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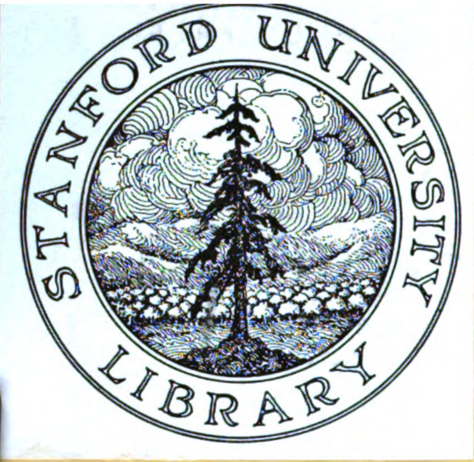

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A CALORIMETRIC PROCEDURE FOR DETERMINING THE HEATS OF SLOW REACTIONS.

I. THE ANALYSIS OF PARTIALLY CONCURRENT HEAT EFFECTS.

BY FREDERICK BARRY.

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The reaction heats of slow chemical changes have not as yet been measured with dependable exactness. The closest approach so far made toward the satisfactory calorimetry of such processes is, without doubt, the very careful work of Brown and Pickering on the heats of mutarotation of glucose and fructose,[1] and on the heats of hydrolysis of starch and sucrose by enzymes.[2] In these investigations Brown and Pickering did not attempt the calorimetry of the whole process; but only that of a part of it, determined in each instance by the change in optical rotation which simultaneously occurred. They thus offered a method of attack which was neither completely general nor wholly calorimetric; and since, when their measurements were made, calorimetric procedure had not yet been developed beyond the stage to which Berthelot had carried it,

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[1] Brown and Pickering, *J. Chem. Soc.*, 71, 756 (1897).

[2] Brown and Pickering, *ibid.*, 71, 783 (1897). For Berthelot's earlier but unsuccessful attempt to measure the heats of mutarotation, see *Compt. rend.*, 120, 1019 (1895); see also Brown and Pickering's remarks upon this work (*loc. cit.*, [1] pp. 757–759); and Nelson and Beegle's criticism (THIS JOURNAL, 41, 571 (1919)).

their work, though admirable for its ingenuity, precision and caution, must have been affected by very considerable error.[1] Their method, none the less, is clearly applicable to many, if not all, of those slow changes which do not involve an appreciable heat of mixture,[2] and their calorimetric errors could now be materially reduced. It is regrettable that their work has not been followed up. As a consequence of this and similar neglect, we still lack dependable knowledge concerning the internal energy relations of all those reactions, the speeds of which are measureable.[3] The obvious effect of such ignorance in limiting the scope and coördination of physicochemical and of physiological research points clearly to the high desirability of developing general and easily adaptable procedures adequate for the precise calorimetry of slow processes.

It was the primary purpose of this investigation to develop such a procedure, more general than that of Brown and Pickering, which should permit the calorimetric examination of complete reactions of various thermochemical character in liquid systems, whether or not these were accompanied by a heat of mixture; and which should be sufficiently exact in principle to make its gradual improvement to the limit of calorimetric precision, defined by minimal thermometric error, not impossible. In order that these conditions should be met, there was chosen for examination and experimental test a reaction of considerable complexity; that, namely, of the complete inversion of sucrose by hydrochloric acid. This reaction possessed many advantages for the purposes in view. Like the greater number of those changes which occur in liquid systems, it is always accompanied by a heat of mixture, that of dry sucrose in acid, or that of acid in sucrose solution, neither one of which can be separately determined; the heat of inversion itself requires, under safe and convenient conditions of temperature and concentration, more than 5 hours for its complete development; and the process as a whole, involves both endothermal and exothermal changes. To measure the heat of this reaction, therefore, it was necessary at the outset to devise means for overcoming the three greatest difficulties likely to be encountered in the calorimetry of

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[1] For example, Brown and Pickering remark (*loc. cit.*, [2] p. 787) that in the determination of the heat of hydrolysis of starch by amylase, the most protracted measurement of which occupied 30 minutes, the correction for thermal leakage was "generally much larger than the actual rise of temperature to be measured."

[2] Brown and Pickering, in their measurements on mutarotation made correction for its progress during dissolution; but their procedure, which is not described in detail, was empirical and probably (in relation to present calorimetric precision) approximate (*loc. cit.*, [1] p. 759).

[3] The current practice of calculating these heats of reaction from heats of combustion, or otherwise by inference from thermodynamical generalizations characteristically inexact, is confessedly a makeshift procedure which yields uncertain, or at best roughly approximate results. See, for instance, the remarks of Brown and Pickering on this point (*loc. cit.*, [2] pp. 783, 784).

protracted processes, which are: the simultaneous determination of two partially concurrent heat effects; the exact maintenance of a negligible or precisely measurable thermal interchange between calorimeter and environment during a long period of time; and the facile adjustment of such control continuously for rising and falling temperatures.

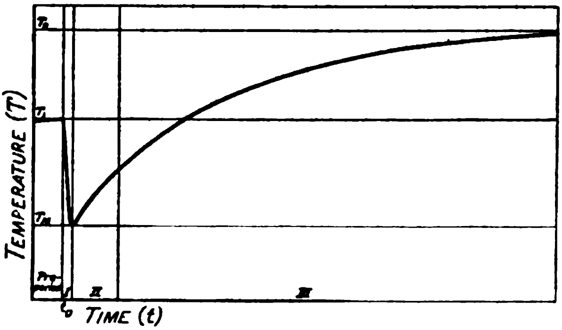
Anticipating the results of work yet to be described, these difficulties, it is believed, have been satisfactorily met, within a margin of error largely determined by the uncertainties of mercury thermometry. The present paper describes a method devised for the analysis of the concurrent heat effects of the sucrose inversion. A second communication will describe the calorimetry of this reaction, and the application of the formulations here developed to the results of actual measurement.

The following analysis will be found applicable to many concurrent effects other than that with reference to which it is developed. The discussion must, therefore, be interpreted as illustrated by, rather than as restricted to, the phenomena of sucrose inversion.

Thermal Effects in the Inversion of Sucrose by Acid Catalysis.

For the determination of any heat of reaction which is accompanied by heat of mixture, two alternative procedures will in general be possible, since the mixture may be accomplished in two ways. For reasons that will soon be apparent,[1] it was decided in actual measurement to initiate the reaction by dissolving dry sucrose in acid, rather than to mix acid with sucrose solution.

The dissolving of sucrose in dilute acid is an endothermal process; the reaction of inversion is exothermal. When, therefore, dry sucrose is mixed with acid there is at first a considerable fall in temperature, which is succeeded almost immediately by a slow rise, the rate of which gradually diminishes as time goes on. If the temperature change in this process be plotted in rectangular coördinates against the time, we have a curve typical of this sort of reaction. Such a curve, drawn from the results of measurement, and divided for convenience into segments marked by the time intervals I, II and III, is shown in Fig. 1. During Period I the dominant effect is the negative heat of solution; in Period II, the positive



REACTION CURVE FROM DETERMINATION Nº3

Fig. 1.

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[1] See page 1302.

inversion heat at first nullifies and then overcomes the effect of solution; in Period III, solution is complete, distribution is uniform, and the heat effect is that of inversion alone. In order to determine the heat of inversion itself from a curve of this character, it is obviously necessary to extrapolate the curve of actual inversion across the entire interval, I + II. This is not altogether a simple matter. Generally speaking such a result may be accomplished by determining from the reaction curve in Period III an empirical formulation, extrapolating by this means, and modifying subsequently the extrapolated segment in accordance with the fact that during the period of concurrent effect spanned by this segment, one reacting substance is present in changing concentration. Disregarding for the present this final complication, it is clear that the first simple extrapolation itself is likely to be somewhat inexact, since it reproduces a segment of greater slope than that from which its formula was derived. The first essential precaution to be taken with respect to this procedure, therefore, would be to make the interval of concurrent effect as short as possible. In practice this would mean to effect solution as quickly as possible. One experimental necessity is thus at the outset clearly indicated. Assuming the task to have been adequately performed, there still remains the desirability of establishing a criterion of normal behavior by means of which the complete theory of extrapolation may be simply developed, and the empirical curve, insofar as it departs from the behavior thus indicated, interpreted and, if necessary, corrected. Such a criterion, in this as in other cases, will be provided by the isothermal equation of reaction speed. In the case of the inversion of sucrose this equation is well established; and for any given conditions of temperature and concentration, its constants, which are not quite invariable, may be determined with high precision by polarimetric measurement, If now, the assumptions be made: first, that in this reaction the energy release is proportional to quantity of sucrose transformed, second, that negligible external work is performed; and third, that during the change the total heat capacity remains constant within measurement error, the temperature-time curve for the isothermal condition will be sensibly of the same form as that of speed. The first of these assumptions is justifiable only if the reaction heat is that of inversion alone; since the measurements which determine the speed equation are made with reference solely to the passage of the reacting system from sucrose and water to the equilibrium mixture of hexoses. It must, however, be tentatively made; and may be so made without much danger of subsequent embarrassment, inasmuch as any superimposed effects to be anticipated are likely to be too small to affect the theory of extrapolation beyond the limit of effective correction. The assumption itself, moreover, offers a possible opportunity for the detection of superimposed heats of consecutive or side reactions if these be measurable. As to the other assumptions made, the second may be granted at once; and the third also, when the heat capacities of factors and products, small in comparison with that of the whole system, are considered.[1]

On the basis of these assumptions, then, the simple theory of extrapolation may be safely developed.

The inversion of sucrose proceeds with negligible variation[2] after the manner of a monomolecular reaction. The familiar speed equation for this type of change,

$$\frac{dx}{dt} = k\,(a - x)$$

and its integrals

$$kt = \log \frac{a}{a - x}, \text{ and } k(t_2 - t_1) = \log \frac{a - x_1}{a - x_2} \tag{1}$$

(in which for a given weight of solvent, a is the initial weight in gram moles; x, x_1, x_2 the amounts transformed in gram moles, at the times t, t_1, t_2; and k the initial rate of transformation for unit mass) yields, on the basis of the assumption first made: namely, that temperature change under the conditions of experimentation will be proportional to quantity transformed,

$$\frac{dT}{dt} = k[(T_f - T_i) - (T - T_i)] = k(T_f - T)$$

and its integrals,

---

[1] In actual determination, during the period of inversion (to which alone this analysis applies), the reacting system passed from sucrose in solution and water, to invert sugar in solution. The molecular heat of dissolved sucrose (14° to 26°) is 152.8 (Magie, *Phys. Rev.*, 16, 381; and 17, 105 (1903)); that of water is 18.0, and that of dissolved invert sugar is (89.6 + 78.8) ÷ 2 = 84.2 (Magie, *loc. cit.*), in gram calorie units. The change in heat capacity per mole in this reaction, is therefore, (152.8 + 18) — 2 (84.2) = 2.4, and for 50 g. of sucrose, a maximal quantity in measurement, 0.35 gram caloric units. Since the heat capacity of the whole system in actual determination was closely that of 1000 g. of water, the change in that capacity due to reaction thus amounted to 0.035 per cent. of the whole, and when not corrected for, caused the same percentage error in the measurement of the reaction heat. This error is beyond the limit of possible experimental accuracy, and is quite negligible. With other reactions, of course, the corresponding values might be large enough to affect the results of measurement. If this were ever the case, the effect of change in heat capacity on the form of the reaction curve could be corrected for with sufficient exactness by modifying the curve of observed temperature change in such a way that the difference between it and the derived curve varied in an approximately exponential manner from zero at the time when the temperature was minimal to the difference defined by the total correction at the time when the reaction came to an end.

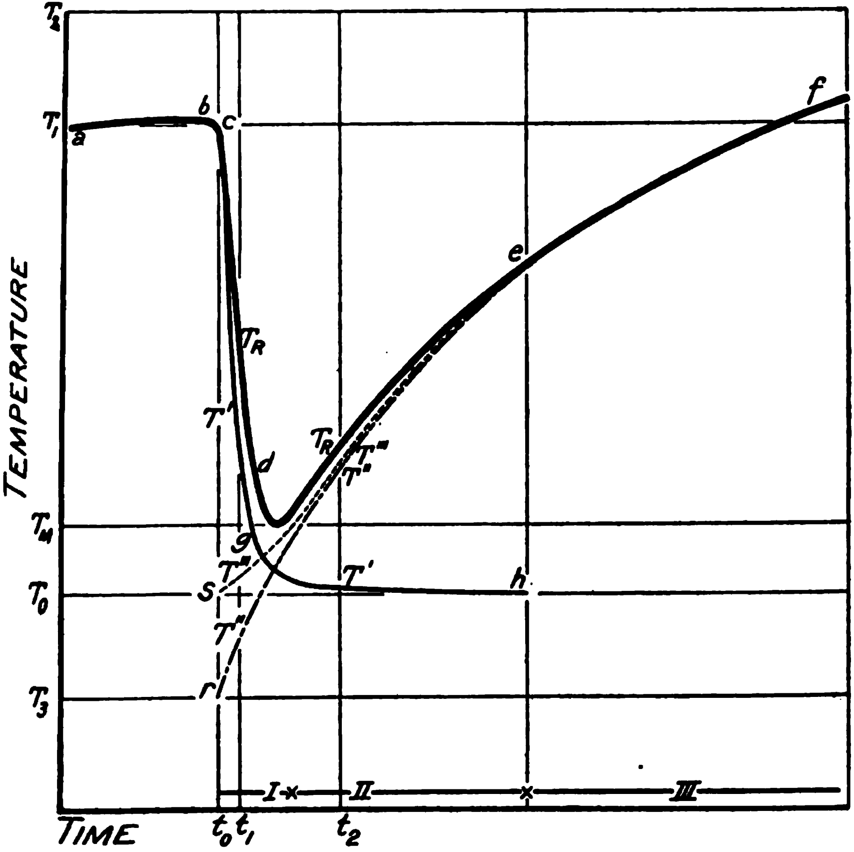
[2] That this was the case under the conditions of experimentation was shown by the results of accessory measurements of isothermal reaction speed under closely similar conditions of temperature and concentration.

$$kt = \log \frac{T_f - T_i}{T_f - T} \text{ and } k(t_2 - t_1) = \log \frac{T_f - T_1}{T_f - T_2} \qquad (2)$$

where T_i and T_f are initial and final temperatures, and T, T_1, T_2, temperatures at the times t, t_1, t_2.

Now, if in actual experience solution were instantaneous, the lowest temperature reached by heat of solution alone—identical with that at which inversion began—would be determined by the point at which the inversion curve, extrapolated from the segment in Period III by Equation 2 cut the ordinate $t = 0$. It remains to consider the effect of the changing sucrose concentration during the time interval covered by the extrapolation. In this period the inversion proceeds, not in accordance with the simple formula of extrapolation discussed above, in which the term $(T_f - T_i)$, corresponding to a in the speed equation, implies maximal initial concentration and, therefore, instantaneous solution, but at all times more slowly; its speed, initially zero, gradually increasing at first with positive and toward the end with negative acceleration, until solution is complete.

The relationships involved in this behavior are graphically represented in Fig. 2, to which subsequent discussion may be conveniently referred. In this figure, the complete curve of reaction obtained by correcting the curve of observed temperatures for temperature changes due to stirring and concomitant superimposed effects, and, if necessary or desirable, for change in heat capacity and other causes of independent variation, is represented by the heavily drawn line, $\overline{abcdef}$. Of this, the branch $\overline{ab}$ represents the temperature change due to initial stirring and concomitant effects before the reaction is initiated; the very short interval $\overline{bc}$ marks the initial lag, neglected in the present discussion, the ordinate $t=0$ being drawn through c, the point from which the observed temperature fall becomes measurably significant; the initial temperature, the abscissa of c, is marked T_1; the final temperature reached, T_2; the minimal temperature, T_m. The inversion curve, extrapolated from Period III by Equation 2 (to be referred to subsequently as the simple curve of inversion), is shown by the line of dashes $\overline{er}$; the point r marking its intersection with the ordinate $t=0$ at the temperature T_3. The curve of solution, which falls sharply from the initial point c with greater slope than that of the reaction curve, and which, after sudden flexure slightly above T_0 rapidly approaches and soon coincides with the abscissa of this temperature, is represented by the lightly drawn whole line $\overline{cgh}$. This curve, the form of which in measurement was not affected by the mechanism of solution, is here plotted from the results of accessory determinations of solution heats, collated in a manner yet to be described, and is very closely exponential. The curve of actual inversion, which lies at all times above that extrapolated from Equation 2, is shown by the dotted line $\overline{es}$; the initial point of which, s, lies on the abscissa T_0. Finally, points on the reaction curve are designated T_R; and those on the solution curve, the simple curve of inversion, and the curve of actual inversion, T', T'' and T''', respectively. The time at which reaction begins ($t = 0$) is marked t_0. These several designations will be used in the following discussion without further remark.



CONCURRENT HEAT EFFECTS IN INVERSION OF SUCROSE BY ACID

Fig. 2.

The problem of extrapolation is, obviously, to determine the temperature T_0. With reference to Fig. 2, we may write the following equations. For the curve of solution,

$$T' = T_0 + (T_1 - T_0)e^{-pt} \tag{3}$$

and for the simple curve of inversion,

$$T'' = T_2 + (T_3 - T_2)e^{-kt}. \tag{4}$$

The rate of actual inversion is at all times proportional to the amount of sucrose in solution.[1] This amount will be, at any instant, the amount dissolved, less the amount inverted up to that instant. That is, the slope of the curve of actual inversion may be formulated:

$$\frac{dT'''}{dt} = A(x - y) \tag{5}$$

where x and y are the amounts of sucrose dissolved and inverted at the time t; and where A is a constant proportional to the constant of inversion, k.

In this equation, since temperature change is assumed to be proportional to quantity transformed, the following relations obtain:

$$\frac{A}{k} = \frac{T_2 - T_0}{a}; \quad \frac{x}{a} = \frac{T_1 - T'}{T_1 - T_0}; \quad \frac{y}{a} = \frac{T''' - T_0}{T_2 - T_0};$$

so that Equation 5 may be written:

$$\frac{dT'''}{dt} = k\,\frac{T_2 - T_0}{a} \cdot a\left(\frac{T_1 - T'}{T_1 - T_0} - \frac{T''' - T_0}{T_2 - T_0}\right)$$

$$= k\left[\frac{T_1 - T'}{T_1 - T_0}(T_2 - T_0) - (T''' - T_0)\right]$$

and, since from Equation 3,

$$\frac{T_1 - T'}{T_1 - T_0} = 1 - e^{-pt},$$

$$\frac{dT'''}{dt} = k\,[(1 - e^{-pt})(T_2 - T_0) - (T''' - T_0)]$$

$$= k\,[T_2 - T''' - (T_2 - T_0)e^{-pt}].$$

From this equation, by suitable transformation and integration, we obtain:

$$T''' = T_2 + (T_2 - T_0)\ 1/k - p\ (pe^{-kt} - ke^{-pt})$$

and since, if T_R represent the observed temperature at the time t,

$$T_R = T' + (T''' - T_0),$$

we obtain finally,

$$T_R = (T_1 - T_0)e^{-pt} + T_2 + \frac{T_2 - T_0}{k - p} - (pe^{-kt} - ke^{-pt}). \tag{A}$$

In this equation, all values save T_0 are known; the temperatures, from observations made in each measurement, the constant k from available

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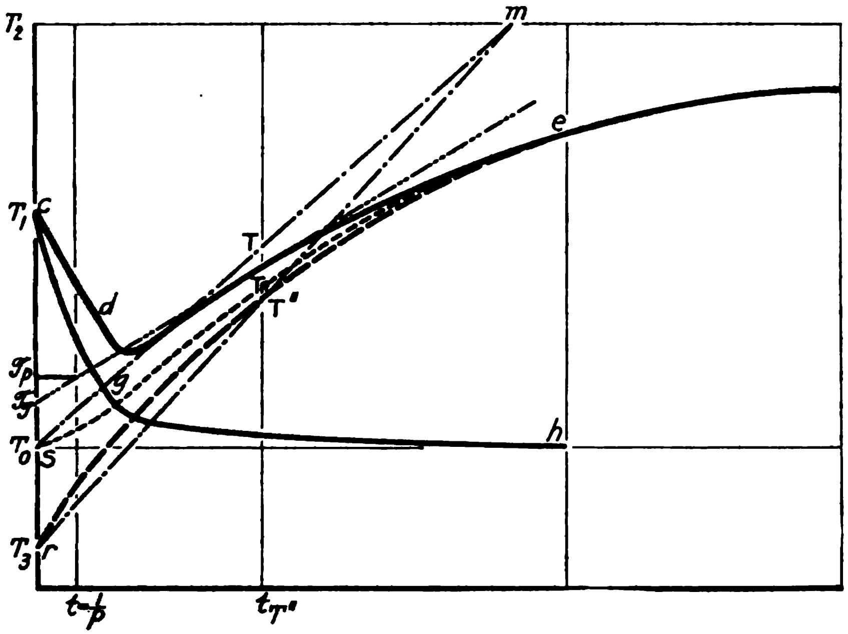
[1] It is for this reason that in actual experiment, mixture was accomplished by dissolving dry sucrose in acid. The relation between speed of inversion and hydrogen ion concentration is too complicated to make possible a simple mathematical treatment of the alternative procedure.

data on the speed of reaction, and p from the results of accessory measurements, already referred to, on the form of the solution curve.

The equation is, nevertheless, difficult to handle. It yields, however, upon differentiation and subsequent algebraic conversion a much simpler formula which permits facile graphical solution:

$$T_2 - T_R - \frac{1}{p} \cdot \frac{dT_R}{dt} = (T_2 - T_0)e^{-kt}.^{1} \qquad \text{(B)}$$

The extrapolation may now be effected graphically as follows.



CONCURRENT REACTION HEATS IN OPPOSITE SENSES

Fig. 3.

A. Exact Tangent Construction.—In Fig. 3 let a secant to the simple inversion curve be drawn through r and any other point on this curve within the time interval II, such as T''; this will intersect the abscissa of T_2 at some point, m. Draw the line $\overline{ms}$; and let the intersections of the ordinate of T'' ($t_{T''}$), with this line and with the reaction curve be T and T_R, respectively. Then

$$\frac{T_2 - T_0}{T_2 - T} = \frac{T_2 - T_3}{T_2 - T''} = \frac{1}{e^{-kt}} \text{ by Equation 4}$$

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[1] NOTE.—For this equation and for invaluable collaboration in its development, the writer is indebted to Professor H. W. Webb of Columbia University.

or,

$$T_2 - T_0 = \frac{T_2 - T}{e^{-kt}}.$$

Substituting this value of $T_2 - T_0$ in Equation B, we have

$$\frac{T_2 - T_R - 1/p \,.\, dT_R/dt}{e^{-kt}} = \frac{T_2 - T}{e^{-kt}}$$

or,

$$T = T_R + \frac{1}{p} \cdot \frac{dT_R}{dt}.$$

The point T is thus determined: For the temperature increment $1/p \,.\, dT_R/dt$ may be found by constructing a tangent to the reaction curve at T_R, intersecting the ordinate $t=0$ at T_T and the ordinate $t=1/p$ at T_p. The temperature interval $T_T - T_p$ then equals $1/p \,.\, dT_R/dt$.

Some uncertainty is involved in this construction, on account of the difficulty of drawing the tangent precisely. This uncertainty will be least when the ratio of the time interval $t_{T'} - t_0$ to the temperature interval $T_2 - T_T$ is smallest, and when the curvature of the reaction curve in the neighborhood of T_R is most nearly uniform. The ordinate $t_{T'}$ should, therefore, be taken on an arc of sensibly uniform curvature as near as is practicable to the minimum temperature of the reaction curve. The approximate magnitude of the uncertainty in any case will be indicated, of course, by the discrepancies shown by independent constructions on the same curve.

B. Approximate Tangent Construction.—An alternative procedure, however, yields a much neater construction, the precision of which, in practise, largely, if not wholly, compensates for the approximation which it involves. In Fig. 4, let the point T_R, taken as common to the reaction curve and the curves of inversion, be chosen for reference: let the line $\overline{rc}$ be drawn tangent to the simple inversion curve at r, intersecting the ordinate $t = 1/p$ at b; and let the intersection of the abscissa T_3 with this ordinate be a. Then, with reference to the inversion curve (since the slope at any point on an exponential curve is proportional to its distance from the asymptote)

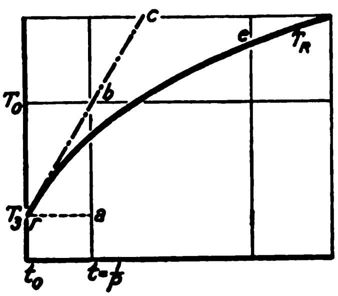


Fig. 4.

$$\overline{ab} = \frac{1}{p} \times (\text{slope of inversion curve at } T_3) = \frac{1}{p} \cdot \frac{dT_R}{dt} \cdot \frac{T_2 - T_3}{T_2 - T_R}.$$

From Equation B, $\frac{1}{p} \cdot \frac{dT_R}{dt} = -(T_2 - T_0)e^{-kt} + T_2 - T_R$

whence

$$\overline{\mathrm{ab}} = -(T_2 - T_0)e^{-kt} \cdot \frac{T_2 - T_3}{T_2 - T_R} + \frac{T_2 - T_R}{T_2 - T_R}(T_2 - T_3) \quad .$$

and since, on the inversion curve, $T_2 - T_R = (T_2 - T_3)e^{-kt}$

$$\overline{\mathrm{ab}} = T_0 - T_3$$

Thus T_0 is determined, and with precision, since the slope at T_3 may be measured in terms of accurately known values; that is, at $t=0$,

$$\frac{dT''}{dt} = k(T_2 - T_3).$$

In drawing the tangent, advantage may be taken of the fact that, as its equation $T = T_3 + kt(T_2 - T_3)$ shows, the point of its intersection with the abscissa T_2 is defined by the condition $t = 1/k$. Since, also, when $t = 1/k$ the equation of the simple inversion curve (Equation 4) becomes

$$T'' = T_2 + (T_3 - T_2)1/e,$$

whence

$$T'' - T_3 = (T_2 - T_3)(1 - 1/e) = 0.63\ (T_2 - T_3).$$

we have in these relations an opportunity of testing both the precision of the construction, and, in some degree, the legitimacy of the premises (see pages 1298 to 1302) which it involves.

C. **Approximate Curve Construction.**—The preceding discussion leads, finally, to a very rapid, though less closely approximate, solution. If the speed of solution is much greater than that of concurrent inversion the simple curve of inversion in the construction shown in Fig. 4 may be taken as coincident with its tangent within the time interval $t=0$ to $t=1/p$; itself intersecting the ordinate $t = 1/p$ at T_0. The temperature T_0 will then be determined with sufficient accuracy merely by extrapolating the simple inversion curve, and constructing the ordinate $t=1/p$ to its point of intersection with this curve. The constant p, however, is the least dependable of all the experimental data. In order to avoid using it, advantage may be taken of the following relations.

Under the above conditions, the curve of reaction, during the short time interval $1/p$, will be sensibly coincident with the curve of solution and may, therefore, be written (compare Equation 4)

$$T_R = T_0 + (T_1 - T_0)e^{-pt}.$$

From this equation, when $t = 1/p$ (and when therefore $T'' = T_0$)

$$T_R = T_0 + (T_1 - T_0)1/e$$

or

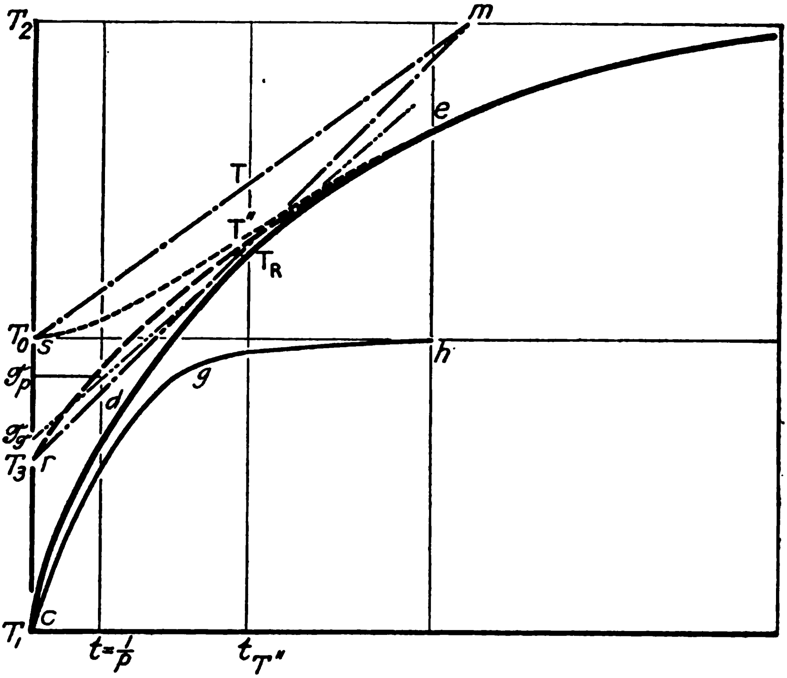
$$T_R = T'' + (T_1 - T'')1/e;$$

whence

$$T_1 - T_R = (T_1 - T'')(1 - 1/e), = 0.63\ (T_1 - T'').$$

The temperature T_0 may, therefore, be determined with the same degree of precision as in the previous case by finding an ordinate ($\equiv [t = 1/p]$) such that measured upon it the distances of the reaction and simple inversion curves from the abscissa T_1 are to each other as 0.63 is to 1. Inasmuch as this can be done very easily by the application of a transparent diagram of converging lines, this approximate solution will be most conveniently rapid. Its adequacy of course depends wholly upon the ratio of the speed of solution to that of inversion within the time interval $1/p$. As this becomes greater, the error of approximation decreases, but more rapidly.

The foregoing analysis, though developed with reference to the sucrose inversion, will apply without essential modification to any partial concurrence between two reactions of the first order. It will have been noted that throughout the discussion no limitation was placed upon the general notion of such concurrence; the formulations apply not only to the case under immediate consideration, in which the heats of reaction



CONCURRENT REACTION HEATS IN THE SAME SENSE

Fig. 5.

are opposed, but also to those in which these heats reinforce each other. The geometrical relations in this latter case are shown in Fig. 5, which thus completes the demonstration. It is likewise clear that similar analysis will be applicable to diverse phenomena involving such concurrence; and the procedure suggests, at any rate, one way in which the analysis of concurrent reactions of the same type not so simply interdependent, or of concurrent reactions of higher order, may be attempted.

D. **Minimum Construction.**—In the particular case of opposed heats of reaction, for instance, in the inversion of sucrose, it may often be useful to effect an independent extrapolation, by taking advantage of the fact that the reaction curve in this case shows a critical point, that of minimum temperature, at which the slopes of the curves of solution and of actual inversion are equal; and those of reaction and actual inversion very closely so. For this condition, $dT_R/dt = 0$. We have then from the general Equation B,

$$T_2 - T_m = (T_2 - T_0)e^{-kt},$$

where $T_m \equiv T_R$ at the minimum point; whence

$$\frac{T_2 - T_0}{T_2 - T_m} = \frac{1}{e^{-kt}}.$$

In the general construction shown in Fig. 3, we have the relation:

$$\frac{T_2 - T_0}{T_2 - T} = \frac{1}{e^{-kt}}$$

It follows, therefore, that for the case of opposed heats of reaction, $T_m = T$; so that in the construction shown in Fig. 3 as applied to this case, T_0 is known from observation and need not be calculated. This procedure is obviously questionable unless the minimum point be sharply defined in the curve of reaction, and is uncertain insofar as the observed minimum differs from the actual in consequence of thermometric lag, which at this point exhibits its most marked effect.

The entire preceding analysis applies, of course, only to the isothermal condition. In the adiabatic condition, the observed heat of reaction, Q, or with negligible error in this case as in the case of any reaction in a condensed system, the actual change of internal energy, U, at any time equals that of the isothermal reaction, U, plus the increment in U due to change of temperature; which we may call ΔU. Now, by Kirchoff's law:

$$\Delta U = \Delta C(\mathbf{T}_2 - \mathbf{T}_1),$$

where ΔU is the increment mentioned, $\mathbf{T}_2 - \mathbf{T}_1$ the observed temperature change, and ΔC the difference between the specific heats of factors and products. Therefore,

$$\mathbf{U} = U + \Delta\mathrm{U} = \mathrm{U} + \Delta C\,(\mathbf{T}_2 - \mathbf{T}_1)$$

or,

$$U = \mathbf{U} - \Delta C(\mathbf{T}_2 - \mathbf{T}_1);$$

and similarly,

$$T = \mathbf{T} - \Delta C/H\ (\mathbf{T}_2 - \mathbf{T}_1) \qquad (7)$$

where H is the heat capacity of the system. If the value of T given in Equation 7 be substituted for T in Equation 2, the resulting equation will be that of the temperature-time curve in terms of the data obtained for the adiabatic condition. In this equation, however, the terms of correction are very small in comparison with the values which they affect,[1] so that, for the purpose of measurement Equations 1 and 2, from which the constant k can be determined and checked, and the curve of inversion simply extrapolated, may be used as applicable to the adiabatic condition without sensible error. Thus, in practice the equations given will be applicable, so far as the heat of reaction alone is concerned, for the separation of concurrent heat effects in the case of any reaction which does not develop an altogether unusual quantity of heat, whatever be the calorimetric method employed.

On the other hand, the form of the sucrose inversion curve is considerably altered even by a small rise of temperature during reaction; and such also will be the case for all reactions for which the temperature coefficient of the velocity constant is correspondingly great. Whenever the coefficient is known for the conditions of experimentation, the reaction curve may, obviously, be corrected for this influence, so that its extrapolation across the short period of concurrent effect will be as precise as necessary. If it be not known in advance, it may always be derived from the reaction curve itself, extrapolated to its value at the time reaction begins, and applied as before.

A more extended discussion of the experimental application of the equations here presented will find its natural place in the record of actual measurement. It is sufficient for present purposes that its general character is thus indicated.

NEW YORK CITY.

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[1] From the data given in a preceding footnote (p. 1299), $\Delta C = (152.8 + 18.0) \div 360 - (84.2 \div 180) = 0.0069$, $\mathbf{T}_2 - \mathbf{T}_1$ will always be less than 0.4°; so that in Equation 7, $\Delta C(\mathbf{T}_2 - \mathbf{T}_1)$ will always be less than 0.0027 gram calorie units. In the same experiments, the heat capacity will always be greater than 1000 gram calorie units; and $T = \mathbf{T} - \frac{\Delta C}{H}(\mathbf{T}_2 - \mathbf{T}_1)$ will, therefore, differ from $\mathbf{T}$ by less than one part in 300,000. This discrepancy will be far beyond the limit of measurement accuracy, not only in these determinations, but in the case of all others of similar character, and may be disregarded.

NEW METHODS OF PREPARING TRIPOTASSIUM LEAD HYDROGEN OCTAFLUORIDE.

By Frank C. Mathers.

Received February 20, 1920.

Introduction.

These experiments were made in connection with the problem of preparing free fluorine. Tripotassium lead hydrogen octafluoride evolves fluorine when heated above 300°, but the preparation of the octafluoride by the known methods was found to be slow and the yields were low. Therefore, new methods of preparing the salt were sought.

The excellent paper by Clark[1] gives complete working details of perhaps the best of the known methods. Potassium plumbate is first formed by heating a mixture of lead peroxide, potassium hydroxide and water. The residue is added to strong hydrofluoric acid and the pure salt, tripotassium lead hydrogen octafluoride, is obtained by crystallization of the filtrate. The review omitted the method[2] of treating lead tetraacetate with hydrofluoric acid and potassium hydrogen fluoride. This, however, is a slow and expensive method. Ruff[3] states that both the ammonium and the potassium double salts can be easily made but no details of the method are given.

Experimental.

Action of Anhydrous Hydrofluoric Acid upon Peroxides of Lead.—Lead peroxide and red lead (Pb_3O_4) are apparently unacted upon by the ordinary conc. hydrofluoric acid (50%). However, the nearly anhydrous acid (96%) acts readily upon the red lead or freshly prepared lead peroxide with formation of good yields of lead tetrafluoride in each case. The reaction with the red lead is very vigorous. The lead peroxide which is split off from the red lead dissolves very quickly in the anhydrous hydrofluoric acid but the waste of the anhydrous acid in the formation of the lead difluoride is objectionable. No black color is noticed except for short intervals in places where the red lead happens to be in excess. Lead peroxide (c. p.) from Eimer and Amend is insoluble in the anhydrous hydrofluoric acid even on standing for several hours. Freshly prepared lead peroxide dissolved in the anhydrous acid but not in the 50% acid. This lead peroxide was prepared by treating red lead with an excess of nitric acid, washing and drying at a low temperature. The undried paste was not soluble. This was probably due to the dilution of the acid. It seemed to make no difference if the dried lead peroxide was used at once or after several days. The tetrafluoride solutions thus obtained were

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[1] This Journal, 41, 1477 (1919).

[2] Brauner, *Z. anorg. Chem.*, 7, 1 (1894); *J. Chem. Soc.*, 65, 393 (1894); Winterfeld, Doktor Dissertation zu Berlin, 1894.

[3] *Z. angew. Chem.*, [2] 20, 1218 (1907).

quickly hydrolyzed by dilution with water—a black precipitate of plumbic hydroxide being formed. The addition of potassium or ammonium fluoride, before dilution, lessens the tendency to hydrolysis. A yield of 62% of the tetrafluoride, based on lead peroxide, was obtained. The only serious objection to this method is the use of anhydrous hydrofluoric acid, which is so very difficult to make and to keep and is disagreeable to use.

By Fusion of Lead Peroxide with Potassium Hydrogen Fluoride.—Any sample of lead peroxide reacts with fused potassium hydrogen fluoride with formation of a double fluoride of lead. Equal weights of potassium hydrogen fluoride (dried by fusion) and lead peroxide in platinum or copper vessels, were used. This gives approximately 3 molecules of potassium hydrogen fluoride to one of lead peroxide, which is the quantity of potassium for the desired salt, but there is insufficient available hydrofluoric acid for complete reaction upon the lead peroxide. It is better to supply the required hydrofluoric acid by the scheme described below than to start with larger quantities of the potassium hydrogen fluoride. The latter substance was fused over a free flame at a temperature of about 200° and the lead peroxide added slowly with stirring. A gas, probably water, was evolved during the reaction. The heating, which need last only for a few minutes, should be discontinued as soon as the mass becomes very pasty. Increase in temperature decomposes the octafluoride. The mass remains black in color. About 30 to 40% of the lead peroxide was changed to a double fluoride at this point. After cooling, the mass was moistened with conc. hydrofluoric acid, the lumps were crushed and the mass thoroughly stirred with a carbon rod. This treatment regenerates potassium hydrogen fluoride. The vessel was then heated in an oven for several hours at about 225°. The residue became much whiter during the heating, thus showing that the lead peroxide was being acted upon. By repeating once or twice the treatment with the hydrofluoric acid followed by the heating, the residue became practically white. Analyses showed that 80% to 86% of the lead peroxide was changed to octafluoride. Analysis was made by extracting the residue with conc. hydrofluoric acid, filtering and washing the residue with 1 : 1 hydrofluoric acid. The filtrate was treated with 5 cc. of conc. nitric acid, and titrated with excess hydrogen peroxide followed with potassium permanganate. Direct fusion with larger amount of potassium hydrogen fluoride (4 : 1) without any further treatment with hydrofluoric acid or heating gave yields of 65% to 70%.

Pure crystals of the double salt, tripotassium lead hydrogen octafluoride, were prepared by digesting the crude residue with conc. hydrofluoric acid, filtering and crystallizing. Analysis, by electrodeposition of lead peroxide from nitric acid solution, gave 50.3% of lead peroxide while that calculated was 50.09%.

A stronger acid was required to avoid hydrolysis of the octafluoride when no excess of potassium was present. One part of hydrofluoric acid (50%) to 0.05 part of water gave no hydrolysis of the pure salt when heated upon a water bath, but one of acid to one of water gave hydrolysis. However, one part of acid, 2 of water and 0.2 part of potassium hydrogen fluoride gave no hydrolysis. Cold solutions hydrolyzed less easily than hot ones. In extracting the crude residue, conc. hydrofluoric acid should be used as otherwise some hydrolysis is likely to occur. Pure crystals of the double salt in glass containers blackened upon the surface. Crystals could be kept without discoloration when sealed in paraffin containers.

Preparation of Fluorine Gas by Heating Tripotassium Lead Hydrogen Octafluoride.—The heating of pure crystals of the double fluoride, $3KF.HF.PbF_4$, as a method of making free fluorine is practically a failure. Heating in an open dish (a platinum retort was not available) has never given enough free fluorine for the writer to detect its odor—a really sensitive test. However, sufficient fluorine is produced to etch the platinum dish. Ruff,[1] who has done more with fluorine and fluorides than anyone except Moissan, says that this method is not successful, although he obtained a sufficient quantity from a platinum retort to detect its odor.

These experiments with the complex octafluoride were discontinued as soon as the really satisfactory method of easily making free fluorine by the electrolysis of melted potassium hydrogen fluoride was discovered.[2]

Summary.

Tripotassium lead hydrogen octafluoride, $3KF.HF.PbF_4$, can easily be prepared by fusing potassium hydrogen fluoride with lead peroxide, followed by treatment with conc. hydrofluoric acid and drying at 225°. The treatment with hydrofluoric acid and drying should be repeated until the residue is almost white. Yields of 86% of the octafluoride can be obtained.

Yields of 62% of the tetrafluoride were obtained by direct solution of freshly prepared lead peroxide in almost anhydrous hydrofluoric acid.

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[1] *Loc. cit.*

[2] *Trans. Am. Electrochem. Soc.*, 35, 335 (1919); *J. Phys. Chem.*, 23, 348 (1919); *Chem. Eng.*, 27, 107 (1919).

[Contribution from the Polytechnic Institute of Warsaw.]

THE THERMOCHEMISTRY OF HYDROCARBONS ACCORDING TO P. W. ZUBOW'S DATA.

By W. Swiętoslawski.

Received March 6, 1920.

In a previous paper[1] I undertook the systematic analysis of the thermochemical data on organic compounds, using the determinations of J. Thomsen, M. Berthelot, Stohmann, W. Louginine, and others. However, the investigations of Emil Fischer and Wrede[2] and of the author[3] have made it clear that all of the data of thermochemistry must be recalculated and corrected before an analysis and a summary of them can be made.

With this in view, I have recently recalculated[4] the very exact experimental material, accumulated between 1892 and 1911 by P. W. Zubow in Louginine's thermochemical laboratory, and in the present communication I wish to examine the results of this recalculation, believing that such an examination will prove useful, even before all the other previous thermochemical investigations have been recalculated.

The Equations of Combustion.

If we denote the heat of formation of the molecules O_2, CO_2, and H_2O from their separate atoms by $2w$, $4z$ and $2u$, and the heats of formation of the atomic linkings, C–H and C–C by x and y, we obtain for a given hydrocarbon C_nH_m, containing only such linkings, the following equation of combustion

$$\left(\frac{4n - m}{2}\right)y + mx + \left(2n + \frac{m}{2}\right)w + A = 4nz + mu,$$

where A signifies the molar heat of combustion of C_nH_m. When the equation is transformed to

$$\left(2n - \frac{m}{2}\right)(y + w - 2z) + m\,(x + w - z - u) + A = 0 \quad (1)$$

we see that the terms $y + w - 2z$ and $x + w - z - u$ are repeated in the equation as many times as the linkings C–C and C–H occur in the hydrocarbon C_nH_m.

We shall call the terms $y + w - 2z$ and $x + w - z - u$ the thermochemical characteristics of the atomic linkings C–C and C–H. They contain the constants w, z and u, and the variables x and y, which depend upon the constitution of the hydrocarbon. It is clear that x and y correspond in Equation 1 to the average values of the heats of formation of the above mentioned linkings.

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[1] *Z. physik. Chem.*, **65**, 513; **67**, 78 (1909); **72**, 49 (1910); *Bull. Acad. Cracovie*, **1909**, 941.

[2] *Sitz. Akad. Wiss. Math.-Nat. Klasse*, **1908**, p. 129.

[3] *J. Russ. Phys.-Chem. Soc.*, **46**, 935, 1284, 1293, 1302 (1914).

[4] This Journal, **42**, 1092 (1920).

If we choose definite values of x and y, so that x = const. and y = const., by comparing several hydrocarbons, Equation 1 must be completed by the addition of $(\Sigma\Delta x + \Sigma\Delta y) = \Sigma\Delta(x, y)$ $(2n - m/2)(y + w - 2z) + m(x + w - z - u) + \Sigma\Delta(x, y) + A = 0$, where $\Sigma\Delta(x, y)$ represents the increase of the heats of formation of the separate atomic linkings C–C and C–H in the hydrocarbons examined.

Thermochemical Characteristics of the C-C and C-H Linkings.

One purpose of this paper is to explain within what limits the values of the thermochemical characteristics $x + w - z - u$ and $y + w - 2z$ can vary in hydrocarbons not containing unsaturated bonds. The analysis of this problem can be performed in two ways, (1) by solving the equations of combustion

$$4(x + w - z - u) + A_1 = 0$$

$$6(x + w - z - u) + (y + w - 2z) + A_2 = 0$$

for methane and ethane; or (2) by computing the average values of x and y for another assumed hydrocarbon, supposing $\Sigma\Delta(x, y) = 0$. Having established values of the thermochemical characteristics of the linkings C–C and C–H, we can then compute the increments $\Sigma\Delta(x,y)$ for other hydrocarbons.

In the previous papers I have chosen the first method, adopting for A_1 and A_2 M. Berthelot's and J. Thomsen's determinations of the heats of combustion of methane and ethane. However, at present it seems to me that the values of A_1 and A_2 are not entirely trustworthy, because at that time the measurements could not be made with the precision now required.

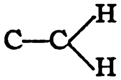
With the intention of using the second method, I have chosen the newly corrected data of P. W. Zubow for the 4 saturated and polymethylene hydrocarbons and the heat of combustion of naphthalene, as redetermined by Dickinson in the Bureau of Standards in 1915, and by the author in 1917 in Louginine's thermochemical laboratory, and have computed, by the method of least squares, the average magnitudes of $(x + w - z - u$ and $(y + w - 2z)$ for the following 5 substances, n-hexane, n-octane, n-decane, cylcohexane and naphthalene.

The heats of combustion of these substances were corrected to the gaseous state at the boiling point, and the computation was performed by supposing $\Sigma\Delta(x, y) = 0$.

Abbreviating: $(x + w - z - u) = X$ and $(y + w - 2z) = Y$ we obtain the following 5 equations:

Cyclohexane	$6Y + 12X + \Sigma\Delta(x,y) + 946.2 = 0$
n-Hexane	$5Y + 14X + \Sigma\Delta(x,y) + 998.5 = 0$
n-Octane	$7Y + 18X + \Sigma\Delta(x,y) + 1317.7 = 0$
n-Decane	$9Y + 22X + \Sigma\Delta(x,y) + 1630.4 = 0$
Naphthalene	$16Y + 8X + \Sigma\Delta(x,y) + 1258.0 = 0$

From which we obtain $X = -52.76$ cal., $Y = -52.25$ cal., $Z = Y + 2X = -157.77$ cal.

The same result can be obtained if the equations are modified by introducing the magnitudes $Z = Y + 2X$, corresponding to the thermochemical characteristic of the  $C{-}C\begin{smallmatrix}H\\ H\end{smallmatrix}$ group. Then, for

$$\begin{array}{lrcl} \text{Cyclohexane} & 6Z & = & -946.2; \\ n\text{-Hexane} & 5Z + 4X & = & -998.5; \\ n\text{-Octane} & 7Z + 4X & = & -1317.7; \\ n\text{-Decane} & 9Z - 4X & = & -1630.4; \\ \text{Naphthalene} & 16Z - 24X & = & -1258.0. \end{array}$$

Whence: $X_1 = -52.78$ cal., $Y_1 = -52.22$ cal., $Z_1 = -157.78$ cal.

It is interesting that if the last equation (for naphthalene) is excluded, the solution of the first 4 equations gives

$$X_2 = -52.82 \text{ cal.}, \quad Y_2 = -52.11 \text{ cal.}, \quad Z_2 = -157.75 \text{ cal.}$$

These numbers differ very little from the above-mentioned ones. The deviations are less than 0.02% for the thermochemical characteristic of the C_2H_2 group, 0.11% for the C–H linking, and about 0.25% for the C–C linking.

If we adopt the values $X = -52.76$ cal., $Y = -52.25$ cal., $Z = -157.77$ cal., and introduce them into our equations of combustion, we obtain the following deviation ($\Delta\%$) between the calculated and measured values.

TABLE I.

Name.	A_{gas}.	$\Sigma X + \Sigma Y$.	Δ.	$\Delta\%$.
n-Hexane	998.5	999.9	+1.4	+0.14
n-Octane	1317.7	1315.4	—2.3	—0.17
n-Decane	1630.4	1631.0	+0.6	+0.04
Cyclohexane	946.2	946.6	+0.4	+0.04
Naphthalene	1258.0	1258.1	+0.1	+0.01
				$\Delta\% = \pm 0.08\%$

The deviations ($\Delta\%$) vary within the narrow limits ± 0.08%, depending evidently on the errors of experiment and on the impurities of the samples burned. Therefore, it is very probable that the thermochemical characteristics of the C–C and C–H linkages really remain constant in these 5 hydrocarbons.

The comparison of the values obtained above with those computed by the first-mentioned method is very interesting, but we must observe that only Thomsen's data are to be considered for this comparison, because the correction of Berthelot's measurements, performed in 1887 and 1901, is attended by many difficulties. Thomsen's data can be in some degree corrected because his apparatus was designed for the combustion of gaseous substances and all the details of his experiments are sufficiently known. When, therefore, we introduce the corrections (1) for changing his thermometer readings to the hydrogen scale (a diminution of about —0.3%), and (2) for the newer determinations of the heat capacity of water (also a diminution of about —0.1%), we are justified in believing that the remaining corrections are small and are due chiefly to impurities in the burned samples.

The corrected and uncorrected values of Thomsen for A_1 and A_2 for methane and ethane, and the thermochemical characteristics X and Y are as follows.

	Uncorr.	Corr.		
Methane	211.9	$A_1 = 211.1$	$X = -52.78$ cal.	$Z = -157.8$ cal.
Ethane	370.4	$A_2 = 368.9$	$Y = -52.22$ cal.	

There is complete agreement between the values for X, Y and Z, calculated in these different ways. As a consequence it is most probable that the thermochemical characteristics of the C–C and C–H linkings in the 7 different hydrocarbons mentioned are really constant.

Furthermore, the values obtained for X, Y and Z can be adopted as a basis for the thermochemical analysis of other hydrocarbons in order to

TABLE II.

No.[1]	Name.	Formula.	A_{gas}.	$\Sigma X \underset{(-)}{+} \Sigma Y$.	$\Sigma\Delta(x,y)$.
	1. Derivatives of Cyclobutane.				
2.	Methyl-cyclobutane..........	C_5H_{10}	792.1	788.9	—3.2
	2. Derivatives of Cyclopentane.				
3.	Cyclopentane................	C_5H_{10}	791.5	788.9	—2.6
7.	Methyl-cyclopentane.........	C_6H_{12}	947.4	946.6	—0.8
16.	1,3-Dimethyl-cyclopentane...	C_7H_{14}	1102.1	1104.4	+2.3
23.	1,2,4-Trimethyl-cyclopentane	C_8H_{16}	1259.2	1262.2	+3.0
29.	1-Methyl-*n*-propyl-cyclopentane	C_9H_{18}	1418.9	1419.9	+1.0
	3. Derivatives of Cyclohexane.				
8.	Cyclohexane.................	C_6H_{12}	946.2	946.6	+0.4
17.	Methyl-cyclohexane..........	C_7H_{14}	1104.2	1104.4	+0.2
24.	1,1-Dimethyl-cyclohexane.....	C_8H_{16}	1256.4	1262.2	+5.8
25.	1,3-Dimethyl-cyclohexane.....	C_8H_{16}	1252.4	1262.2	+9.8[2](?)
26.	1,4-Dimethyl-cyclohexane.....	C_8H_{16}	1243.2	1262.2	+19.0(?)
30.	1,2,3-Trimethyl-cyclohexane....	C_9H_{18}	1413.3	1419.9	+6.6
31.	1,3,3-Trimethyl-cyclohexane...	C_9H_{18}	1411.5	1419.9	+8.4
37.	1-Methyl-*n*-propyl-cyclohexane	$C_{10}H_{20}$	1572.8	1577.7	+4.9
	4. Derivatives of Cycloheptane.				
18.	Cycloheptane................	C_7H_{14}	1100.6	1104.4	+3.8
27.	Methyl-cycloheptane.........	C_8H_{16}	1260.2	1262.2	+2.0
32.	Ethyl-cycloheptane..........	C_9H_{18}	1426.1	1419.9	—6.2[2](?)

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[1] The numbers correspond to those in the tables of Zubow's data published in THIS JOURNAL, 42, 1092 (1920).

[2] It seems to me that the values for the 2 dimethyl-cyclohexanes (1,3) and (1,4) are too small, and that for ethyl-cycloheptane too great. The heats of combustion for these compounds should be redetermined.

find out whether the heats of combustion of the C–C and C–H linkages remain constant or change with the constitution.

The Polymethylene Hydrocarbons.

The equation of combustion for a polymethylene hydrocarbon C_nH_{2n} is $nY + 2nX + \Sigma\Delta(x, y) + A = 0$; or, $nZ + \Sigma\Delta(x, y) + A = 0$. Whence we can compute the increment, $\Sigma\Delta(x,y) = -A - nZ$.

In Table II are given the corresponding data for the 17 polymethylene hydrocarbons, burned by P. W. Zubow.

Examining the above mentioned values of $\Sigma\Delta(x, y)$ we note that the heats of formation of the atomic linkings C–C and C–H are not constant, but depend upon the structure of the hydrocarbons. Indeed, if we should simplify the analysis by supposing x = const., or $\Sigma\Delta x = 0$, then by dividing the increments $\Sigma\Delta y$ by the number of the C–C linkings in the ring, we obtain the following comparison.

TABLE III.

	Formula.	$\Sigma\Delta y/n$.
Polymethylene Hydrocarbons.		
Cyclopentane	C_5H_{10}	—0.5
Cyclohexane	C_6H_{12}	+0.1
Cycloheptane	C_7H_{14}	+0.5
Methyl Derivatives.		
Methyl-cyclobutane	C_5H_{10}	—0.8
Methyl-cyclopentane	C_6H_{12}	—0.2
Methyl-cyclohexane	C_7H_{14}	+0.0
Methyl-cycloheptane	C_8H_{16}	+0.3
Dimethyl Derivatives.		
1,3-Dimethyl-cyclopentane	C_7H_{14}	+0.5
1,1-Dimethyl-cyclohexane	C_8H_{16}	+1.0
1,3-Dimethyl-cyclohexane	C_8H_{16}	+1.7 (?)
1,4-Dimethyl-cyclohexane	C_8H_{16}	+3.1 (?)
Trimethyl Derivatives.		
1,2,4-Trimethyl-cyclopentane	C_8H_{16}	+0.6
1,2,3-Trimethyl-cyclohexane	C_9H_{18}	+1.1
1,3,3-Trimethyl-cyclohexane	C_9H_{18}	+1.4
Methyl-*n*-propyl Derivatives.		
1-Methyl-3-*n*-propyl-cyclopentane	C_9H_{18}	+0.2
1-Methyl-3-*n*-propyl-cyclohexane	$C_{10}H_{20}$	+0.8

Table III is self-explanatory. We see that increasing the number of carbon atoms in the ring causes a remarkable increase in the heat of formation of the C–C linkings, and that the introduction of the methyl or the methyl and *n*-propyl groups does not affect this property.

On the other hand, the heat of formation of C–C linkings increases on the introduction of methyl groups in the polymethylene hydrocarbons.

TABLE IV.

Derivatives of Cyclopentane.		Derivatives of Cyclohexane.	
Name.	$\Sigma\Delta y/n$.	Name.	$\Sigma\Delta y/n$.
Cyclopentane	—0.5	Cyclohexane	+0.1
Methyl-cyclopentane	—0.2	Methyl-cyclohexane	+0.0
1,3-Dimethyl-cyclopentane	+0.5	1,1-Dimethyl-cyclohexane	+1.0
1,2,4-Trimethyl-cyclopentane	+0.6	1,2,3-Trimethyl-cyclohexane	+1.1

These facts show that the constancy of the heat of formation of the C–C and C–H linkings found in the 7 hydrocarbons first chosen cannot be accepted as a general property, but on the contrary the variability in the heat of formation of these linkings must be accepted as definitely confirmed. This variation is, however, not considerable and can be discovered only by means of very exact measurements, and by burning very pure substances.

The Unsaturated Hydrocarbons.

Our equations of combustion for hydrocarbons containing unsaturated C=C linkings, do not differ from the above mentioned ones for saturated hydrocarbons and for naphthalene, but the introduction of the symbol $2y_2$ for the heat of formation of the C=C linking is more convenient for computation. The equation of combustion for an unsaturated hydrocarbon $C_nH_{2n} + m$ is then as follows

$$(n-2)(y+w-2z) + 2n(x+w-z-u) + 2(y_2+w-2z) + \Sigma\Delta(x,y) + A = 0.$$

Rearranging, we obtain.

$$n(y+w-2z) + 2n(x+w-z-u) + \Sigma\Delta(x,y) - 2(y-y_2) + A = 0$$

or

$$nY + 2nX + \Sigma\Delta(x,y) - 2(y-y_2) = 0$$

and finally

$$2(y-y_2) - \Sigma\Delta(x,y) = A + \Sigma X + \Sigma Y,$$

The term $2(y-y_2)$ shows the difference between the heats of formation of 2 single bonds C–C and of a double one C=C.

P. W. Zubow burned a considerable number of unsaturated polymethlene hydrocarbons, and 2 aliphatic hydrocarbons. In Table V are collected the corresponding data and the computed values.

Table V shows a marked variability in the magnitude of $2(y-y_2) - \Sigma\Delta(x,y)$. The small number of aliphatic hydrocarbons investigated do not permit of any generalization. It is clear only that the heat of formation of the C=C linking is smaller than that of 2 single C–C linkings. If we accept this variability of the two terms $2(y-y_2)$ and $\Sigma\Delta(x,y)$, it is also very probable that the sum $2(y-y_2) - \Sigma\Delta(x,y)$ can increase, diminish, or remain constant, depending upon how the separate terms change.

TABLE V.

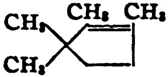
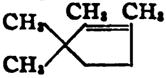
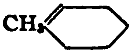
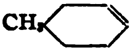
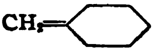
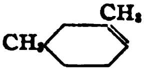
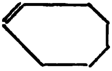
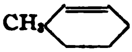
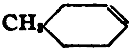
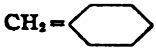
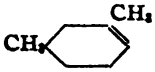
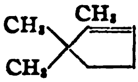
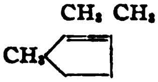
No.	Name.	Formula and Structure.	A_{gas}.	$\Sigma X + \Sigma Y$ (—)	$2(y-y_2)$ — $\Sigma\Delta(x,y)$.
		Aliphatic Hydrocarbons.			
9.	Hexylene................	C_6H_{12} $C_3H_7.CH = CH.CH_3$	961.9	946.6	15.3
1.	Trimethyl-ethylene......	C_5H_{10} $(CH_3)_2C = CH(CH_3)$	803.2	788.9	14.3
		Derivatives of Cyclopentene.			
20.	Trimethyl-cyclopentene.	C_8H_{14} 	1206.9	1208.9	—2.0
21.	Laurolene.............	C_8H_{14} 	1207.0	1208.9	—1.9
		Derivatives of Cyclohexene.			
6.	Cyclohexene...........	C_6H_{10} 	900.9	893.4	7.5
11.	Methyl-(1)-cyclohexene-(1)...............	C_7H_{12} 	1053.6	1051.1	2.5
12.	Methyl-(1)-cyclohexene-(3)...............	C_7H_{12} 	1055.9	1051.1	4.8
13.	Methylene-cyclohexene..	C_7H_{12} 	1056.6	1051.1	5.5
22.	1,3-Dimethyl-cyclohexene...............	C_8H_{14} 	1209.5	1208.9	0.6
		Derivative of Cycloheptene.			
15.	Cycloheptene...........	C_7H_{12} 	1063.0	1051.1	11.9

TABLE VI.

No.	Name.	Formula.	Structure.	$2(y-y_2)$— $\Sigma\Delta(x,y)$.	$\Sigma\Delta(x,y)$.	$2(y-y_2)$.
6.	Cyclohexene..................	C_6H_{10}		7.5	0.0	7.5
11.	Methyl-cyclohexene-1,1.........	C_7H_{12}		2.5	0.2	2.7
12.	Methyl-cyclohexene-1,3.........	C_7H_{12}		4.8	0.2	5.0
13.	Methylene-cyclohexane.........	C_7H_{12}		5.5	0.2	5.7
22.	1,3-Dimethyl-cyclohexene-3.....	C_8H_{14}		6.6	5.8	6.4
20.	Trimethyl-cyclopentene.........	C_8H_{14}		—2.0	3.0	1.0
21.	Laurolene....................	C_8H_{14}		—1.9	3.0	1.1

With regard to polymethylene hydrocarbons containing the C=C linking, the diminution of $2(y-y_2)-\Sigma\Delta(x,y)$ is very remarkable. It can depend upon 2 causes: upon the diminution of the heat of formation of the

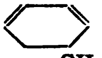
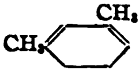
C=C linking, $2y_2$; or upon the increase of $\Sigma\Delta(x,y)$. But above we observed in the case of methyl derivatives of polymethylene hydrocarbons the increase of these numbers, then simplifying the analysis we can suppose that the increases $\Sigma\Delta(x,y)$ remain the same in the case of saturated and unsaturated hydrocarbons, C_nH_{2n} and C_nH_{2n-2}.

Accepting this supposition, Table VI gives the corresponding data.

In spite of the approximate nature of these calculations, it is clear that the heat of formation of the unsaturated C=C linking varies within very wide limits. It is also probable that $2(y - y_2)$ can in separate cases be equal to zero, when $2y = 2y_2$ (for example in naphthalene), or may differ but little from zero as in the case of laurolene and isolaurolene.

The data for hydrocarbons containing 2 unsaturated bonds could also be used for the confirmation of the above statements, if the number of hydrocarbons which have been investigated were not so few.

TABLE VII.

No.	Name.	Formula.	Structure.	$A_{gas.}$	$\frac{\Sigma X+\Sigma Y}{(-)}$	$\frac{4(y-y_2)-}{-\Sigma\Delta(xy)}$.
4.	Dihydrobenzene...............	C_6H_8		843.1	840.1	3.0
13.	1,3-Dimethyl-dihydrobenzene,	C_8H_{14}		1162.7	1155.6	7.1

If we accept the constancy of $\Sigma\Delta(x,y)$ in the saturated and unsaturated hydrocarbons, we obtain the following numbers for $2(y - y_2)$,

	$4(y-y_2)-\Sigma\Delta(x,y)$.	$\Sigma\Delta(x,y)$.	$2(y-y_2)$.
Dihydrobenzene[*].....................	3.0	0.0	1.5
1,3-Dimethyl-dihydrobenzene..........	7.0	5.8	6.4

[*] It must also be noted that Zubow's value 843.1 for dihydrobenzene does not agree with Stohmann's. The latter made a correction for the gaseous state of +9.9 cal., for the hydrogen scale of —0.3%, and for the true heat capacity of water of —0.1%, giving 856.4. If we accept this number, we obtain $4(y - y_2) - \Sigma\Delta(x,y) = 16.3$ or $2(y - y_2) = 8.1$.

The same results can be obtained in another way, namely, by using data corresponding not to the substances in the gaseous state, but to the liquid at 18°. If we subtract, for example, the equation of combustion of cyclohexene from the one for cyclohexane,

$$\text{Cyclohexane:}\quad 6Y + 12X + \Sigma\Delta(x,y) + A_1 = 0.$$

$$\text{Cyclohexene:}\quad 2(y - y_2) + 7Y + 10X + \Sigma\Delta'(x,y) + A_2 = 0$$

we obtain,

$$-2(y - y_2) + 2X - Y + \Sigma\Delta(x,y) - \Sigma\Delta'(x,y) + A_1 - A_2 = 0.$$

Assuming $\Sigma\Delta(x,y) = \Sigma\Delta'(x,y)$, we can compute $2(y - y_2) = A_2 - A_1 - 2X + Y$, where $X = -52.76$ cal., $Y = -52.25$ cal., $A_1 = 936.3$ cal., and $A_2 = 891.2$ cal. Finally $2(y - y_2) = 8.2$ cal. Similarly, by the first method of computation, we obtained $2(y - y_2) = 7.5$ cal.

Table VIII gives several examples of this computation.

TABLE VIII.

Compared hydrocarbons.	A_2.	A_1.	$2(y - y_2)$.	Computated by the first method.
Methyl-1-cyclohexene-1. Methyl-cyclohexane....	1040.9	1091.8	2.4	2.7
Methyl-1-cyclohexene-3..........................	1043.6	1091.8	5.1	5.0
1,1,2-Trimethyl-cyclopentene-2. 1,2,4-Trimethyl-cyclopentane......................	1193.3	1245.4	1.2	1.0

The complete agreement of the results obtained shows that both methods can be used to evaluate $2(y - y_2)$.

Summary.

1. By analysis of the equations for the combustion of hydrocarbons we obtain the terms $(y + w - 2z) = Y$ and $(x + w - z - u) = X$, corresponding to the heats of combustion of the linkings C–C and C–H. These terms have been named the thermochemical characteristics of the C–C and C–H linkings.

2. The analysis showed the constancy of the thermochemical characteristics of the C–C and C–H linkings in the following 5 hydrocarbons, *n*-hexane, *n*-octane, *n*-decane, cyclohexane, and naphthalene. Therefore, if the molecule of naphthalene contains the double bond C=C, the heat of formation of this double bond is exactly the same as that of 2 single C–C linkings.

3. Likewise the thermochemical characteristics of C–H and C–C bonds are the same in methane and ethane as in the above mentioned 5 hydrocarbons, the computation being based on the corrected data of Thomsen.

4. The following values for the thermochemical characteristics of C–C and C–H linkages and of the homologous difference were computed and adopted, $x = -53.72$ cal., $Y = -52.25$ cal., $Z = 2X + Y = -157.77$ cal.

5. In spite of the proved constancy of the thermochemical characteristics of the C–C and C–H linkages in 5 saturated, one polymethylene and one aromatic hydrocarbons, further analysis has shown its variability in other hydrocarbons which have been examined.

6. It is definitely established, that the heat of formation of the C–C linking increases with the increase in the number of carbon atoms in the ring of polymethylene hydrocarbons, and that the heat of formation of the same linking is increased by the replacement of a hydrogen atom by a methyl or *n*-propyl group.

7. The increase in y is not considerable. In the case of polymethylene hydrocarbons it varies within the limits -0.5 to $+0.5$ in the series of cyclopentane, cyclohexane, and cycloheptane. It varies within the limits -0.8 to $+1.7$ when 1, 2, or 3 methyl groups are introduced in the molecule of the polymethylene hydrocarbons which have been studied.

8. The analysis of the data on unsaturated hydrocarbons shows a very

important difference 2 $(y - y_2)$ between the heat of formation of 2 single linkages, C–C, and of the double one, C=C. This difference, due to the change of constitution of the hydrocarbons examined, varies within the very large limits +8.0 cal. to +1.0 cal. In special cases it is possible that $2(y - y_2)$ can be equal to zero (for example, in naphthalene).

All of these computations are based on the newly corrected, very exact measurements, accumulated by only one investigator, P. W. Zubow.

The values of thermochemical characteristics can at present be considered as rough material for further mathematical elaboration of theories of valence.

WARSAW, POLAND.

[THIRTIETH CONTRIBUTION FROM THE COLOR LABORATORY, BUREAU OF CHEMISTRY, DEPARTMENT OF AGRICULTURE.]

"THE ABSORPTION SPECTRA OF THE NITRIC ESTERS OF GLYCEROL."

BY ELLIOT QUINCY ADAMS.

Received March 18, 1920.

Hepworth,[1] from a study of the absorption spectra of the nitric esters of glycerol, concludes that it is evident that:

"(1) The labile and stable forms of nitroglycerin are physical isomerides, and both forms are identical in aqueous solution.

"(2) Commercial nitroglycerin is more absorptive than pure nitroglycerin.

"(3) The order of increasing absorption in aqueous solution is β-mononitrate, α-mononitrate, α,γ-dinitrate, α,β-dinitrate, and tri-nitrate.

"(4) α-Methylin[2] dinitrate is rather more absorptive than glycerol α,β-dinitrate.

"(5) The displacement of a hydrogen atom of one of the hydroxyl groups of glycerol by a nitro group produces a much more profound change in the absorption spectrum than the displacement of one or both hydrogen atoms of the remaining hydroxyl groups.

"(6) There does not appear to be any numerical proportionality between the number of hydrogen atoms of the hydroxyl groups displaced by nitro groups and the degree of absorption for any particular dilution."

The absorption spectra are given in 3 plots of the logarithm of the relative thickness in mm. of 0.00005 *N* aqueous solution against the oscillation frequency.[3]

To determine whether there is any proportionality between the number of nitrate radicals and the absorption, it is necessary first to consider

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[1] Harry Hepworth, *J. Chem. Soc.*, 115, 840–7 (1919).

[2] α-Methylin is glycerol α-methyl ether. The parts of the summary in fine print are not referred to again in this paper.

[3] In the scales of logarithms a decimal point has been omitted. It is fairly evident that the standard concentration is 1/20,000 *gram molecular*. The oscillation frequency is the reciprocal of the wave length in mm.

what relation is to be expected. A solution showing the normal relation between concentration and absorptive power is said to obey Beer's Law, if the product of concentration and thickness of layer be kept constant, the absorption will remain the same. For such a solution the logarithm of the ratio of incident to transmitted light divided by the concentration and by the thickness gives a constant, known as the "specific extinction coefficient" or the "molecular extinction coefficient" according, respectively, as the concentration is in grams per liter or mols per liter. A fair comparison of substances of different molecular weight requires the use of the molecular extinction coefficient, or of some quantity proportional to it. To obtain such a value for the *relative molecular extinction coefficient*, or more briefly the absorptive power, from the plots of Hepworth, the intercepts of the ordinates for oscillation frequencies $\nu = 4200$ mm.$^{-1}$ (reciprocal millimeters) and $\nu = 4300$ mm.$^{-1}$ between the several curves and the top lines of the plots (log relative thickness = 4) have been read and the numbers corresponding to these logarithms recorded in Table I as A_ν/C.

The "calculated" values of the absorptive power assume equal effect for each nitrate radical, and have been obtained by taking at each oscillation frequency $^1/_9$, $^2/_9$, and $^1/_3$, respectively, of the sum of the absorptions of the 5 nitrates. It will be seen that the agreement is all that can be expected until account is taken of the difference between isomers.

Table I.—Relative Molecular Extinction Coefficients.

Designation according to			$\nu = 4200$ mm.$^{-1}$.			$\nu = 4300$ mm.$^{-1}$.			Mean.[c]	
Will.	Adams.		log.[a]	A_ν/C.	Calc.[b]	log.[a]	A_ν/C.	Calc.[b]	A_ν/C.	Calc.[d]
-	-	Glycerol	[$-\infty$]	0	0	[$-\infty$]	0	0	0	0
β-	α-	Mononitrate	0.18	1.5	1.7	0.62	4.2	4.2	2.8	2.5
α-	β-	Mononitrate	0.30	2.0		0.74	5.5		3.8	3.8
$\alpha\gamma$-	$\alpha\gamma$-	Dinitrate	0.39	2.5	3.3	0.84	6.9	8.5	4.7	5.0
$\alpha\beta$-	$\alpha\beta$-	Dinitrate	0.54	3.5		0.95	8.9		6.2	6.2
$\alpha\beta\gamma$-	$\alpha\beta\gamma$-	Trinitrate	0.74	5.5	5.0	1.10	12.6	12.7	9.0	8.8

[a] Obtained by reading down from top line of plots of Hepworth, *loc. cit.*, p. 842. The succession of integers and half-integers at $\nu = 4200$ mm.$^{-1}$ suggests that readings were taken at this oscillation frequency (among others) and with an accuracy of 0.5 unit of the (arbitrary) scale of relative absorptive power (relative molecular extinction coefficient).

[b] Assuming equal effect for each nitrate radical; this is, of course, only a first approximation.

[c] Since the experimental error in such measurements is considerable, the final comparison is made on the mean of the 2 absorption values.

[d] Assuming 2.5 for the effect of a nitrate radical in $\alpha(=\gamma)$ position and 3.75 for one in the β-position. See Figs. 1 and 2.

The difference between isomers is most simply explained as due to the difference in the absorptive effect of a nitrate radical according as its attachment to carbon is primary or secondary. As the designations

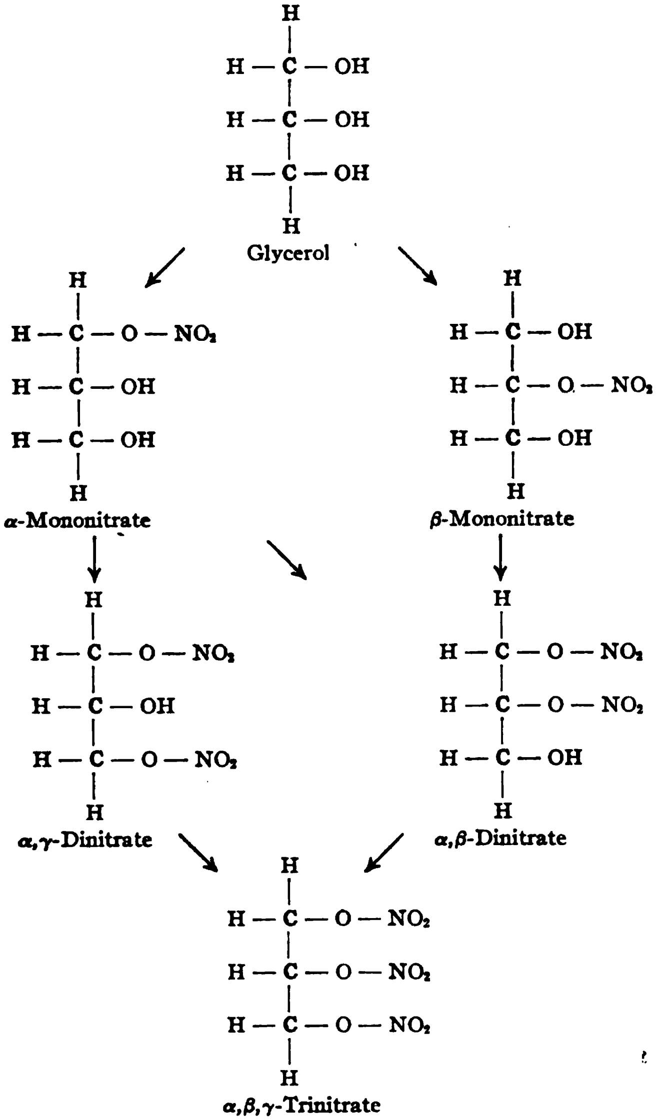

Fig. 1.

for the isomers, as given by Hepworth, are not compatible with such an explanation, it will be well to examine the evidence for those designations.

Hepworth (*loc. cit.*) gives no evidence for the designations, other than that given by the work of Nef[1] and Will.[2] Nef prepared "Glycidnitrat"

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[1] J. U. Nef, "Dissociationsvorgänge in der Glycol-Glycerinreihe," *Ann.*, 335, 238 (1904).

[2] W. Will, "Über Glycerin-nitrate," *Ber.*, 41, 1107–25 (1908).

by the interaction of epi-iodohydrin and silver nitrate. This substance, on heating with water at 100°, gave an oil easily soluble in water and ether, "welches wohl α-Mono-nitroglycerin darstellt." Will prepared the entire series of nitrates and established their composition by the analysis of their derivatives, particularly the nitrobenzoyl esters. He inferred the constitution of the isomeric mono- and dinitrates from the products resulting from the further nitration of the mononitrates (see Fig. 1), the mononitrate from which 2 dinitrates were obtained being called α, and that from which only one dinitrate resulted, β. Since mixed melting point observations prove the identity of his α-mononitrate with that prepared by the method of Nef, the results of these two investigators agree, and both must be accounted for before any change can be made in the designations of the mononitrates.

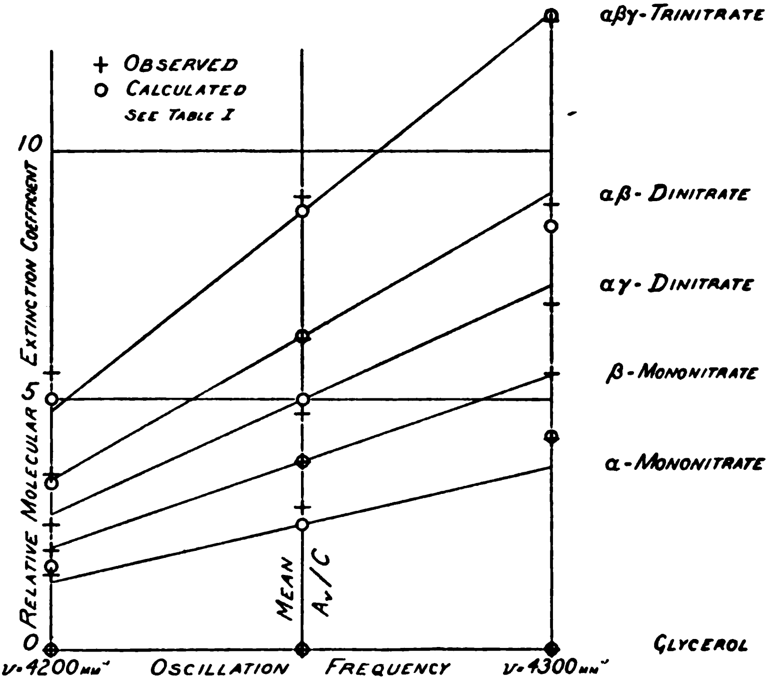

Fig. 2.

Will states[1] "In the investigation of the nitration it is further shown that the β-mononitrate is more readily nitrated to the trinitrate than is the α-mononitrate. By cautious nitration to the dinitrate the β-mononitroglycerin does not furnish both dinitroglycerins, as the mononitrate melting at 58° does, but it was possible to obtain only one such, namely,

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[1] *Loc. cit.*, pp. 1119, 1121. In one case conc. nitric acid, sp. gr. 1.52, was used; in the other dilute acid (20% H_2O).

the dinitrate designated above as dinitroglycerin F." The trinitrate was formed also in both cases. The significance of this marked difference in ease of nitration must be considered further.

Differences in the rates of nitration of the various mono- and dinitrates will be due to 2 factors, an intrinsic difference in the reactivity of hydroxyls in the α- and β-position, and the steric effect of the nitrate radicals already present. These may act in 2 ways, they may, by their size or mass, decrease the reactivity of neighboring groups, the familiar "steric hindrance;" and they may be so situated as to render the molecule optically active. Since nitric acid is a substance optically inactive, and since in no case do enantiomorphs behave differently with inactive reagents, there is no reason to expect the possibility or impossibility of optical activity to have any effect on the rate of nitration. If the α-hydroxyl were the reactive one, no great difference in the reactivity of the two mononitrates should be expected (see Fig. 1), since both have at least one such hydroxyl, and the steric hindrance will be less in the case of the α-mononitrate which has only one. If, on the other hand, the β-hydroxyl is the more reactive, the α-mononitrate, which has it, should be appreciably more reactive.

On the basis of this assumption the following behavior with dil. nitric acid is to be expected with the β-mononitrate little or no action, since it has only unreactive hydroxyls blocked by an adjacent nitrate radical; with the α-mononitrate the principal product, by replacement of the reactive hydroxyl, will be the α,β-dinitrate which will not react further, but the unblocked α-hydroxyl may be expected to react to some extent, giving the α,γ-dinitrate, the reactive β-hydroxyl of which will be replaced to give the trinitrate. This agrees in all details with the *results* of Will,[1] but requires a reversal of his designations α- and β- for the mononitrates.

The relatively unreactive β-mononitrate, on treatment with conc. nitric acid would give in the first instance the α,β-dinitrate, by the further nitration of that compound the trinitrate; the rise in temperature resulting from the dilution of the excess of conc. nitric acid with water[2] would cause a partial hydrolysis of the trinitrate to give the α,γ-dinitrate; hence the ether extract of the resulting solution will contain (as Will found) both dinitrates and some trinitrate.

It remains to account for the production of the β-mononitrate by the method of Nef from "glycidnitrat,"[3] by the action of boiling water. By reference to Fig. 3 it will be seen that "glycidnitrat" contains 2 particularly reactive groups; an ethylene oxide ring and a double bond. If a

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[1] W. Will, "Das α-mononitrat schied, unter gleichen Bedingungen nitriert, überhaupt kein Öl ab," *loc. cit.*, p. 1121.

[2] W. Will, *loc. cit.*, p. 1119.

[3] J. U. Nef, "Glycid is γ-hydroxy-propylene oxide," *loc. cit.*

rearrangement occurs, there would be formed glyceryl orthonitrate[1] which, by the addition of water, could give either mononitrate. Again, "glycidnitrat" is insoluble in water; hydrolysis to "glycid" and nitric acid would permit it to go into solution. In a subsequent addition of nitric acid to the ethylene oxide ring the negative nitrate radical would be expected, by analogy to additions to unsaturated hydrocarbons, to add to the β-carbon atom. Finally, if the "glycid" should first hydrate to glycerol, the nitration of this, according to the results of Will,[2] should

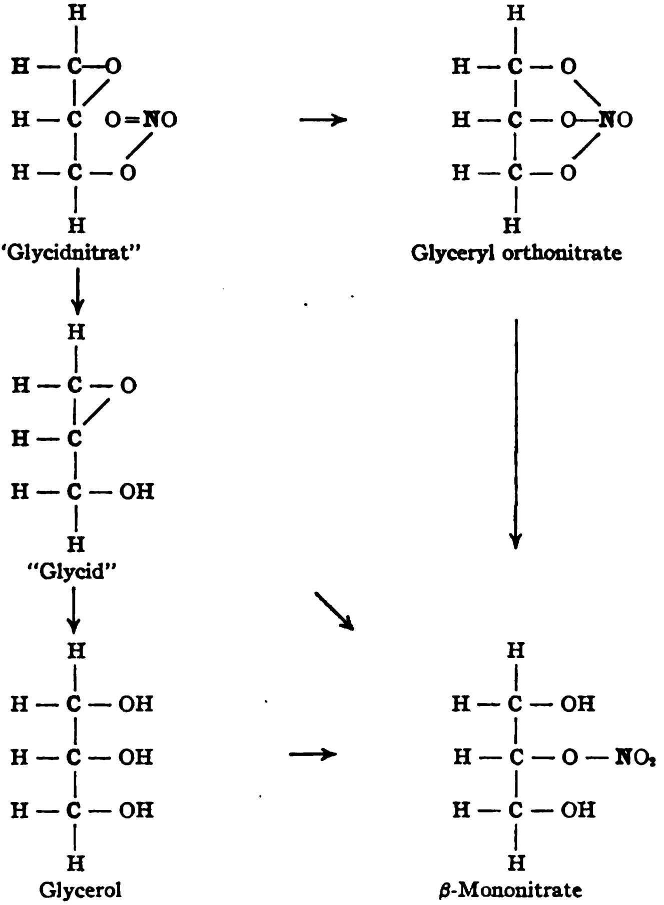

Fig. 3.

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[1] Orthonitrates have not been described. Orthophosphates and orthosilicates are well known; orthocarbonates are unknown as salts but have been prepared as esters, and by analogy the same should be true of the orthonitrates.

[2] W. Will, *loc. cit.*, p. 1121. It should be borne in mind that Will's use of the prefixes α- and β- is exactly the reverse of that in the text above, as concerning the substances designated; in both cases it signifies the structure assigned to the compounds.

give a product 96–97% of which would be the same β-mononitrate. While no one of these reactions is proved to occur, the formation of a mononitrate from "nitroglycid" cannot be said to prove that it is the α-mononitrate when it is possible to account for the production of the β-mononitrate in 3 different ways.

To return to a consideration of the relation between constitution and absorptive power; the last two columns of Table I compare the mean of the absorptions observed at ν = 4200 mm.$^{-1}$ and ν = 4300 mm.$^{-1}$ with values calculated, assuming that each "primary" nitrate radical contributes 2.5 to the mean relative absorptive power, and each "secondary" nitrate radical 3.75.[1] The agreement between the absorptions observed and calculated is well within the probable error (about 0.35 unit).

Summary.

1. In plotting absorption spectra the use of the *logarithm* of the specific (or molecular) extinction coefficient should be avoided, since it tends to obscure the relation between constitution and absorption.

2. The designations α- and β- applied by Will[2] to the two mononitrates derived from glycerol, should be interchanged.

3. It is possible that the "glycidnitrat" described by Nef[3] is glyceryl orthonitrate.

4. The absorption spectra of the nitric esters of glycerol, as given by Hepworth,[4] can be completely accounted for on the assumption that each nitrate radical has an absorptive effect dependent upon its location in the molecule, but independent of the presence or absence of other nitrate radicals.

5. The absorptive effect of the nitrate radical is about 1.5 times as great when it replaces the β-hydroxyl of glycerol as when it replaces an α-hydroxyl.

WASHINGTON, D. C.

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[1] The accuracy of the data does not warrant expressing these numbers to better than quarter-units. The ratio of 2 : 3 between them is accidental.

[2] W. Will, "Über Glycerin-nitrate," *Ber.*, 41, 1107–25 (1908).

[3] J. U. Nef, *Ann.*, 335, 238 (1904).

[4] Harry Hepworth, *J. Chem. Soc.*, 115, 840–7 (1919).

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

A FORCE, APPARENTLY DUE TO MASS, ACTING ON AN ELECTRON, AND THE NON-IDENTITY OF ISOTOPES IN SPECTRA AND OTHER PROPERTIES.

BY WILLIAM D. HARKINS AND LESTER ARONBERG.

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Both electrostatic and gravitational forces follow an inverse square law, and the constants are such that the gravitational force is only 4.1×10^{-40} times the electrostatic,[1] when one of the masses consists wholly of positive, and the other of negative electrons. The smallness of such a gravitational force would seem to indicate that when an electron in the outer part of an atom vibrates under the restraining force due to the attraction of the positive charge on the nucleus of the atom (modified by the effects of the adjacent negative electrons), its vibration will depend wholly upon the charge and not at all upon the mass of the nucleus, insofar as experimental methods are able to decide. It need not, then, be surprising that Bohr's first equation[2] for the possible frequencies emitted by the simplest atoms, such as hydrogen and helium, contained no term which took account of the mass of the nucleus. However, Fowler, in a discussion in *Nature*,[3] pointed out that certain of the formulas which had been used did not give accurately the lines found by him, and this led Bohr to show that the deviations could be accounted for by the introduction of a term for the mass of the central nucleus. Thus the Bohr equation[4] became

$$\nu = \frac{2\pi^2 e^2 E^2\, mM}{h^3\,(M + m)} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

where ν is the frequency of the emitted light, e and E, and m and M, are the charge and mass of the electron and the nucleus, respectively. It is clear that this equation does not assume the existence of any force due to the mutual action of the masses of the positive and the negative electron, since the mass term is introduced for the purpose of correcting for the displacement of the nucleus from the center of gravity of the system, negative electronucleus, with a change in the mass of the nucleus.

Five years ago it occurred to one of the writers that the best test of the effect of mass as independent of a net charge, in attracting a negative electron, could be made by the use of isotopes, such as those of lead, for the net positive charge on the nuclei of isotopes is the same, but the mass is

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[1] Richardson, "The Electron Theory of Matter," p. 590. Cambridge University Press, 1914.

[2] *Phil. Mag.*, 26, 10 (1913).

[3] *Nature*, 92, 95 (1913).

[4] *Ibid.*, 92, 231 (1913).

different. It seemed, however, both from the standpoint of theory and of past experimental experience, that there was little chance for the discovery of such an effect, since the Bohr theory predicted a difference between the wave length of the principal line in the spectrum of ordinary lead and of that derived from radium (radium G), of only 0.00005 Ångstrom, which is too small a difference to detect by the use of even the eschelons and gratings which give the highest dispersion. In addition to this prediction of theory, there was the fact that at least 7 careful experimental investigations had all resulted in the conclusion that the spectra of isotopes are *identical*. These investigations were as follows: those of Russell and Rossi,[1] and of Exner and Haschek,[2] using thorium and ionium; that of Aston[3] on the isotopes of neon; that of Soddy and Hyman[4] on lead from thorium and ordinary lead, and finally those of Richards and Lembert,[5] Hönigschmidt and St. Horivitz,[6] and of Merton,[7] on Radium G and ordinary lead. Merton used a grating, and finally a Fabry and Perot étalon, and concluded from his work with the latter that there is no difference in wave length as great as 0.003 Å. for the line λ4058 in the spectrum of ordinary lead and of radium G.

The Nature of Isotopes.

Isotopes are atomic species whose atoms contain the same number of planetary electrons, and, as is evidenced by the great likeness in their spectra, these electrons must form a system of almost, but, probably not quite, identical configuration. The net positive charge on the nuclei of isotopic atoms is the same, but either the stability or else the mass of the nuclei are different. In the radioactive series, isotopes derived from the same ancestor, either uranium or thorium, if they differ at all in mass, have nuclei which differ by an α-particle (the nucleus of a helium atom) and by 2 electrons, which may be called cementing electrons. If η is taken as the symbol of the hydrogen nucleus—the positive electron—and β as that of the negative electron, then the α-particle is $(\eta_4{}^+\beta_2{}^-)^{++}$. The α-particle together with the 2 cementing electrons which unite it to the rest of the nucleus, may be said to have the formula $((\eta_4{}^+\beta_4{}^-)$, which will be described by the term "helio group," and this has a zero net charge. That is, isotopes of different masses, if derived from the same ancestor, have nuclei which differ by one or two helio groups. Isotopes which are derived from different ancestors (uranium and thorium) have nuclei which differ by the group $(\eta_2{}^+\beta_2{}^-)$, which may be called the mu (μ) group,

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[1] *Proc. Roy. Soc. (London)*, 87, 478 (1912).

[2] *Sitz. Akad. Wiss., Wien (Abt. IIa)*, 121, 175 (1912).

[3] *Brit. Assoc. Meeting*, 1913, p. 403.

[4] *J. Chem. Soc.*, 105, 1402 (1914).

[5] THIS JOURNAL, 36, 1329 (1914).

[6] *Sitz. Akad. Wiss., Wien (Abt. IIa)*, 123, Dec. (1914).

[7] *Proc. Roy. Soc. (London)*, 91, 198 (1914).

by the difference between a mu and a helio group or by both a mu and a helio group. Among the light atoms the only known isotopes, those of neon discovered by Thomson, and those of chlorine, presumably separated by Harkins and Broeker,[1] and with atomic weights 35 and 37 as determined by the positive ray method by Aston,[2] differ by the mu group. It is probable too, that the isotopes of magnesium and silicon, claimed by Harkins to exist (provided the most recent atomic weights, 24.3 for magnesium and 28.1 for silicon are sufficiently exact), differ also by the mu group.

In addition to the groups specified above, there is another, which, like the α-group without its cementing electrons, does not by itself give rise to the existence of an isotope, since its net charge is one positive. This is either the λ^{+++} group, (lithium nucleus group) or the nu (ν^+) group. Which of these is the primary group cannot well be decided at the present time. If it is the ν or $(\eta_3{}^+\beta_2{}^-)^+$ group, then λ is equivalent to $\alpha\nu$. For the sake of simplicity the latter representation will be chosen. It is evident that isotopes might be formed by the addition of one ν group, together with one cementing electron. This would be equivalent in the sense of composition, to the inclusion of a group $\nu\beta$, or $\eta_3{}^+\beta_2{}^-\beta^-$, but does not imply that the third negative electron is directly associated with the other two. Isotopes might also be formed by the inclusion of one positive and one negative electron $(\eta^+\beta^-)$, though members of this last class have not been discovered, nor have those which contain the $\eta_3{}^+\beta_2{}^-\beta^-$ electron addition, but the latter may, and probably will, be discovered later in the range between atomic numbers 28 and 82.

The formula of lead from radium (radium G) is, according to Harkins,[3] $(\alpha_{51}{}^{++}\beta_{20}{}^-\mu)^{82+}e'_{78}e_4$, where e represents an electron in the valence shell, and e' a planetary electron in an inner shell. That of lead from thorite, of atomic weight 208, is $(\alpha_{52}{}^{++}\beta_{22}{}^-)^{82+}e'_{78}e_4$. Ordinary lead is either a mixture of these two isotopes, or it is an individual of the formula $(\alpha_{50}{}^{++}\lambda^{+++}\beta^-{}_{21})^{82}$ $e'_{78}e_4$ or $(\alpha_{51}{}^{++}\nu^+\beta_{21}{}^-)e'_{78}e_4$. These last two are simply two different symbolic expressions for the same composition. The atomic weight evidence is slightly in favor of the idea that it is a mixture of the two isotopes. Also, ordinary lead is much more stable than is to be expected in general for an atom of such high nuclear charge whose nucleus contains an *odd* number of *negative* electrons, since relative instability usually accompanies the presence of an odd number of negative electrons. If ordinary lead is an individual isotope, then each of its nuclei contains one positive and one negative electron in excess of those contained in the lead from radium, and, in any case, this is the average difference.

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[1] *Phys. Rev.*, **15**, 74 (1920); *Science, N. S.*, **51**, 289–91 (1920); *Nature*, **105**, 230–1 (1920).

[2] *Nature*, **104**, 392 (1919).

[3] *Phys. Rev.*, **15**, 73–94 (1920).

The Spectra of Isotopes.

The use of the conception of gravitational fields in an atom may be elucidated in the future by the newer relativity theory of Einstein, but such applications of the theory have not, as yet, been made. Since the gravitational fields upon which experiments are carried out are due to a large scale phenomenon, and to the resultant effect of 2 or more bodies which are practically neutral electrically, the effect of the addition of a neutral mass to the nucleus of an atom upon the vibration of an electron, a very small scale phenomenon, cannot be accurately predicted from the ordinary law of gravitation, which, as stated in the first paragraph, leads to the idea that such an effect is entirely negligible.

The details of the experimental work on the spectra of ordinary lead and a lead from radium of atomic weight 206.318, very kindly supplied by Professor T. W. Richards, were presented in 2 short notes[1] published 2 years ago. It was found that the wave length of the line λ4058 as obtained from the radio-lead was 0.0044 Å. greater than that from ordinary lead; that is, the difference in wave length found is *one-millionth of the total wave length,* or one-ten-thousandth of one per cent. *It is to be noted that this is an effect 100 times greater than that predicted by the theory of Bohr* and enormously greater than that predicted by the simple gravitational theory. This result was obtained in a most careful joint investigation carried out by Professor H. G. Gale and the writers. Sixteen comparison plates were taken, and a number of exposures were taken in which the spectra of 2 specimens of ordinary lead were compared. In every case, when the radio-lead and the ordinary lead were interchanged in their position with reference to the spectrograph, the shift in wave length followed the shift in position. The experimental work, carried out by the use of the Michelson 10-inch grating with a 30-foot Littrow mounting, used in the sixth order, was of such a character that there seemed to be no reasonable doubt of its correctness. There was certainly no doubt that the shift was real, since it could be easily seen. However, on account of the smallness of the wave length difference, and because it was nevertheless much greater than that predicted by Bohr's theory, it seemed best to defer our discussion of the meaning and importance of the result until it had been confirmed in a totally independent investigation. Recently[2] Merton has obtained such a confirmation, and finds that not only the direction, but also the magnitude of the shift obtained by him is the same within the limits of error, as that obtained by us. He did not use a grating, but a Fabry and Perot étalon. Our source of light was a Wali-Mohammed vacuum arc, Fig. 1, run at 0.04 mm. pressure, with a

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[1] Harkins and Aronberg, *Proc. Nat. Acad. Sci.*, 3, 710–15 (1917). "Note on the Spectrum of the Isotopes of Lead," Aronberg, *Astrophys. J.*, 47, 96–103 (1918).

[2] *Proc. Roy. Soc.* (*London*), 96A, 388–95 (1920).

current of 1.1 amperes and a voltage of 40. Merton used an arc produced between the lead and a piece of tungsten, and a current of one ampere at 100 volts, burning under a bell jar at a "fraction of a millimeter" of pressure. In our experiments the amperage and voltage were varied intentionally in some of the experiments, but without any noticeable effect upon the results. The shift in wave length found by Merton was 0.0050 Å. ± 0.0007 Å., while the average of 16 measurements as found by us was 0.0044 Å., an agreement within about twelve one-millionths of one per cent. of the total wave length which is not far from the experimental error. As stated, our radio-lead had an atomic weight equal to 206.312, while that of the lead used by Merton is not given in his paper. He found, also, a difference of 0.0022 Å. ± 0.0008 Å. between the wave length of ordinary and that of thorite lead, but the latter contained about 20% of ordinary lead, so its atomic weight is about 207.84. When it is considered that the difference in the atomic weights of the 2 forms of lead used by us is 0.89, while that between the thorite lead and ordinary lead used by Merton was about 0.6, it is seen that all of the measurements are in as good agreement as could be expected, *the electron in the heavier atom always showing the greater frequency, as would be predicted from theory if it is the additional mass in the nucleus which produces the effect.*

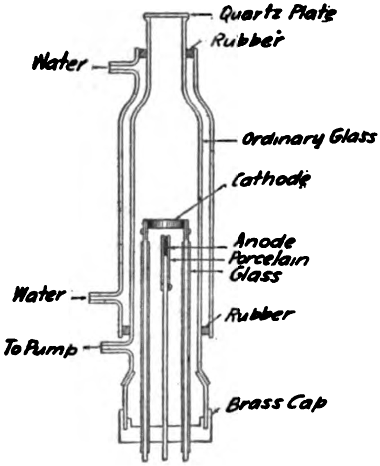

Fig. 1.

Thus there has been discovered an effect upon the vibration of an electron, the only apparent cause of which is the change in the mass of the nucleus of an atom, which must then be accompanied with a change in the force acting upon the electron, otherwise the vibration period of the latter would not be changed. The interest in this phenomenon lies in its close relationship to gravitation, and also in the fact that its magnitude far exceeds ordinary gravitation, which would seem to indicate that such small scale mass effects do not follow the same simple form of the law as large scale gravitational effects. It is possible that the effect discovered is due to the fact that the positive and negative electrons added to the nucleus, in the change from a lighter to a heavier lead, are not coincident in space, but this lack of coincidence is also present in the rest of the nucleus, and may also be related in some way to gravitational effects. Thus it is not unlikely that this newly-discovered effect is related in some way to the electromagnetic field in the atom, which is related in some unknown way to the large scale gravitational field.

The newer relativity assumes a proportionality between mass and weight, and by the results which it obtains, makes it seem probable that such a proportionality exists, but, on the other hand, the experimental tests of this relationship, though they have been carried out with great care and precision, as in the work of Eötvös, do not give as conclusive evidence as could be desired, since they have been carried out with materials of such a nature that the crucial test has not, as yet, been made, at least not with the attainable degree of accuracy. The newer theories of the constitution of the nucleus of the atom as worked out by Harkins,[1] suggest that for such a test one of the masses should consist wholly, or as largely as is possible, of hydrogen, while the other should contain no hydrogen, since the percentage change of mass which occurs in the formation of complex atoms is practically independent of the atom which is formed, provided hydrogen is taken as the material for their formation. Thus when hydrogen changes into helium, it seems probable that there is a decrease of mass equal to 0.77%, but when helium changes into any other complex atomic species, the change of mass is very much smaller, so small indeed that the present atomic weights are not sufficiently accurate to indicate that there is such a change. By taking one of the masses in the form of hydrogen and the other in the form of any other element or elements, it is thus possible to compare the weights and masses of 2 bodies, one of which is composed of material which *has not* been subject to this considerable packing effect, while the other *has* been affected by it. We do not mean to indicate that the results of such an experiment are likely to show that mass is not proportional to weight, but only wish to point out that the crucial experimental test of this relationship has not, as yet been made. It is likely that some of Newton's experiments were made with materials which would meet the above conditions for such a test, except for the fact that the technique had not been developed sufficiently at that time to give the work a sufficient degree of accuracy.

Spectra as a Means of Distinguishing between Isotopes.

Since the work reported here, and also that of Merton, indicates a change in wave length with a change in the atomic weight of isotopes, it is apparent that isotopes which differ in atomic weight may be distinguished by their spectra. It might seem, also, that when a mixture of isotopes is available, as in the case of the common element chlorine, the grating spectograph might be used as an instrument to detect their existence

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[1] THIS JOURNAL, 37, 1367–1421 (1915); 39, 856–79 (1917); *Phys. Rev.*, 15, 73–94 (1920).

in the mixture, without either subjecting it to an extremely lengthy and tedious separation. However, this supposition does not seem to be justified, at least in the case of lead, since the line seems to be shifted and not broadened. Let us make the assumption already presented, that ordinary lead is a mixture of about 60% of lead from thorium to 40 from radium. Line λ4058 has a width which depends upon the conditions in the arc, particularly the pressure. The lead from radium which we used would be composed, on the above basis, of about 85% of lead from radium, and 15% of lead from thorium, yet when its spectrum was taken under the same conditions, line λ4058 was found to be shifted as a whole in the direction to be expected as the result of a smaller atomic weight, that is to a greater wave length, the width of the line remaining about the same. In other words, the position of the line seems to correspond to the mean atomic weight of the lead in the specimen under investigation. It is, of course, possible, though not so probable, that the atomic weight of ordinary lead is slightly lower than the determined value, and that ordinary lead is an individual. In this case it is to be expected that the spectrum of the specimen of radium-lead used by us, which contained on this basis 25 or 30% of ordinary lead, would show a broadened line, but this was not the case.

Non-Identity of Isotopes in Chemical Properties.

The differences in the vibration frequencies of the *electrons* in isotopes indicate that they are not held by identical forces, so isotopes should not be identical from the chemical standpoint, though the difference should be exceedingly slight, and not capable of detection by chemical means now available, insofar as it is due to the mass effect upon the electrons. There is another effect due to the action of the different nuclear masses upon the vibration frequencies of the *atoms*, which may or may not be of a sufficient magnitude to give differences in vapor pressure and in chemical affinity which may be detected experimentally. This effect has been discussed from the standpoint of the quantum theory by Lindemann,[1] and by Lindemann and Aston.[2] Unfortunately the quantum theory is itself so indefinite that the deductions from it are altogether uncertain. The results of Soddy seem to indicate that lead and lead from thorium have the same atomic volume, and Richards[3] has shown in very precise experiments that both the atomic volumes and the melting points of lead and lead from radium are the same within the experimental errors. The wave length of the spectrum lines is the first property, aside from mass and atomic stability, in which isotopes have been found to differ, and it is the first property

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[1] *Phil. Mag.*, 38, 173–81 (1919).

[2] *Ibid.*, 37, 523–34 (1919).

[3] T. W. Richards, "Presidential Address to the American Association for the Advancement of Science" (1918), THIS JOURNAL, 38, 221 (1916).

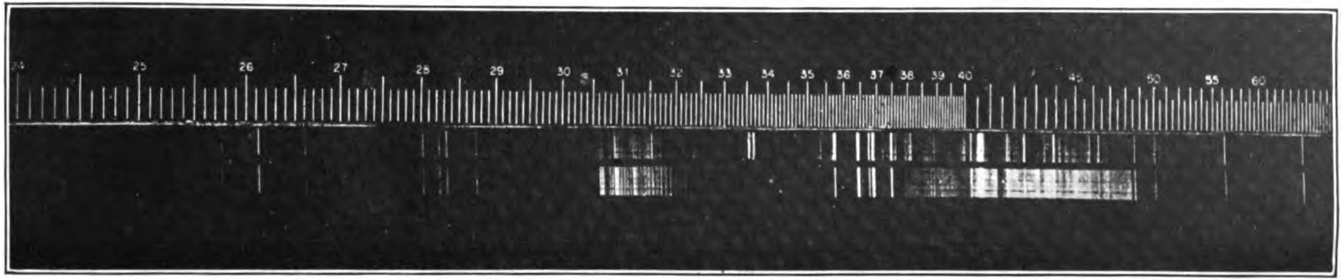

Fig. 2.—Spectrum of lead from radium (below) and ordinary lead (above). Differences in the spectra are due to small amounts of impurities. The specimens of lead used in the 16 final measurements were more highly purified than those whose spectra are given above. On the final plates comparison spectra for ordinary lead were taken both above and below. The dispersion was so high, however, that the plates give very few lines due to lead.

showing such a difference which is due to an effect on the planetary electrons.

CHICAGO, ILL.

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY. NO. 127.]

THE EQUILIBRIUM BETWEEN CHLORINE AND PLUMBOUS AND PLUMBIC CHLORIDES IN AQUEOUS SOLUTION.

BY ERNEST W. WESCOTT.

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1. Introduction.

Solutions of lead chloride in strong hydrochloric acid absorb chlorine in much larger quantities than can be accounted for by the solubility of the gas. The solutions exhibit a strong yellow color, and on the addition of ammonium chloride throw down a precipitate of clear yellow octahedral crystals. The composition of these crystals, which can be obtained in a state of great purity, has been found to be represented by the formula $(NH_4)_2PbCl_6$. Cesium and other chlorides produce precipitates of similar composition which in all cases are salts of the hypothetical acid, H_2PbCl_6. By treating the crystals of the ammonium salt with pure sulfuric acid at zero, there has been obtained the tetrachloride of lead, $PbCl_4$. This substance is a heavy yellowish oil, which reacts violently with water.

These facts suggest that the reaction occurring when chlorine is passed into a suspension of lead chloride in hydrochloric acid may be written as follows

$$PbCl_2(s) + Cl_2(g) + 2HCl = H_2PbCl_6;\ \text{or}$$

$$PbCl_2(s) + 2Cl^- + Cl_2(g) = PbCl_6^{--}.$$

The purpose of this investigation was to determine the equilibrium conditions of this reaction, with a view also to estimating the plumbous-plumbic reduction potential. Experiments were also made with acid concentrations small enough to permit the precipitation of solid lead dioxide; and the free energy of this compound was calculated from the equilibrium conditions of the reaction

$$PbCl_2(s) + 2H_2O + Cl_2(g) = PbO_2(s) + 4HCl.$$

This research has been carried out with the coöperation of Professor A. A. Noyes and with the aid of the grant made to him by the Carnegie

Institution of Washington. For all this assistance I wish to express my great indebtedness.

2. Preparation of the Equilibrium Mixtures.

The solutions were prepared in a great variety of ways during the preliminary work in an effort to approach equilibrium from both sides. Two of these may be mentioned.

In the first of these preliminary methods glass bombs were filled with lead chloride, hydrochloric acid, and chlorine in such excess that a layer of liquid chlorine was present. After shaking a month at 25°, these bombs were cautiously opened, the excess of chlorine was allowed to escape, and the solutions were then quickly analyzed. The concentration of the complex was shown to be much higher than in solutions prepared at atmospheric pressure. The experiments made by this method established the reversibility of the reaction, even in extreme cases, and showed the influence of chlorine pressure; but it proved not to be susceptible of accurate manipulation.

The other preliminary method tried was the direct production of the lead complex in excess, by allowing lead tetrachloride to act on the acid solution. This method was used with some success, but was abandoned because of the laboriousness of preparing the lead tetrachloride in the pure state.

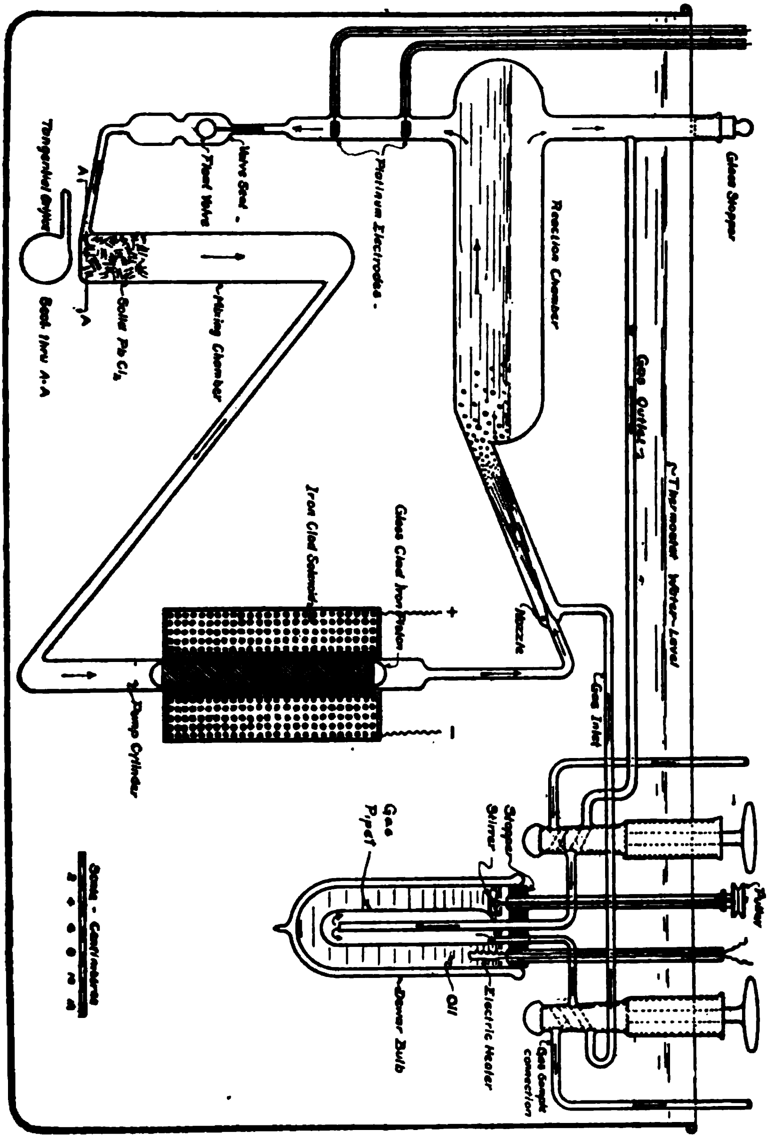
In the method finally adopted the equilibrium (at somewhat different chlorine pressures) was approached from both sides. Solutions of hydrochloric acid in contact with solid lead chloride were treated with chlorine (in the apparatus described below) for periods varying from days to weeks; and samples for analysis were taken. The same solution was then subjected to a lower chlorine pressure for another extended period, and analyses were again made. Even though equilibrium might not be fully reached in either case, it must certainly lie between the values obtained at the higher and lower chlorine pressures.

The chlorine employed was drawn as needed from a tank of electrolytic liquid chlorine. The lead chloride was purified by recrystallization from water.

3. Apparatus.

As the equilibrium conditions are only slowly attained, it is obvious that the chlorine pressure would not remain constant if the gas escaped against the fluctuating atmospheric pressure. Therefore, the systems worked with were always "closed," that is, they were not subject to atmospheric pressure; and the method employed was to stir together the liquid, solid, and gas, and to circulate the gas through some side bulb or pipet, so that a sample of the gas, as well as of the liquid, could be removed for analysis.

The first apparatus consisted of a horizontal glass tube 3 cm. in diameter with smaller vertical tubes at each end. The tops of these tubes were connected through a 25-cc. bulb joined to the tubes by short capillaries. The whole apparatus was then immersed in a thermostat and rocked slowly to and fro about a horizontal axis perpendicular to the plane of the apparatus, so that the liquid flowed repeatedly past the solid in the tube, and at the same time acted as a piston on the gas, forcing it back and forth through the 25-cc. bulb. In the use of this apparatus, a rather



surprising difficulty was met with. The plan was to seal off the 25-cc. bulb as a gas sample; but it was unexpectedly found that considerable quantities of water collected in the capillaries and in the bulb. This form of apparatus was, therefore, abandoned.

After a great deal of experimenting the aparatus shown in the figure was devised. In this apparatus a "gas-pipet" provided with two 3-way stopcocks was introduced between the "gas inlet" and "gas outlet," it being placed in the thermostat within a "Dewar bulb," which was maintained by electric heating at a temperature one degree higher than the rest of the system to prevent condensation. An essential part of the apparatus is the magnetic pump. This consists of an "iron-clad solenoid" and of a "pump-cylinder," within which is a glass-covered bar of iron serving as the piston. The terminals of the solenoid are connected to the 110-volt circuit through a switch operated at intervals of 10 or 15 seconds by a cam (not shown in the sketch). When the solenoid is activated the piston snaps up into the position shown in the drawing, forcing a stream of solution through the "nozzle." This stream of liquid carries large quantities of gas into the main "reaction chamber;" and this gas then circulates through the "gas outlet" and the "gas-pipet" back into the apparatus at the "gas inlet." At the same time, a stream of liquid flows down past the glass "float-valve" and through the "mixing chamber," where it stirs the solid lead chloride thoroughly. When the solenoid is disconnected from the electric circuit the float valve has already closed, and the piston slowly settles to the bottom of the cylinder, restrained by the slow flow of the liquid up the narrow annular space between the piston and the cylinder. All glass connections, including those with the gas-pipet, were made by fusing the parts together.

The only stopcocks were those on the gas-pipet; these were lubricated with paraffin which had been chlorinated at a little above its melting point until on cooling it became of the consistency of vaseline, after which it reacted only very slightly with the chlorine.

In the upright tube between the "reaction chamber" and the "float-valve" were sealed 2 platinum wires enlarged at the ends into disks. These were platinized and served as electrodes to determine the conductance of the solution.

It is hoped that the general plan of this apparatus will be of use in many other investigations. It is frequently desirable to have thorough stirring in an absolutely closed glass system which cannot be rotated or shaken; and there is probably no other method so simple and energetic as this magnetic pump.

4. Methods of Analysis.

The gas pipet was disconnected from the rest of the apparatus by turning the 3-way cocks; the chlorine contained in it was completely driven out by a slow stream of carbon dioxide gas into potassium iodide solution; and the iodine liberated was titrated with thiosulfate. From the known volume and temperature of the pipet the partial pressure of chlorine was calculated with the aid of the perfect-gas law.

Samples of the solution for the analyses were withdrawn into a vacuum pipet. This was done by fitting the pipet with an extension tube, which passed through the opening ordinarily closed by the "glass stopper." The extension tube was thrust 7 or 8 cm. below the surface of the liquid so as to get a sample not affected by the change in chlorine pressure at the surface, which might arise from diffusion of air admitted by the removal of the stopper. In most of the experiments 2 samples were analyzed. In one the lead was determined directly as chloride by evaporating the solution in platinum dishes. In the other the oxidizing chlorine was determined by drawing potassium iodide solution into the vacuum pipet and titrating the liberated iodine in the pipet itself, it having been proved by experiments with known solutions that the presence of lead does not affect the titration.

5. Solubility of Chlorine Gas and of Lead Chloride in Hydrochloric Acid Solutions.

In calculating the concentration of the substances involved in the equilibrium, there is needed, in addition to the analytical data, the solubilities of chlorine gas and of solid lead chloride in the various solutions. The solubilities of the chlorine in hydrochloric acid solutions were obtained as will now be described; and in the subsequent computations with the equilibrium mixtures it is assumed that these solubilities are not influenced by the extent to which the hydrochloric acid initially present is converted into chloroplumbic acid.

The solubility of chlorine in hydrochloric acid of various concentrations was determined in the same apparatus and by the same method as that used in the equilibrium experiments. The values at 25° of the distribution-ratio (that is, the ratio of the millimols of Cl_2 per 1000 g. of water to the partial pressure of the chlorine gas in atmospheres) for various concentrations of hydrochloric acid were found to be as given in Table I. The partial pressures are calculated here, and also in the main equilibrium experiments, from the concentration of the chlorine in the gas with the aid of the perfect-gas law.

TABLE I.—SOLUBILITY OF CHLORINE IN HYDROCHLORIC ACID SOLUTIONS.

Millimols of HCl in 1000 g. of water.........	103.7	286.0	802.0
Distribution-ratio.........................	62.3	60.0	61.1

For the solubility of lead chloride in hydrochloric acid solutions the data of von Ende[1] were used, his values having been checked at 3 points

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[1] *Z. anorg. Chem.*, 26, 129 (1901).

by determinations of my own. A plot of his values was made for interpolating at the special concentrations involved in the equilibrium mixtures.

6. The Results of the Equilibrium Measurements.

Fifteen equilibrium mixtures were prepared and analyzed. In the first 8 of these the formation of the complex was independently derived both by determining the total lead content and the content in oxidizing chlorine; in the last 7 the latter was alone determined. In 11 of the experiments the chloride initially present was only hydrochloric acid; while in the 4 other experiments this was partially replaced by sodium chloride, with the object of determining whether the equilibrium was affected by the hydrogen ion concentration when the chloride ion concentration was kept constant.

The data resulting from the analysis of the equilibrium mixtures and the values computed from them are given in Tables II and III, which are for the most part self-explanatory.

The temperature was always 25°. All concentrations, indicated by symbols in parentheses, are expressed in millimols per 1000 g. of water.

The sodium thiosulfate solution used for titrating the chlorine gas sample and the oxidizing chlorine (ΣCl_2) in the solution was 0.09711 *N* in Expts. 1–6, and 0.09763 *N* in Expts. 7–15.

The lead chloride present as such in the equilibrium mixtures was obtained, with the aid of the plot of von Ende's data above referred to, on the basis of the assumption that the solubility in the mixtures is determined solely by the concentration of the uncombined chloride in it; that is, by that quantity of the hydrochloric acid and sodium chloride initially present which has not been converted into chloroplumbate complex. According to whether this complex is assumed to be $PbCl_6^{--}$ or $PbCl_5^-$, this uncombined chloride has different values, which are found by subtracting from the initial (HCl) or (HCl + NaCl) in the one case twice the concentration of the chloroplumbate complex, and in the other case the concentration itself of that complex. And correspondingly 2 values of the lead chloride present as such, represented by $(PbCl_2)_1$ and $(PbCl_2)_2$ in the tables,[1] were derived from the plot. By subtracting these last quantities from the total lead content (ΣPb) as found by the gravimetric analysis, the concentration of the chloroplumbate complex $(\Delta Pb)_1$ or $(\Delta Pb)_2$, was found. This procedure evidently requires for the determination of either quantity a knowledge of the other; but this difficulty was met by first estimating approximately the complex concentration, and then making a series of successive approximations.

The concentration of free chlorine (Cl_2) in the solution was found by

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[1] In general, symbols with the subscript 1 denote quantities computed under the assumption that the complex acid is H_2PbCl_6; those with the subscript 2 under the assumption that the complex acid is $HPbCl_5$.

multiplying the partial pressure p_{Cl} by the value of the distribution ratio given in Table I for a hydrochloric acid concentration equal to the initial total chloride concentration (HCl + NaCl) in the mixture. By subtracting this chlorine concentration from the total oxidizing chlorine content (ΣCl_2) as determined by the titration of samples of the solution, an independent value, denoted[1] by (ΔCl_2), of the chloroplumbate concentration was obtained. A comparison of these values of (ΔCl_2) with those of $(\Delta Pb)_1$, and $(\Delta Pb)_2$ shows the agreement of the 2 analytical methods.

The concentration of the chloride ion constituent in the solution, represented for the 2 cases of complex formation in the tables by $(Cl^-)_1$ and $(Cl^-)_2$ is found by the expressions:[2]

$$(Cl^-)_1' = (HCl + NaCl) - 2(\Delta Pb)_1 + 2(PbCl_2)_1',$$

or

$$(Cl^-)_1'' = (HCl + NaCl) - 2(\Delta Cl_2) + 2(PbCl_2)_1''.$$

$$(Cl^-)_2' = (HCl + NaCl) - (\Delta Pb)_2 + 2(PbCl_2)_2',$$

or

$$(Cl^-)_2'' = (HCl + NaCl) - (\Delta Cl_2) + 2(PbCl_2)_2''.$$

Equilibrium constants were calculated under the 2 assumptions that the chloroplumbate complex has the formula $PbCl_6^{--}$ and that it has the formula $PbCl_5^-$; and that, correspondingly, the equilibrium involved is that of the first or second of the following reactions:

$$PbCl_2(s) + Cl_2(g) + 2Cl^- = PbCl_6^{--}.$$

$$PbCl_2(s) + Cl_2(g) + Cl^- = PbCl_5^-.$$

The corresponding mass-action expressions are:

$$\frac{(PbCl_6^{--})}{(Cl^-)^2(p_{Cl})} = K_1; \text{ and } \frac{(PbCl_5^-)}{(Cl^-)(p_{Cl})} = K_2$$

In calculating the values of the equilibrium constants by these equations, the concentrations were expressed in mols (instead of millimols), and the ionization of all the substances was assumed to be complete. This assumption probably does not lead to results very far from the truth, owing to the partial compensation of the incomplete ionization of the hydrochloric acid by that of the $HPbCl_5$ or H_2PbCl_6.

7. Discussion of the Equilibrium Results.

An examination of the equilibrium constants given in Tables II and III shows that the check determinations on the same mixture by the same analytical method are in general in good agreement, the average devia-

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[1] These symbols (ΔPb) and (ΔCl_2) used for the chloroplumbate complex are increments in the sense that they represent the increase in lead content or oxidizing chlorine content that results from formation of the complex.

[2] In general, symbols to which single "accents" are appended, denote quantities calculated from the determination of the lead content; those to which double "accents" are attached denote quantities calculated from the determination of the oxidizing chlorine content.

TABLE II.—THE RESULTS OF THE EQUILIBRIUM MEASUREMENTS.

Equilibrium Mixture. No.	1.	2.	3.	4.	5.	6.	7.	8.
Initial concentration of acid (HCl)	103.7	103.7	103.7	103.7	286.0	286.0	286.0	286.0
Cc. $Na_2S_2O_3$ for Cl_2 in 62.01 cc. of gas	47.36	44.69	48.30	37.01	46.46	40.96	47.40	38.02
Partial pressure of Cl_2 in atmospheres (p_{Cl})	0.905	0.854	0.924	0.708	0.888	0.783	0.906	0.727
Grams of sample for lead determination	49.21	55.57	47.59	51.46	47.27	38.16	58.87	65.44
Grams of $PbCl_2$ found in this sample	0.3210	0.3592	0.3104	0.3094	0.3441	0.2607	0.4352	0.4228
Total lead content (ΣPb)	23.71	23.49	23.71	21.83	26.78	25.14	27.29	23.73
$(PbCl_2)'_1$ from solubility plot, assuming H_2PbCl_4	17.31	17.26	17.31	16.90	8.36	8.32	8.40	8.28
$(\Delta Pb)_1$ equal to $(\Sigma Pb) - (PbCl_2)'_1$	6.40	6.23	6.40	4.93	18.42	16.82	18.89	15.45
$(PbCl_2)_2'$ from solubility plot, assuming $HPbCl_3$	16.44	16.40	16.44	16.28	7.94	7.90	7.98	7.86
$(\Delta Pb)_2$ equal to $(\Sigma Pb) - (PbCl_2)_2'$	7.27	7.09	7.27	5.55	18.84	17.24	19.31	15.87
$(Cl^-)_1'$ equal to $(HCl) - 2(\Delta Pb)_1 + 2(PbCl_2)_1'$	125.5	125.7	125.5	127.6	265.9	269.0	265.0	271.7
$(Cl^-)_2'$ equal to $(HCl) - (\Delta Pb)_2 + 2(PbCl_2)_2'$	129.3	129.4	129.3	130.7	284.1	284.6	282.7	293.8
Grams of sample for oxidizing chlorine	32.95	28.69	37.57	25.16	19.83	27.03	21.08	23.36
Cc. $Na_2S_2O_3$ solution used for this sample	42.53	33.54	48.34	25.02	29.20	35.02	31.49	28.30
Oxidizing chlorine content (ΣCl_2)	63.1	57.5	63.0	48.9	72.0	63.3	73.1	59.2
(Cl_2) from p_{Cl} by distribution ratio	56.4	53.2	57.2	44.2	53.3	47.0	54.4	43.6
(ΔCl_2) equal to $(\Sigma Cl_2) - (Cl_2)$	6.7	4.3	5.8	4.7	18.7	16.3	18.7	15.6
$(PbCl_2)_1''$ from solubility plot, assuming H_2PbCl_4	17.4	16.8	17.2	16.9	8.4	8.3	8.4	8.3
$(PbCl_2)_2''$ from solubility plot, assuming $HPbCl_3$	16.4	16.2	16.3	16.2	8.4	8.3	8.4	8.3
$(Cl^-)_1''$ equal to $(HCl) - 2(\Delta Cl_2) + 2(PbCl_2)_1''$	125.1	128.6	126.4	128.0	265.4	270.0	265.4	271.4
$(Cl^-)_2''$ equal to $(HCl) - (\Delta Cl_2) + 2(PbCl_2)_2''$	129.8	131.8	130.5	131.4	284.1	286.3	284.1	287.0
K_1' equal to $1000(\Delta Pb)_1 \div [((Cl^-)_1')^2 p_{Cl}]$	0.449	0.462	0.440	0.428	0.293	0.297	0.297	0.288
K_1' mean	0.445		(A.D., 0.005)		0.294		(A.D., 0.002)	
K_1'' equal to $1000(\Delta Cl_2) \div [((Cl^-)_1'')^2 p_{Cl}]$	0.473	0.304	0.393	0.405	0.299	0.285	0.293	0.291
K_1'' mean	0.394		(A.D., 0.022)		0.292		(A.D., 0.002)	
K_2' equal to $(\Delta Pb)_2 \div [(Cl^-)_2' p_{Cl}]$	0.0621	0.0641	0.0608	0.0600	0.0747	0.0774	0.0754	0.0743
K_2' mean	0.0617		(A.D., 0.0007)		0.0754		(A.D., 0.0005)	
K_2'' equal to $(\Delta Cl_2) \div [(Cl^-)_2'' p_{Cl}]$	0.0570	0.0382	0.0481	0.0505	0.0703	0.0728	0.0725	0.0746
K_2'' mean	0.0485		(A.D., 0.0047)		0.0726		(A.D., 0.0005)	

TABLE III.—RESULTS OF THE EQUILIBRIUM MEASUREMENTS.

Equilibrium Mixture. No.	9.	10.	11.	12.	13.	14.	15.
Initial concentration acid (HCl)	802	802	802	286	286	103.7	103.7
Initial concentration of chloride (HCl + NaCl)	802	802	802	802	802	286.0	286.0
Cc. $Na_2S_2O_3$ solution for Cl_2 in 62.01 cc. of gas	40.85	48.81	41.86	46.19	42.61	49.42	43.30
Partial pressure of Cl_2 in atmospheres (p_{Cl})	0.786	0.824	0.806	0.889	0.821	0.952	0.84
Grams of sample for oxidizing chlorine	16.84	23.36	20.54	25.13	17.14	51.99	40.97
Cc. $Na_2S_2O_3$ solution used for this sample	37.78	55.67	48.03	51.16	36.44	77.60	53.95
Oxidizing chlorine content (ΣCl_2)	111.7	118.8	117.0	102.5	106.7	73.5	64.8
(Cl_2) from (p_{Cl}) by distribution ratio	48.8	51.2	50.0	55.2	51.0	57.1	50.0
(ΔCl_2) equal to (ΣCl_2) —(Cl_2)	62.9	67.6	67.0	47.3	55.7	16.4	14.9
$(PbCl_2)_1$ from solubility plot, assuming H_2PbCl_4	4.9	4.9	4.9	4.8	4.8	8.3	8.3
$(PbCl_2)_2$ from solubility plot, assuming $HPbCl_3$	4.8	4.8	4.8	4.7	4.7	7.9	7.9
$(Cl^-)_1$ equal to (HCl + NaCl) — $2(\Delta Cl_2)$ + $2(PbCl_2)_1$	686	677	678	717	701	270	273
$(Cl^-)_2$ equal to (HCl + NaCl) — (ΔCl_2) + $2(PbCl_2)_2$	750	745	745	764	755	285	287
K_1 equal to 1000 (ΔCl_2) ÷ $[(Cl^-)_1^2\, p_{Cl}]$	0.170	0.178	0.180	0.103	0.114	0.236	0.238
K_1 mean	0.176	(A.D., 0.002)		0.108		0.237	
K_2 equal to 1000 (ΔCl_2) ÷ $[(Cl^-)_2\, p_{Cl}]$	0.107	0.109	0.112	0.070	0.090	0.060	0.061
K_2 mean	0.109	(A.D., 0.001)		0.080		0.061	

tion of the mean (the A. D. values[1]) exceeding about 1% in only 3 out of the 14 sets of values. Moreover, those based on the determination of the total oxidizing chlorine agree with those based on that of the total lead content in the case of the solutions of medium concentration (HCl = 286.0), but not in the case of the most dilute solution (HCl = 103.7) for which the values based on the chlorine determinations are obviously affected by fairly large errors.

It may also be pointed out that, while the partial pressure of the chlorine gas was not varied within wide limits, yet within the limits involved the concentration of the complex formed is proportional to the partial pressure. This is seen best by comparing Expts. 3 and 4 and Expts. 7 and 8, in which the chlorine pressure differs in the ratio about 9:7, while the corresponding equilibrium constants differ by only 1 to 3%.

The further conclusions to be drawn appear much more clearly from a consideration of the summary of best values derived from the means in the preceding tables and presented in Table IV.

TABLE IV.—BEST VALUES OF THE EQUILIBRIUM CONSTANTS.

HCl in mols...............	0.104	0.104	0.286	0.286	0.802
HCl + NaCl in mols.......	0.104	0.286	0.286	0.802	0.802
$K_1 = (PbCl_6^{--})/p_{Cl}(Cl^-)^2$..	0.44	0.24	0.29	0.11	0.18
$K_2 = (PbCl_5^-)/p_{Cl}(Cl^-)$....	0.062	0.061	0.074	0.080	0.109

An examination of the values in Table IV leads to the following conclusions.

The values of K_1 (corresponding to the complex $PbCl_6^{--}$) increase somewhat each time the acid concentration is increased, while the total chloride is kept constant; but they decrease very rapidly each time the total chloride concentration is increased, while the acid concentration is kept constant; thus between the acid concentrations 0.104 and 0.802 *N* the value of K_1 varies 2.5 fold. This fact makes it clear that the plumbic lead is not present mainly in the form of the complex acid $H_2^+PbCl_6^{--}$.

The values of K_2 (corresponding to the complex $PbCl_5^-$), on the other hand, remain remarkably constant each time the total chloride concentration is increased while the hydrogen ion concentration is kept constant. This fact indicates that $H^+PbCl_5^-$ is the complex acid which is mainly present in these moderately dilute solutions. The values of K_2 do however, increase not inconsiderably (20–40%) each time the acid concentration is increased while the total chloride concentration is kept constant. This shows that hydrogen ion has an effect of secondary magnitude on the equilibrium—an effect arising perhaps from a more rapid decrease in the ionization of the complex acid $HPbCl_5$ than in that

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[1] These are calculated by the expression $\Sigma\delta/(n\sqrt{n})$, where $\Sigma\delta$ is the sum of the deviations of the separate values from the mean value, and n is the number of these separate values.

of hydrochloric acid, with increasing concentration. The fact that the effect of increasing the hydrogen ion concentration is to increase the proportion of complex in the solution, and not to decrease it, shows that there is no considerable hydrolysis of the complex into such products as $HPbCl_4(OH)$. The fact that the solid salts that have been separated are salts of the acid H_2PbCl_6, and not of $HPbCl_5$, is doubtless because the former acid is produced, in accordance with the mass-action law, in considerable proportion in hydrochloric acid solutions of larger concentrations than those involved in these measurements.

For the equilibrium constant $(PbCl_5^-)/(Cl^-)p_{Cl}$ of the complex ion $PbCl_5^-$ the mean of the values obtained with the 4 more dilute acid solutions may be adopted, namely the value 0.070; the concentrations being expressed in mols per 1000 g. of water, the partial pressure of the chlorine being given in atmospheres, and the ionizations of the hydrochloric acid and $HPbCl_5$ being assumed equal. If greater accuracy is desired, the equilibrium constant may be expressed as a function of the concentration c_H of the hydrogen ion constituent, namely by the equation $K_2 = 0.055 + 0.07\ c_H$; and 0.055 may be regarded as the value for complete ionization of the hydrochloric and the chloroplumbic acids.

8. Computation of the Plumbous-Plumbic Reduction Potential.

From the mean value (0.070) of the equilibrium constant derived in the last section we may calculate by the familiar thermodynamic expression $-\Delta F = R\ T \log K$ the free energy decrease attending the reaction

$$PbCl_2(s) + Cl_2(1\ atm.) + Cl^-(1\ M) = PbCl_5^-(1\ M).$$

By proper substitutions the equation becomes $-\Delta F = 8.31 \times 298.1 \times 2.303 \log_{10} 0.070$, and the free energy decrease is thus found to be —6590 joules.

The above reaction results when 2 faradays (2 F or 193,000 coulombs) of electricity are passed from left to right through the cell,

$$PbCl_2(s),\ PbCl_5^-(1\ M) + Cl^-(1\ M)\ ||\ Cl^-(1\ M),\ Cl_2(1\ atm.).$$

The electromotive force of this cell is, therefore, —6590/193000, or —0.034 volt. The value corresponding to the equilibrium constant 0.055 for complete ionization is —0.037 volt. Adding to the value —0.034 the specific electrode potential of chlorine, that is, the electromotive force (—1.356 volts) of the cell[1]

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[1] This value is derived as follows. From a critical consideration of the measurements of Wolff (*Z. Elektrochem.*, 20, 19 (1914)), and of Lewis and Rupert (THIS JOURNAL, 33, 306 (1911)), made by J. B. Dickson in this laboratory, 1.086 volts has been obtained as the best value of the electromotive force at 25° of the cell $Hg + Hg_2Cl_2$ (s), HCl (1M), Cl_2(1 atm.). Noyes and Ellis (THIS JOURNAL, 39, 2541 (1917), found 0.270 volt for the cell H_2(1 atm.), H^+ (1 M) || Cl^-(1 M), Hg_2Cl_2 (s) + Hg. Taking the sum of these 2 quantities and changing its sign, we get —1.356 volts as the specific electrode-potential of chlorine.

$$Cl_2(1 \text{ atm.}), Cl^-(1\ M) \ || \ H^+(1\ M), H_2(1 \text{ atm.}),$$

we obtain —1.390 volts for the electromotive force of the cell

$$PbCl_2(s), PbCl_5^-(1\ M) + Cl^-(1\ M) \ || \ H^+(1\ M), H_2(1 \text{ atm.}).$$

This is the specific electrode potential or reduction potential of the combination constituting the left-hand part of this cell.

The corresponding reduction potential of the combination Pb^{++} $(1\ M) + Cl^-(1\ M) + PbCl_5^-(1\ M)$ may be found by noting that the solubility-product[1] of plumbous chloride, $(Pb^{++}) \times (Cl^-)^2 = 0.0000418$, is the value of (Pb^{++}) in a solution 1-molal in Cl^-, and that the reduction potential is increased by the amount $(R\ T/2\ F) \log (1/Pb^{++})$ when the plumbous ion concentration is increased from (Pb^{++}) to 1-molal. The value of this expression when $(Pb^{++}) = 4.18 \times 10^{-5}$ is $+ 0.130$ volt, and the specific reduction potential of the $Pb^{++} + PbCl_5^- + Cl^-$ combination is, therefore, —1.260 volts.

9. Determination of the Equilibrium in the Presence of Lead Dioxide.

At somewhat lower concentrations of acid than those involved in the preceding equilibrium measurements the hydrolysis of the chloroplumbic acid goes so far that lead dioxide is precipitated according to the equation:

$$HPbCl_5 + 2H_2O = 5HCl + PbO_2(s)$$

The corresponding reaction starting with solid lead chloride is:

$$PbCl_2(s) + 2H_2O + Cl_2(g) = Pb_2O(s) + 4HCl$$

The reaction was first studied in the apparatus used for the previous measurements. The resistance of the solution, measured between the pair of platinized electrodes sealed into the apparatus as shown in the figure, served as an index of equilibrium. This test is very sensitive, inasmuch as 4 hydrochloric acid molecules are formed for each molecule of plumbous chloride that reacts.

The reaction was found to take place much more slowly than in the preceding measurements; and, since in this case an error in the measurement of the partial pressure of the chlorine produces little error in the result, a simpler apparatus was devised which made it possible to carry on several experiments at the same time. This apparatus consisted of 4 tubes, 3 cm. in diameter and 25 cm. long, lying side by side in a horizontal position. The tubes were half filled with liquid; and chlorine gas was passed in series through the spaces above the liquid, escaping finally at atmospheric pressure. The whole arrangement was given a reciprocating motion in a horizontal plane by means of a motor and eccentric. Connection with the chlorine source was maintained through a flexible system of spiral glass tubes, entirely free from rubber joints.

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[1] Taking the molal solubility as 0.0389 (Noyes, *Z. physik. Chem.*, **9**, 623 (1892)) and the ionization as 0.562 as derived from the conductance ratio (Hunt, THIS JOURNAL, **33**, 802 (1911); see also THIS JOURNAL, **39**, 1543 (1917).

Two of these tubes were filled with lead chloride and distilled water, and two with 0.2 *N* hydrochloric acid, solid lead chloride, and solid lead dioxide. The dioxide used in one experiment was prepared by precipitating it electrolytically on a platinum anode; that used in another experiment was made by diluting a chloroplumbic acid solution with water. Chlorine was passed through; and at intervals of several days the resistances of a certain conductivity cell of pipet form filled successively with the several solutions was determined. The results are tabulated in Table V.

TABLE V.—RESISTANCE OF THE EQUILIBRIUM MIXTURES WITH LEAD CHLORIDE AND DIOXIDE.

Initial State.	4 days.	7 days.	11 days.	17 days.
$PbCl_2(s) + H_2O$	365	332	310	298
$PbCl_2(s) + H_2O$	334	320	310	300
$PbCl_2(s) + PbO_2$(electrolytic) + 0.2 *N*.HCl	294	294	295	295
$PbCl_2(s) + PbO_2$(precipitated) + 0.2 *N*.HCl	235	269	272	273

From the results in Table V the mean resistance of the final equilibrium mixture is found to be 292 ± 5 ohms. This value, which is the resistance in ohms of the pipet cell filled with the equilibrium mixture, was compared with the resistances of the same cell filled with known hydrochloric acid solutions saturated with lead chloride. By this comparison the concentration of the acid ($HCl + HPbCl_5$) in the equilibrium mixture was found to be 0.099 molal. This method of comparison is reliable since previous measurements had shown that there is only a small change in resistance when a hydrochloric acid solution saturated with lead chloride is saturated with chlorine gas.

10. Computation of the Free Energy of Lead Dioxide.

From the value (0.099 molal) of the acid concentration in the equilibrium mixture and from the equilibrium constant K_2 (0.062) at this concentration, we may compute the fraction x of the total acid that is in the form of the complex acid by means of the equation

$$K_2 = \frac{(PbCl_5^-)}{(Cl^-)p_{Cl}} = \frac{0.099x}{(0.099 - 0.099x + 0.034^{a})\ 0.97} = 0.062.$$

[a] This term is equal to $2(PbCl_2)$, that is, twice the concentration of lead chloride present as such in the solution as read off the solubility plot.

The value of x is thus found to be 0.076, and that of the chloride ion constituent in the solution (as given by the parenthesis in the preceding expression) to be 0.125 molal.

The equilibrium constant K of the reaction

$$PbCl_2(s) + Cl_2(g) + 2\ H_2O = PbO_2(s) + 4\ H^+Cl^-$$

is, therefore, given by the expression

$$K = \frac{(H^+)^4(Cl^-)^4}{p_{Cl}} = \frac{(0.099)^4\ (0.125)^4}{0.97} = 2.4 \times 10^{-8}.$$

For the corresponding free energy decrease, when the concentrations of H^+ and of Cl^- are one molal and the partial pressure of Cl_2 is one atmosphere, we have

$$-\Delta F = R\,T \log K = 8.31 \times 298.1 \times 2.303 \log_{10} 2.4 \times 10^{-8} = -43{,}500 \text{ joules.}$$

This reaction takes place when 2 faradays are passed from left to right through the cell

$$\left.\begin{matrix}PbCl_2(s)\\ PbO_2(s)\end{matrix}\right\} Cl^-(1\,M) + H^+(1\,M)\ \|\ Cl^-(1\,M),\ Cl_2(1 \text{ atm.}).$$

The electromotive force of this cell is, therefore, —43,500/193,000 or —0.225 volt.

Adding to this the specific electrode potential of the chlorine electrode we get —1.581 volts as the specific electrode potential of the $PbCl_2$, PbO_2 half-cell referred to the molal hydrogen electrode.

Adding to this the quantity (+0.130 volt) computed in the last section for changing the Pb^{++} concentration to one molal from that prevailing in a solution one molal in chloride ion saturated with plumbous chloride, we get —1.451 volts as the specific electrode potential of $Pb^{++} + PbO_2(s) + H^+$.

Adding this to the specific electrode potential (+0.132)[1] of Pb(s), Pb^{++} we get —1.319 volt as the electromotive force of the double cell

$$Pb(s),\ Pb^{++}(1\,M)\ \|\ H^+(1\,M),\ H_2;\ Pb^{++}(1\,M) + H^+(1\,M),\ PbO_2(s)\ \|\ H^+(1\,M),\ H_2.$$

In this double cell when 2 faradays pass from left to right the following reaction takes place

$$Pb(s) + 2\ H_2O = PbO_2(s) + 2\ H_2(1 \text{ atm.}).$$

The free energy decrease attending this reaction is, therefore, 193,000 × (—1,319) or —254,600 joules.

This same reaction evidently takes place when 4 faradays are passed through the cell

$$Pb(s) + PbO_2(s) + H^+(1\,M),\ H^+(1\,M),\ H_2(1 \text{ atm.}).$$

The electromotive force of this cell, or the specific electrode potential of the combination Pb(s), $PbO_2(s) + H^+$ is, therefore, —254,600/386,000 or —0.660 volt.

Finally, by adding to the free-energy equation just derived,

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[1] Noyes and Toabe (This Journal, 39, 1544 (1917)) found 0.132 for this potential; while Lewis and Brighton (This Journal, 39, 1909 (1917)) found 0.1295. The first of these values is here employed, since it was derived from cells involving lead chloride, using the same ionization value, namely that corresponding to the conductance ratio.

$$Pb(s) + 2H_2O = PbO_2(s) + 2H_2(1\ atm.) - 254{,}600\ joules,$$

the following one computed by Lewis and Randall,[1]

$$2H_2(1\ atm.) + O_2(1\ atm.) = 2H_2O + 473{,}600\ joules,$$

we get for the free energy of formation of lead dioxide

$$Pb(s) + O_2(1\ atm.) = PbO_2(s) + 219{,}000\ joules.$$

11. Summary.

In this article has been described an investigation of the equilibrium between solid plumbous chloride and chlorine in hydrochloric acid solutions, including the case where the acid is so dilute that lead dioxide separates as a solid phase. The apparatus required for accurate experiments on this equilibrium has been represented by a detailed drawing and has been fully described.

The results of this investigation show that the complex chloroplumbic acid has the composition $HPbCl_6$; for with a given chlorine pressure the quantity of this complex acid present in equilibrium with solid plumbous chloride was found to be proportional to the first power of the chloride ion concentration. The hydrogen ion concentration, which would not be involved in the equilibrium if the ionization of the substances were complete, was found to have a small secondary effect, probably owing to an influence on the ionization of the chloroplumbic acid.

The equilibrium constant corresponding to the expression $(PbCl_6^-)/(Cl^-)p_{Cl}$ is given by the expression $K' = 0.055 + 0.07\ c_H$, the concentrations being expressed in mols per 1000 g. of water, the partial pressure of the chlorine being given in atmospheres, and the ionizations of hydrochloric acid and $HPbCl_6$ being assumed equal.

The equilibrium constant of the reaction $PbCl_2(s) + Cl_2(g) + 2H_2O = PbO_2(s) + 4H^+Cl^-$, as given by the expression $K = (H^+)^4(Cl^-)^4/p_{Cl}$ was found to be 2.4×10^{-8}, under the assumption that the ionization of the hydrochloric acid and $HPbCl_6$ is complete.

From these equilibrium constants and from other data existing in the literature the values of the free energy decreases at 25° were calculated for the case that the concentrations of all dissolved substances are one molal (except that of the chlorine whose partial pressure is one atmosphere), and were found to be those expressed by the following free energy equations:

$$PbCl_2(s) + Cl_2(g) + Cl^- = PbCl_6^- - 6590\ joules.$$
$$PbCl_2(s) + 2H_2O + Cl_2(g) = PbO_2(s) + 4H^+Cl^- - 43{,}500\ joules.$$
$$Pb(s) + O_2(g) = PbO_2(s) + 219{,}000\ joules.$$

CAMBRIDGE, MASS.

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[1] THIS JOURNAL, 36, 1992 (1914).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TENNESSEE COLLEGE OF MEDICINE.]

FLUOREMETRY, QUANTITATIVE ANALYSIS BY COMPARATIVE FLUORESCENCE.[1] PRELIMINARY REPORT.

BY L. J. DESHA.

Received April 22, 1920.

In connection with a study of the effects of ultra-violet radiation upon biological substances which has been undertaken in this laboratory, it occurred to me that the visible fluorescence which is excited in the solutions of so many substances by these invisible rays might be utilized, under appropriate conditions, as the basis of a new general method for the quantitative determination of such compounds. When visible radiation falls perpendicularly upon the walls of a cylinder with an opaque bottom, containing a solution or liquid, little or no light is transmitted to the eye of an observer placed above the cylinder except such as may be reflected by any suspended particles. A comparatively simple relationship between the amounts of light thus reflected by 2 such suspensions forms the now familiar basis of nephelometry.[2,3,4] I imagined that if 2 such cylinders containing different concentrations of a fluorescent substance in solution were similarly exposed in a nephelometer to a source of ultraviolet radiation, all, or most all, of the visible rays from the latter being excluded by a suitable filter, the heights of the 2 columns required to produce an optical balance in the eye piece of the instrument should bear some readily calculable relationship to the concentrations. Experiment has demonstrated that this assumption is correct.

In the present paper the arrangement of apparatus is described, the conditions essential to concordant determinations are outlined and results are reported in which it is shown that determinations may be made upon acid solutions of quinine sulfate containing from $^1/_2$ to 2 parts per million and alkaline solutions of aniline iodeosine containing 2 to 4 parts per million. A further communication will include a report upon some experiments designed to increase still further the accuracy and delicacy of the method, a study of the influence of added non-fluorescent substances, a further investigation of the form of the curves obtained and certain practical applications.[5] The present results are sufficient, however, to demonstrate that we have here a new method of microanalysis of at least

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[1] Presented by title before the Section on Physical and Inorganic Chemistry of the American Chemical Society at the St. Louis meeting, April 15, 1920.

[2] P. A. Kober, *J. Biol. Chem.*, **13**, 485 (1913); **29**, 155 (1917).

[3] Kober and Graves, *J. Ind. Eng. Chem.*, **7**, 843 (1915).

[4] P. A. Kober, *ibid.*, **10**, 556 (1918).

[5] These studies will include the use of comparison cylinders of transparent silica, a determination of the effects of added substances and applications to the determination of urobilin in body fluids and of quinine in the blood of patients treated for malaria.

the same order of sensitiveness as colorimetry and nephelometry and requiring no special technique for the preparation of solutions to be examined, which should prove exceedingly useful in the estimation of small amounts of the numerous substances which are either fluorescent themselves or become so upon the addition of suitable reagents, but which do not readily lend themselves to determination by either of the other methods.

On account of the analogy of the procedure to colorimetry and nephelometry, the natural term by which to designate the new method would be either "fluorometry" or "fluoremetry." The latter is preferred as being less liable to confusion with the process of determining fluorine in an instrument which has been given the name "fluorometer." Even a slight misunderstanding as to meaning of the term "fluoremetry" in the sense now proposed is regarded as less objectionable than the introduction of such a cumbersome word as "fluorescometry."

Arrangement of Apparatus.

The source of radiation employed is a mercury vapor lamp in quartz tube of the type designed for use with a transformer actuated by ordinary 110-volt alternating current,[1] giving an arc about 12 cm. in length. In order to cut off from the eye of the observer the powerful visible radiation from the lamp, the latter must be enclosed in a suitable light-tight box which, on account of the large heat evolution, should not be too small and must be provided with some means of ventilation. Practically I found it convenient to install the lamp in an ordinary chemical hood, the interior of which was painted white, several coats of black paint applied to the glass of the sash windows and all cracks made tight by cotton wool or putty. Beneath one of the partially raised sashes was closely fitted a section of "beaver" wall board in which an opening 8.75 cm. square

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[1] This lamp and transformer are manufactured by the Hanovia Chemical Company of Newark, N. J., and billed by them as "A. S. type quartz lamp for 110 volts A. C., with transformer to operate." In a letter from this company it is stated that the lamp emits 3000 candle power visible radiation and that the 110-volt actuating current is stepped up by the transformer to 390 volts. A plug on the transformer is pushed in after the lamp has been in operation some 7 to 10 minutes, thus cutting out part of the external resistance and giving the maximum of radiation both visible and ultra-violet. The current consumption is stated to be 3.5 amperes while operating and somewhat greater at the moment of establishing the arc. These figures I have not personally attempted to verify.

The attempt has been made to render fluoremetric methods available to more workers by the substitution of a source of illumination more generally accessible than the quartz-enclosed mercury arc. A marked, though less intense, fluorescence is observed when a 750 watt "Mazda, Type C" lamp is used in connection with the filter G 586 AW. With this arrangement comparisons may be made with a fair degree of accuracy upon fully acidified solutions of quinine sulfate about 10 times more concentrated than those used with the mercury arc.—June 14, 1920.

had been cut at the level of the lamp tube. On the outside of the hood was installed a Kober nephelometer[1] with the end of the lamp house (from which the incandescent bulb, the lens and glass plate had been removed) directly against and surrounding the opening in the "beaver" board. Radiation from the lamp (which is used "side-on") therefore falls upon the walls of the comparison cylinders when placed in their proper holders at a distance of 50 to 80 cm. from the source of illumination, depending upon the position of the lamp with reference to the front of the hood.

When the cylinders are thus exposed to the intense full radiation of the lamp there is so much reflection of visible rays from the walls of the cylinders and other parts of the instrument, that there is considerable light visible in the eye piece when only distilled water is present in the cylinders—or, in fact, when the cylinders are removed. It is, therefore, absolutely essential that the greater part of the visible rays be eliminated by a suitable filter so placed as to tightly close the opening in the beaver board. Plates of glass of the Uviol type are best adapted to this purpose.[2] With one of these ("Violet Ultra") it was possible to reduce the visible radiation to such an extent that, with the lamp at 50 cm. from the cylinders, one of the latter filled with distilled water or *N* sulphuric acid to a depth of 100 mm. gave a barely discernible haze—of the order produced

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[1] This is one of the newer types of the instrument, differing from that described by Kober (*J. Biol. Chem.*, **29**, 155 (1917)) in that the optical arrangement is not such as to produce the Lummer-Brodhun effect (square within a circle) but gives a simple divided circle as in most other instruments. Unlike the Duboscq, however, the *right* field corresponds to the *right* cup and not the reverse. The instrument is also provided with the pin-hole aperture in the observation tube, the importance of which has been emphasized by Kober (*J. Ind. Eng. Chem.*, **10**, 556 (1918)).

[2] Two glasses suitable for this purpose may be obtained from the Corning Glass Works, Corning, N. Y. One of these, known as "Red-Purple Ultra, G 586 A," comes in a thickness of about 5 mm. As visually observed with the spectroscope, this glass transmits the 2 faint red lines at the extreme left of the mercury spectrum (in the neighborhood of 7080 and 6920), and a barely distinguishable trace of the brilliant green line at 5461 while all of the lines in the violet from 4078 to the end of the visible spectrum are strongly transmitted. The second glass "Violet Ultra G 586 AW," is about 10 mm. in thickness and transmits no visible radiation of wave-length greater than 3984. Both of these are claimed to be, and apparantly are, extremely transparent to the rays in the neighborhood of 3650, the region of greatest intensity of ultraviolet radiation in the mercury arc. The choice of the one or the other as a filter in fluoremetry will depend somewhat upon the intensity of the source of illumination. The "Red Purple Ultra" appears to transmit somewhat more of the ultra-violet as well as the longer waves than does the "Violet Ultra" but in order to obtain zero illumination when using it with a strong lamp the latter must be removed to a considerably greater distance from the comparison cylinders than when using the "Violet Ultra."

The use of these glasses was suggested to me by Dr. E. K. Carver in connection with the qualitative observation of fluorescence.

by 3 to 4 mm. of a one part to 20 million solution of quinine sulfate in N sulfuric acid.

In the early experiments, the laboratory was darkened by curtains for the purpose of making the readings, but when it was found that the experiment was yielding results which would justify considerable work, a small dark room was built against the front of the hood. The greater ease and accuracy with which readings could be made, clearly demonstrated that for this work a dark-room is a practical necessity. A black cloth hung around the instrument, to aid in cutting off such rays as pass the openings of the side doors, may be used without interfering with the operation of adjusting the column heights, and may be lifted for reading the scale. The latter is accomplished by the aid of a very dim light to keep the eyes sensitive for the next setting.

Precautions.

Workers accustomed to the use of the colorimeter and nephelometer will instinctively guard against such sources of error pointed out by Folin, Kober and others, as eye fatigue, bodily strain, dust upon the optical parts, incorrect adjustment of verniers, failure to dry the exterior of cylinders or to rinse these properly and to wash and dry the plungers when solutions are changed. They will also naturally adopt a regular routine under which settings are made alternately from dark to light, and *vice versa*, and the mean of an even number in each direction taken for the average. Special mention should perhaps be made of the recent observations of Lamb, Carleton and Meldrum,[1] who point out the errors which may arise through rotation of the eye piece and suggest the marking of cups to insure their replacement in exactly the same positions. The latter I have found particularly important in the work now reported.

In addition to these, and to the lighting conditions already discussed, certain special precautions are to be observed. The source of illumination being neither at an infinite distance, as in the Duboscq colorimeter, not attached to the instrument base as in the regular Kober nephelometer, it is desirable to adjust the position of the lamp from right to left, or *vice versa*, until an approximate balance of the fields has been secured, after which the relative positions of lamp and instrument must be maintained throughout any series of readings. Even so, however, it has not yet been possible so to control conditions that the ratio between standard solutions contained in both cylinders remains exactly the same for many minutes. Thus in a series of readings in which the standard in the left-hand cup remains at the same height and the same solution in the right-hand cup was read against it at intervals of about 20 minutes such values (each an average of 4 settings) as 19.75, 19.1, 18.7 and 19.0, were obtained. Practically, this source of error may be overcome with reasonable

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[1] This Journal, **42**, 251 (1920).

accuracy by reading the standard both before and after the unknown and taking the mean of these two as the true basis for comparison.

Such a shifting of the relative values of the fields is observed in nephelometry, but according to most reports it occurs less rapidly. I am of the opinion that in the present case it must be due to variations in the intensity of the mercury arc at different points, caused probably by changes in the outside voltage.[1] If this is the case, it would seem possible to correct it by using, instead of the direct radiation, the rays brought to a focus by a suitable quartz lens or system of metallic mirrors, but neither of these has been available. As stated above, the lamp has been so placed that it is radiation from one side of the quartz tube which is utilized; using it in the end-on position results only in diminution of the intensity without improvement in constancy. The shifting is not due, as I at one time imagined, to a photolysis of the fluorescent substance standing in the left-hand cell during a whole series of comparisons. This is shown by the fact that the shift is not always in the same direction and persists even when the solution in the left cylinder is changed after the comparison of each unknown. The possibility of such a photolysis should, however, be borne in mind when dealing with substances which are particularly sensitive to photochemical change.

A further precaution is that of adequate dilution of the solutions examined. We have here a situation much more important than the errors which arise in colorimetry through the comparison of columns widely differing in depth. In fluoremetry we are dealing with a phenomenon in which the light is a function not only of the amount of dissolved fluoregene, but also of the amount of exciting radiation absorbed. It is to be expected, therefore, that when the concentration of a solution is already such that it *completely* absorbs the exciting rays, further increases in concentration will produce little or no increase in the amount of fluorescence observed.[2] Thus it has been found that 3.6 mm. of a 400 mg./liter solution of quinine sulfate is matched by 22 mm. of a solution con-

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[1] In this connection it should be noted that this shifting of the fields is more marked soon after lighting the lamp than later on. The lamp does not develop its full intensity until it has been in operation some 20 minutes and it has been found advantageous to allow it to remain lighted for even a longer period before starting an important series of readings.

[2] This result would naturally be anticipated from the reports of numerous investigations which show that the rate of a photochemical reaction does not follow the law of mass-action when the active rays are completely absorbed. Thus Luther and Forbes (THIS JOURNAL, 31, 777 (1909)), found that for the reaction between quinine and chromic acid "in ultra-violet light the velocity appears independent of the concentration of quinine, but in violet light these two quantities are roughly proportional to each other." This is explained by the fact that the ultra-violet light is completely absorbed while the violet light is absorbed only slightly. The fluorescent light with which the present paper is concerned is due entirely (within the limits of our power of

taining 1 mg. per liter (both of the same acid concentration). The assumption that the column heights will be inversely proportional to the concentrations, would call for a ratio of 1 : 400 whereas, in fact, it is only about 1 : 6. Yet, as noted below, when it is a question of comparing among themselves solutions containing from 0.5 to 2 mg. per liter a relationship closely approximating inverse proportionality is found to exist.

As a practical means of securing adequate dilution, it is suggested that the solution of any unknown substance be diluted by known stages until a point is found where further dilution produces a marked reduction in the luminescence of the flask or test-tube when held in the path of the screened ultra-violet radiation. It is better still to dilute the solution of the unknown substance until, when poured into a flat-walled vessel 10 mm. in thickness (spectroscopic cell) placed between the source of radiation and the parent solution contained in an observation cylinder standing in the instrument, enough radiation is transmitted by the solution in the cell to produce a marked fluorescence in the cylinder.[1]

Finally, it is to be observed that for the substances so far examined the reaction of the solution bears an important relationship to the amount of fluorescence as shown by the data in Table I. In this case the marked increase in fluorescence of aniline-iodeosine solutions in passing from 0.001 N acid to neutrality, as compared with the change from neutral to 0.1 N alkali, indicates that provided the solutions are distinctly non-acid, such

TABLE I.

Influence of Hydroxyl Ion Concentration upon Fluorescence of Aniline-Iodeosine Solution Containing 4 Mg. per Liter.

Reaction of solution.	Height of column required to match standard. Mm.	Comparative fluorescence. %.
0.005 N H_2SO_4	128.0	13
0.001 N H_2SO_4	57.0	29
Neutral	16.7	97
0.1 N NaOH	16.2	100
1.86 N NaOH	23.0	70

(The standard solution, *i. e.*, the one 0.1 N with respect to NaOH, was placed in the left cup of the instrument at 15 mm., which gave a reading of 16.2 for the same solution in the right-hand cup. The other solutions were then read in the right-hand cup, the standard remaining the same on the left, except in the case of the stronger acid where it had to be set at a lower value. The diminution in fluorescence found with the 1.86 N NaOH was probably due less to any interference by the excess of alkali as such than to its gradual destruction of the color body, for this solution became colorless after standing for several days.)

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measurement) to the ultra-violet rays as shown by the fact that no trace of it can be observed when the exciting radiation is made to pass first through 10 mm. of a strong solution of quinine sulfate (1 : 2500) though the latter does not diminish, so far as I have been able to observe, the intensity of any of those visible lines of the mercury arc which are passed by the glass filter "G 586 A."

[1] If comparison cylinders of transparent silica and a cell of the same material

minor differences in alkali concentration as would be incurred in practical determinations would be without appreciable effect. A similar condition was found for quinine sulfate when an acidity about normal is maintained. The presence of considerable quantities of non-fluorescent substances (neutral salts) in solution has also been shown to reduce the fluorescence though the change here is of a much lower order than that caused by variations in the reaction. A more complete study upon these points is in progress.[1] For the present it should be emphasized that for comparable results the concentration of salts and of hydrogen or hydroxyl ion in the standard and unknown solutions should be approximately the same.

Results of Measurements.

Quantitative comparisons have been made with solutions of quinine sulfate and aniline iodeosine. Among the known fluorescent substances which happened to be available, these selections were made for the preliminary work because they exhibit their fluorescence in acid and in alkaline solution, respectively, because an application of the quinine determination in a biochemical connection was contemplated and because the aniline-iodeosine solutions may likewise be studied in the colorimeter, thus affording a direct comparison with that method. No special attention was given to the purification of the original specimens used since, for the present, comparisons were to be made only between different dilutions of the same parent solution.[2] The results of these com-

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were used it would be a simple matter to determine what concentration of any substance in the cell when placed in front of *one* of the cylinders would reduce the fluorescence therein to a definite fraction of the former value required to match the companion cylinder not so screened. It is suggested that such measurements may be useful when, in the absence of the difficultly obtainable quartz spectrograph and accessories it is desired to determine in a semi-quantitative way the extinction coefficient for the longer ultra-violet rays.

[1] The referee to whom this paper was submitted by the Editor has kindly called my attention to an observation by Buckingham (*Z. physik. Chem.*, **14**, 129 (1894)), that quinine behaves differently in chloride and in sulfate solutions. In my note book under date of March 3, 1920, there appears a memorandum showing that the addition of conc. hydrochloric instead of conc. sulfuric acid to a certain solution of quinine sulfate gave very little fluorescence. This observation was the basis of the work on the effect of foreign substances here referred to which will be reported in a later communication.

[2] One gram of quinine sulfate, U. S. P., was dissolved in 100 cc. of dil. sulfuric acid and a portion of this still further diluted until a concentration of 2.5 mg. per liter was obtained (the solution having been neutralized in the meanwhile by the addition of the amount of 0.1 *N* sodium hydroxide solution indicated by the titration of a portion, using methyl red as the indicator). To volumes of from 10 to 40 cc. of this neutral stock solution 10 cc. of 5 *N* sulfuric acid was added in each case and the whole made up to 50 cc. The resulting solutions, used for the comparisons, therefore, contained from 0.5 to 2 mg. per liter of quinine sulfate in *N* sulfuric acid.

For the aniline-iodeosine solutions, 0.5 g. of the substance was dissolved in distilled water and diluted to a stock solution containing 20 mg. per liter. Of the latter, parisons are given in Tables II and III and graphically represented by the continuous curves in the upper parts of Figs. 1 and 2. They will be discussed presently.

TABLE II.

Fluoremetric Readings of Quinine Sulfate Solutions in *N* Acid Compared with Standard (*s*) Containing one mg.of Quinine Sulfate per Liter.

Concentrations in mg./L.	2.0 Mm.	1.7 Mm.	1.4 Mm.	1.2 Mm.	(*s*.) 1.0 Mm.	0.8 Mm.	0.6 Mm.	0.5 Mm
Individual Settings	10.3	12.0	14.7	17.0	19.7	24.6	31.4	....
	10.7	11.95	14.6	17.0	19.6	25.0	32.0	....
	10.6	12.0	14.7	17.3	20.0	24.6	32.1	....
	10.3	...	14.8	17.2	19.1	25.3	31.8	....
Av. 1st series..........	10.45	12.0	14.7	17.1	19.6	24.9	31.8	....
Av. 2nd series..........	10.3	12.1	14.6	16.7	19.8	24.3	31.5	....
Av. 3rd series..........	10.2	11.8	14.3	16.4	19.0	23.0	30.7	36.6
Av. 3 series...........	10.32	11.97	14.53	16.73	19.47	24.07	31.53	36.6
Adjusted av. (a)........	10.28	11.98	14.53	16.76	19.5	24.10	31.15	36.6

[a] These "adjusted averages" are the values obtained by averaging the 3 series after the results in each had been calculated (on the assumption of exact proportionality for differences of not more than 0.5 mm.) to what they should have been had the standard (*s*) read in each case 19.5 mm. instead of 19.6, 19.8 and 19.0 as actually found. It will be observed that the results thus obtained differ only inappreciably from those in the line above them, which are the plain averages of actual readings.

TABLE III.

Fluoremetric Readings of Aniline-Iodeosine Solutions in 0.1 *N* Alkali Compared with Standard (*s*) Containing 4 Mg. of Aniline Iodeosine per Liter.

Concentrations in mg./L.	(*s*.) 4 Mm.	3.6 Mm.	(*s*.) 3.2 Mm.	2.6 Mm.	2.0 Mm.
Av. 1st series..................	16.25	18.0	20.1	24.4	31.5
Av. 2nd series..................	16.10	18.0	20.1	24.2	30.6
Av. 3rd series..................	16.05	17.9	20.0	24.7	31.4
Av., 3 series...................	16.10	17.97	20.07	24.43	31.17
Adjusted (b) average............	16.00	17.83	19.90	24.25	30.90

[b] Obtained as in Table II by calculating the figures in each series to a common basis of $s = 16.0$ mm.

The results of comparing the same aniline-iodeosine solutions by colorimetry and fluoremetry (Table IV) are interesting. In addition to showing the divergence in ratios of readings to concentrations for the 2 methods, elsewhere discussed, they indicate that the fluoremetric readings are somewhat more concordant. The latter is not surprising in this case when it is considered that the color compared in the colorimeter is pink,

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volumes of from 10 to 20 cc. were measured, 10 cc. of *N* 1 sodium hydroxide solution added in each case and the whole diluted to 100 cc. The resulting solutions thus contained from 2 to 4 mg. of aniline iodeosine per liter in 0.1 *N* sodium hydroxide solution.

to which the eye is much less sensitive than to the greenish blue of the fluorescent light.

Table IV.

Fluoremetric and Colorimetric Comparisons of the Same Solutions of Aniline Iodeosine.

Fluoremetric Readings.		Colorimetric Readings. (Duboscq Colorimeter.)	
Left. (4 mg./L.)	Right. (2 mg./L.)	Left. (4 mg./L.)	Right. (2 mg./L.)
$s = 16.0$[a]	30.6	$s = 16.0$[a]	32.2
	30.6		34.3
	31.5		34.3
	31.5		35.0
	31.6		32.0
	32.0		32.7
	32.0		33.0
	31.5		34.8
16.0	31.4	16.0	33.5

[a] In each instrument the stronger solution was set at such a height in the left hand cup as to give a value of 16.0 mm. in the right-hand cup when the latter was filled with the same. The right cup was then emptied, filled with the weaker solution and readings made as indicated, the left remaining unchanged throughout.

Discussion of Results.

The results obtained with the sets of solutions of quinine sulfate and aniline-iodeosine, equal among themselves in content of acid and alkali, respectively, are expressed graphically by the solid curves in Figs. 1 and 2, in which the readings obtained are plotted as ordinates against the concentrations, in mg. per liter, as abscissas. The dotted curve in each figure represents the colorimetric or theoretical curve drawn on the assumption that $y = s/x$ (s being the reading of the standard).

The relationships of these 2 sets of curves naturally suggest that existing between the colorimetirc and nephelometric curves which has been discussed by Kober[1] and it was considered interesting to inquire whether the formula developed by him for the nephelometric curve would represent the results of fluoremetry.

Kober's formula is as follows

$$y = (s/x) - (1 - x)sk/x^2)$$

in which y is the height of the column of unknown solution, x the ratio of its concentration to that of the standard, s the height of the standard and k a constant to be determined (for any particular instrument and set of solutions) by substituting in the formula the standardization values of y, x and s.

In Col. 4 of Table V will be found the values obtained by solving for k, ($k = x\ (/1 - x) - (x^2y/(1 - x)s)$, when the values for y, s and x in fluoremetric measurements (Tables II and III and Cols. 2 and 3 of Table

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[1] *Loc. cit.*

V) are substituted. These values for k do not possess the same claim to constancy as those found in nephelometric work,[1] a condition which may or may not be altered by the elimination of further sources of error in the measurements. More significant than this is the fact that in the case of quinine sulfate where solutions both stronger than the standard and more dilute are compared with it, 2 distinctly different sets of values are encountered for k, the one corresponding to the range of higher concentrations, the other to the lower. The divergences are not of a type to indicate that they are due primarily to errors in measurements and it has, therefore, been considered preferable to use the average value of k as actually found for each range of concentration in determining the correction factor (Col. 6) for the solutions included within that range.

TABLE V.

COMPARISON OF FLUOREMETRIC READINGS WITH COLORIMETRIC AND NEPHELOMETRIC CURVES.

1. Conc. mg./L.	2. Ratio to Standard. x.	3. Fluoremetric Readings. $y_{Fluor.}$	4. Constant $\left(\frac{x}{1-x} - \frac{x^2 y}{(1-x)s}\right) = k$.	5. $y = \frac{s}{x}$ $y_{Color.}$	6. Neph. Correc'n. $\left(\frac{(1-x)\,sk}{x^2}\right)$	7. $y_{Neph.}$	8. $\frac{y_{Color.}}{y_{Fluor.}}$	9. $\frac{y_{Neph.}}{y_{Fluor.}}$
Quinine Sulfate in N 1 H_2SO_4. Standard contains one mg. per liter; s = 19.5 mm.								
					(k = 0.139).			
		Mm.		Mm.	Mm.	Mm.	%.	%.
2.0	2.0	10.28	0.109	9.75	+0.68	10.43	94.8	101.5
1.7	1.7	11.98	0.107	11.47	+0.66	12.13	95.7	101.3
1.4	1.4	14.53	0.151	13.86	+0.55	14.41	95.4	99.2
1.2	1.2	16.76	0.188	16.25	+0.38	16.63	97.0	99.2
			Av. 0.139					
1.0	1.0	19.5 (s)	...	19.5	0.00	19.5	...	...
					(k = 0.056).			
0.8	0.8	24.10	0.045	24.38	—0.34	24.04	101.2	99.8
0.6	0.6	31.15	0.062	32.50	—1.21	31.29	104.3	100.4
0.5	0.5	36.60	0.062	39.00	—2.18	36.82	106.6	100.6
			Av. 0.056					
Aniline Iodeosine in 0.1 N NaOH. Standard contains 4 mg. per liter; s = 16.0 mm.								
					(k = 0.024).			
4.00	1.0	16.00 (s)	...	16.00	—0.00	...	...	...
3.6	0.9	17.83	0.024	17.78	—0.05	17.73	99.7	99.4
3.2	0.8	19.90	0.010	20.00	—0.12	19.88	100.5	99.9
2.6	0.65	24.25	0.027	24.62	—0.32	24.30	101.5	100.2
2.0	0.50	30.90	0.034	32.00	—0.77	31.23	103.6	101.3
			Av. 0.024					

Column 5 gives the colorimetric or inverse proportionality curve, $y = s/x$, to which the nephelometric correction (Col. 6) is added algebraically to obtain the values for the nephelometric curve, Col. 7. The

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[1] Compare S. S. Graves, THIS JOURNAL, 37, 1176 (1915).

figures in Cols. 8 and 9 show, respectively, the percentage of the fluorescent substance actually present which would be indicated if the results of fluoremetric comparisons were read off directly from the colorimetric and nephelometric curves. The errors thus occasioned are represented graphically by the curves in the lower parts of Figs. 1 and 2. It is obvious that the nephelometric curve, as modified by the use of different constants for the 2 ranges of concentration, expresses the results of fluoremetric comparisons with an average error of about $^1/_6$ the magnitude which is encountered in the use of the inverse proportionality curve. This gives ground for the hope that work with other substances will demonstrate the possibility of a further modification which may render the nephelometric formula applicable to fluoremetry.

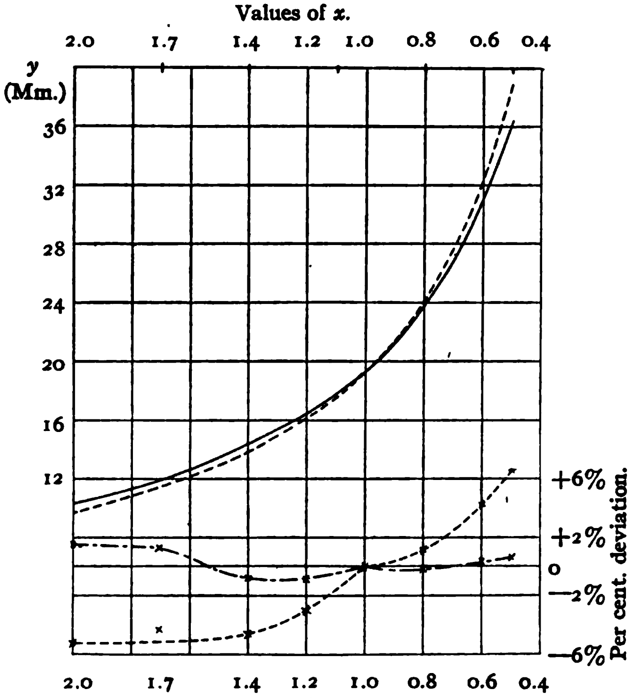

Fig. 1.—Relationship between Fluorescence and Concentration. Quinine sulfate in N H_2SO_4. Upper curves: $x = \frac{\text{Conc. sol'n compared}}{\text{Conc. standard (1 mg./L)}}$; y = height of column required for fluoremetric match with 19.5 mm. of standard; solid line is the curve of observed relationships; broken line is the inverse proportionality (colorimetric) curve. Lower curves: dash line shows the error (%) in actual concentrations of solutions resulting from interpreting fluoremetric readings from colorimetric curve; dot-dash line shows the error (%) from interpretation by modified nephelometric curve.

In further justification of the use of separate constants for the ranges of concentration greater and less than the standard of comparison, it seems desirable to call attention to certain facts regarding the magnitude and sign of nephelometric correction. It will be observed that in the formula

$$y = (s/x) - ((1 - x)sk/x^2)$$

the expression $-((1 - x)sk/x_2)$ represents the correction which must be applied to the colorimetric curve as given by the term s/x. In all of the curves published by Kober and his co-workers (so far as they have come under my observation) the *strongest* solution in a series is the one uniformly taken as the standard. In consequence, no value of x greater than one is encountered. When, however, an intermediate concentration is used for the standard of measurement, ratios greater than one will appear and, from the form of the expression $-((1 - x)sk/x^2)$ it will be seen that whenever x becomes greater than one, the sign of the resulting correction must necessarily change. That is to say, if the nephelometric

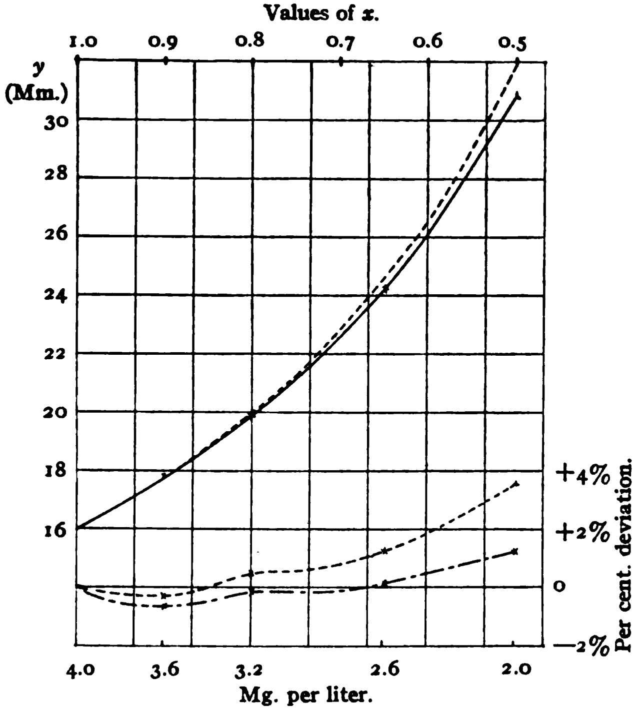

Fig. 2.—Relationship between Fluorescence and Concentration. Aniline Iodeosine in 0.1 N NaOH. Upper curves: $x = \frac{\text{Conc. sol'n compared}}{\text{Conc. standard (4 mg./L)}}$; y = height of column required for fluoremetric match with 16.0 mm. of standard. The several curves have the same significance as those in Fig. 1.

curve lies below the colorimetric for the region where $x < 1$ it should lie *above* the other for any values of x greater than one. As stated, I have seen no nephelometric curves which could be used for ascertaining whether this relationship holds good and I have not yet had the time to make appropriate measurements myself. But in plotting the observed results of fluoremetric measurements I was at once struck with the regular reversal of the positions of the actual and inverse proportionality curves whenever I passed from solutions weaker than the standard to those more concentrated. This observation led me to calculate the magnitude of the nephelometric correction, $-((1-x)sk/x^2)$, for considerable variations in x on both sides of $x = 1$. The results of such a calculation for the case in which $k = 0.052$ and $s = 20.0$ mm. are plotted in Fig. 3. In addition to the change in sign of the correction on the two sides of $x = 1$, it is noted that the absolute value for the interval between $x = 1$ and $x = 2$ is only about $^1/_{10}$ of that between $x = 1$ and $x = {}^1/_2$; that a maximum occurs at $x = 2$ and that thereafter the value is practically constant. So far, therefore, from expecting exactly the same form of

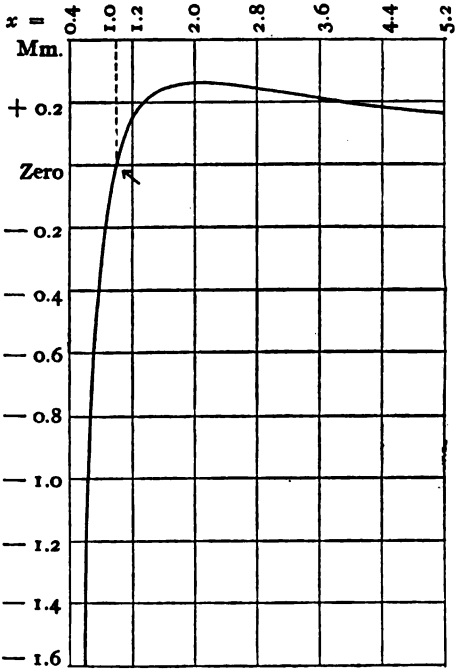

Fig. 3.—Variations in the sign and magnitude of the nephelometric correction factor, $\frac{(1-x)\,s\,k}{x^2}$, (ordinates of this curve) with changes in ratio of concentrations on both sides of $x = 1$. Calculated for standard (s) set at 20 mm. and $k = 0.052$.

expression to hold good on both sides of $x = 1$, it would be rather surprising if this were found to be the case.[1] In a practical way, the comparison of unknown stronger solutions with a fairly tall column of a weaker standard might give some interesting results.

Summary.

A new method of micro-analysis is described, of the same order of sensitiveness as colorimetry and nephelometry, which should prove generally applicable to the determination of minute quantities of the considerable number of substances which are either fluorescent themselves or may be rendered so by the addition of a suitable reagent.

Ultra-violet rays from a quartz-enclosed mercury arc, filtered from most of the visible radiation, are used to excite fluorescence in solutions of such substances contained in the comparison cylinders of the Kober nephelometer. The intensity of the fluorescent light thus produced, as observed in the eye piece of the instrument, is equalized in the usual manner by altering the heights of the exposed columns.

For sufficiently dilute solutions the curves obtained by plotting the scale readings against concentrations are quite regular. These calibration curves are drawn for solutions containing 0.5 to 2 mg. per liter of quinine sulfate in N sulfuric acid and for solutions of 2 to 4 mg. per liter of aniline iodeosine in 0.1 N alkali.

Such a curve differs from that of inverse proportionality (the colorimetric curve) much more than from one drawn according to the nephelometric formula. Some peculiarities of the latter are indicated and it is shown that when 2 constants are used (one for solutions stronger than the standard and the other for those more dilute) the values corresponding to the fluoremetric readings may be taken from the nephelometric curve with an average error of less than 1%. It is expected that this can be reduced by the further elimination of errors in measurement or a further modification of the formula, or by both together.

Various phases of the work, including certain applications, are receiving attention.

MEMPHIS, TENN.

[1] This is in no wise intended as a criticism of Kober's formula which is remarkably accurate for the particular purpose and region of concentrations for which it was designed and used. On the contrary, the present suggestions are only intended to indicate a possible widened usefulness.

[CONTRIBUTION FROM THE BUREAU OF STANDARDS, U. S. DEPARTMENT OF COMMERCE.]

GLASS TO METAL JOINTS.

BY E. C. McKELVY AND C. S. TAYLOR.[1]

Received April 22, 1920.

1. Introduction.

In the handling of volatile liquids and liquefied gases and in the manipulation of gases in general in the laboratory, it has been found very useful to have a method for connecting glass and metal tubing by means of a joint which combines the qualities of mechanical strength, resistance to internal pressure, tightness and stability over a considerable range of temperature and which also is suitable for use with a variety of gases. Several methods possessing the above qualities in various degrees have been in use in the laboratories of the Bureau for a number of years. The principles involved in these methods are not new, but in view of the possible wide applicability of joints of this type in laboratory work and their very limited use up to this date, it is desirable to bring together in one place the necessary information for making full use of them. In conjunction with proper auxiliary devices such as metal unions and valves, either of the needle or diaphragm type, a method is provided for joining metal to glass or glass to glass in such a way that in connecting and disconnecting, if proper care is used the weight of each part remains unaltered.

The purpose of this paper is, first, to give a detailed account of the best methods for the construction of these joints so that they can be reproduced by others; second, to give the results of certain tests upon them; and finally, to outline some of the applications of the joints in laboratory work.

2. Earlier Work.

The 2 types of joints considered in this work which possess the qualities mentioned above are the platinized glass-tin-metal joint, and the direct glass to metal joint.

Röntgen[2] soldered into a sheet of metal, a piece of glass, several sq. cm. in area which had been platinized by Dode's method. The plate was then dipped into boiling water without injury to it. Solder was observed to cling very tenaciously to the platinized surface, but by too long contact with the melted solder the platinum was dissolved from the surface of the glass. These observations have been corroborated by us.

Kundt is referred to by Kohlrausch[3] as the discoverer of the process of

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[1] Published by permission of the Director of the Bureau of Standards.

[2] Röntgen, *Pogg. Ann.*, 150, 331–3 (1873); *Dingl. Poly. J.*, 211, 136 (1873).

[3] Kohlrausch, "Lehrbuch d. prakt. Physik," 12*te* Auflage, 1914, p. 37.

soldering metal to platinized glass, which had been covered electrolytically with copper. The original publication on which this reference is based has not been found. As one of the foremost experimentalists of his time, Kundt may very well have discovered this process though no trace of it is found in his publications available to us. The procedure used in platinizing glass is the subject of many publications in the period from 1859 to 1870. The older work has to do with platinizing by means of a colloidal solution of platinum in lavender oil, while later publications are confined largely to platinizing by means of the cathode discharge, which is preferable for mirrors.

Cailletet[1] described a joint between glass and metal tubing made by covering platinized glass with a coating of copper electrolytically and soldering it into the metal tube as if it were metal. Adequate directions are given for making this joint, and he reported that on his apparatus for the liquefaction of gases a joint of this character, the size not being given, held 300 atmospheres internal pressure. Very little use of this valuable joint has been made since that time, particularly for high pressure work with gases. The Cailletet joint has been used at this Bureau for many years, especially for joining metal thermostat parts to the glass U-tube in which the mercury is actuated, and for sealing metal resistance thermometer bulbs to glass.

Very recently Koenig[2] has used a joint somewhat similar to the Cailletet joint, to join a glass manometer to a steel osmotic pressure cell. The glass tube was roughened by rubbing with glycerol and emery dust. It was then platinized by painting on a mixture of about two parts of ether to one of alcohol containing 3% of platinic chloride and 2% of stearic acid. After drying, the coated glass was heated gently in a Bunsen flame until a platinum coating was obtained. The platinum was first plated electrolytically with gold and then with nickel. A strip of zinc foil was wound around the nickel and soldered into place. This tube was then soldered to the steel cell.

The glass-platinum joint in the form in which a platinum wire is sealed into glass is one of the most familiar of laboratory devices. Joints in which a glass tube is fused to a platinum tube have been in use for a number of years in resistance thermometers of the calorimetric type.[3] Travers[4] attributes this type of joint to Callendar, and describes its construction. Karrer[5] has also recently described this type of joint.

A direct glass-to-metal joint was devised by C. A. Kraus.[6] Its prepara-

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[1] Cailletet, *Séances Soc. franc. phys.*, 1890, p. 242–3; *Séance*, Dec. 19, 1890.

[2] Koenig, *J. Phys. Chem.*, 22, 461 (1918).

[3] Dickinson and Mueller, Bur. Standards *Bull.* 9, 486 (1913); (*Sci. Paper* 200).

[4] Travers, "Experimental Study of Gases," p. 22. Macmillan and Co., 1901.

[5] Karrer, THIS JOURNAL, 40, 928 (1918).

[6] U. S. pat. 1,046,084, Dec. 3, 1912.

tion and application to the construction of many ingenious pieces of apparatus have been frequently described by him in his lectures throughout the country. Primarily designed for introducing large electrodes into glass vacuum tubes, its usefulness in the laboratory was readily apparent. The procedure as worked out has been applied only to joints between soft glass and iron or steel. A flux glass of low melting point is applied to the metal surface, to dissolve the metallic oxide and the metal to some extent, and thus give very intimate contact with the glass. The flux is applied to the inner side of the metal tube and the seal is then made to the flux glass.

For some years E. O. Sperling, glassblower at this Bureau, has successfully made soft glass to steel joints without the use of a flux glass. In this case it is necessary to heat the steel much hotter. The soft glass acts as its own flux, though it dissolves the iron oxide to a much smaller extent than is the case in the Kraus joint.

3. Construction of the Joints.

A. Soldered Joints.—The following procedure in making these joints has been used with gratifying results. Although, as will be shown later, it is possible that certain steps may be omitted without interfering seriously with the strength of the joint, the procedure as given has been found to give certain and reliable results. It has been applied only to the joining of glass and metal tubing. The glass tube is so chosen as to fit snugly for from 15 to 20 mm. of its length into the metal tube. It is convenient to have the end of the glass tube fit against a shoulder in the metal tube as shown in Fig. *1a*. The inside of the metal tube is tinned up to the shoulder with commercially pure tin, leaving a slight excess of tin on the surface, particularly if the tubes do not fit very closely. In place of tin, common solder or pure lead has been used successfully. The glass tube after roughening slightly with sand or emery paper is platinized over a length of 20 mm. or more by applying a colloidal solution of platinum[1] in

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[1] Several methods for preparing this solution, which has been extensively used for the preparation of platinum mirrors, have been proposed. Practically every method is some variation of the original solutions patented in England by Basserot in 1859 ("Repertory of Patent-Inventions, June," 1859, p. 485; *Dingl. Poly. J.*, 153, 42) and in France by Dodé in 1865 (described by Salvétat. *Bull. Soc. Encouragement*, Sept., 1865, p. 526; *Dingl. Poly. J.*, 177, 79). Solutions prepared as follows have been found very satisfactory. 1. Ten per cent. platinic chloride solution, equivalent to one g. of platinic chloride, is evaporated to dryness in a porcelain evaporating dish, and dissolved in a minimum quantity of absolute alcohol. This solution is added very slowly with stirring to 6 cc. of lavender oil in a container cooled in ice. Burgundy pitch is added to the warmed solution until the latter has the desired consistency. 2. One part of pure neutral platinic chloride prepared by evaporating the 10% solution to dryness is moistened with a few drops of absolute alcohol and ground finely in an iced mortar with 10 parts of lavender oil, adding the latter gradually in small quantities. 3. (Ascribed to Kundt by Kohlrausch, "Lehrbuch der prakt. Physik," 12*te* Auflage, 1914,

lavender oil mixed with Burgundy pitch. One or two drops of this mixture are applied to the slightly warmed surface and flowed into a film, which is then heated carefully to drive off the volatile material, and finally heated to an incipient red heat to burn off the carbonaceous material and fuse the platinum into the glass.

One application of any of the platinum solutions made up as described, is generally sufficient. If the coating seems too thin, the operation may be repeated. Using a slightly acid solution of zinc chloride as soldering flux, the two parts are heated gradually over a Bunsen flame until the tin is well melted. The glass part is inserted into the metal tube and the whole is allowed to cool slowly and uniformly. The platinum surface should not be tinned before making the joint as the platinum is likely to be removed in this operation. Much less care is required in platinizing and in making the joint if Pyrex glass tubing is used.

Joints have been made by this method with glass tubing up to 40 mm. external diameter, but the smaller sizes are much more easily made. Wall thicknesses of metal tubing from 0.5 to 2 mm. have been successfully used, but the lesser thicknesses give more certain results. Iron, steel, copper, brass and nickel have been successfully used, the only requirement being that the metal part must be wetted by tin.

B. Fused Joints.—Glass-platinum joints have been made with platinum tubing of either 0.1 or 0.15 mm. wall thickness. The glass should preferably have the same coefficient of expansion as the platinum. The best joints so far made were of Jena 397^{III} glass,[1] although one fairly good joint was made with Pyrex. The platinum forms the inner member of the joint and the length of the seal is usually from 5 to 10 mm. The construction of the joint requires skill in glass blowing but no special manipulation. There are numerous references in the literature to joints of this kind.

The flux for the Kraus joint is made by melting in a crucible equal parts by weight of zinc oxide, borax and powdered soda glass. The flux may be drawn or cast into rods for convenience in use. Its composition and use are covered by patent.

A method of making such joints which is particularly applicable to large tubes is described in U. S. Patent No. 1,046,084 by C. A. Kraus. Joints of the smaller sizes are comparatively much easier to make and

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p. 37). One g. of platinic chloride is dissolved in 3.5 cc. of absolute alcohol. Ten cc. of a concentrated alcoholic solution of boric acid is added and the whole is treated with 25 cc. of a mixture of lavender oil and Venetian turpentine in proportions to give the desired consistency. For giving a coating suitable for joints of the character described in this paper, the consistency of the platinizing solution is of little importance. Platinizing solutions which have been kept for several years gradually thicken when exposed to the air but deposit no platinum, and can still be used with satisfactory results.

[1] The Corning Glass Works also make a special glass for sealing to platinum.

considerable variations in construction are permissible. The metal shell has been made in a number of different shapes, some of which are shown in Fig. 1. Kraus uses a spun shell of steel (Fig. 1*d*). The spun shell is lined with a thin layer of flux and then with soda glass by blowing the glass into the shell. The glass tube to be sealed in is flared out to a flat ring of a width equal to from one to three times the thickness of the wall of the tube. The plane of this ring is normal to the axis of the tube. The tube and shell are heated and the tube introduced into the shell so that the edge of the ring presses against the shoulder in the shell. Fusion is completed by heating the outside of the shell, in such a way as to keep the glass tube cool enough to avoid deformation.

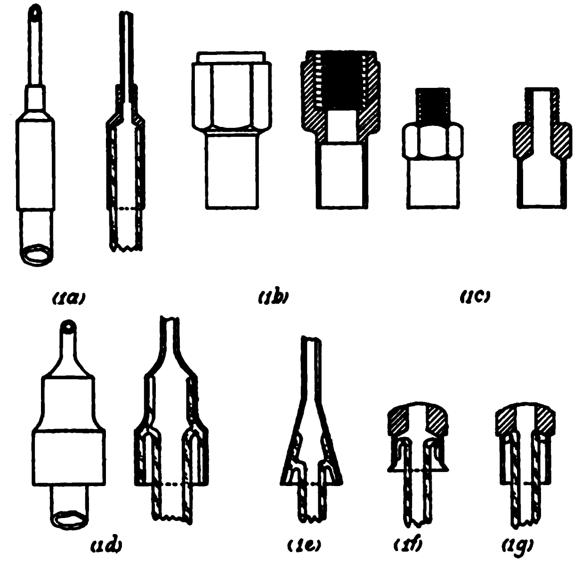


Fig. 1 Various types of glass-metal joints and caps.

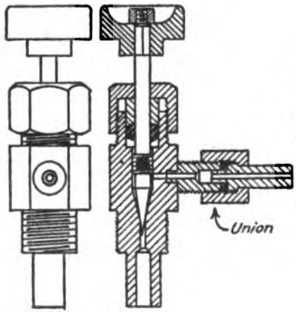


Fig. 2a. Needle valve
Scale - Full size

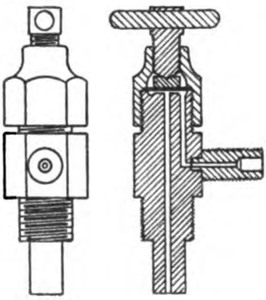


Fig. 2b Diaphragm valve
Scale - Full size

The construction described has been simplified in various ways. The necessity of using a shouldered shell may be avoided by the use of a conical shell (Fig. 1*e*). Cylindrical shells flared at the end have also been used. In these the lining of soda glass may be omitted, its function being performed by the outer part of the flared ring on the glass tube which is deformed on insertion, as shown in Fig. 1*f*. A simple cylindrical shell with the glass pressed against the bottom of the shell as shown in Fig. 1*g* has also been successfully used. In all cases, the flared ring should meet the outer member at nearly a right angle. It is not essential that the metal shell be thin.

Attempts at this Bureau to make joints between metal and Pyrex glass or porcelain have so far been unsuccessful.

4. Auxiliary Metal Parts.

The metal caps used in making the joints are made of such form that connection to other apparatus can be conveniently made. The simplest form of cap is one into which a metal tube is brazed or soldered. More generally useful forms are those which have a threaded connection which forms one member of a union. Several of the types of caps which have been used are shown in Fig. 1. In quantitative work with compressed and liquefied gases the ordinary stopcocks are not applicable, and valves must be used instead. The 2 types, a needle and a diaphragm valve, which have been most used, are shown in Fig. 2. An important feature of these valves is their small size and light weight. The needle valves are preferred except where the presence of the packing may prove objectionable; since, on account of the manner of seating, the diaphragm is not as easily closed and the closure is likely to be affected by small irregularities on the seating surfaces.

The valves are screwed into the metal caps, with a tin washer to make the joint tight. Metal to metal joints, which, if the proper care is used, may be made and broken without changing the weight of either part, are satisfactorily made by the union shown in Fig. 2*a*, which has a tin washer between the 2 metal surfaces. A fiber washer may be substituted for the tin in cases where contamination of the material will not result.

5. Tests of Joints.

Joints of this type have been used for several years for a variety of purposes which required them to be vacuum tight and to hold pressures up to 50 or 60 atmospheres. In addition, a few tests in which they were submitted to extreme conditions have been carried out. The pressure was attained by means of a hydraulic gage tester and the pressures could be read to about 5 atmospheres and held stationary for a short time. The limit of the apparatus was 400 atmospheres, a pressure well above the safety point for glass tubing in general.

Soldered Joint.—The internal pressure at which a joint of this type disrupts will depend upon the form and material of the metal cap, the manner of soldering, and the thickness and uniformity of wall of the glass tubing. Most of the tests were carried out on joints of the dimensions found most useful in our laboratory work, that is a steel or brass cap (Figs. 1*b* and *c*) with wall thickness of 0.5 mm. and glass tubing of 8.5 mm. external diameter and from 6 to 7 mm. internal diameter. In addition tests were carried out to obtain some information on the effect of each of the main factors involved. A considerable number of joints of this size, made as described in the section on construction of joints, which were first tested and found vacuum tight, were disrupted at pressures ranging from 100 to 220 atmospheres, the glass tubing shattering in every case. When a brass cap and capillary glass tubing of 1 mm. bore were used, the tubing was forced out at 250 atmospheres. When a steel cap was used, joints with such capillary tubing still held at 400 atmospheres. Two joints made with glass tubing 11 mm. outside diameter and about 1 mm. thick (but rather non-uniform) and with brass caps, held to 140 and 160 atmospheres, respectively. One joint with a steel cap 2 mm. thick, was much more difficult to make tight, but held to 320 atmospheres, when the glass shattered. Joints made with tubes up to 40 mm. in diameter have been found to be vacuum tight. Joints made with steel or brass caps were repeatedly immersed in oil at 200°, and cooled in air after each immersion without any noticeable effect upon their ability to hold a vacuum or internal pressure. When 4 joints thus treated were subsequently tested, the glass tubing shattered at from 130 to 200 atmospheres. Joints exposed to liquid air temperatures were vacuum tight at that temperature and remained so on warming up to room temperature.

No specific tests were made to determine the resistance of the joints to mechanical shock. However, experience in the use of this joint has shown no case of breaking except where the glass tubing itself might well be expected to break.

Certain modifications in making this type of joint were tested. In order to obtain good results it does not seem necessary to roughen the glass before platinizing. Joints can also be made without platinizing the glass. Six joints were made in this way, using brass caps in all cases and capillary glass tubing. In 3 cases where the glass was roughened, the tubes blew out at 80, 100 and 150 atmospheres; in 3 cases where the glass was not roughened, the tubes blew out at 160, 170 and 230 atmospheres. It seems probable that roughening the glass without subsequent platinizing merely interrupts the continuity of contact between the tin and glass, thus decreasing the strength. The tin appears to wet the glass and the strength of the unplatinized joint is probably due to that phenomenon rather than to the soft metal acting as a washer between the brass or steel and the glass. Inspection of the platinized joints after separation of the glass and metal shows that the tin flows on and clings to the platinized glass as if the latter were entirely of metal. More reliable and apparently stronger joints are, however, more easily obtained with the platinized glass, since in only one case with such glass was it possible to blow out the tube before the glass shattered. Soft solder ($^1/_2$ lead and $^1/_2$ tin) may be substituted for tin, but the joint will be more difficult to make and the result will be less certain.

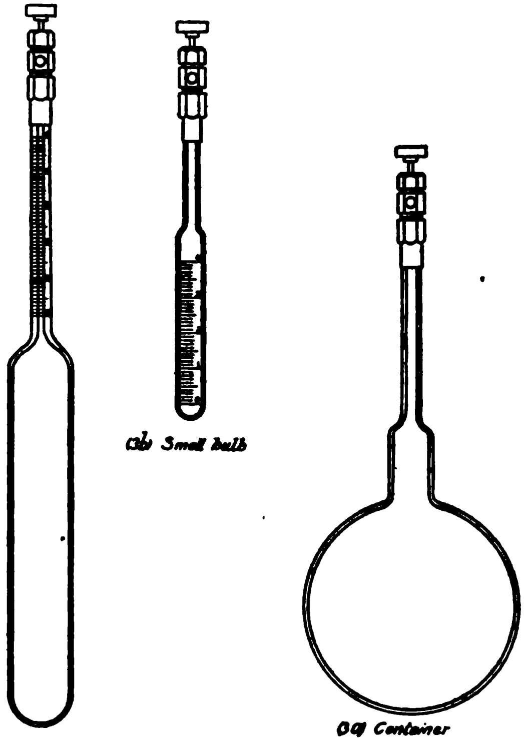
Four joints were made using pure lead as the solder between the thin-walled platinized glass and the steel cap. When tested the glass tubing shattered at from 175 to 275 atmospheres. A similar joint using capillary glass tubing held up to 400 atmospheres when the glass tubing shattered. A lead joint will remain vacuum tight up to 250°. Six joints were made according to Cailletet's directions; that is, platinizing the glass, copper plating the platinum, and then soldering the copper plated glass to the metal with tin. When tested they failed between 200 and 300 atmospheres pressure, the glass tubing being disrupted in every case. The joints were made by nickel-plating the platinized glass and then soldering the nickel-plated glass to the metal, using tin as solder. These joints held to almost 300 atmospheres when the glass finally disrupted.

Fused Joints.—Failure in the construction of joints of the Kraus type is at once evidenced by cracks or by the glass tube shattering at comparatively low pressures. To allow for the proper disposition of the seal in joints of this type in a steel tube 9 mm. internal diameter, the external diameter of the glass tube must be not more than 7 mm., thus making the internal diameter of the tube considerably smaller than in the case of the soldered joint. Joints of this character hold from 70 up to, in a few cases, 360 atmospheres. It appears, however, that the tube fails first at the joint. In one case a crack was heard at 20 atmospheres, but the joint held to 60 atmospheres. The experience at this Bureau with this type of joint indicates that it is somewhat more difficult to make, and is considerably more fragile than the soldered joint. It has rendered best service where it can be clamped into position, or where it is to be used with mercury, since mercury attacks the solder in a soldered joint. Joints made without flux glass have been successfully used in such cases, and have held pressures of many atmospheres. Joints of this type are put together at a temperature very much higher than that at which they are to be used. In spite of the great strains undoubtedly existing in the glass tubes near the joint, they have given surprisingly good results both in handling and in their resistance to internal pressure.

No test of the glass-platinum joints under pressure were made. Joints of this type were not injured by repeated immersion in the vapor of boiling sulfur (445°) or in liquid air (—190°).

6. Applications.

A.—The soldered joint was devised for and has been used mostly in connecting glass bulb containers to metal valves, thus permitting the introduction, observation, withdrawal and accurate weighing of comparatively large quantities of liquefied gases under pressure. It has been very useful in conducting the analysis and testing of liquid anhydrous ammonia[1] in which bulbs up to 125 cc. capacity have been employed. A metal to glass joint made with hard de Khotinsky cement will hold liquid ammonia for at most only a few hours. Keyes[2] has employed a shellac and oil of tar composition for this purpose, but says nothing as to the length of time it resists the action of ammonia. Round-bottom flasks of 500 cc. capacity with necks drawn down to 9 mm. outside diameter have served in the handling of ethyl chloride (Fig. 3*a*). Small bulbs up to 10 cc. have been used in handling liquid carbon dioxide (Fig. 3*b*).



(3b) Small bulb

(3a) Container

(3c) Picnometer

Fig. 3 *Illustration of use of glass-metal joints. Scale one third full size.*

B.—Inasmuch as it was found that the containers mentioned above could be weighed reproducibly to 0.1 mg. and with proper care in handling

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[1] E. C. McKelvy and C. S. Taylor, *Am. Soc. Refrig. Eng.*, 3, 36 (1917).

[2] Keyes, THIS JOURNAL, 40, 28 (1918).

and the proper type of valve, remained constant in weight for long periods, similar apparatus was constructed with a graduated capillary to serve as a picnometer in determining the density of liquefied gases and volatile liquids (Fig. 3*c*). With due precautions and the necessary corrections, picnometers of this kind have given results on the density of liquid ethyl chloride at 25°, which are reproducible with precision and are in excellent agreement with determinations carried out in sealed glass dilatometers. A few determinations of the density of liquid ammonia and of liquid methyl chloride have also been made with this container.

C.—This type of container has been applied to the determination of the density of ammonia under normal conditions of temperature and pressure by using it as a small easily weighed container into which the gas can be condensed from the calibrated bulb of large volume in which the temperature and pressure of the gas are measured. A somewhat similar method was first used by Prof. E. W. Morley[1] in determining the density of hydrogen, and by Maass and Russell.[2] It was found that the tube containing the liquefied gas under its own vapor pressure, and the empty container, could be weighed with great reproducibility when the necessary care and precautions in making and breaking joints were observed. The advantages of such a method are readily apparent.

D.—The Kraus joint could doubtless be used for the above mentioned applications, but it has been mainly applied to uses not involving the weighing of the part.

Both types of joints have been applied to the following uses. First, to connect apparatus such as steel cylinder used for fractional distillations at high pressures, to glass apparatus in which distillations at pressures below atmospheric are conducted. In this way contamination in transfer may be avoided. Second, in making up by a direct weighing procedure binary mixtures of known concentration of liquefied gases or volatile liquids.

The Kraus joint has been successfully applied in the construction of a multiple U-tube mercury pressure gage[3] for the reading of pressure differences up to 15 atmospheres, where it was necessary for mercury to pass through the joint. Such joints are regularly tested to 140 atmospheres pressure. Similar joints of a variety of sizes have been used with success in the construction of apparatus for use in the calorimetry of gases where the joints are required to be vacuum tight and resistant to internal pressure over a considerable range of temperature.

The joints made without flux glass have been applied successfully to apparatus for measuring by the static method vapor pressures up to 30

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[1] Morley, *Smithsonian Inst. Pub. Contributions to Knowledge*, **980**, 64–72 (1895).

[2] Maass and Russell, THIS JOURNAL, **40**, 1847–52 (1918).

[3] Dickinson and Meyers, *Bur. Standards Bull.* (to be published shortly).

atmospheres, under conditions where the possible passage of mercury must be provided for. These joints were tested to 50 atmospheres before use.

Acknowledgments are due to H. F. Stimson and C. H. Meyers, of this Bureau, for assistance and suggestions.

7. Summary.

1. Methods for the construction of 2 types of metal to glass joints have been given together with the results of tests upon their behavior on handling, their vacuum tightness and their resistance to internal pressure.

2. A reproducible and quantitative method for making and breaking connections between metal and glass or glass and glass is given.

3. Several types of apparatus and laboratory work in which these joints can be successfully used have been outlined.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY OF HARVARD UNIVERSITY.]

A CALORIMETRIC METHOD FOR STANDARDIZING THERMOMETERS BY ELECTRICAL ENERGY.

BY THEODORE W. RICHARDS AND SETSURO TAMARU.

Received April 23, 1920.

In 1915 Dr. Thorbergur Thorvaldson, in collaboration with one of the present authors, showed that it was possible to calibrate an interval in the thermometric scale near the temperature of the room with considerable accuracy by means of a definite chemical reaction repeated step by step at intervals over the scale.[1] This method (which demands only very simple apparatus) might serve, when properly carried out, a useful purpose for those whose experimental appliances are limited. Nevertheless, the change in heat capacity, and of heat of reaction with the temperature, cause complications in the calculation; and these data demand more thorough study as to their details before the method can attain the highest accuracy of which it is capable.

Another somewhat similar method is the subject of the present paper. In this method, the source of energy is not a chemical reaction, but rather electrical energy supplied at known voltage through a definite constant resistance. The method consists simply in thus supplying heat in successive small equal quantities to a calorimeter, noting the reading of the thermometers produced by each step. From the known heat capacity of the system, the rise of temperature which ought to occur is easily calculated. The comparison of the actual rise in each case with that calculated should give the error of the thermometer over each interval concerned. The accuracy clearly depends first, upon the accuracy of meas-

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[1] Richards and Thorvaldson, THIS JOURNAL, 37, 81 (1915).

urement of the time and the several electrical dimensions; secondly, upon the precision of the calorimetry; and lastly, upon the accuracy with which the specific heat of the system (consisting largely of water) is known.

The mode of experimentation is, of course, such as might be suited to the determination of heat capacity, if the temperature intervals were known. Instead, the heat capacity of water is assumed to be known and the temperature scale thus determined. The well-known work of Barnes[1] has placed our knowledge of the specific heat of water at ordinary room temperatures in a position adequate for the present purpose.

Apparatus.—The calorimeter was adiabatic, being contained in a closed vessel submerged in a bath capable of being heated electrically at the same rate as the inner calorimeter itself. The heating coil for the inner vessel was made of seasoned manganin coated with a firm insulating film of Bakelite; its 2 stout leads were suitably insulated by glass tube and sealing wax. This coil was immersed deeply in 0.9 liter of water in the calorimeter proper. The calorimeter was separated by an air space about 5 mm. thick from the walls of the submerged container. Such an air space was found to be sufficient, a wider space effected no important gain. The stirring was accomplished by means of the up-and-down motion of a stirrer composed of 2 perforated flat, silver rings which were thermally insulated from the operating mechanism by means of vulcanized rubber, so that there was no heat exchange through this agency. The mercury thermometers to be calibrated were immersed in the inner calorimeter vessel to a definite depth, kept constant throughout the experiments.

The surrounding bath was provided with a vigorous stirrer to cause very rapid attainment of uniformity in the temperature of the bath. Suitable rheostats and electrical measuring instruments were provided for both the inner and the outer circuits. The accurate measurement made necessary in the inner heating coil was made by means of a potentiometer so arranged that the potential between the terminals of the heating coil should be kept constant within 0.02% (at a value definite in any given series and usually about 3 volts). A stop watch measured the equal intervals of time. Neither potentiometer nor heating resistance need be carefully calibrated if the object is simply to subdivide a given interval of the thermoelectric scale and absolute values are not needed. A normal cadmium cell which was sufficiently constant served as the standard of electromotive force.[2]

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[1] H. T. Barnes, *Phil. Trans.*, **199A**, 149 (1902).

[2] The arrangement was not unlike that used by F. Daniels and one of us, except that, of course, the calorimeter and heating coil were much larger in the present case (THIS JOURNAL, **41**, 1746 (1919)).

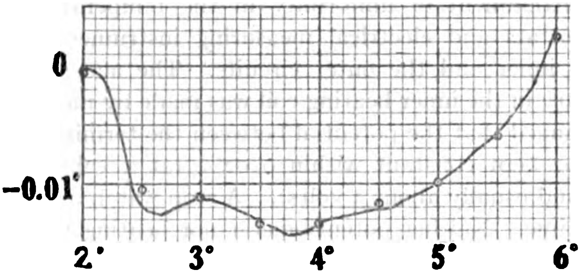
The successive readings indicated on a Fuess Beckmann thermometer (set so that 2.000° on its scale = 16.00°) through successive additions of a given amount of electrical energy in one of the series of trials are given by the following figures: 2.0505, 2.5555, 3.051, 3.5475, 4.044, 4.5375, 5.032, 5.5225 and 6.008.

The several differences between the successive pairs of these 9 figures are: 0.5050, 0.4955, 0.4965, 0.4965, 0.4935, 0.4945, 0.4905, and 0.4855.

If the specific heat of water at 18° is taken as 1.0000, those at 16° and 20° may be taken as 1.0005 and 9.9995, respectively. Evidently the corrections to be applied to the various differences on account of these small changes are very small,—beyond the accuracy of reading; but collectively they are worth considering. The values of the differences thus corrected become as follows: 0.5053, 0.4957, 0.4966, 0.4965, 0.4935, 0.4944, 0.4903 and 0.4858. The sum total of these 8 figures is 3.9581.

Careful determinations of this total interval by a standard platinum resistance thermometer showed that it was really 3.961°. Hence each interval should have been 0.4951°. The difference between this number and each of the 8 before mentioned gives the error of that particular range. Thus the error of the thermometer between 2.05 and 2.55 on its scale is found to be +0.0102°, between 2.55 and 3.05 +0.0006°, and so on. The corrections to be applied of course, bear the opposite sign.

The average of 6 trials thus made with this thermometer gave the results for its corrections indicated in the diagram, where they are compared with a careful standardization of the same thermometer by means of an accurate platinum resistance thermometer (standardized at the Bureau of Standards), kindly made by Mr. O. C. Bridgeman.



Corrections to the Beckmann thermometer are plotted in the direction of ordinates; scale readings of the thermometer in the direction of abscissas. The black line indicates standardization by platinum thermometer; the circles, the average results of the method under consideration.

The 6 trials of which the average is represented above were the last executed of a number in which the earlier trials served as preparation and training. The intervals were not always half a degree, as in the case cited, some being less and some more. Of the 60 observations included in these 6 series of results, only 2 deviated from the smooth curve drawn among them by more than 0.001°. Thus it is clear that with adequate practice and care this method may serve very satisfactorily to calibrate a thermometer.

We are indebted to the Carnegie Institution of Washington for generous pecuniary support in this work, which was incidental to a careful research having as its main object the determination of the heat of solution of cadmium in acids. This will soon be reported in full. The experimental work was completed in 1915.

Summary.

In this brief paper, it is shown that a thermometer may be accurately calibrated by successive additions, to a known heat capacity, of heat from electrical energy. The experimentation is essentially like that suitable for the determination of heat capacity where temperature changes are accurately known.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM CHEMICAL LABORATORY, EDGEWOOD ARSENAL, EDGEWOOD.]

FREEZING-POINT SOLUBILITY CURVE FOR SULFUR AND DICHLORO-ETHYL SULFIDE.[1]

By J. A. WILKINSON, CHRIST NEILSON AND H. M. WYLDE.

Received April 28, 1920.

In the preparation of dichloro-ethyl sulfide or mustard gas by the reaction between ethylene gas and sulfur monochloride according to the equation

$$2C_2H_4 + S_2Cl_2 = (C_2H_4Cl)_2S + S$$

one atom of sulfur is set free for every molecule of mustard gas formed, that is, about 20% of sulfur by weight. When first prepared this sulfur stays in solution, but on standing it may precipitate out in such a way as to form a hard cake in the settling tanks or pipe lines. Later methods of manufacture overcame this difficulty, however.

It was the purpose of this investigation to determine the solubility of sulfur in liquid mustard gas and also the nature of the solid phase which separates out at different temperatures.

Preparation of Materials.

The first experiments were made with a very high grade of roll sulfur without purification. Afterwards pure rhombic, monoclinic and amorphous sulfur were prepared and their solubilities determined.

Rhombic sulfur was prepared by recrystallizing the roll sulfur from carbon disulfide solution.

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[1] Published with the approval of Lt. Col. Amos A. Fries, Chief Chemical Warfare Service, U. S. A.

Monoclinic sulfur was prepared by melting the roll sulfur, allowing the melt to cool until nearly all solid, and then breaking the crust and allowing the remaining liquid to run off. The crust and the liquid were discarded and only the fine needle crystals used. This was kept in an oven at 109° to 110° until used. *Amorphous sulfur* was prepared by melting the roll sulfur and allowing it to run in a fine stream into water. After standing for some time this was dried, ground to a fine powder in mortar, and then extracted repeatedly with carbon disulfide to remove all but the amorphous form. The material was used immediately after driving off the excess of carbon disulfide.

Dichloro-ethylsulfide.—A sample of crude mustard gas, from Edgewood Arsenal, which was quite brown and had a large amount of sulfur dissolved in it, was placed in a bath of ice and salt and frozen. On remelting the mustard gas most of the sulfur remained as a precipitate. The clear amber liquid was poured off from this and fractionally distilled twice under reduced pressure. On the second distillation the part which came over under a pressure of 21 millimeters of mercury at a temperature of 98° to 99° was almost water-white and had a freezing point of 13.82°. This was used in the experiments.

Method.

Mixtures of sulfur and mustard gas were weighed into a large test-tube which was inserted into a larger one and held in position by a rubber stopper. This gave an air space between the two, making the rate of heating and cooling slower and more regular. The inside tube was closed by a rubber stopper with 2 holes for the introduction of the thermometer and stirrer. A 2-liter beaker of water or oil, heated with a Bunsen burner, was used as a temperature control.

The temperature of the bath was raised slowly at the rate of about 2° in 5 minutes and the mixture stirred constantly. The temperature was noted at which the 2 phases became one, and then the system was slowly cooled and the temperature again noted when the second phase appeared. The determination was then repeated, heating and cooling at a slower rate and thus increasing the delicacy of the transition point. This method gave very accurate results for that portion of the curve where 2 liquid layers formed. Where the solid phases separated a different procedure was used. The freezing-point determination method developed by the American University Research Division of the Chemical Warfare Section was used where the solid phase was mustard. Where the solid phase was sulfur the method of plotting time against temperature during the cooling was used.

Where the per cents. of sulfur were below 1% a Beckmann thermometer was used for the determination of the lowering of the freezing point. For all the other determinations a thermometer graduated in single degrees and capable of being read to 0.1° was used.

The mustard gas was placed in the test-tube first and weighed accurately to the third decimal place. The sulfur was weighed on a watch glass and transferred to the test-tube. From these weights the per cents. of the components were calculated. After one determination, a second weight of sulfur was introduced into the apparatus. Each point was checked several times with each quantity weighed and the whole series was checked twice. The results given in the data are averages of many readings.

Solubility of Roll Sulfur.

Table I gives the temperature at which the second phase was formed with the different per cents. of sulfur. Also the nature of the second phase is shown, whether it was solid mustard gas, solid sulfur or a second liquid layer.

TABLE I.—SOLUBILITY OF ROLL SULFUR.

Temperatures.

	Nature of the solid phase.		
% S.	Solid mustard. °C.	Solid sulfur. °C.	Liquid phase. °C.
0	13.82	...	...
0.1	13.79	...	...
0.3	13.75	...	...
0.7	13.70	...	...
0.9	13.66	...	...
1.48	...	24.0	...
2.44	...	43.0	...
3.38	...	54.0	...
4.31	...	61.0	...
6.10	...	74.0	...
9.09	...	85.0	...
16.66	...	99.0	...
20.00	...	102.5	...
25.18	...	...	110.0
31.00	...	...	120.0
32.00	...	...	122.0
35.00	...	...	127.0
40.00	...	...	133.5
60.00	...	...	143.0
78.00	...	...	135.0
85.00	...	...	124.0
87.00	...	...	117.5
90.00	...	...	105.0
94.00	...	108.0	...
100.00	...	114.0	...

These results are shown in Figs. 1 and 2, Fig. 1 giving all the data and Fig. 2 being drawn on a larger scale so that it will show the part of the curve below 1% sulfur.

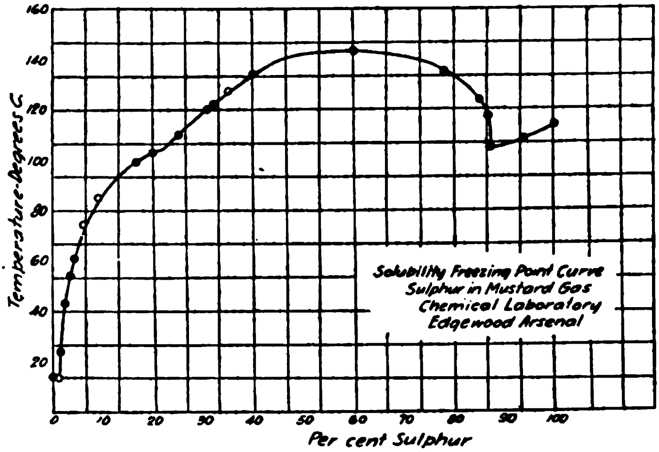

Fig. 1.

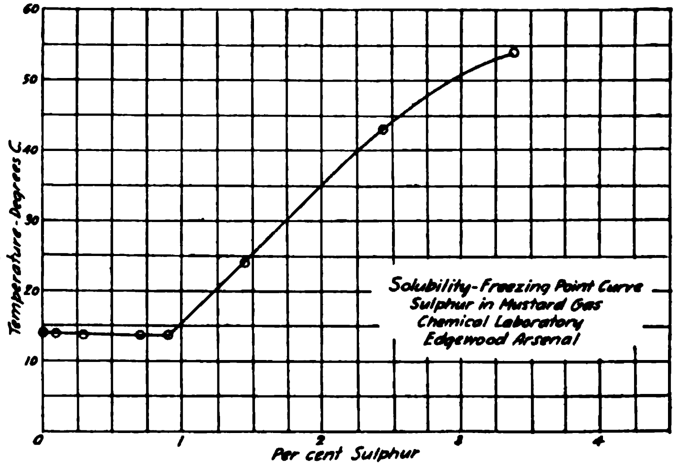

Fig. 2.

Solubility of Rhombic Sulfur.

This determination was made for the purpose of checking the results with those on roll sulfur. Table II gives the data and the comparison with the roll sulfur of the same per cent. composition.

TABLE II.—SOLUBILITY OF RHOMBIC SULFUR.

	Temperature.			
Rhombic. %.	Sol. °C.	Freezing. °C.	Roll sulfur. %.	Temp. freezing. °C.
7.6	80	79	7.6	79
11.3	90	90	11.3	90
17.5	100	100	17.5	100
21.0	104	103	21.0	103

These values show that the solubility of the 2 samples of sulfur is the same.

Solubility of Monoclinic Sulfur.

The solubility of monoclinic sulfur was found to agree with that of rhombic. The question then presented itself as to which of the 2 forms was the stable phase in contact with mustard gas at the different temperatures.

On cooling solutions of sulfur in mustard gas until crystals of sulfur separated out, it was found that the nature of the solid phase depended upon the temperature at which it was formed. If above 78° the crystals were monoclinic needles while below that they were rhombic crystals.

These experiments lead to the conclusion that in crystallizing at temperatures below 78° the rate of transformation is too rapid to allow the monoclinic to be stable, while above that temperature we are approaching near enough to the true transition point to make the rate slow enough to allow the monoclinic to form and remain as the solid phase under the liquid.

This is, as would be expected, that the metastable phase or monoclinic crystals would form first and then would change to the stable or rhombic crystals. The rate at which transition would take place would increase the farther one went below the transition temperature (95.5°) until at 78° it would change so rapidly that the presence of the monoclinic form could not be detected. It does not necessarily mean that the transition point of the 2 forms of sulfur is lowered by the presence of the liquid mustard gas.

Solubility of Amorphous Sulfur.

A mixture of 0.14% of amorphous sulfur and 99.86% of mustard gas was heated slowly from 30° to 120°, holding the temperature constant for 10 minutes at every 10° and stirring continuously. There was no evidence of solution of the sulfur until the temperature was raised to 120° at which point the sulfur melted and all went into solution immediately. The solubility of amorphous sulfur is, therefore, less than this amount at temperatures below its melting point.

Conclusions.

(1) The complete solubility curve for sulfur in mustard gas has been determined.

(2) The solubility of rhombic and monoclinic sulfur in mustard gas is the same.

(3) Below 78° the solid phase that crystallizes is rhombic sulfur while above that temperature it is monoclinic sulfur.

(4) The solubility of amorphous sulfur in mustard gas is less than 0.14% at temperatures below 120° at which temperature the sulfur melts.

In conclusion the writers desire to express their appreciation of the helpful suggestions of Major Wm. Lloyd Evans of the Chemical Laboratory of Edgewood Arsenal.

AMES, IOWA.

[CONTRIBUTION FROM CHEMICAL LABORATORY, EDGEWOOD ARSENAL, EDGEWOOD, MD.[

DENSITY AND COEFFICIENT OF EXPANSION OF DICHLORO-ETHYL SULFIDE.[1]

JOHN A. WILKINSON AND CHRIS WERNLUND.

Received April 28, 1920.

One of the physical constants of dichloro-ethyl sulfide or mustard gas, which is of great importance in filling gas shells, is the density and the variation of this with changes in temperature. This last is of importance since upon it is based the calculations of the voids necessary to be left in filling the shells in order to prevent the development of leaks. The liquid expanding as the temperature rises completely fills the shells and crushes the threads on the adaptors which hold the boosters.

Since the density at different temperatures was desired, the determinations were made in a dilatometer tube. The same sample could be used to determine the density at the different temperatures and thus the coefficient of expansion could be calculated.

Preparation of Dichloro-ethyl Sulfide.

A sample of mustard gas supposed to be about 97% pure was first distilled by passing the vapor from a constant boiling hydrochloric acid solution through it. The heavier layer of the distillate was then extracted with ether and the ether layer dried over calcium chloride for 12 hours. It was then poured from the calcium chloride into a distilling flask and the ether evaporated off, and the residue distilled *in vacuo*, the middle portion being taken for the density determination. This liquid was almost water-white, having but a very faint yellow tinge. Its freezing point was 13.5°.

Determination of Density.

The stem of the dilatometer was calibrated before sealing to the bulb by weighing the amounts of mercury delivered by the different lengths of the capillary. The volume of the bulb was determined by weighing the dilatometer empty and filled to the zero mark with mercury.

The mustard gas was introduced into the dilatometer through a very fine capillary tube made by drawing out a piece of glass tubing. The dilatometer was immersed in a water bath at 15° and filled with mustard gas adjusting the level to the zero mark after equilibrium had been reached. The top of the dilatometer was then sealed off and it and the contents

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[1] Published with the approval of Lt. Col. Amos A. Fries, Chief Chemical Warfare Service, U. S. A.

weighed. The increase in the weight over that of the empty dilatometer gave the weight of the mustard gas.

Data.

The values obtained are as follows:

Weight of mustard gas used........................	6.0835 g.
Volume of dilatometer..............................	4.7564 cc.

$$\text{Density at } 15^\circ = \frac{6.0835}{4.7564} = 1.2790.$$

Coefficient of Expansion.

The dilatometer was then immersed in a tall glass vessel filled with water which served as a constant temperature bath. The temperature was raised slowly and the height of the meniscus in the capillary read by means of cathetometer. The following table gives the volume occupied by the 6.0835 g. of mustard gas at the different temperatures, and from these values are calculated the densities or specific gravities compared to water at 4° as unity. In the last column are the differences in density for each 5 degrees. Several readings being made at each point with both rising and falling temperatures.

The volume read on cooling to 15° after having raised the apparatus to 90° was exactly the same as it was before being heated. This showed that the apparatus recovered its original volume very quickly after being heated.

TABLE I.

Weight of Mustard Gas = 6.0835 g.

Volume Cc.	Temp., ° C.	Density.	Diff.	
4.7564	15	1.2790	..	
4.7748	20	1.2741	0.0051	
4.7956	25	1.2686	0.0055	
4.8147	30	1.2635	0.0051	
4.8345	35	1.2584	0.0051	
4.8547	40	1.2531	0.0053	
4.8752	45	1.2479	0.0052	
4.8957	50	1.2426	0.0053	
4.9168	55	1.2373	0.0053	
4.9386	60	1.2318	0.0055	
4.9607	65	1.2263	0.0055	
4.9823	70	1.2210	0.0053	
5.0034	75	1.2158	0.0052	
5.0249	80	1.2106	0.0052	
5.0481	85	1.2051	0.0051	
5.0633	88	1.2015	0.0036	0.0055
5.0710	90	1.1996	0.0019	

The variation in density per degree between 15° and 90° is 0.001058. The variation in volume of one gram per degree between the same temperature is 0.0006895 cc. The variation in volume in cc. per cc. per degree is 0.000881 cc.

TABLE II.

Thermal Expansion of Dichloro-ethyl Sulfide.

Volume at 15° = 1.

Temperature, ° C.	Vol.
15	1.00000
20	1.00324
25	1.00824
30	1.01226
35	1.01642
40	1.02067
45	1.02497
50	1.02901
55	1.03372
60	1.03830
65	1.04295
70	1.04747
75	1.05193
80	1.05648
85	1.06133
88	1.06452
90	1.06614

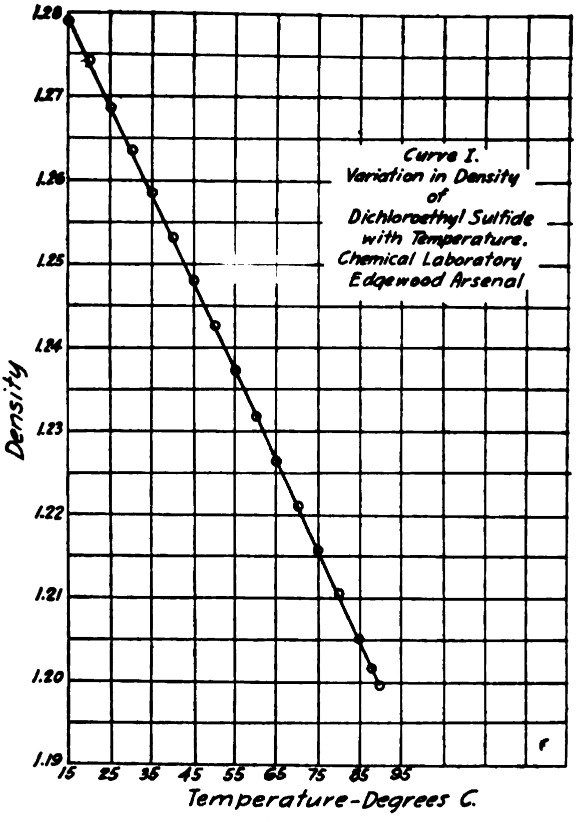

Fig. 1.

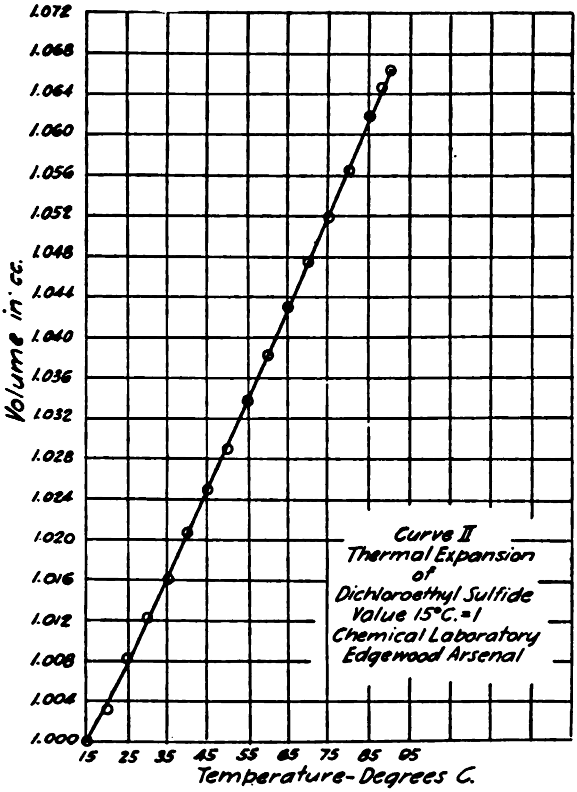

Fig. 2.

In the accompanying curves, I shows the relationship between density and temperature and II change in volume of one cc. of mustard gas with increase in temperature, *i. e.*, the coefficient of expansion.

Conclusions.

(1) The density of dichloro-ethyl sulfide at 15° is 1.2790 and at 90° it is 1.1996, a change of 0.001058 per degree.

(2) The coefficient of expansion of dichloro-ethyl sulfide between 15° and 90° is 0.06614 cc. per cc., an increase of 0.000881 cc. per degree.

(3) The expansion between these temperatures is practically uniform.

In conclusion the writers wish to express their appreciation of the help and suggestions of Major Wm. Lloyd Evans, of the Chemical Laboratory of Edgewood Arsenal.

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[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR., CHEMICAL LABORATORY OF HARVARD COLLEGE.]

THE VAPOR PRESSURES OF CERTAIN SUBSTANCES: CHLOROPICRIN, CYANOGEN BROMIDE, METHYL-DICHLORO-ARSINE, PHENYL-DICHLORO-ARSINE, DIPHENYL-CHLORO-ARSINE AND ARSENIC TRICHLORIDE.[1]

BY G. P. BAXTER, F. K. BEZZENBERGER AND C. H. WILSON.[2]

Received May 3, 1920.

In collaboration with the Bureau of Mines and the Research Division of the Chemical Warfare Service the vapor pressures of various compounds were determined at the Harvard Branch Laboratory. While the necessities of the situation demanded speed rather than a high degree of accuracy, the observations are probably correct with a very few per cent. in most cases, and seem on the whole worth while making a matter of permanent record. This paper contains the results obtained with the following substances: chloropicrin, cyanogen bromide, methyl-dichlorarsine- phenyl-dichloro-arsine, diphenyl-chloro-arsine and arsenic trichloride.

All the observations were made by the "air current" or "transference" method, except in the case of arsenic trichloride at higher temperatures where a static method was employed. A known volume of air, as determined by the measured volume of water run out of an aspirator, was saturated with the vapor of the substance in question by passing through a weighed receptacle maintained at constant temperature in a water thermostat. The loss in weight of the saturating tube furnished the weight of evaporated substance. From the latter quantity the volume of vapor was calculated on the assumption that the volume of a gram molecule under standard conditions is 22.41 liters. Even with the most volatile substances this assumption is probably true within the accuracy of the experiments. The per cent. of vapor by volume multiplied by the interior pressure, as determined by the barometric reading and an open-arm water manometer attached to the aspirator, gives the vapor pressure.

The control of temperature in the thermostats was within 0.1° except when a freezing mixture was employed where the uncertainty may have been as large as one degree at —18°.

Since nearly all the substances investigated hydrolyze readily, the air was dried, usually by passing over sodium hydroxide, before entering the saturating tube. The saturating tube was constructed as shown in Fig. 1 with 3 U-tubes joined together. The inlet, which could be closed with a glass stopcock, was located above the water of the constant tem-

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[1] Published by permission of the Director of the Chemical Warfare Service.

[2] Sergeant, C. W. S., U. S. A. Died, January 10, 1919.

perature bath; the outlet in most cases was immersed in the bath so as to avoid condensation of the vapor when used at temperatures above that of the room, and was connected to a U-tube immersed in the bath and then to the aspirator system by stout rubber tubes. Between the U-tube and the aspirator, when the more volatile substances were under examination, a U-tube immersed in a freezing mixture was introduced, both as a matter of safety and in order to avoid pressure complications in the aspirator bottle.

The coils of the saturating tube were nearly filled with glass beads. If the substance under examination was a liquid, barely enough was introduced to seal the bends of the coils. If the substance was a solid it was either introduced in the molten state or was melted in the tube and caused to solidify over as much of the interior surface of the coils as possible.

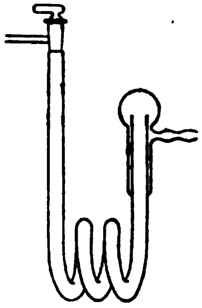
Fig. 1.

No variations in the results with the rate of flow of air were found up to 4 liters of air per hour, but the rate was ordinarily between 2 and 3 liters per hour, and with the more volatile substances such as cyanogen bromide was much less. While all the materials furnished were apparently fairly pure, they all gave evidence of containing a small proportion of more volatile impurities, since the initial results were higher than later ones. In order to provide for this difficulty the first step after filling the saturating tube was to pass a comparatively large volume of air through the tube at an elevated temperature before making any attempt to weigh the tube. After such treatment, constant values for the vapor pressure were always obtained. There is, however, the uncertainty as to less volatile impurities which may have lowered the vapor pressure.

The tubes were weighed by substitution for similar counterpoises, after the usual precautions of wiping with damp cotton cloth and prolonged standing near the balance. Many hours' immersion in the water of the thermostat even at as high a temperature as 75° was found to have no perceptible solvent effect upon the glass.

With all the substances investigated a plot of the logarithm of the vapor pressure against the reciprocal of the absolute temperature gives a very nearly straight line, which therefore, can be represented by an empirical equation of the form

$$\log v.\,p. = A + \frac{B}{273 + t}.$$

Satisfactory values of A and B have been computed for each substance.

Vapor pressures calculated by means of these equations agree with the observed values within the experimental error. For a higher degree of accuracy the equations are not adequate, however, and cannot be trusted for extrapolation over any considerable range.

Details follow for the individual substances.

Chloropicrin.—The original material was distilled in a partial vacuum in 2 portions. The first was used at 35°, 25°, 15° and 0°, the second at the other temperatures. The first 2 experiments, at 25°, which gave discrepant results, are not included in the table.

TABLE I.

Chloropicrin.

$$\log v.p. = 8.2424 - \frac{2045.1}{273 + t}$$

Temperature. °C.	Volume of air at 0° and 760 mm. Cc.	Loss in weight of tube. G.	Interior pressure. Mm.	Vapor pressure observed. Mm.	Vapor pressure calculated. Mm.	Difference. Calc. — obs. Mm.
35	2151	0.9200	731.0	40.27		
	2575	1.0690	749.5	40.13		
	2317	0.9445	748.0	(39.36)		
	1828	0.7776	730.3	40.01		
			Av.,	40.14	40.04	—0.10
30	2784	0.8638	763.3	30.97		
	2085	0.6505	765.8	31.23		
			Av.,	31.10	31.10	0.0
25	2805	0.6808	742.6	23.78		
	2535	0.6048	756.5	23.83		
			Av.,	23.81	23.97	+0.16
20	2008	0.3626	759.4	18.24		
	2361	0.4300	758.9	18.38		
			Av.,	18.31	18.30	—0.01
15	3287	0.4454	761.3	13.81		
	2657	0.3653	752.0	13.83		
			Av.,	13.82	13.85	+0.03
10	2588	0.2651	758.5	10.45		
	2903	0.2930	758.0	10.29		
			Av.,	10.37	10.37	0.0
0	2407	0.1386	733.2	5.71		
	2712	0.1551	737.5	5.71		
			Av.,	5.71	5.64	—0.07
—18	3299	0.0611	754.1	1.90	1.67	—0.23
—19	3400	0.0566	751.5	1.70	1.55	—0.15
—20	3125	0.0459	751.8	1.50	1.44	—0.06

The approximate volume of air and loss in weight of the saturating tube are given briefly in the following table for the individual experiments with the remaining substances:

	Volume of air. Liters.	Loss in weight of tube. G.
Cyanogen bromide	1–2	1.8 –0.07
Methyl-dichloro-arsine	1–3	0.17 –0.01
Phenyl-dichloro-arsine	6–25	0.025–0.001
Diphenyl-chloro-arsine	14–32	0.007–0.0001
Arsenic trichloride	2–6	0.85 –0.14

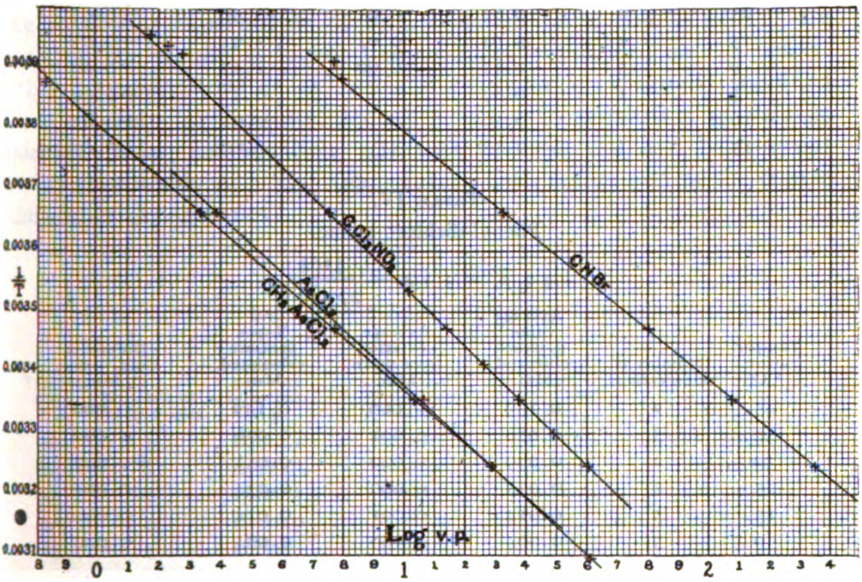

Fig. 2.

TABLE II.

Cyanogen Bromide.

$$\log v.p. = 10.3282 - \frac{2457.5}{273 + t}$$

Temperature. ° C.	Number of observations.	Average vapor pressure observed. Mm.	Average deviation from mean. Mm.	Vapor pressure calculated. Mm.	Difference. Calc. — obs. Mm.
35	4	223.5	2.9	223.5	0.0
25	3	119.5	0.9	120.6	+1.1
15	2	63.3	0.1	62.4	—0.9
0	2	21.2	0.1	21.2	0.0
—15.5	1	6.3	...	6.1	—0.2
—17.3	1	5.9	...	5.2	—0.7

Phenyl-dichloro-arsine.—This material contained a relatively large proportion of volatile impurity, which eventually was removed by sweeping out the saturating tube with a current of air for many hours at about 70°.

TABLE III.

Methyl-dichloro-arsine.

$$\log v.\ p. = 8.6944 - \frac{2281.7}{273 + t}$$

Temperature. °C.	Number of observations.	Average vapor observed. Mm.	Average deviation from mean. Mm.	Vapor pressure calculated. Mm.	Difference. Calc. — obs. Mm.
35	2	19.33	0.06	19.33	0.00
25	2	10.83	0.01	10.90	+0.07
15	2	5.94	0.01	5.91	—0.03
0	3	2.17	0.00	2.17	0.00
—15	1	0.67	..	0.71	+0.04
—16.8	1	0.56	..	0.61	+0.05
—17	1	0.53	..	0.60	+0.07

TABLE IV.

Phenyl-dichloro-arsine.

$$\log v.\ p. = 9.150 - \frac{3164}{273 + t}.$$

Temperature. °C.	Number of observations.	Average vapor pressure. observed. Mm.	Average deviation from mean. Mm.	Vapor pressure calculated. Mm.	Difference. Calc. — obs. Mm.
45	2	0.159	0.000	0.159	0.000
35	5	0.076	0.001	0.076	0.000
30	2	0.049	0.000	0.051	+0.002
25	2	0.035	0.000	0.034	—0.001
15	5	0.014	0.001	0.014	0.000
0	3	0.004	0.000	0.004	0.000

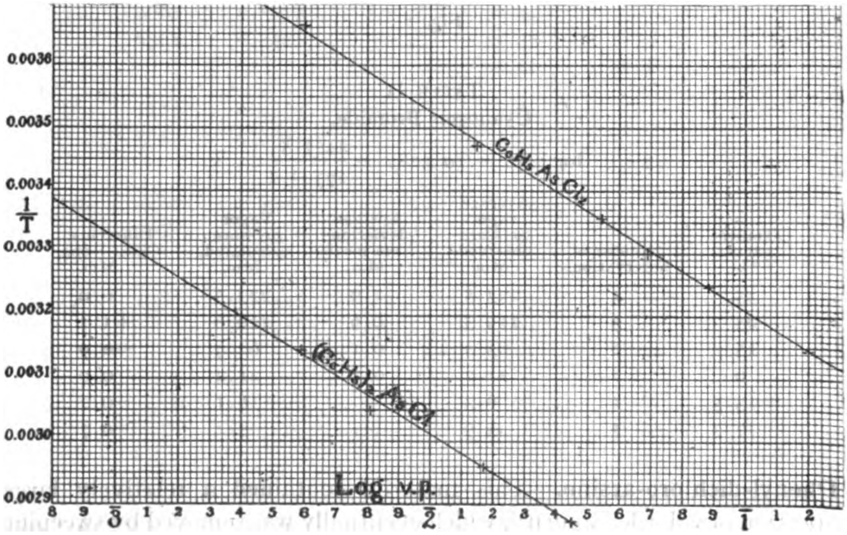

Fig. 2.

Diphenyl-chloro-arsine.—Two samples of material were furnished, one of which had been purified by distillation, one by crystallization. No difference could be detected between the 2 samples. The solid substance gave irregular results at temperatures below its melting point, 44°. Therefore, values were found at temperatures above the melting point, with the expectation of extrapolating to lower temperatures. As it turned out, the melted substance remained supercooled long enough to make possible 4 experiments at 25°, although these results at 25° are lower than the results at higher temperatures would lead one to expect. Further determinations at 25° after the substance eventually solidified gave excessively high results, probably owing to separation of volatile impurities during solidification, although the material had been swept out very thoroughly at a high temperature both before and in the course of the earlier experiments.

TABLE V.
Diphenyl-chloro-arsine.

$$\log v.p. = 7.8930 - \frac{3288}{273 + t}.$$

Temperature. °C.	Number of observations.	Average vapor pressure observed. Mm.	Average deviation from mean. Mm.	Vapor pressure calculated. Mm.	Difference. Calc. — obs. Mm.
75	4	0.0282	0.0013	0.0278	—0.0004
65	5	0.0148	0.0008	0.0146	—0.0002
55	2	0.0065	0.0003	0.0074	+0.0009
45	4	0.0039	0.0001	0.0036	—0.0003
25	4	0.0003	0.0001	0.0008	+0.0005

Arsenic Trichloride.—After experiments at temperatures up to 50° had been completed by the air-current method, the observations were extended to nearly 100° by the "submerged bulblet" method of Smith and Menzies.[1] Conc. sulfuric acid was used as the immersion liquid and the capillary ascension in the tube constituting the outlet of the bulb was determined. Four series of measurements were made and the results plotted against the temperature. From the curve, vapor pressures at

TABLE VI.
Arsenic Trichloride.

$$\log v.p. = 7.5183 - \frac{1720}{241.2 + t}.$$

Temperature. °C.	Number of observations.	Average vapor pressure observed. Mm.	Average deviation from mean. Mm.	Vapor pressure calculated. Mm.	Difference. Calc. — obs. Mm.
50	3	40.90	0.20	40.90	0.00
35	3	19.53	0.03	19.54	+0.01
25	2	11.65	0.04	11.40	—0.25
0	2	2.44	0.02	2.44	0.00

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[1] Smith and Menzies, THIS JOURNAL, 32, 907 (1910).

Submerged Bulblet Method.

Temperature. °C.	Observed.				Interpolated. Mm.	Calculated. Mm.	Difference. Calc. — obs Mm.
	I. Mm.	II. Mm.	III. Mm.	IV. Mm.			
100.0					301	300	—1
98.9			290				
98.0		274					
97.9			287				
96.0			264				
94.2		244					
90.7			221				
90.0					211	211	0
89.8		208					
85.7		177					
85.4			181				
81.1		152					
80.3			148				
80.0					145	146	+1
79.4				143			
76.3			124				
76.1		122					
74.5				117			
73.2		109					
71.4	108						
71.0				100			
70.9		99					
70.0					97	98	+1
67.8	89						
67.6		82					
65.6				76			
64.3	79						
61.3				63			
60.2	64						
60.0					64	64	0
58.2				57			
54.7	48						
51.2	43						

10° intervals between 50° and 100° were read off and are given in the column of "interpolated" values. Since the results between 0° and 100° cannot be adequately expressed by the logarithmic equation of the simpler type, the modification of Antoine,[1] $\log v.\ p. = A + \dfrac{B}{C + t}$, has been used.

The boiling points of arsenic trichloride calculated from the equation are 129.3° and 129.6° at 752 mm. and 760 mm., respectively, while Walden[2] found the boiling point to be 129° at the former and Thorpe[3] 130.2° at the latter pressure.

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[1] Antoine, *Compt. rend.*, 110, 632 (1890).

[2] *Z. physik. Chem.*, 43, 420 (1903).

[3] *Proc. Roy. Soc.*, 24, 283 (1876).

The foregoing data obviously furnish evidence from which the heats of vaporization may be computed. Using the Clausius-Clapeyron equation ($L = T \frac{dp}{dt} (V_{gas} - V_{liquid\text{-}solid})$ and values for the vapor pressures calculated from the logarithmic vapor pressure equations, this has been done for the 3 most volatile substances at various temperatures. The results are expressed in kilogram calories per gram molecule.

TABLE VII.

Heats of Vaporization.

Temperature. ° C.	Chloropicrin.	Cyanogen bromide.	Arsenic trichloride.
100	..	..	6.86
50	..	..	7.29
35	6.77	8.08	..
0	7.10	8.60	7.42

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, PRINCETON UNIVERSITY.]

STUDIES IN THE ADSORPTION BY CHARCOAL.

I. THE RELATION OF SERVICE TIME TO ADSORPTION AND ABSORPTION.

BY H. H. LOWRY AND G. A. HULETT.

Received March 29, 1920.

Introduction.

Because of the prominence of gas warfare in the recent world war, means of protection against gas had to be developed. Naturally charcoal played a prominent part because of its remarkable properties as an absorbent. Also naturally one sample of charcoal prepared in one way might be better than another for a given use and the test developed to show superiority of one charcoal over another became known as the "service time" test. This method of testing has been described by Lamb, Wilson, and Chaney[1] and was purely an empirical test developed to approximate field conditions. Briefly, it consisted in passing air containing a known concentration of a toxic gas, as chloropicrin, at a definite rate through a sample of charcoal of standard dimensions until the gas could be detected in the effluent air. The test gave the desired data but had no theoretical basis, though many speculations had been made on this point. No known property of a charcoal could, however, lead one to say that it would give a better test than another without actually submitting it to these empirical conditions.

The lack of relation between service time and some physical properties of various charcoals is shown in Table I.

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[1] *J. Ind. Eng. Chem.*, 11, 430 (1919).

TABLE I.[1]

	A909.	Nela.	English.	German.
Density:				
True	1.84	1.89	1.86	1.70
Apparent	0.55	0.46	0.13	0.24
Vol. capillaries per cc.	0.23	0.31	0.39	0.38
Service Time:				
Cal. minutes (accelerated)	17.3	53.5	8.8	60.2[a]
% wt. $C(NO_2)Cl_3$ at break point	14.6	48.7	32.0	110.0[a]

[a] This value was obtained not on the charcoal as taken from the canisters but after having been treated as described later.

Most of the speculations on service time have connected this property with either the well known great adsorptive power of charcoal or with capillary action due to its porous structure. We wished to investigate this relation and decided to measure the adsorptive power of these charcoals for nitrogen, carbon dioxide and water vapor. These were chosen because they were well defined, stable substances not very difficult of preparation in the pure state, and were widely different as to critical temperatures. Attention is called to this fact that at 25°, the temperature chosen for the measurements, water is normally a liquid, carbon dioxide is a gas just below its critical temperature, and nitrogen a gas and far above its critical temperature.

It was also realized that we had an opportunity to obtain adsorption measurements on charcoals which had been prepared in a very definite way and their other characteristics determined in the work on the various charcoals used for gas masks. Previous measurements, as given in the literature, may be considered to have doubtful value because of their non-reproducibility, since no special attention was given to the preparation of the charcoal, to activation, and to the other physical properties of the charcoal. Only in this sense was it intended to supplement the

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[1] NOTE.—The method of determination of these properties follows:

True Density.—Charcoal placed in sample tube and evacuated at 445° and sealed *in vacuo*. Weighed in air, then opened under water and, after the "drift" had disappeared, the weight determined, and volume obtained from weight of water displaced (THIS JOURNAL, 42, 391 (1920)).

Apparent Density.—These figures are calculated on a moisture- and gas-free basis.

Volume of Capillaries.—Values obtained by centrifuging the sample of charcoal opened under water in the density determination for a definite period of time and approximately 1000 r. p. m. The excess weight of the sample over the true weight of the charcoal represented the water retained by the capillaries and is essentially the same as if the external water were removed by filter paper.

Service Time.—These tests were made by Dr. N. K. Chaney, of the National Carbon Co., by the standard accelerated method except that the rate was 500 cc. per minute instead of the usual 1000 cc., *i. e.*, the test is only half as accelerated as the standard. From the actual weight of the chloropicrin absorbed, the minutes service was calculated. We wish to express here our sincere thanks to Dr. Chaney for furnishing us with this data.

enormous amounts of data already collected on the adsorption of gases by charcoal. Special interest, however, was attached to the adsorption of water vapor, first because no accurate measurements of the adsorption of vapors by charcoal, which could normally exist as liquids at the temperature of the measurements, have previously been recorded in the literature, and secondly, because the so-called toxic "gases" of warfare were usually such vapors.

Description of the Charcoals.

A909.—This charcoal was prepared at Astoria in August, 1918, from cocoanut shells. The preliminary carbonization was at 950° for 10 hours. The sample was then steam-activated at 950° for 45 minutes according to a method described in detail elsewhere.[1] The sample used was 18–20 mesh, *i. e.*, that which would pass through an 18-mesh screen but was retained by a 20-mesh screen.

A909 Es.—This was the same charcoal as the preceding, the only difference being in the size of the particles. It was prepared by grinding the coarse A909 in a ball mill and collecting by electrical precipitation the dust which was too fine to settle.[2] The maximum diameter of the particles as determined microscopically was one micron, 0.001 mm.

Nela.—This was a mixture of cocoanut charcoals prepared and activated in the C. W. S. Laboratory at Nela Park, Cleveland. The charcoals composing this mixture were very similar but of various degrees of activity. The preliminary carbonization was made at 950° for 10 hours and the charcoals were then activated with steam at 950° for approximately 45 minutes.

English.—This was a mixture of English charcoals which were very similar. These charcoals were made from birch wood in gas retorts, that is, they were really air activated. The method of preparation was the standard adopted for the preparation of British war charcoals.

German.—For the details of the method of preparation of this charcoal, the reader is referred to an article by J. F. Norris.[3] Briefly, the carbonization was affected as follows. The wood in pieces of uniform size was soaked in a hydrochloric acid solution of zinc chloride for about $^1/_2$ hour. The acidified wood was then heated in a closed muffle furnace at a cherry-red for at least 6 to 8 hours. The charcoal obtained was washed with hydrochloric acid until the soluble ash was reduced to a minimum. The finished product contained about 0.01% of zinc. It was finally washed free from acid, drained on a grill, and dried in a vacuum at 70° to 80°. This sample of charcoal was taken from unused canisters which had been captured in September, 1918, and was further treated

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[1] *J. Ind. Eng. Chem.*, 11, 430 (1919).

[2] THIS JOURNAL, 42, 391 (1920).

[3] Norris, *J. Ind. Eng. Chem.*, 11, 829 (1919).

before using it in the measurements, including those of the service time, as follows. It was boiled in distilled water for 2 hours, its water decanted and this treatment repeated 7 times. It was then boiled for 3 hours in dil. (1 : 7) hydrochloric acid, the acid decanted and then again treated as at first 3 times with water. It was dried in the air on filter paper, and then for 5 hours at 110–115° in air free from carbon dioxide and water vapor.

Preparation of Nitrogen, Carbon Dioxide, and Water.

Nitrogen.—A mixture of air with hydrogen from a Kipp generator using dil. hydrochloric acid and zinc metal, was forced through a combustion tube in the proper proportions to remove completely the oxygen and hydrogen, using copper-copper oxide as the indicator.[1] The effluent gases, nitrogen and argon, were collected and stored in a large glass gasometer over a dil. alkaline pyrogallate solution in order that they might not be contaminated with the oxygen originally dissolved in the water. Subsequent analysis showed no traces of oxygen, carbon monoxide, carbon dioxide, or hydrogen, Assuming that the air originally contained 78% of nitrogen and 1% of argon, the "nitrogen" used contained 1.25% argon. The gas, as used, was dried by passage over calcium chloride and phosphorus pentoxide.

Carbon Dioxide.—The carbon dioxide was prepared by dropping 1 : 1 sulfuric acid, kept in an atmosphere of carbon dioxide, on a saturated solution of sodium hydrogen carbonate. The sulfuric acid had been previously saturated with carbon dioxide to displace the dissolved gases. The gas was dried over calcium chloride and phosphorus pentoxide. Analysis showed a residue of less than 0.1% of gas not absorbed by a caustic potash solution. The gas was generated as used.

Water.—The water used was ordinary distilled water freed from dissolved gases as follows. About 10 cc. of distilled water was placed in the tube T, Fig. 1, and the system partially evacuated through the stopcock M by means of a Töpler pump. The water was then carefully frozen with solid carbon dioxide and ether and the system evacuated to the vapor pressure of water at that temperature. After closing the

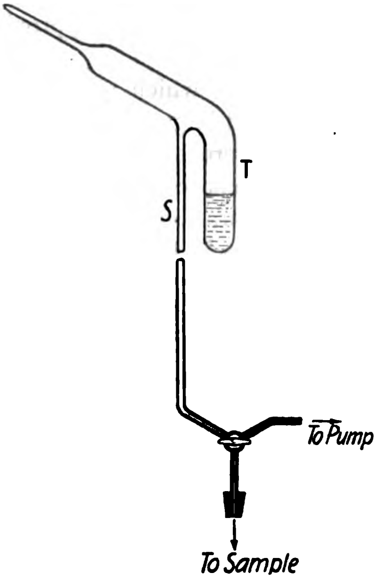

Fig. 1.

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[1] This Journal, 27, 1415 (1905).

stopcock M, the ice was allowed to melt and M opened again momentarily. Any air dissolved in the water would be given up to the vacuum. To remove this air, which was always less than 0.02 cc., the water was again frozen and the system re-evacuated.

Description of Apparatus.

A diagram of the apparatus is shown in Fig. 2. This consisted of a quartz tube, NP, 15 mm. inside diameter, and about 25 cm. in length. The sample of charcoal was placed in the lower 8 to 10 cm. of the tube and above this, in order to reduce the amount of dead space as much as possible, there was placed another quartz Tube, O, sealed at both ends and fitting tightly in NP. A ground glass, vacuum-tight joint at N joined the quartz tube containing the sample to a 3-way Stopcock, M. By means of this stopcock, the charcoal could be directly opened to the reservoir holding the gas to be absorbed or to a manometer S and through the stopcock R to a Töpler mercury pump, by which the evacuation of the system was effected. Pressures from a fraction of a millimeter to 400 mm. could be read from the manometer by means of a cathetometer and a scale placed between the 2 arms of the manometer. The pressure was read to the nearest 0.1 mm. The volume of the apparatus enclosed by the stopcock R and the quartz tube NP was measured directly by putting the quartz tube and filler, O, in place empty, with R closed and the system evacuated to R, and subsequent opening of R and evacuation of the rest of the apparatus, the gas being collected at the delivery of the pump and measured in a gas buret to the nearest 0.01 cc. Since the inside diameter of the manometer was previously measured and was of uniform bore, the volume of the apparatus at 0 mm. pressure could be calculated, as also the increase in volume with each millimeter pressure. For determining the free space in the apparatus when the charcoal was in place, the volume of the charcoal, calculated from the weight of the gas- and moisture-free sample and its previously determined true density, was subtracted from these values.

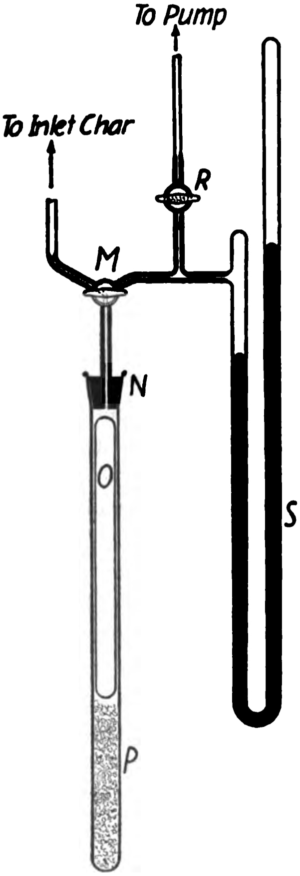

Fig. 2.

Method.

In practice, a sample of charcoal, containing an unknown weight of gas and moisture, was weighed directly into the quartz tube NP. The weight of the sample used depended on the apparent density of the charcoal since the volume of the charcoal used was a constant—about 14 cc. In the line between the pump and the stopcock R was sealed a small glass condenser (Fig. 2*a*), which was immersed in solid carbon dioxide and ether after the system had been completely evacuated to the stopcock M. This stopcock was then opened and simultaneously an electric heater was placed around the quartz tube, the ground glass connection at N being cooled by a lead coil through which cold water was passing. The heater had been calibrated and sufficient current was passed through to raise the sample of charcoal to 750° and this temperature was maintained until, with continual evacuation by means of the Töpler pump, less than 0.1 cc. was given off in each 10-minute interval. This condition was usually obtained only after 5 to 7 hours heating. Previous experience had shown that until such a temperature had been reached the effluent gases contained fairly large percentages of the oxides of carbon. The gas as given off was collected at the delivery of the pump and stored in a large gas buret over mercury, in which the total volume of gas was measured. An analysis of a sample of this allowed easy calculation of the weight of gas given up by the charcoal during the treatment. This varied with the charcoals used from 1% to 10% of the original weight of the charcoal. The moisture in the charcoal, having been retained in the condenser by freezing, was determined directly by cutting the condenser out of the line, the stopcock R being closed, and weighing the condenser with the water and then empty. This moisture varied from 1% to 13% of the original weight of the charcoal. After the quartz tube had cooled, it was kept immersed in a thermostat at 25° ± 0.2°, while the pressure concentration measurements were being made. Fairly close adjustment of the temperature was necessary because of the large though undetermined temperature coefficient of pressure with temperature. After the measurements with one gas were obtained, the charcoal was re-evacuated at 184° (aniline b. p.) to remove the last traces of the adsorbed gas.

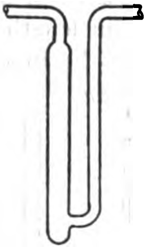

Fig. 2*a*.

Admission of Nitrogen and Carbon Dioxide.

Since both these substances are gases, their pressures and concentrations were measured similarly, though necessarily differently from the method followed with water, a description of which will be given later.

For the admission of nitrogen, the apparatus shown in Fig. 3 was sealed to the stopcock M (Fig. 2). This apparatus consisted essentially of a small gasometer, R, of known volume, kept immersed in a jacket of water NP, the temperature of which was recorded by the thermometer, T. The rest of the apparatus was the large gasometer in which the nitrogen was stored, and drying tubes containing calcium chloride and phosphorus pentoxide. By opening the stopcock, M, this apparatus, including the small gasometer R, could be completely evacuated to J. The line was then "washed out" several times with nitrogen from the large gasometer. When this was accomplished, the small gasometer was opened to the nitrogen supply and simultaneously the line to the gasometer from the pump closed by turning the 3-way stopcock K. The stopcock J being opened, the gasometer R was filled with nitrogen to the zero mark at atmospheric pressure by means of the leveling bulb L. The temperature and pressure of this volume being known, it was readily reduced to N. T. P. The volume of the gasometer was 94.62 cc. Now the stopcocks K and M were so turned as to connect the sample of charcoal with the nitrogen in the gasometer and the levels of mercury in L and R kept approximately level while the gas was being adsorbed. Equlibrium was very rapidly reached and the 2 levels carefully adjusted. The stopcock M was then turned so the line

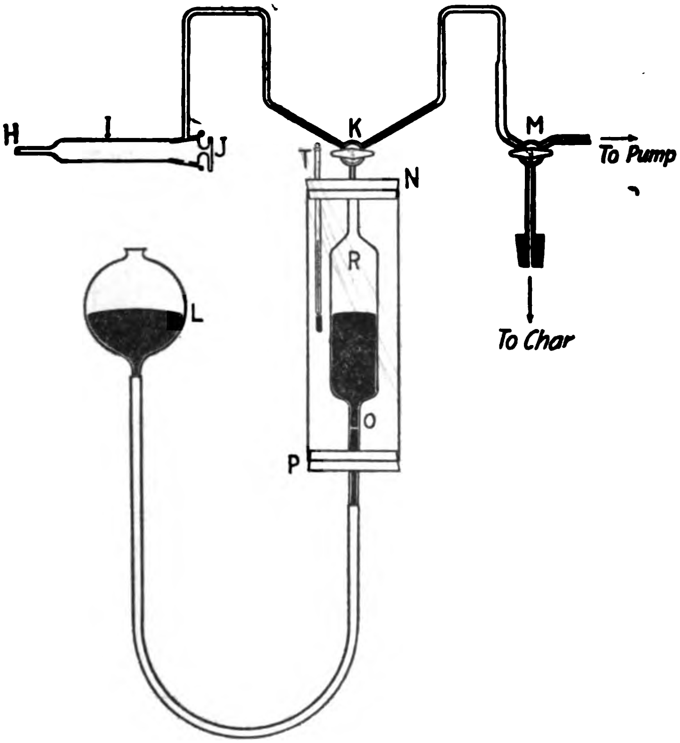

Fig. 3.

between K and M and the gasometer R could be evacuated. In this way the excess of gas remaining in the gasometer could be measured by collecting it as pumped off at the delivery of the Töpler pump and its volume determined in a gas buret. By subtracting this volume, corrected to N. T. P., the amount of nitrogen in the quartz tube NP, Fig. 2, was known, and by subtracting from this value the nitrogen in the previously determined free space of the tube, also corrected to N. T. P., the amount of nitrogen in cc. N. T. P. adsorbed at 25° and atmospheric pressure was determined. By a series of evacuations, and collecting and measuring each volume of gas as pumped off, and subtracting this from the previous volume of gas in the system, the amount of nitrogen in the system at several pressures could be measured. Since the volume of the system was known for each pressure, the volume of nitrogen adsorbed on the charcoal could be easily calculated. The nitrogen could be completely pumped off at 25°. A typical table is given in Table 2 as an example of the method of recording results. Fig. 4 represents the concentration

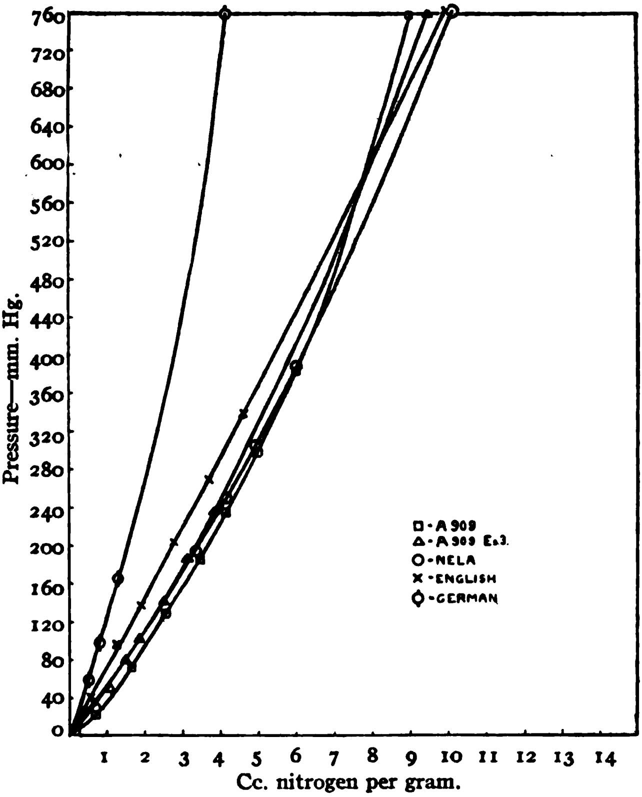

Fig. 4.—Adsorption isotherms for nitrogen on charcoals at 25°.

pressure curves for nitrogen as plotted from the data obtained with the various charcoals.

TABLE II.

Adsorption of Nitrogen by A909 Es. 3.

	Cc. admitted.		Cc.	Press.	Room	Vol. system.		Gas in	Gas on	Cc. gas
	T.	P.	N. T. P.	Mm. Hg.	temp.	Bulb.	Line.	Sys. N.T.P.	char.	per g.
75.89	19.0	760	70.99	760.0	....	10.66	....	10.66	60.33	9.46
32.38	19.5	760	30.21	235.8	19.8	3.32	2.58	5.90	24.31	3.84
26.06	19.5	760	24.32	186.0	19.8	2.67	1.83	4.50	19.82	3.11
20.38	19.5	760	19.01	142.0	20.0	1.99	1.26	3.25	15.76	2.48
14.97	19.5	760	13.97	101.5	20.0	1.42	0.80	2.22	11.75	1.84
11.96	19.7	760	11.16	80.0	19.7	1.12	0.60	1.72	9.44	1.48
8.62	20.0	760	8.03	48.9	20.3	0.69	0.34	1.03	7.00	1.10
4.66	20.2	760	4.34	21.7	20.6	0.30	0.13	0.43	3.91	0.61
1.98	20.2	760	1.84	5.1	20.3	0.07	0.03	0.10	1.74	0.27
0.18	20.3	760	0.17	0.2	20.6	...	....	...	0.17	0.03

The measurements of the concentration pressure relation with carbon dioxide were made in exactly the same way as those with the nitrogen except for the necessary modifications due to the much larger amounts

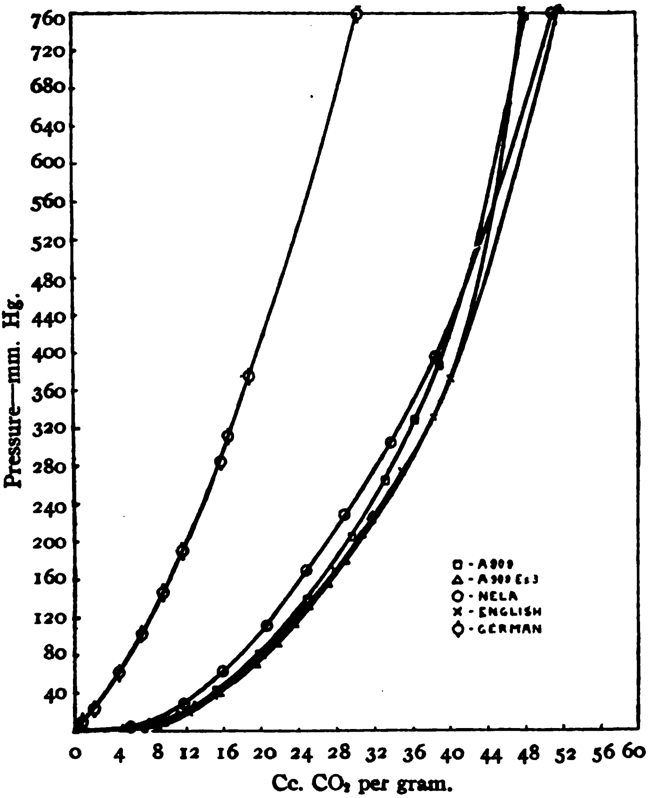

Fig. 5.—Adsorption isotherms for carbon dioxide on charcoals at 25°.

adsorbed. This necessitated several fillings of the gasometer R. For the admission of carbon dioxide, the generator was sealed to the apparatus shown in Fig. 3 at H. The generator was furnished with a mercury valve immediately before a stopcock which separated it from the rest of the system. Carbon dioxide was generated and allowed to escape through this valve until tests showed that the gas was completely adsorbed by a caustic potash solution. The concentration pressure curves obtained for carbon dioxide on the different charcoals are shown in Fig. 5. It was found that the complete removal of the carbon dioxide from the charcoal *at the temperature of adsorption* was a slow and tedious process. The gas came off very slowly at the lowest pressures, as much as 8 cc. per g. of charcoal being retained by one of the charcoals at a pressure of 1.4 mm. Hg. The only exception to this was in the case of the German charcoal, with which the amount adsorbed per g. was about half that of the amount adsorbed by the other charcoals, and where the carbon dioxide was readily pumped off at 25°. In order, therefore, to free the surface from adsorbed gas, the tube was immersed in a tube of boiling aniline vapor. It was very readily possible at this temperature, 184°, to recover completely the amount of carbon dioxide originally admitted.

Admission of Water.

To admit water to the charcoal, the apparatus shown in Fig. 1 was sealed to the stopcock M, Fig. 2, in place of the apparatus used for the admission of the gases. The preparation of the water for use has been described previously. After the last freezing in the preparation, the ice in T was allowed to melt and a beaker of warm water was placed around the bulb containing the water. Since the apparatus was filled only with water vapor, the water distilled and filled the tube S, which had been calibrated with a thread of mercury (0.123 cc. per cm. tube) completely to the stopcock M. A scale—one division = 0.581 mm., was fastened to the tube S and in this way the amounts of water admitted to the charcoal could be directly read to 0.007 cc. and estimated one place farther. Since the adsorption was to be measured at 25°, which is several degrees higher than ordinary room temperature, means had to be provided to prevent distillation from the charcoal to the line which was in the air above the thermostat. At first, heating by means of a Nichrome wire wound around that part of the line was tried, a small current, which was sufficient to keep the line at about 30° as determined experimentally, being passed through the wire. Later it was found to be more convenient to raise the room temperature to 27–30°, thereby removing this difficulty. This necessitated the cooling of the thermostat by means of ice. It was customary to cool the bulb to 10–15°, causing more rapid distillation from the line to the charcoal, and then allowing the temperature to slowly rise. The pressure was read when the temperature reached 25°. As this pressure approached that of water at 25°, 23.5 mm., it was sometimes necessary to repeat this cooling before the pressure would remain constant. It frequently required 3 to 5

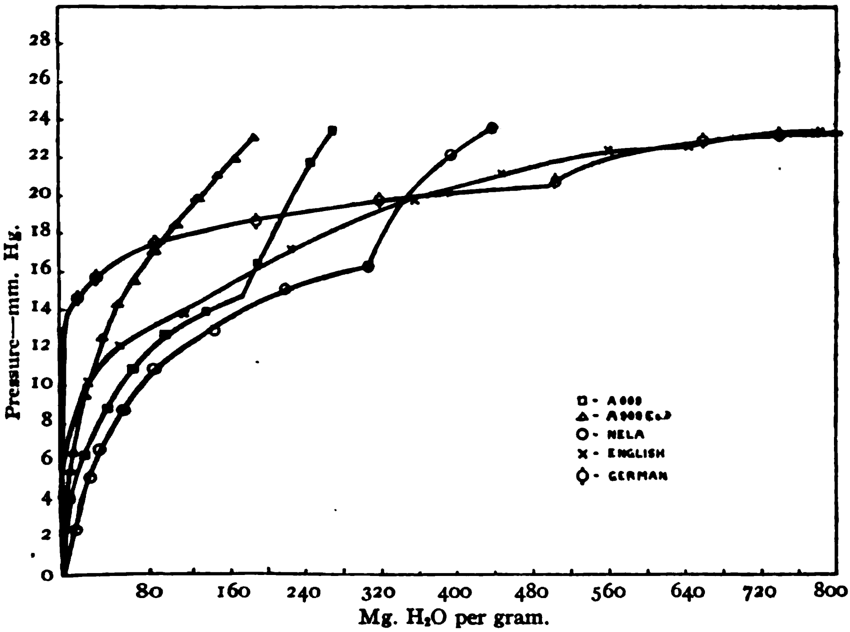

Fig. 6.—Adsorption isotherms for water vapor on charcoals at 25°.

hours for equilibrium to be reached. The curves of concentration pressure of water on the various charcoals are shown in Fig. 6. A typical table of experimental data is also appended in Table III:

TABLE III.

Adsorption of Water by English Charcoal at 25°.

Cc. of water admitted.	Pressure mm. Hg.	Room temp.	Cc. of water in system.	Cc. of water on charcoal.	G. of water on charcoal.	G. of water per g. of charcoal.
0.0357	10.2	27.8	0.00015	0.0355	0.0354	0.0277
0.0743	12.1	29.2	0.00015	0.0741	0.0738	0.0577
0.1458	13.8	29.6	0.00017	0.1456	0.1449	0.1133
0.2886	17.2	30.4	0.00026	0.2883	0.2872	0.2247
0.4314	19.8	29.4	0.00030	0.4311	0.4295	0.3360
0.5742	21.2	29.6	0.00032	0.5739	0.5720	0.4473
0.7184	22.4	30.2	0.00034	0.7181	0.7156	0.5595
0.8262	22.6	30.3	0.00034	0.8259	0.8230	0.6441
1.0047	23.4	29.9	0.00036	1.0043	1.0009	0.7831

Discussion.

A consideration of these data on adsorption shows that the isotherms obtained for nitrogen and carbon dioxide on the various charcoals are of the same general form as previously obtained by other investigators, *i. e.*, Homfray,[1] Titoff,[2] Travers,[3] Baerwald.[4] Furthermore, the quantities adsorbed do not vary much among themselves for equal weights of the various charcoals, except for the specially treated German charcoal. A slightly larger adsorptive capacity for nitrogen and carbon dioxide was noticed for the finely divided A909 than for the large grained sample. This is taken to indicate that the increase in surface due to pulverizing the charcoal was small, less than 8%, in comparison with the total available surface present in the larger grained material.

In Table IV there are given the amounts of nitrogen and carbon dioxide adsorbed by one cc. of the different charcoals, at 25° and 760 mm., together with their service times. It is necessary to use equal volumes of the charcoals for this comparison with the service time, as this latter test is made on a constant volume of charcoal. This can be obtained by multiplying the volume adsorbed per gram charcoal by the apparent density of the charcoal. It is very readily seen from this table that there is no relation between the capacity for a charcoal to adsorb a gas, as nitrogen or carbon dioxide, and its service time.

TABLE IV.

	Cc. N. T. P. per cc. of charcoal.		Minutes service.
	N_2.	CO_2.	
A909	4.97	26.53	17.3
Nela	4.89	25.04	53.5
English	1.29	6.21	8.8
German	1.01	7.35	60.2

In the exponential formula, $q = a.p^{1/n}$, for adsorption isotherms, Titoff[5] found that the value of n is very close to unity for gases which at ordinary temperatures may be called "perfect gases" and that it increases in value for gases of increasingly high critical temperatures. This would give approximately a straight line to the isotherms of the perfect gases and the curves would become more and more concave to the pressure axis for gases with increasingly higher critical temperatures. If this generality could be applied even to cases where the measurements were made on a vapor which could exist normally as a liquid under the conditions of the measurements, as water in our experiments, we should expect that the isotherm for water would be very much more concave to the pressure axis than that for carbon dioxide. However, the curves obtained for water are of a form exactly opposite, that is, they are concave to the concentration axis.

Charcoal, being of a porous nature, besides presenting enormous sur-

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[1] Homfray, *Z. physik. Chem.*, 74, 129 (1910).

[2] Titoff, *ibid.*, 74, 641 (1910).

[3] Travers, *Proc. Roy. Soc.*, 78, 9 (1907).

[4] Baerwald, *Ann. Physik.*, 23, 90 (1907).

[5] *Loc. cit.*

face and accordingly having high adsorptive capacity, also offers the opportunity of capillary action, especially to the vapor of a liquid which has as high a surface tension as water. The isotherms for water must, therefore, be taken to show that in this case the capillary action is greater than the surface attraction of adsorption, since they are just what would be expected from the assumption that water was taken up predominatingly by capillary action. In this case, the smaller capillaries would be filled first since they would give the lower vapor pressures. The smaller the diameter of the capillaries, the more rapidly would they be filled by a given amount of water and so the pressure would increase more rapidly at first in relation to the concentration than when the capillaries were of a larger diameter. This would satisfactorily explain the concavity to the concentration axis obtained for the isotherms for water.

A further indication that water vapor is not *ad*sorbed, but *ab*sorbed, by charcoal is given by the comparison of the ratios of nitrogen, carbon dioxide, and water taken up per g. of the various charcoals. These ratios are for A909, Nela, English and German charcoals, respectively, 1 : 5.3 : 29.9; 1 : 5.0 : 54.2; 1 : 4.8 : 98.1; and 1 : 7.4 : 226.4. It is seen that while there is more or less regularity between the ratios of nitrogen and carbon dioxide, the water varies between the wide limits of 29.9 and 226.4. This must surely mean that if charcoal adsorbs gases, it does not *ad*sorb water vapor, but that this is a different phenomenon, which may be called *ab*sorption.

A quite pronounced break can be seen in the isotherms for water on the different charcoals, with the exception of the finely divided A909. In a study on the "adsorption" of water by silica gel, Anderson[1] obtained a similar break. He seems justified, from his later work on the study of the velocity of adsorption, to conclude that this break marks the intersection of 2 phenomena, the first smooth part of the curve represents the taking up of water vapor by capillary action, the break occurs only when the capillaries have filled up and the further increase in vapor pressure is due merely to the flattening of the meniscus at the ends of the capillaries.

Anderson developed in his paper a formula which can be used for the calculation of the diameters of the capillaries from the vapor pressure measurements. By means of this formula, it is also possible to calculate the surface of the charcoal since the volume of each size capillary can be obtained directly by reference to the concentration axis. The formula is

$$r = \frac{2T . s_0 . 0.4343}{d . p_0 . \log(p_0/p_1)}$$

where r = radius of the capillary; T = surface tension in dynes per cm.

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[1] Anderson, *Z. physik. Chem.*, **88**, 191 (1914).

at 25° = 72.1; s_0 = vapor density of water vapor above water at 25° = 22.75×10^{-6}; d = density of water at 25° = 0.99707; p_0 = vapor pressure in dynes of water at 25° = $23.517 \times 13.534 \times 980.1 = 31.20 \times 10^4$; and p_1 = the vapor pressure in the capillary.

The lowest pressure measured in our experiments was 2.3 mm. on the Nela charcoal when 16 mg. of water had been absorbed per g. of charcoal. This corresponds to a capillary diameter of 9.1×10^{-8} cm. A vapor pressure of one mm. represents a pore with a diameter of 6.7×10^{-8} cm. In Table V are listed the smallest, largest and mean diameters of the capillaries in each charcoal, as calculated from this equation, together with the surface as calculated by applying this formula as indicated above.

TABLE V.

	Capillary diameters.			Cal. surface.	
	Smallest. Cm.	Largest. Cm.	Mean. Cm.	Per g. M.	Per cc. M.
A909........	6.7×10^{-8}	4.1×10^{-7}	2.8×10^{-7}	230^{-2}	130^{-2}
Nela........	6.7×10	5.5×10	3.7×10	440	200
English......	1.6×10	1.9×10	8.3×10	300	40
German......	2.0×10	1.3×10	9.5×10	160	40

Lamb, Wilson, and Chaney[1] have estimated that the surface of one g. of an activated charcoal is about 1000 square meters, which from our data would appear to be too great. Recently A. M. Williams,[2] in developing a new interpolation formula for the adsorption of gases, was able to calculate that the surface of the charcoal used by Dr. Ida F. Homfray[3] was 131 square meters, which agrees well with the values we have obtained, especially when one considers that this was a pre-war product and not activated. With a surface of the magnitude given by our calculations, adsorption of nitrogen and carbon dioxide at ordinary temperatures and to pressures as high as atmospheric could well be in a monomolecular layer, such as is characterized as true adsorption by Langmuir,[4] since 50 cc. of carbon dioxide at N. T. P. would occupy in a monomolecular layer a surface of less than 150 square meters. Also the fact that, while the differences in the calculated surfaces of A909, Nela, and English charcoals is considerable, there is not a corresponding difference in the adsorption of the gases, this would make the concept of "elementary spaces" postulated by Langmuir[5] necessary. The difference in the adsorptive capacity of a given charcoal for nitrogen and carbon dioxide would then depend solely on the difference in "time-lag" of the condensation evaporation process of adsorption.

Since it has been shown that the taking up of water vapor is a different

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[1] Lamb, Wilson and Chaney, *J. Ind. Eng. Chem.*, 11, 430 (1919).

[2] Williams, *Proc. Roy. Soc.*, **96A**, 287 (1919).

[3] *Loc. cit.*

[4] Langmuir, THIS JOURNAL, 40, 1361 (1918).

phenomenon from adsorption, it is interesting to see whether there is any relation between this phenomenon, absorption, and service time. The necessary data for this comparison is collected in Table VI. In this table the per cent. weight of chloropicrin held by the charcoal at the break point, the saturation point, and the "retentivity" point are calculated to volume of chloropicrin. The retentivity signifies the amount of chloropicrin left in the charcoal on reversing the test until no trace of chloropicrin can be detected in the effluent air. The density of chloropicrin at 25° has been taken to be 1.651, the density determined at the American University being $d_4^{20} = 1.6539$.

TABLE VI.

	Vol. chloropicrin in cc. at.			Vol. capillaries per g.	
	Break.	Saturation.	Retentivity.	Total.	At break in curve.
A909........	0.0884	0.1762	0.0806	0.2728	0.1735
Nela.........	0.2948	....	....	0.4406	0.3083
English......	01.938	0.3967	0.0696	0.7828	0.6435
German......	0.6561	0.8174	0.1726	0.8543	0.4948

Here, also, we see no relation between service time and capillary action. Further, there does not appear to be any relation between the volume of the capillaries and retentivity or saturation, except as might be expected the saturation occurs in each case before the capillaries were completely filled, due to the fact that the lower layers of charcoal had not yet reached saturation.

This complete lack of quantitative relation between service time with the phenomena of adsorption and absorption is not startling. The test, as developed, was only empirical and such factors as size of mesh of the sample and resistance to the passage of air were known to have a marked influence on the service time. It is this "sieve effect" of removing the vapors from the air that is the uncertain and indeterminate factor in the minutes service that a charcoal can give. We know of no other phenomena, however, which can explain the mechanism of this removal of gases, or vapors, of high critical temperature from those of much lower, than adsorption and absorption. We must conclude, therefore, that both of these phenomena are probably involved in the determination of service time, and, from our work on the absorption of water vapor, that capillary action predominates over the influence of unmodified surface action or adsorption.

Conclusions.

1. No relation between service time and adsorption of a gas, as nitrogen or carbon dioxide, by various charcoals has been found to exist.

2. Measurements of the adsorption of these gases by charcoals have shown that, according to the original preparation of the charcoal, the adsorptive capacity per gram of charcoal at 25° and 760 mm. may vary as much as 100%.

3. It has been shown that the adsorption of nitrogen and carbon dioxide by charcoal may be considered to be in a condensed layer one molecule deep.

4. Measurements of the isothermal adsorption of water vapor by charcoal at 25° show that water is not *ad*sorbed by charcoal but is held by capillary action, *i. e.*, is *ab*sorbed.

5. Using Anderson's formula connecting the radius of a capillary with vapor pressure, the mean diameters of the capillaries of the 4 charcoals used have been calculated and have been found to vary between 2.8×10^{-7} cm. and 9.2×10^{-7} cm. The maximum diameter in any of the charcoals was determined to be 1.3×10^{-6} cm.

6. By means of this same formula and the isothermals for water, the surfaces of the various charcoals were found to vary from 160 square meters to 436 square meters per gram of charcoal.

7. It was pointed out that this variation in surface was not always accompanied by a corresponding variation in adsorptive capacity. This makes the concept of "elementary spaces" as postulated by Langmuir necessary.

8. No relation between the service time of the different charcoals with the volume of the capillaries was found. The same was true for the saturation point and the retentivity of these charcoals. This lack of relation must indicate that other indeterminate factors must influence largely the minute service of a charcoal; *i. e.*, the 2 phenomena, adsorption and capillary action are insufficient in themselves to explain this test.

PRINCETON, N. J.

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, PRINCETON UNIVERSITY.]

STUDIES IN THE ADSORPTION BY CHARCOAL.

II. RELATION OF OXYGEN TO CHARCOAL.

BY H. H. LOWRY AND G. A. HULETT.

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De Saussure,[1] in one of the first quantitative measurements of adsorption by charcoal, was unable to obtain results for oxygen because it alone of the gases would not apparently come to equilibrium even after a year. This anomalous behavior in the adsorption of oxygen by charcoal has been largely overlooked by recent investigators though previously recognized and recorded by R. Angus Smith,[2] who found that the adsorption of oxygen continued for at least a month, though this was not true for hydrogen, nitrogen or carbon dioxide; and that, when it was sought to remove the oxygen by heat, carbon dioxide was given off in place of

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[1] De Saussure, *Gilb. Ann.*, 47, 113 (1814).

[2] R. A. Smith, *Proc. Roy. Soc.*, 12, 424 (1863).

oxygen, by H. Kayser,[1] who found that the adsorption of oxygen had not reached an end after two weeks; and by J. Böhm,[2] who found that nitrogen absorbed by charcoal could be completely removed but that oxygen could be only partly removed "even by boiling water."

However, in the exhaustive work on adsorption by Dr. Ida F. Homfray,[3] as in that of Baerwald[4] and in that of Lemon,[5] no such peculiarities in the behavior of oxygen were noticed. Dr. Homfray obtained equilibrium with the various gases in from a few minutes to $^1/_2$ hour, depending on the temperature, and so apparently missed this peculiar effect first recorded by De Saussure. These later investigators also were not concerned with the recovery of the adsorbed gases as such, so they did not observe the second peculiarity mentioned by Smith, *i. e.*, the fact that the oxygen may be recovered only partly as oxygen, the rest being recovered only as oxides of carbon.

In our work on the adsorptive power of the war charcoals we noticed this singular difficulty of obtaining equilibrium with oxygen. Furthermore, in attempting to determine the moisture and gas content of these charcoals,[6] it was noticed that gases continued to be given off to a vacuum as the temperature was raised. Up to 900°, these gases consisted almost entirely of carbon dioxide and carbon monoxide, the first predominating at the lower temperatures and the latter at the higher. At about 1000°, carbon dioxide and monoxide practically ceased to be obtained. Above 1000° hydrogen began to be more noticeable and to come off in increasingly large quantities as the temperature was raised. The hydrogen was presumably from hydrocarbons undecomposed in the original preparation of the charcoals.

When a charcoal has been thoroughly "outgassed" at 900° to 1000° and allowed to cool to room temperature in a vacuum and gases admitted, it was found possible to recover completely such gases as hydrogen, nitrogen, and carbon monoxide at room temperature, though the rate at which they could be collected in a Töpler pump was increased by raising the temperature; 90% of the carbon dioxide could be recovered, and smaller percentage of the water, at room temperature, but both could be quantitatively obtained at 184° (aniline b. p.) as rapidly as possible to collect them with a Töpler pump for the carbon dioxide and with a condenser cooled with solid carbon dioxide for the water.

However, when oxygen was admitted and allowed approximately to come to equilibrium, only about half was recovered by evacuating at

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[1] H. Kayser, *Wied. Ann.*, 12, 526 (1881).

[2] J. Böhm, *Bot. Z.*, 1883, 32–34.

[3] F. Homfray, *Z. physik. Chem.*, 74, 129 (1910).

[4] Baerwald, *Ann. Physik*, 23, 90 (1907).

[5] Lemon, *Phy. Rev.*, [2] 14, 281, 394 (1919).

[6] C. W. S. Reports, Sept.–Dec., 1918.

room temperature and only traces on increasing the temperature to 184°, though on again cooling to room temperature and again admitting oxygen, this second lot was readily recovered. Therefore attempts were made to recover completely this oxygen, which had apparently disappeared, by increasing the temperature still further, and soon carbon dioxide and monoxide began to appear, but not until a temperature of 900° to 1000° was again reached was all the oxygen recovered and then *not as oxygen* but as these *oxides of carbon*. We have interpreted this to indicate that there were here 2 phenomena, adsorption and "fixation" or "combination" of the oxygen with the charcoal. The adsorbed oxygen was regarded as that which was recoverable by evacuating at room temperature, and the "fixed" oxygen that which was recovered only as the oxides of carbon at higher temperatures.

These facts led us to a more thorough investigation of this fixation of oxygen by charcoal, both as to the length of time necessary to reach saturation and also as to the amounts of oxygen which could be held in this way by the charcoal. For this purpose we used 3 samples of war charcoal described in the preceding paper as A909, English, and German. Their moisture and adsorbed gas contents were known, and the samples were kept in carefully stoppered bottles.

Experimental.

A. Determination of Equilibrium of Charcoal and Oxygen at 250 and 760 mm.—For this purpose, 3 bulbs of about 25 cc. capacity each were filled with the above named charcoals and each was sealed to a line which led either to a Töpler pump or to a buret containing pure electrolytic oxygen. Each bulb was separated individually from the line by a one-way stopcock, and during the measurements was kept immersed in a thermostat at 25° ± 0.1°. As a preliminary treatment, the samples were thoroughly freed from adsorbed gases by outgassing at 184°, leaving in them, however, the fixed oxygen they originally contained. When the bulbs had been cooled in the thermostat, oxygen was admitted at 760 mm. by a constant pressure arrangement. From the temperature of the buret, the amount of oxygen admitted to the bulb was reduced directly to N. T. P. After the first correction for the dead space in the bulb, the amount taken up each time was divided by the weight of the moisture and gas-free sample, reducing the results to cc. of oxygen per g. of sample.

Fresh oxygen was admitted from time to time and the amounts recorded. At the end of the first 100 hours, when the amounts of oxygen taken up at successive intervals were becoming less, each sample was evacuated thoroughly at 25°. In no case was the amount of oxygen originally admitted recovered. In some cases traces of carbon dioxide and carbon monoxide were found in the gases collected. Since the samples were largely oxygen, it was thought possible that the small amounts of carbon monoxide were from the alkaline pyrogallate used to absorb the oxygen. Oxygen was then admitted and its course followed. This was repeated until equilibrium was reached. This was most quickly reached by the English charcoal at the end of 1600 hours or 66 days, while the German charcoal took just about twice this length of time. The data is presented in the form of curves as shown in Figs. 1, 2 and 3.

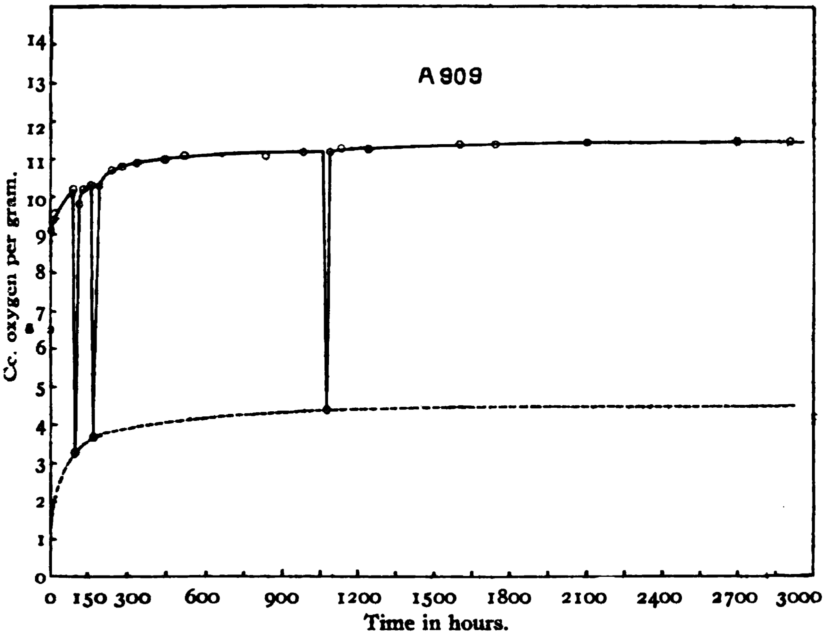

Fig. 1.—Adsorption and fixation of oxygen at 25° and 760 mm. by A909 charcoal.

It will be noticed that we really have 2 curves from each series of measurements. The upper curve represents in each case the total amount of oxygen taken up at 25° and 760 mm., while the lower dotted curve represents that which cannot be obtained by evacuation at 25°. It is also apparent that the slopes of the 2 curves are very similar. From our previous experience, we are led to the conclusion that the lower curve represents the rate of saturation of the charcoal by what we have called "fixed" oxygen, and that the upper curve is the sum of 2 effects, true adsorption and fixation. Since this is the case, it can readily be seen that the long time necessary to reach equilibrium is due to this fixation and that the true adsorption of oxygen by charcoal occurs as rapidly as for other gases.

These measurements have, therefore, shown not only that the equilibrium between oxygen and charcoal is attained only after months of

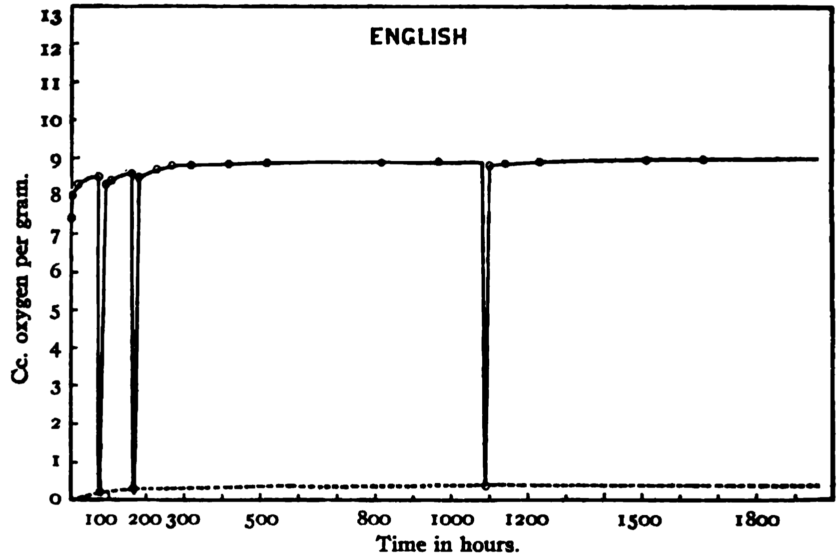

Fig. 2.—Adsorption and fixation of oxygen at 25° and 700 mm. by English charcoal.

contact, but also that the cause of this is the presence of 2 effects, true adsorption and "fixation."

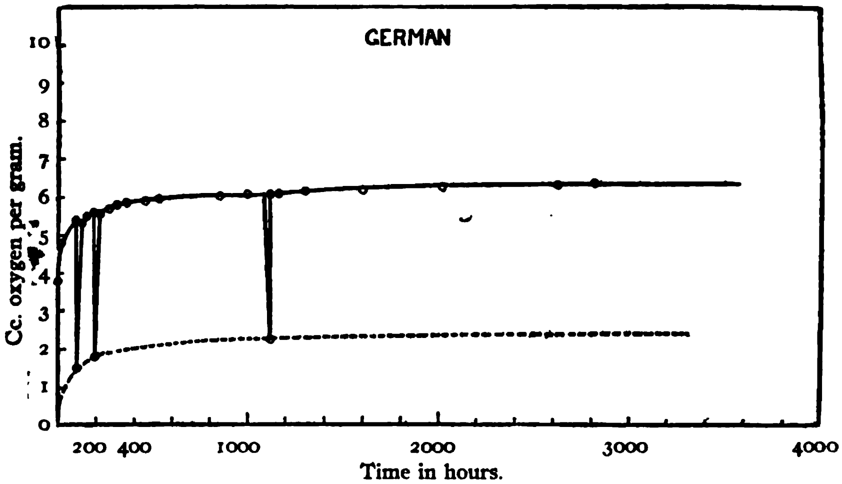

Fig. 3.—Adsorption and fixation of oxygen at 25° and 760 mm. by German charcoal.

B. Determination of Total "Fixed" Oxygen.—In order to obtain all the fixed oxygen from charcoal, it seemed necessary only to heat the sample in a vacuum, after first removing all the adsorbed gases and vapors, and to collect and analyze the evolved gases. The carbon dioxide and monoxide are calculated to cc. of oxygen, N. T. P., per g. of charcoal. The procedure first adopted was as follows: the charcoal was heated in a fused quartz tube in an aniline bath and thoroughly outgassed, then in a Nichrome resistance furnace to 1050°. Gases continued to be slowly given off for several hours at this temperature and still contained small percentages of the oxides of carbon. Since even at this temperature the charcoal acted on the fused quartz, we suspected that we were not getting the true oxygen content of the charcoal. We observed that the inner surface of the tube was markedly etched and suspected the reduction of the silica to a sub-oxide so that some of the oxides of carbon might well have been from this reduction. In view of this situation, it seemed necessary to devise a method which would obviate these difficulties and allow us to go to still higher temperatures.

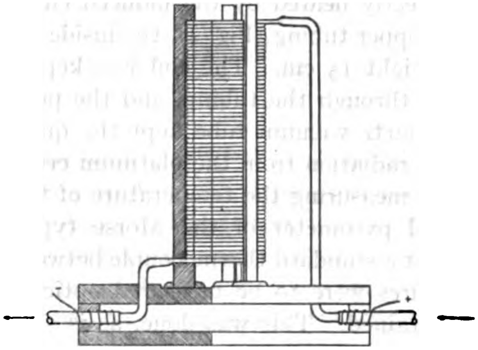

Fig. 4.

The development of the high frequency induction furnace by E. F. Northrup[1] seemed to offer a means of solving our difficulties. The compactness of the apparatus afforded by this method of heating was recognized to be one of its many advantages over other forms of electrical heating. Using this method of heating, we have found it possible to heat charcoal in a platinum cup supported in a quartz vacuum tube, keeping the quartz at a low temperature even when the cup and charcoal were at 1400°. In this way the possibility of a leak through hot quartz and reduction of the silica to a sub-oxide were prevented.

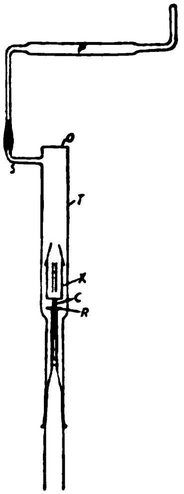

Fig. 5.

The apparatus designed for this experimental work is shown in Fig. 5. It consists primarily of a fused quartz tube, T, 25 cm. long and 2.5 cm. outside diameter, with a side tube, S, connected to a glass tube by a de Khotinsky joint leading to a Töpler pump through a phosphorus pentoxide tube, P. The upper end of the quartz tube was closed by an optically clear piece of fused quartz; and the lower end by a stopper of Pyrex glass with a ground joint, which also served indirectly as a support for a platinum-rhodium crucible, X. The crucible was 3.5 cm. long and 1.5 cm. in diameter and had a platinum pin riveted to the bottom. This pin fitted in a fine porcelain tube, C, which in turn was held in the Pyrex

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[1] Northrup, *Trans. Am. Electrochem. Soc.*, 35, 69 (1919).

support. In order to prevent radiation downwards, a porcelain disk, R, was fastened to the small porcelain tube. The crucible served as the resistor and was rapidly heated by the induced currents from the primary. When the charcoal was heated it also became a conductor and so could be directly heated by the induced currents. The primary was a coil of flat, copper tubing (Fig. 4), the inside diameter of which was 3.6 cm. and the height 15 cm. The coil was kept cool by passing a stream of cold water through the tubing, and the proximity of this coil to the walls of the quartz vacuum tube kept the quartz at a low temperature in spite of the radiation from the platinum crucible.

For measuring the temperature of the charcoal, a Leeds and Northrup optical pyrometer of the Morse type was used. This was calibrated against a standard thermocouple between 800° and 1400°. Since the temperatures were to be measured optically, black body conditions had to be obtained. This was done, as is shown in the cut, by placing a very thin, platinum truncated cone over the top of the crucible to minimize the radiation from the surface; and then a platinum tube of very thin foil of 0.4 cm. diameter was placed in the center of the sample and focusing was made on the surface of the charcoal at the bottom of this tube.

The procedure in making a determination was as follows: The crucible was filled with a known weight of charcoal and the apparatus assembled as described. The heater shown in Fig. 6, containing naphthalene (b. p. 218°), was placed around the quartz tube and the lower end stoppered and covered with mercury. The naphthalene was then brought to boiling and the vapors allowed to condense to C above the position of the platinum crucible. During the heating the charcoal was continually outgassed by means of the Töpler pump and this gas, being regarded as adsorbed gas, discarded. Then the naphthalene bath was replaced by the primary coil of the induction furnace and the charcoal heated rapidly. All the gas was collected by the Töpler pump and was stored in a large gas buret over mercury and a sample of this analyzed.

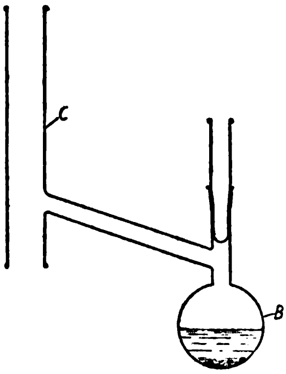

Fig. 6.

A preliminary run was made on the A909 in order to determine at what temperature the oxides of carbon ceased to be obtained. The results of this experiment are shown in Table I.

They show that the amounts of oxygen remaining combined with the charcoal above 1180° are extremely small and could be neglected. It seemed important to see what gases could be obtained at still higher temperatures, however, and so in 2 of the experiments the temperature was raised to 1400°. The gas at these high temperatures was more than 99% hydrogen and was slowly decreasing in amounts obtained as the temperature was raised.

TABLE I.

	Total gas. Cc. per g.	Temp. limits.	Time of heating.	Cc. per g.				Fixed oxygen. Cc. per g.
				CO_2.	CO.	H_2.	CH_4.	
I....	36.42	200–1000°	2 hrs.	4.66	23.40	8.32	0.04	16.36
II....	17.60	1000–1180°	$2^1/_2$ hrs.	0.08	0.53	16.93	0.06	0.35
III....	4.78	1180–1260°	$1^1/_4$ hrs.	0.00	0.07	4.76	0.04	0.03

Since the object of this part of the work was to obtain quantitatively the amount of oxygen capable of being fixed by charcoals, after standardization of the method with ordinary A909, the determinations were made on the 3 samples which had been saturated in pure electrolytic oxygen. The results obtained are presented in Table II. In this table are first given the results from 2 successive runs on two samples of A909 in order to get some idea as to the reproducibility of the results. Considering that charcoal is not a pure substance, the agreement is regarded as very good

TABLE II.

	Total gas. Cc. per g. (N. T. P.)	Maximum temp.	Time of heating.	Cc. N. T. P. per g.				Fixed O_2 per g	
				CO_2.	CO.	H_2.	CH_4.	Cc. N. T. P.	Wt. %.
A909 (1)	54.99	1100° ± 50	$2^1/_2$ hrs.	5.19	22.11	27.57	0.12	16.25	2.32
A909 (2)	58.89	1260°	$5^3/_4$ hrs.	4.74	24.00	30.01	0.14	16.74	2.39
(O_2 sat.)									
A909	56.90	1226°	3 hrs.	5.76	24.80	26.19	0.15	18.16	2.59
English	43.79	1412°	$2^1/_4$ hrs.	2.76	18.36	22.56	0.11	11.94	1.71
German	201.00	1412°	$3^1/_4$ hrs.	9.76	32.92	154.5	3.79	26.25	3.75

The data in this table show that the larger part of the oxygen held by the charcoal had been fixed before the samples had been "soaked" in pure oxygen. A comparison of the amounts of oxygen which is fixed by the different charcoals with the amounts adsorbed is given in Table III, together with the ratio of fixed to adsorbed oxygen. This shows that as much as 6 times the amount of oxygen adsorbed by a charcoal may be held as "fixed" oxygen.

TABLE III.

	Cc. N T. P. oxygen per g. of charcoal.		Ratio of fixed to adsorbed O_2.
	Fixed.	Adsorbed.	
A909........................	18.16	7.2	2.5
English......................	11.94	8.6	1.4
German......................	26.25	4.2	6.3

In Table IV are given the actual observations on a run, in order to give an idea of how an experiment proceeded, after the sample had been thoroughly outgassed at 200°.

TABLE IV.

Sample Used—A909 = 2.948 g.

Time.	Cc. gas.	Temp.	Time.	Cc. gas.	Temp.
2 : 05	0.00	25°	...	....	...
2 : 15	97.4	959	3 : 45	2.5	1190°
2 : 25	19.0	1045	3 : 55	1.7	1226
2 : 35	13.0	1091	4 : 05	1.2	1208
2 : 45	17.0	1160	4 : 15	1.10[a]	1196
2 : 55	10.5	1178	4 : 25	1.06	1211
3 : 05	10.0	1172	4 : 35	0.90	1211
3 : 15	6.0	1181	4 : 45	0.72	1205
3 : 25	4.0	1196	4 : 55	0.61	1211
3 : 35	2.7	1166	5 : 05	0.46	1208

[a] These small volumes were measured in the fall tube of the Töpler pump (*J. Ind. Eng. Chem.*, **12**, 40 (1920)).

At the end of each determination, the walls of the quartz tube held on their inner surface a thin film of a solid varying in color from white to brown, which had vaporized from the charcoal at the high temperatures. A similar observation has been recorded by A. Schuller,[1] who concluded that this was organic matter. On attempting to remove this film, however, the odor of acetylene was noticed. This suggested that a carbide had been formed during the determination and that accordingly some of the oxides of carbon obtained might well have been from reduction of mineral matter contained in the ash. In order to determine what might be the magnitude of this effect on the data obtained, the percentage of ash was determined for each charcoal and the ash analyzed. In the A909 and English charcoals this was mostly alkali carbonates with slight traces of alkaline earths, iron, and alumina. In the German charcoal the ash was principally iron with some alkali carbonates. Table V presents this data and the maximum amount of oxygen which could under any circumstances be attributed to the ash. It is thought, however, that the amount of reduction at these comparatively low temperatures was in all cases much less than these figures would indicate. In any case, as shown in this table, the ash can account for only a small part of the oxygen obtained in the experiments as oxides of carbon.

TABLE V.

	% ash.	Calc. cc. O_2 per g. of charcoal.	Cc. O_2 remaining "fixed" by charcoal.
A909	1.11	3.00	15.16
English	2.04	5.41	6.53
German	1.91	4.35	21.90

Discussion.

Since it has been definitely shown that oxygen can be "fixed" by charcoal, other than by adsorption, it becomes an interesting problem to consider the origin and state of this oxygen. The original material from which

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[1] Schuller, *Wied. Ann.*, **18**, 317 (1883).

all these charcoals were prepared was organic matter and as such contained in the molecular complexes both oxygen and hydrogen. It seemed possible that *both* the oxygen and hydrogen obtained by us were from some of the original material which had not been decomposed in the preparation of the charcoals, but against this view we find the following facts. The temperature of charring this original material was in all cases very close to the temperature, above which no oxides of carbon were obtained and only above which hydrogen and methane were obtained. This would lead us to the conclusion that the hydrogen alone was from the original undecomposed organic material. This conclusion is supported by the fact, which was pointed out in the introduction, that the oxygen obtained as oxides of carbon on heating in a vacuum was reversible while the hydrogen was irreversible. An actual experiment showed that 90% of the oxygen obtained as oxides of carbon above 184° was fixed by the charcoal a second time in 99 hours. On the other hand, in every case hydrogen admitted to a charcoal after outgassing at 1050° and cooling to room temperature could be readily and quantitatively recovered at room temperature.

In view of these facts, we have concluded that this fixed oxygen is held by the charcoal as a surface compound or compounds. These compounds would be, therefore, solid oxides of carbon high in carbon and low in oxygen content, but not necessarily in which the ratio of carbon to oxygen was constant. These oxides must be stable at ordinary temperatures, or at least have a very low rate of decomposition, the decomposition not taking place appreciably until a temperature of about 200° is reached. The data shows that these oxides then break down slowly, giving carbon dioxide and carbon monoxide and presumably leaving a residue of carbon. Although the carbon dioxide predominates at the lower temperatures in the decomposition and carbon monoxide at the higher, no conclusions as to the mechanism of the original decomposition can be made, since carbon dioxide liberated in immediate contact with carbon at the higher temperatures would react immediately with the carbon and be reduced to the monoxide, *i. e.*, there would be a tendency to attain equilibrium between carbon, carbon monoxide and carbon dioxide at any given temperature.

This conception of a solid oxide of carbon, stable at ordinary temperatures, is not new. Brodie[1] isolated 2 oxides of carbon which were amorphous, brown and transparent solids to which he assigned the formulas C_6O_4 and C_4O_3, and indicated that he considered that they belonged to a series of oxides corresponding to the hydrocarbons of the acetylene series. Berthelot[2] showed that these oxides decomposed on heating to 300° in an

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[1] Brodie, *Ann.*, 169, 270 (1873).

[2] Berthelot, *Bull. soc. chim.*, 26, 102 (1876).

atmosphere of nitrogen to an oxide still higher in carbon content by loss of equal volumes of carbon dioxide and carbon monoxide and to which he assigned the formula $C_{10}O_8$. Mellitic anhydride, $C_{12}O_9$, has recently been prepared and its properties described in 2 independent investigations.[1] The most recent work on graphitic acid[2] and work done in this laboratory (which has not yet been published) indicates that this is a colloidal oxide of carbon with an empirical formula approaching C_3O.

Furthermore, H. E. Armstrong,[3] in his studies on the combustion of carbon, concluded that the simple oxides, carbon dioxide and carbon monoxide, were obtained only by the breakdown of the more or less completely oxidized carbon complex. The later extensive researches of Rhead and Wheeler[4] on the same subject lead to the conclusion that oxygen combines with a mass of carbon directly to form a "physico-chemical" complex C_xO_y of variable composition, which is decomposed by heat into carbon monoxide and dioxide. These investigators performed some interesting experiments to determine the amount of this solid carbon-oxygen complex present at temperatures from 100° to 900° during the combustion of carbon. Their results indicate that the higher the temperature, the less the amount of the complex present. If we extrapolate their results, it would appear that at room temperature practically no carbon monoxide or dioxide would be formed but only the complex, while above about 1200° very little of the complex would be formed. This agrees entirely with our observations, which, interpreted by means of assuming the formation of this C_xO_y complex, shows that the first stage in the combustion of carbon takes place at ordinary temperatures. Langmuir[5] has shown that a similar complex of carbon and oxygen, presumably an extremely stable solid oxide of carbon, was formed by a highly graphitized filament of very pure carbon. This decomposed only slowly at 1425° but readily at 1925° and seems to have been even more stable than the complex formed by oxygen with amorphous carbon. These facts all indicate that oxygen does combine with carbon to form a complex, C_xO_y, high in carbon and low in oxygen content, which decomposes on heating to give the ordinary oxides of carbon.

We are led further to the conclusion that this complex must be formed on the surface of the charcoal. This would therefore be likely to alter the adsorptive capacity of a charcoal, which would thus depend in part on the amount of this complex on the surface, No conclusive data on this point have been collected, however, since, although it was observed

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[1] Meyer and Steiner, *Ber.*, **46**, 813 (1913); and Jarrad, *J. Chem. Soc.*, **29**, 106 (1913).

[2] Kohlschütter and Haenni, *Z. anorg. Chem.*, **105**, 121 (1919).

[3] Armstrong, *J. Soc. Chem. Ind.*, **24**, 473 (1905).

[4] Rhead and Wheeler, *J. Chem. Soc.*, **101**, 831 (1912); and **103**, 461 (1912).

[5] Langmuir, THIS JOURNAL, *Chem. Soc.*, **27**, 1154 (1915).

that the adsorptive power of the German charcoal with the most fixed oxygen was the lowest and the English charcoal with the least fixed oxygen the highest, the presence of undecomposed hydrocarbons was also greatest in the German and least in the English charcoal. So, since in the preliminary treatment of the charcoals (Part I), most of the fixed oxygen was removed while the hydrocarbon content was not much altered, the differences observed are more likely due to this latter cause.

Conclusions.

1. The anomalous behavior of the adsorption of oxygen by charcoal extending over long periods of time, overlooked by recent investigators, has been confirmed. This is shown to be due to the presence of 2 phenomena, adsorption and surface combination.

2. A method has been developed for heating charcoal in a vacuum out of contact of oxygen-containing materials, as quartz, to high temperatures by use of the Northrup induction furnace. The gases evolved were collected and analyzed.

3. The formation of a carbon-oxygen complex, essentially a stable solid oxide of carbon, has been shown to occur on the surface of charcoal at ordinary temperatures. This complex decomposes on heating to carbon dioxide and carbon monoxide and can thus be considered to be an intermediate step in the combustion of charcoal, which supports the view suggested by Armstrong and supported with experimental evidence by Rhead and Wheeler and by Langmuir.

4. The amounts of oxygen thus combined to the charcoal has been found to vary with 2 samples of charcoal from 1.71% to 3.75% of the *weight* of the charcoal.

PRINCETON, N. J.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

POLARITY AND IONIZATION FROM THE STANDPOINT OF THE LEWIS THEORY OF VALENCE.

BY WENDELL M. LATIMER AND WORTH H. RODEBUSH.

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Some years ago Abegg and Bodlander[1] discussed the general facts concerning strong and weak electrolytes, the solubility of salts and the formation of complex ions in solution. They showed that these facts may be coördinated and explained to a surprising extent by attributing to each element or radical, in greater or less degree, a property which they called electro-affinity. This property has been more commonly designated as electropositive or electronegative character, and its relation to position in the periodic table is clearly recognized. It now seems possible to go

[1] Bodlander, *Z. anorg. Chem.*, 20, 453 (1899).

further and show this property to be a consequence of the structure of the atom.

In accordance with the Rydberg relationship, the elements from lithium to argon may be arranged in order of their atomic numbers, so that they fall in 2 short series of 8 each. Starting with potassium, there follow 2 series of 18 elements each, and with cesium, 2 series of 32 elements each, the last series, however, being incomplete. The elements in the middle of these long series are peculiar in their behavior, although it is difficult to say with what particular element the abnormality begins or leaves off. However, the elements at the beginning and end of the long series show the same gradation of properties as the elements in the first 2 series of 8. If we somewhat arbitrarily omit the elements of peculiar behavior in the middle of the long series, we can construct a simplified periodic table in series of 8 throughout, each column then consisting of a group of elements of the same valence. Thus, for example, the first group will contain the alkali metals from lithium to cesium, the fifth group the elements from nitrogen to bismuth, and the seventh group, the halogens.

The theory proposed and outlined by G. N. Lewis[1] gives us a definite picture of the structure of the atom for the elements in this simplified periodic table. From the standpoint of the Lewis theory, if the net positive charge upon the kernel be assumed to behave as if centered in the nucleus, the amount of the attraction of this charge for the valence electrons determines the degree of electronegativity of the element. The element becomes more electronegative as we go across the table from left to right because of the increasing net positive charge upon the kernel. As we go down any valence group the attraction of a positive nucleus for the valence electron is decreased because of the increased distance of the valence electron due to the interposition of additional shells of electrons between it and the nucleus. Thus sulfur with a net positive charge on the kernel of 6 is more electronegative than phosphorus with a net positive charge of 5. On the other hand, phosphorus is less electronegative than nitrogen because the valence electrons are separated from the nucleus by an additional shell of electrons.

The term polar[2] has been used in connection with many different properties, but we shall consider it here in its simplest sense. A compound will be said to be polar in which a valence electron has passed from one atom to another, leaving a positive charge upon the one atom and giving a negative charge to the other, thus forming, if the compound contain but the two atoms, an electric dipole. In the extreme case it seems probable that the electron passes completely from the one atom

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[1] Lewis, THIS JOURNAL, 38, 762 (1916); Langmuir, *ibid.*, 41, 868, 1543 (1919).

[2] Bray and Branch, THIS JOURNAL, 35, 1440 (1913); Lewis, *ibid.*, 35, 1448 (1913).

to the other and that the two atoms behave as though the respective charges of positive and negative electricity were located at the centers of the atoms themselves. All the intermediate stages between polar and non-polar compounds doubtless occur, depending upon the extent to which the neutrality of the molecule is disturbed as the electron is more or less completely displaced from one atom to the other.

It follows from the Lewis theory of valence that the degree of polarity of a compound of 2 atoms would depend upon the difference in electronegative character of the 2 atoms, and this conclusion is readily verified by consideration of the facts. Thus in lithium chloride the lithium atom has a net positive charge on the kernel of one, the chlorine atom has a net charge of 7, and we should expect the valence electron to be completely taken away from the lithium and drawn into the outer shell of the chlorine, forming an extremely polar compound. This we find to be the case. Beryllium chloride is not as polar as lithium chloride, since beryllium has a net positive charge on the kernel of 2, and consequently the attraction of the kernel for the valence electrons is twice as great. Boron trichloride shows very little polarity, owing to the fact that the net positive charge of 3 on the boron kernel exerts a powerful attraction for the valence electrons. Carbon tetrachloride is non-polar. Here the net positive charge of 4 on the carbon kernel exerts so strong a pull on the valence electrons that the carbon and the chlorine atoms are simply drawn closer together and the valence electrons may be said to exist in the shells of both atoms. If the compounds of the elements are considered at random we find that whenever there is sufficient difference between the attraction of the positive kernels of 2 atoms for the electrons forming the bond between them, the compound is polar, and the degree of polarity can always be predicted from the structure of the atoms.

Ionization of Polar Compounds.

The criteria by which we shall judge whether a compound is ionized or not will depend on our definition of ionization. The X-ray spectrum of a crystal of sodium chloride shows that each atom of sodium is surrounded by 6 atoms of chlorine, and each atom of chlorine by 6 atoms of sodium. Presumably the valence electron of the sodium has been entirely removed from the sodium atom and forms a part of the shell of the chlorine atom. We cannot say to which particular chlorine atom the electron of the sodium has gone. Sodium chloride does not conduct a current because the atoms are not free to move. However, if we bring the sodium chloride into the liquid state, by fusion for example, it becomes a very good conductor indeed. In the fused state the arrangement of the atoms of sodium chloride is probably not greatly different from that in the crystal, except as it is disturbed by the mobility of the liquid. Since a sodium atom is surrounded on all sides by chlorine atoms it is free to move in any direction upon the application of an electric field, and conduction in the fused salt consists presumably of the movement of atoms of one kind of electric charge through the nearly uniform field produced by a mesh of atoms having the opposite electric charge.

It seems logical to say that a polar molecule is ionized when the ions are able to move independently of each other under the influence of an applied electric field. By this definition fused sodium chloride appears to be completely ionized, but solid sodium chloride, while completely polar, would not of course be considered ionized.

When we form a dilute solution of sodium chloride in an ionizing solvent of negligible conductivity, we meet with a new phenomenon. The most conspicuous characteristic of an ionizing solvent is an abnormally high dielectric constant. The connection between the high dielectric constant and the ionizing power of the solvent has often been explained as follows. In order that sodium chloride in solution may ionize, the powerful electrostatic forces between the ions must be overcome. It is necessary that the solvent act as a depolarizing medium and partially neutralize these forces. The power of the solvent to do this is presumably measured by the dielectric constant. From these considerations the Nernst-Thomson rule was formulated, which states that the ionizing power of a solvent should vary more or less directly with the dielectric constant.

The Nernst-Thomson rule presumes that if a sodium and a chloride ion are separated in solution by a greater distance than they are in the crystal there are strong electrostatic attractions between them. This may not be the case. The molecular volume of sodium chloride is only about half the sum of the atomic volumes of metallic sodium and solid chlorine. Atomic volume of course has no significance as far as actual size of the atoms is concerned, but it does indicate the strength of the forces between the atoms of the crystal. When an atom of chlorine approaches within a certain distance of an atom of sodium there must be some sort of a repulsive force which opposes a closer approach of the 2 atoms. The distance between an atom of sodium and at atom of chlorine in the crystal then represents the distance at which the repulsive forces just balance the attractions between the atoms. If the attractive force between the atoms is less than in sodium chloride, as it is in metallic sodium, the equilibrium positions are farther apart. Now when we dissolve sodium chloride in water which has a dielectric constant of 80, the attractive force between the atoms is reduced to a little more than 1% of its original value. If the repulsive forces between the atoms, of the nature of which we are entirely ignorant, be not reduced to a proportional amount, the interatomic distance for equilibrium between the 2 forces may be considerably increased. In a concentrated solution of sodium chloride the average distance between the sodium and the chloride ions is only about twice that of the crystal, and from the foregoing considerations it is by no means certain that the ions would tend to approach each other any closer than this average distance, especially since an ion is not in the field of a single ion of opposite charge but is acted upon by a number of ions in different directions, the forces of which more or less neutralize each other. In other words, a concentrated solution of sodium chloride may be analogous to fused sodium chloride, except for somewhat greater interatomic distances.

If the foregoing picture is correct, a concentrated solution of sodium chloride is completely ionized.[1] At infinite dilution where the ions are so far separated as to be out of each other's fields we must also have complete ionization. At intermediate concentrations, where the average distance between ions is greater than the equilibrium distance and yet not so great that the ions are out of each other's fields, there may be a tendency for the ions to form in pairs separated from each other by the equilibrium distance. Now since the independent movement of an ion depends upon its being acted upon by several other ions at such distances and directions as to neutralize each other, such a pair can hardly be said to be ionized. There seems to be some evidence that this effect is most pronounced at about molal concentration for sodium chloride.[2]

From the foregoing considerations, in a solution of a polar salt like sodium chloride the ions must always be separated by greater distances than in the solid. In order that a liquid may act as a solvent for a polar substance it must be a depolarizing agent of sufficient strength to permit the separation of ions which takes place when the salt dissolves. This seems to be the chief significance of dielectric constant. Obviously the minimum value of dielectric constant which a liquid must have in order to function as a solvent for polar substances will depend upon the forces between the ions in the solid. Sulfur dioxide, with a dielectric constant of about 14, is able to dissolve many salts. When we consider liquids of dielectric constant below 8 we find that salts do not dissolve in them appreciably as a rule. Solubility is of course affected by many factors, but it seems quite probable that the reason for the slight solubility of salts in these liquids is the inability of the solvent to neutralize the electrostatic forces between ions.

In the few cases[3] in which there is electrolytic conduction in solution

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[1] Cf. Noyes and MacInnes, This Journal, 42, 239 (1920).

[2] Allmand and Polack, *J. Chem. Soc.*, 115, 1036 (1919).

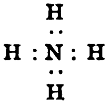
[3] Examples are: Methyl Alcohol in Liquid Hydrogen Chloride (Archibald, This Journal, 34, 584 (1912)); Potassium Iodide in Liquid Iodine (Lewis and Wheeler, *Z. physik. Chem.*, 56, 179 (1906)); Ether and Bromine (Plotnikow, *J. Russ. Phys. Chem. Soc.*, 38, 1096 (1906)); Magnesium Iodide in Ether (unpublished investigation by Mr. R. F. Newton of this laboratory). See also Kraus and Bray, This Journal, 35, 1393 (1913).

in a solvent of low dielectric constant, we find the conductivity very small in dilute solutions, but increasing very rapidly with increasing concentration until it reaches a maximum at some concentration at which the ratio of mols of solvent to mols of solute is a small number, usually not greatly different from unity.

In all these cases the solubility appears to be due to the formation of more or less stable compounds between the solute and the solvent. The behavior of the conductivity is precisely what we should expect. The depolarizing action of the solvent is so small that positively and negatively charged ions are unable to separate and move freely with respect to each other. Hence conductivity in the dilute solution is negligible, the ions being in a condition precisely analogous to sodium chloride vapor, grouped in pairs or molecules. What little conductivity there is, is due to an accidental separation of ions not different from that which takes place in salt vapors. As the concentration approaches the composition of the molecular compound we approach the condition of a fused salt, where an ion is surrounded by ions of opposite sign and can move freely in any direction. The increased conductivity in concentrated solutions is then precisely analogous to fused salt conductivity.

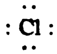
Ionization of Compounds Not Highly Polar.

So far we have discussed polarity the mechanism of which consisted of the transfer of electrons from one atom to another in the molecule. We shall now consider polarity due to the transfer of a hydrogen nucleus from one molecule to another. For example the formation of the ammonium ion



$$\begin{array}{c} \mathrm{H} \\ \cdot\cdot \\ \mathrm{H : N : H} \\ \cdot\cdot \\ \mathrm{H} \end{array}$$

and the chloride ion



$$\begin{array}{c} \cdot\cdot \\ : \mathrm{Cl} : \\ \cdot\cdot \end{array}$$

by the transfer of a hydrogen nucleus from a molecule of hydrogen chloride to a molecule of ammonia. In discussing compounds of hydrogen it must be borne in mind that the hydrogen kernel is also the hydrogen nucleus and as such is very different from the kernel of any of the other elements. Here in all probability we are dealing with the elementary unit of positive electricity, seemingly a particle of minute size even in comparison with the electron. It has already been pointed out that the relative electronegativity of the elements depends upon the net nuclear charge and the distance of the valence electrons from the nucleus as determined by the number of electron shells. Now the hydrogen nucleus, though its nuclear charge is but one, has no surrounding shell of electrons, and may for that reason approach many times closer to the electrons of a valence bond than any other element. What knowledge we have concerning the structure of the nuclei of the elements of higher atomic weight indicates that hydrogen nuclei and electrons may be packed together very closely indeed. In one sense, then, hydrogen is the most electronegative of all the elements,[1] and it is doubtful if the hydrogen nucleus ever gets very far away from one or more electrons. It is this unique character of the hydrogen nucleus which differentiates the polarity of hydrogen compounds. In the pure state, although differing a good deal in degree, they are all extremely non-polar. Thus even as strong an acid as hydrochloric acid is in the pure liquid state a nonconductor of the same order as water. Nor is its conductivity appreciably increased when dissolved in acetone or nitrobenzene,[2] substances with fairly high dielectric constants. Even in liquid hydrogen cyanide, which has a very high dielectric constant, hydrogen chloride does not show a conductivity comparable with that of some salts in the same solvent.[3] Walden[4] has shown that ionization of acids in solvents is independent of the Nernst-Thomson rule of dielectric constant and is greater the more basic the solvent. In the light of the experimental facts, then, the ionization of acids, or indeed extreme polarity of any compounds involving hydrogen, must be interpreted as due to the transfer of a hydrogen nucleus from one molecule to another, thus forming a complex ion. Indeed, from the nature of the hydrogen nucleus, it seems as unlikely that in a solution hydrogen ions should exist as such, as that the electrons should be present moving about freely. It is true that hydrogen shows great mobility in water solutions, but it will appear later that this does not of necessity argue the existence of free hydrogen ions.

Obviously any discussion of the degree of ionization from the standpoint of atomic structure[5] must deal not only with the tendency of the acid to give up hydrogen, but also with the tendency of the solvent to take it up. Let us first consider the hydrogen compounds

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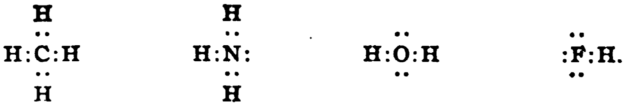
[1] This conclusion is borne out by the fact that atomic hydrogen has such a powerful tendency to form H_2. Extremely electronegative elements such as nitrogen, oxygen and the halogens all show this tendency to form a "saturated" diatomic molecule, that is one of very low or at least uniform external field. Since the external fields of these molecules are nearly neutral, these strongly electronegative substances are extremely volatile in the molecular state. The ease of replacement of acid hydrogen by metals and the volatility of the diatomic gas are both due to the powerful tendency for the formation of molecular hydrogen.

[2] Sackur, *Ber.*, 35, 1248 (1902).

[3] Kahlenberg and Schlundt, *J. Phys. Chem.*, 6, 447 (1902).

[4] Walden, *Trans. Faraday Soc.*, 6, 71 (1910).

[5] Some of the conclusions reached in the following paragraphs have been indicated by Langmuir in a paper, THIS JOURNAL, 42, 274 (1920), which appeared while the present paper was yet in the manuscript.



$$\mathrm{H}:\overset{\mathrm{H}}{\overset{\cdot\cdot}{\underset{\mathrm{H}}{\underset{\cdot\cdot}{\mathrm{C}}}}}:\mathrm{H} \qquad \mathrm{H}:\overset{\mathrm{H}}{\overset{\cdot\cdot}{\underset{\mathrm{H}}{\underset{\cdot\cdot}{\mathrm{N}}}}}: \qquad \mathrm{H}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{O}}}:\mathrm{H} \qquad :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{F}}}:\mathrm{H}.$$

The increasing charge on the kernels of the elements from carbon to fluorine must tend to pull in closer the electrons of the groups of 8, or, as Langmuir has called them, the octets formed about the kernels; and at the same time the hydrogen is held off by the increasing repulsion between the positive nuclei. Consequently, the total force holding the hydrogen becomes less, that is, the compound becomes more acid when dissolved in a solvent, the molecules of which have a field sufficiently negative to pull the hydrogen away. Now let us consider the tendency of these same hydrides to take up hydrogen kernels, in other words their ability as solvents to ionize other acids. One of the fundamental postulates of the Lewis theory is that a valence bond in those elements which form octets consists of a pair of electrons held in common by 2 atoms. An octet about an atom is then capable of uniting with 4 other atoms, providing of course that the total number of electrons in the atom is such as to complete all the shells. This tendency to complete the group of 4 atoms about an octet of electrons is in many ways as striking as the tendency to complete the octet of electrons about a positive kernel. Now methane has completed its group of 4 atoms and has no free pairs of electrons left; while ammonia has one free pair of electrons, water 2, and hydrogen fluoride 3. Moreover the force with which a pair of electrons of an octet is holding a hydrogen nucleus gives us a good indication of the tendency of a free pair of electrons of the same octet to add another hydrogen nucleus. From these considerations, we should expect ammonia to form readily the ion NH_4^+ and water and hydrogen fluoride to show strong but decreasing tendencies to form at least the ions, H_3O^+ and H_2F^+. It follows that for an acid dissolved in liquid ammonia a relatively larger number of the molecules will react with the solvent to form a polar compound than for the same acid dissolved in water. And in general it may be said that the degree of ionization of weak acids as determined by conductivity measurements will be greater the more basic the solvent. However, the situation is somewhat different when we compare solutions of a strong acid, for example, hydrochloric acid, in water and liquid ammonia, since in both solvents the hydrogen chloride has probably completely reacted with the solvent to form polar molecules. In fact Kraus and Bray,[1] from comparative measurements, have calculated the degree of ionization of hydrochloric acid to be greater in dilute solution in water than for solutions of corresponding concentration in ammonia.

We have seen that for a horizontal row in the periodic system the

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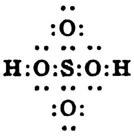
[1] Kraus and Bray, This Journal, 35, 1337 (1913).

acidity of the hydride is greater the more electronegative the element. Consideration of the hydrides of any valence group leads to the conclusion that in this case the hydride is more acid the less electronegative the element. For example, hydrogen chloride is more acid than hydrogen fluoride, hydrogen sulfide more acid than water, phosphine more acid than ammonia. The elements sodium to chlorine differ from the corresponding elements lithium to fluorine in that the valence electrons are forming a new group of 8 around the first group of 8. Then in hydrogen chloride the valence electrons are (1) farther from the center of the kernel, and (2) farther from each other than in hydrogen fluoride. As a consequence of (1), an electron is held by less force, and, as one continues down the valence group, it becomes increasingly less difficult for the hydrogen to take the electron completely away from the halogen, and we find hydrogen iodide gas dissociating largely into molecular hydrogen and iodine. From (2) it seems reasonable to expect hydrogen chloride to be more acid than hydrogen fluoride in that the hydrogen, in the case of chlorine, is held by a pair of electrons which are farther apart than in fluorine. Indeed in the latter the octet may be sufficiently small so as to enable electrons other than the pair to exert considerable attraction upon the hydrogen nucleus.

The strength of an oxy-acid may be considered in terms of the forces tending to distort the oxygen octet. Lewis,[1] in his paper on "The Atom and the Molecule," has discussed the effect of substituting a chlorine in acetic acid. The ideas which he expressed may be extended considerably in connection with the inorganic oxygen acids. Thus in sulfuric acid



$$\begin{array}{c} \cdot\cdot \\ :\mathrm{O}: \\ \cdot\cdot\;\cdot\cdot\;\cdot\cdot \\ \mathrm{H}:\mathrm{O}:\mathrm{S}:\mathrm{O}:\mathrm{H} \\ \cdot\cdot\;\cdot\cdot\;\cdot\cdot \\ :\mathrm{O}: \\ \cdot\cdot \end{array}$$

the attraction of the sulfur kernel for electrons held in common with the oxygen, and the repulsion between the sulfur and the oxygen kernels tend to distort the oxygen octet from the cubical arrangement. Obviously this pulling of electrons in toward the sulfur and pushing of the oxygen kernel out will weaken the force with which the hydrogen is holding a pair of electrons in common with the oxygen. The higher the positive charge on the central kernel, the greater will be this distortion. Then for any horizontal row of the periodic system, the oxygen acids of highest valence, for example silicic acid (H_4SiO_4), orthophosphoric, sulfuric and perchloric acids, will become stronger as the atomic number increases. The close agreement of the densities of the last 3 acids above indicates that their structures are very similar and emphasizes the fact that rela-

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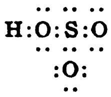
[1] Lewis, *loc. cit.*, p. 782.

tively small distortions of the oxygen octet may produce large differences in the degree of ionization when water is the solvent.

We have seen in any vertical or valence periodic group that as the atomic weight increases, that is, as each new shell is formed about the preceding one, both the attraction for the valence electron and the repulsion of a neighboring kernel decrease. Then in the case of an oxy-acid the distortion of the oxygen octet due to the central atom must become less as one goes down the group; their form doubtless approaches more and more that of the oxygen in the water molecule and the hydrogen consequently is held with corresponding firmness. In fact the attraction of the central kernel for the electrons may become so weak that the oxygen octet is no longer held in position but ionizes to form hydroxyl. Thus we have the amphoteric compounds. For illustration we need only mention HNO_3, H_3PO_4, H_3AsO_4, H_3SbO_4, $Bi(OH)_3$. Putting the two cases together we have the well known generalization that the more negative the element the stronger the oxygen acids. The condition for maximum distortion of the oxygen octet would be found in perfluoric acid. Doubtless this is the very reason that no oxygen compounds of fluorine are known.

The generalization may be made in terms of the older idea of valence, that the oxygen acids of any element become stronger the higher the positive valence of the element. The reason for this becomes clear if considered in reference to the position of the electrons in the atoms. For example consider sulfurous acid



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 .. .. ..
H:O:S:O:H
 .. .. ..
   :O:
    ..
```

Six of the 8 electrons around the sulfur are held in common with the 3 oxygens. The remaining 2 electrons may then be drawn in by the sulfur to such an extent as practically to reduce the positive charge on the sulfur from 6 to 4. The distortion of the oxygen octet then corresponds more to carbonic acid than to sulfuric acid, although of course the neutralization is not complete, and sulfurous acid is somewhat stronger than carbonic acid. It may then be stated that weakness of the acids containing less oxygen is due to the presence of one or more pairs of electrons on the central kernel which are not shared with other atoms.

The acids of phosphorus offer an exception to the rule as ordinarily stated regarding the dependence of the strength of an acid upon the valence of the element. The following table is quoted from "Leitvermögen der Elektrolyte."[1]

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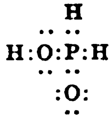
[1] Kohlrausch, "Leitvermögen der Elektrolyte," pp. 160, 167 (Teubner, Leipzig, 1898).

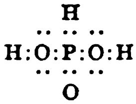
MOLECULAR CONDUCTIVITY AT 25°.

V in liters.	2.	8.	32.	128.	512.	1024.
H_3PO_4	64	96	156	246	317	341
H_3PO_3	129	187	257	318	351	358
H_3PO_2	140	207	281	335	361	367

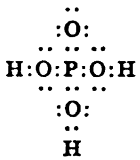
The acids of lower valence are apparently even more highly ionized than phosphoric acid. Considering the inability to replace but one of the hydrogens in H_3PO_2 and but two in H_3PO_3, whereas all three are replaceable in H_3PO_4, the following structural formulas are probably correct.



$$\begin{array}{c} \mathrm{H} \\ \cdot\cdot\ \cdot\cdot \\ \mathrm{H:O:P:H} \\ \cdot\cdot\ \cdot\cdot \\ \mathrm{:O:} \\ \cdot\cdot \end{array}$$



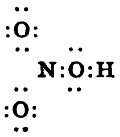
$$\begin{array}{c} \mathrm{H} \\ \cdot\cdot\ \cdot\cdot\ \cdot\cdot \\ \mathrm{H:O:P:O:H} \\ \cdot\cdot\ \cdot\cdot\ \cdot\cdot \\ \mathrm{O} \end{array}$$



$$\begin{array}{c} \cdot\cdot \\ \mathrm{:O:} \\ \cdot\cdot\ \cdot\cdot\ \cdot\cdot \\ \mathrm{H:O:P:O:H} \\ \cdot\cdot\ \cdot\cdot\ \cdot\cdot \\ \mathrm{:O:} \\ \cdot\cdot \\ \mathrm{H} \end{array}$$

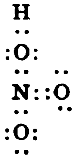
Here the tendency to pull in a pair of electrons which took place in sulfurous acid is prevented, in this case by hydrogen attached directly to the central atom. That the acids which have the hydrogen attached to the phosphorus are even stronger than phosphoric acid is in agreement with our postulate regarding the electronegative hydrogen and with other facts to be considered later.

The structure of nitric acid may be either



$$\begin{array}{l} \ \cdot\cdot \\ \mathrm{:O:} \\ \ \cdot\cdot\ \ \ \ \cdot\cdot \\ \quad\ \mathrm{N:O:H} \\ \ \cdot\cdot\ \ \ \ \cdot\cdot \\ \mathrm{:O:} \\ \ \cdot\cdot \end{array}$$

or

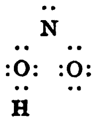


$$\begin{array}{l} \ \mathrm{H} \\ \ \cdot\cdot \\ \mathrm{:O:} \\ \ \cdot\cdot\ \ \cdot\cdot \\ \ \mathrm{N::O} \\ \ \cdot\cdot\ \ \cdot\cdot \\ \mathrm{:O:} \\ \ \cdot\cdot \end{array}$$

Under the pull of a strong electronegative element such as oxygen, the nitrogen octet may not be stable and a sextet is formed instead. The structures of the nitrate group in sodium nitrate from X-ray analysis[1] seems to bear out this idea. The same is doubtless true of boric and carbonic acids. Indeed molecular nitrogen may be explained on the tendency of nitrogen to form sextets as

$$:\ddot{\mathrm{N}}:\ddot{\mathrm{N}}:$$

The structure of nitrous acid then may be written as



$$\begin{array}{c} \cdot\cdot \\ \mathrm{N} \\ \cdot\cdot\quad\cdot\cdot \\ \mathrm{:O:\ :O:} \\ \cdot\cdot\quad\cdot\cdot \\ \mathrm{H}\qquad \end{array}$$

Here we have another example of a free pair of electrons on the central atom. This accounts for nitrous acid being weaker than nitric acid.

The ionization of organic acids may be explained along similar lines.

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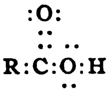
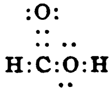
[1] Bragg and Bragg, "X-Rays and Crystal Structure."

As mentioned before, Lewis has discussed chloro-acetic acid at some length. In general it may be said of acids of the type



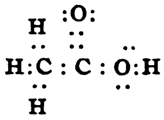
$$\mathrm{R}:\overset{\overset{:\mathrm{O}:}{\cdot\cdot}}{\mathrm{C}}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{O}}}:\mathrm{H}$$

that whenever the nature of R is such as to exert a strong pull upon the electrons holding it to the carboxyl carbon, the acid will be correspondingly strengthened. Oxalic acid, in which the electrons in question are presumably half way between the two carboxyl carbons, is a strong acid. The strong neutralizing power of the hydrogen kernel considered in connection with the acids of phosphorus is observed again in formic acid



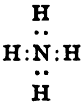
$$\mathrm{H}:\overset{\overset{:\mathrm{O}:}{\cdot\cdot}}{\mathrm{C}}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{O}}}:\mathrm{H}$$

which is considerably stronger than acetic acid



$$\mathrm{H}:\underset{\mathrm{H}}{\underset{\cdot\cdot}{\overset{\mathrm{H}}{\overset{\cdot\cdot}{\mathrm{C}}}}}:\overset{\overset{:\mathrm{O}:}{\cdot\cdot}}{\mathrm{C}}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{O}}}:\mathrm{H}$$

Thus as far as concerns the carboxyl carbon the field due to the electrons of the bond is more nearly neutralized by the hydrogen than by the kernel of the methyl carbon. In view of their relative positive charges the opposite effect might have been expected. This emphasizes again the difference between the hydrogen kernel or nucleus and the kernel of any other element; the one a single positive unit and the other a complex structure of both positive and negative units. The amines are another excellent example of this characteristic of hydrogen. If one of the hydrogens in the ammonium group



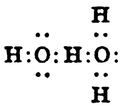
$$\mathrm{H}:\underset{\mathrm{H}}{\underset{\cdot\cdot}{\overset{\mathrm{H}}{\overset{\cdot\cdot}{\mathrm{N}}}}}:\mathrm{H}$$

be replaced by a carbon radical, the remaining hydrogens are held more firmly, that is the amine is more basic. This is the result to be expected if the field of the electron bond is less neutralized by the methyl group than by the hydrogen. The pair of electrons is shifted in toward the nitrogen; the positive charge on the nitrogen somewhat neutralized; and the remaining 6 electrons held less firmly by the nitrogen but more firmly by the remaining 3 hydrogens.

Associated Liquids.

The phenomenon of association in liquids has long been recognized as related to dielectric constant and ionizing power as a solvent. According to one view, a so-called polar solvent contains dipoles of considerable moment, that is, positive and negative charges separated by a considerable distance. The high dielectric constant of such a liquid is considered to be due to the orientation of these dipoles in an electric field. Likewise association is supposed to take place because of the attraction of two dipoles for each other. This explanation is open to serious objections. In the first place it is hard to see why the compounds of very high dielectric constant should be chiefly hydrogen compounds. Also hydrogen chloride should contain dipoles of greater moment than water or hydrogen fluoride, yet it has a much lower dielectric constant both in the vapor and liquid. Nor does hydrogen chloride appear to be associated. It seems then that the explanation is to be sought along other lines.

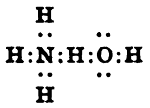
Let us compare again the compounds ammonia, water and hydrogen chloride. Ammonia adds a hydrogen readily but has little tendency to give one up. Hydrogen chloride, on the other hand, shows just the opposite tendencies. Water occupies an intermediate position and shows tendencies both to add and give up hydrogen, which are nearly balanced. Then, in terms of the Lewis theory, a free pair of electrons on one water molecule might be able to exert sufficient force on a hydrogen held by a pair of electrons on another water molecule to bind the two molecules together. Structurally this may be represented as



$$\mathrm{H}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{O}}}:\mathrm{H}:\underset{\mathrm{H}}{\underset{\cdot\cdot}{\overset{\overset{\mathrm{H}}{\cdot\cdot}}{\mathrm{O}}}}:$$

Such combination need not be limited to the formation of double or triple molecules. Indeed the liquid may be made up of large aggregates of molecules, continually breaking up and reforming under the influence of thermal agitation.

Such an explanation amounts to saying that the hydrogen nucleus held between 2 octets constitutes a weak "bond."[1] Ammonium hydroxide



$$\mathrm{H}:\underset{\mathrm{H}}{\underset{\cdot\cdot}{\overset{\overset{\mathrm{H}}{\cdot\cdot}}{\mathrm{N}}}}:\mathrm{H}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{O}}}:\mathrm{H}$$

is an example in which the union is fairly strong. This is contrary to the view commonly held that the weak basicity of ammonium hydroxide is due to the fact that it consists largely of a solution of ammonia in water. The idea also departs somewhat from the view taken by Lewis in regard to the polarity of NH_4^+. However, there seems to be no reason for be-

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[1] Mr. Huggins of this laboratory in some work as yet unpublished, has used the idea of a hydrogen kernel held between two atoms as a theory in regard to certain organic compounds.

lieving that gradations may not exist all the way from the case of ammonium chloride, where the hydrogen is definitely transferred from the chlorine to the ammonia, to the case in the association of water where the hydrogen is still held quite firmly to the original water molecule. Ammonium chloride is probably nearly as completely polar with respect to the separation of charges as sodium chloride, and the crystal, at ordinary temperatures, is held together in a similar manner by forces only slightly less. As we raise the temperature, however, the hydrogen of the bond, being a heavy particle, acquires vibrational energy very rapidly. This breaks up the crystal structure and causes ammonium chloride to dissociate and volatilize without melting. Hydrogen chloride forms a compound of this type with water just as it does with ammonia, but it is even less stable than ammonium chloride for obvious reasons.

It is not assumed that all association is of this type. In acetic acid, for instance, the association doubtless takes place with the formation of definite polymers of 2 molecules. This kind of association however will produce properties radically different from those of a liquid like water.

If our picture of the association of water is correct, a hydrogen nucleus may be held between two oxygen octets by forces which, for quite a distance, obey Hooke's law. Such a hydrogen would be capable of considerable displacement by an electric field. This is just the mechanism postulated by the mathematical theory of dielectric polarization as giving rise to high dielectric constant. It is quite possible in the case of the hydrogen compounds of the most electronegative elements, hydrogen fluoride, for example, that the simultaneous attraction of a highly concentrated octet of electrons, and the repulsion of the powerful positive nucleus for the hydrogen, may result in the hydrogen in the single molecule being held elastically. The association of the molecules is, however, very probably the factor that produces the extremely high dielectric constant.

The high mobility of the hydrogen ion in water solution may be explained as due to a shifting of hydrogen nuclei from one water molecule to another, a sort of Grotthus chain effect, rather than to a rapid motion of any one H_3O^+ ion. Obviously such a mechanism is possible only when the molecule of the solvent adds and gives up hydrogen nuclei readily. This is not true of ammonia and the NH_4^+ ion does not show a high mobility in liquid NH_3. It seems worth while to emphasize that the so-called "Associated Liquids" or "ionizing solvents" are quite non-polar insofar as no considerable separation of positive and negative charges in the molecule takes place. One of the properties of a completely polar compound is that of crystallizing in a space lattice, of which the individual ions are the units. The ions are held together by powerful electrostatic forces, and the melting point of such a crystalline substance is high.

Non-polar compounds, on the other hand, crystallize presumably with the molecule as the unit. Since the intermolecular forces are of the nature of stray fields from the atoms, which are relatively weak, non-polar compounds do not have high melting points. The "ionizing solvents" are, however, quite different in properties from a non-polar liquid of the type of liquid nitrogen. The atoms of the nitrogen molecule are "saturated." This is another way of saying that the stray fields around the molecule are not strong enough nor diversified enough to produce much interaction between the molecules. On the other hand, the properties of the "ionizing solvent" depend upon the existence of moderately strong intermolecular fields.[1] Dielectric constant is a measure of this type of "polarity" but has no significance with regard to highly polar compounds.

The metals in the middle of the long groups of the periodic table, which we have previously avoided discussing, form compounds intermediate in character between the highly polar salts and the non-polar acids. They show to a high degree the property which Werner has designated as coördination number. Abegg and Bodlander[2] point out that the solubility and ionization of the salts of these metals is connected with this tendency to form ionic complexes. In other words the simple salts of these elements, which are in themselves not highly polar, become more polar through reaction with the solvent or other molecules. It is not surprising that a salt such as cadmium chloride should be slightly dissociated in water solution but rather that any salt of these metals should be a good electrolyte.

BERKELEY, CALIF.

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE S. S. WHITE DENTAL MANUFACTURING COMPANY.]

THE SYSTEM ZINC OXIDE, PHOSPHORUS PENTOXIDE AND WATER AT 25° AND 37°.

BY N. E. EBERLY, C. V. GROSS AND W. S. CROWELL.

Received May 4, 1920.

Introduction.

The zinc salts of phosphoric acid are of interest in the study of dental cements. The following is a part of a more extended investigation of the reactions and equilibria involved in the manufacture and use of such plastic compounds.

The phosphates of zinc, particularly the acid salts, have been very little studied. Graham describes an acid salt, $ZnHPO_4.H_2O$. Heintz[3]

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[1] Cf. Harkins and King, THIS JOURNAL, 41, 971 (1919).

[2] Abegg and Bodlander, *loc. cit.*

[3] Heintz, *Ann.*, 143, 356 (1867).

was not able to prepare it. Demel[1] describes the salt $Zn_2(HPO_4)_2.2H_2O$ as separating in stable, triclinic crystals from concentrated acid solutions of sp. gr. 1.5 or more, and states that it is decomposed by water.

The neutral zinc orthophosphate, $Zn_3(PO_4)_2$, has been studied more fully. The tetrahydrate has been obtained from zinc carbonate and orthophosphoric acid at 100°. A monohydrate is also reported.[2]

Various investigators have reported the preparation of hydrates of zinc orthophosphate by precipitation. The evidence of higher hydrates than $4H_2O$ is based upon the analyses of precipitates filtered from solutions. Owing to the colloidal nature of these preciptiates, the existence of such hydrates is questionable. The tetrahydrate occurs in nature as the mineral hopeite.

In view of the scanty information obtained from the literature, the investigation of the ternary system, zinc oxide, phosphorus pentoxide and water, was undertaken. Since we are concerned with the stability of the system at ordinary temperatures and the reactions occurring in it at body temperature, the isotherms at 25° and 37° were traced.

Materials Used.

The zinc oxide used was the U. S. P. grade. Careful analysis indicated that it contained only traces of impurities, chiefly iron and silica. It was practically 99.8% zinc oxide.

The phosphoric acid used was U. S. P. 85% phosphoric acid. It was found to contain traces of nitrates (diphenylamine gave a faint blue color), and an undeterminably small quantity of alkali. It was free from chlorides, sulfates and pyrophosphoric acid.

Experimental Method.

The experiments were carried out as follows. After preliminary experiments had shown the approximate course of the curve, solutions were made in small Erlenmeyer flasks of Pyrex glass containing zinc oxide and phosphorus pentoxide in sufficient quantity to be slightly supersaturated. The more dilute solutions, up to 35% of phosphorus pentoxide, were allowed to crystallize spontaneously. The more concentrated were seeded with the proper crystalline phase, since they showed great reluctance to crystallize of themselves.

In the case of the equilibrium at 25°, the tightly-stoppered flasks and their contents were placed in a mechanically-stirred gas-heated water bath, provided with a toluene regulator which kept the temperature constant without attention to about 0.1° for months at a time. With occasional agitation, the flasks were allowed to remain in the bath for some weeks. The liquid and solid were removed and analyzed, returned

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[1] Demel, *Berl. Ber.*, 12, 1171 (1879).

[2] Fredel, *ibid.*, 9, Ref. 794 (1876); Friedel and Sarasin, *J. Ber.*, 1892, p. 519; also Debray, *Compt. rend.*, 52, 46 (1861) and 59, 40 (1864).

and the analyses repeated at 2-week intervals until constant results were obtained. At 37° the flasks were kept in a bacteriological incubator which was observed to be constant to 0.25° over a long period.

Considerable difficulty was experienced in making up solutions with less than 20% phosphorus pentoxide, since the solid phase was more soluble in the cold than at the boiling point. The following procedure was adopted. The preliminary experiments had shown the approximate course of the curve. Concentrated solutions were prepared such that on dilution they would be of the proper composition. They were cooled rapidly in ice and diluted with the proper quantity of cold water, shaken vigorously and placed at once in the bath at the proper temperature. The rise in temperature caused crystallization.

Methods of Analysis.

Samples of the liquid phase were withdrawn with a pipet provided with a filter of cotton wool. Zinc and phosphoric acid were determined in the same solution. It was found that phosphoric acid in such large quantities caused errors in the determination of zinc by titration with potassium ferrocyanide. The phosphoric acid was removed by precipitation with magnesia mixture. The first precipitate was washed with 2.5%

Equilibrium at 25°.

	Solution.		Crystals and mother liquor.		
No.	% P_2O_5.	% ZnO.	% P_2O_5.	% ZnO.	
1......	5.08	2.38	15.62	22.75	Locate $Zn_3(PO_4)_2 : 4H_2O$ ZnO 54.3%. P_2O_5 31.0%. H_2O 14.7%.
2......	9.76	4.65	17.04	20.89	
3......	12.42	6.13	.....	.....	
4......	13.52	6.56	.....	.....	
5......	14.00	6.74	.....	.....	
6......	14.15	6.92	.....	.....	
7......	14.37	6.97	.....	.....	
8......	14.83	7.34	.....	.....	
9......	15.98	7.71	.....	.....	
10......	17.15	8.26	.....	.....	
11......	18.33	8.73	19.50	11.15	Indeterminate.
12......	22.75	10.74	23.92	13.70	
13......	26.48	12.47	27.05	14.18	Locate $ZnHPO_4$: $3H_2O$. ZnO 37.8%. P_2O_5 33.0%. H_2O 29.2%.
14......	28.70	13.48	29.82	19.47	
15......	30.09	14.16	31.03	20.78	
16......	32.55	15.40	33.07	23.98	
17......	33.79	15.82	33.82	21.58	
18......	37.15	17.30	36.73	21.50	
19......	37.76	17.65	.....	.....	
20......	39.61	18.04	.....	.....	
21......	42.05	16.14	47.77	27.48	Locate $Zn(H_2PO_4)_2 : 2H_2O$ ZnO 27.3%. P_2O_5 47.9%. H_2O 24.8%.
22......	44.53	13.20	.....	.....	
23......	48.70	9.58	48.00	27.13	
24......	52.25	7.64	.....	.....	
25......	55.97	7.23	.....	.....	

Equilibrium at 37°.

	Solution.		Crystals and mother liquor.		
No.	% P_2O_5.	% ZnO.	% P_2O_5.	% ZnO.	
1......	4.87	2.08	.....	.....	
2......	9.46	4.12	.....	.....	
3......	13.60	6.27	.....	.....	
4......	18.13	8.78	.....	.....	
5......	19.48	9.66	.....	.....	
6......	20.32	10.16	.....	.....	
7......	21.96	10.88	.....	.....	
8......	26.75	13.26	.....	.....	
9......	29.65	14.77	.....	.....	
10......	33.39	17.06	.....	.....	
11......	34.58	17.92	.....	.....	
12......	36.13	16.00	.....	.....	
13......	37.80	15.78	38.92	34.38	Locate
14......	39.93	16.12	39.54	41.30	$ZnHPO_4 : H_2O$
15......	42.42	15.81	40.58	34.05	ZnO 44.1%. P_2O_5 38.5%.
16......	42.65	16.82	40.09	39.08	H_2O 17.4%
17......	44.89	17.83	.....	.....	
18......	46.11	18.05	.....	.....	
19......	46.41	14.74	.....	.....	
20......	48.99	12.55	.....	.....	
21......	51.35	11.26	.....	.....	
22......	51.92	11.12	.....	.....	
23......	54.32	10.82	.....	.....	

ammonium hydroxide, dissolved and reprecipitated carefully by the method of Schmitz,[1] filtered on a Gooch crucible, dried, ignited and the phosphoric acid weighed as magnesium pyrophosphate. The zinc oxide, was determined in the combined filtrate by careful titration with potassium ferrocyanide by the method of Lowe.[2]

The drained crystals, with mother liquor adhering, were analyzed in the same way, thus giving 2 points on the straight line connecting the composition of the solid phase and that of the liquid phase.

Before considering the ternary system, the binary systems zinc oxide water and phosphorus pentoxide water should be considered. The first can be dismissed by stating that zinc oxide is relatively insoluble in water at ordinary temperatures. The second has been very completely investigated by Smith and Menzies.[3] Their results were expressed in terms of orthophosphoric acid and water. We have recalculated them in terms of phosphoric pentoxide and water and find that the solubility of phosphoric pentoxide in water will not affect our results until high concentrations are reached. The isotherm at 25° intersects the solubility curve in 3 points, 62.5%, 68.4% and 68.7% pentoxide. It would be

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[1] Schmitz, *Z. anal. Chem.*, 45, 512 (1906).

[2] Low, "Technical methods of Ore Analysis," Sixth edition, p. 284.

[3] Smith and Menzies, THIS JOURNAL, 31, 1183 (1909).

interesting to trace the equilibrium relations around these concentrations. Unfortunately, the experimental difficulties are great and lack of time restricted our work to concentrations below 55%.

The isotherms at 25° and 37° are plotted in Fig. 1. The first branch of the curves represents the solubility of neutral zinc orthophosphate tetrahydrate, $Zn_3(PO_4)_2.4H_2O$, in phosphoric acid of increasing concentration. It will be noted that the 37° isotherm lies below the 25°, showing that the solubility decreases as the temperature increases. At 25° this branch of the curve ends at P_2O_5 = 15.2%, ZnO = 7.5%. At 37° it ends at P_2O_5 = 20.3%, ZnO = 10.1%. The lower solubility and higher acidity at the quadruple point at 37° can be attributed to greater hydrolysis at the higher temperature. The tetrahydrate separates in shining plates similar in appearance to magnesium ammonium phosphate. If caused to form slowly, large transparent plates or short prisms can be prepared.

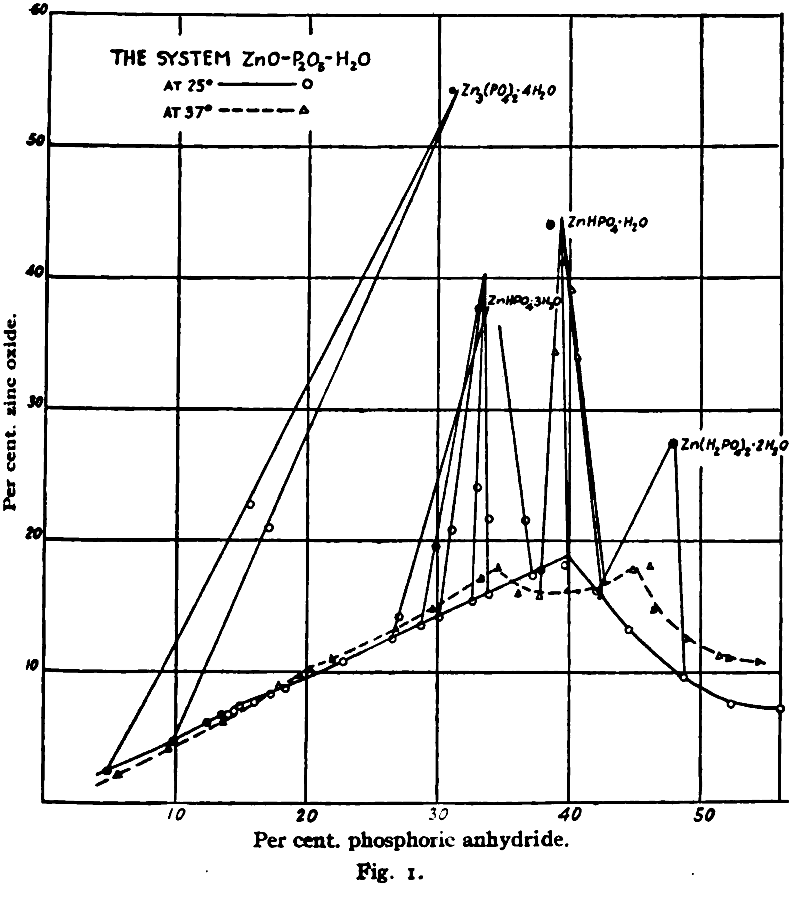

Fig. 1.

At the quadruple point $Zn_3(PO_4)_2.4H_2O$, $ZnHPO_4.3H_2O$, solution and vapor are in equilibrium.

The second branch of the curve represents the solubility of zinc hydrogen orthophosphate trihydrate, $ZnHPO_4.3H_2O$, in phosphoric acid solutions. The curve at 37° lies above that at 25°, showing an increase of solubility with increasing temperature. The curve at 37° ends at about 34% phosphorus pentoxide, while that at 25° continues to the quadruple point at 40% pentoxide and 18.8% zinc oxide. At 37° a new phase makes its appearance at 34% pentoxide. Transparent needles of Graham's phosphate, $ZnHPO_4.H_2O$, separate from solutions of this and higher concentrations. The salt seldom separates pure, but is always contaminated at first with the adjacent phases. Equilibrium is very slowly reached even when the solutions are seeded with crystals of the proper phase. Efforts were made to crystallize this salt at 25°, but without success, and no evidence of its existence could be obtained except from a slight irregularity of the curve near the second quadruple point. Either the upper end of the curve at 25° represents a metastable condition which we were not successful in destroying or the monohydrate does not appear at this temperature. In any event, Heintz' failure to prepare this salt can be readily understood.

At 25° the second quadruple point represents the equilibrium between $ZnHPO_4.3H_2O$, $Zn(H_2PO_4)_2.2H_2O$, solution and vapor. Above this point large, transparent rhombohedrons of the latter salt separate slowly from the solutions. The solubility decreases rapidly as the concentration of the pentoxide increases.

At 37° another branch is inserted between the $ZnHPO_4.3H_2O$ curve and the $Zn(H_2PO_4)_2.2H_2O$ curve, which represents the solubility of the $ZnHPO_4.H_2O$, Graham's phosphate. Great difficulty was experienced in determining the curve since equilibrium was reached very slowly. Nearly 6 months elapsed before the composition of the solutions became constant. In some instances the trihydrate separated first in spite of seeding with the monohydrate, and a long time elapsed before this salt redissolved. In the more concentrated solutions a salt of the composition $Zn(H_2PO_4)_2$ separated, and the crystals slowly broken down into needles of the monohydrate. There is some uncertainty as to the exact location of these 2 quadruple points, but we feel that they are located to within 1%. The quadruple point $ZnHPO_4.3H_2O$, $ZnHPO_4.H_2O_7$ solution, vapor, is at 34.6% pentoxide and 17.6% zinc oxide. The quadruple point $ZnHPO_4.H_2O$, $Zn(H_2PO_4)_2.2H_2O$ solution, vapor, is at 45.7% pentoxide and 18.5% zinc oxide.

The hydrolytic precipitation of the zinc orthophosphate tetrahydrate from dil. phosphoric acid solutions leads to a simple method for its preparation in a pure state. A solution containing 50% pentoxide (85% phosphoric acid diluted with $^1/_5$ of its weight of water) is saturated at the boiling point with zinc oxide. The water lost by evaporation is replaced and the solution rapidly cooled first to room temperature, then in cracked ice. About 10 volumes of ice-cold water are added and the solution violently stirred and poured through a filter into a large porcelain dish. The dish and its contents are heated with stirring on a water bath. A large quantity of shining plates of the neutral tetrahydrate will separate. The crystals are filtered out and washed clean with boiling water, sucked dry on a plate and spread out in a thin layer to air dry. This gives a pure product of constant composition, uncontaminated with alkalies and without excess zinc or phosphoric acid.

A microscopic study of the various phases was made with the following results.

$Zn_3(PO_4)_2 : 4H_2O$. Shining orthorhombic plates.

$ZnHPO_4 : 3H_2O$. Sticky, threadlike crystals agglomerating into cotton-wool-like masses. Optical properties could not be observed.

$ZnHPO_4 : H_2O$. Small, hard, transparent needles. Extinction oblique to long axis, probably triclinic.

$Zn(H_2PO_4) : 2H_2O$. Large, transparent triclinic rhombohedra.

Summary.

The isotherms at 25° and 37° of the ternary system $ZnO.P_2O_5 : H_2O$ have been traced to 55% phosphorus pentoxide.

The following solid phases separated at 25°: $Zn_3(PO_4)_2.4H_2O$, $ZnHPO_4.3H_2O$ $Zn(H_2PO_4)_2.2H_2O$.

At 37° an additional phase was noted, *viz.:* $ZnHPO_4.H_2O$.

A method of preparing pure neutral zinc orthophosphate tetrahydrate has been described.

PHILADELPHIA, PENN.

[CONTRIBUTION FROM THE BUREAU OF STANDARDS, U. S. DEPARTMENT OF COMMERCE.]

THE DETERMINATION OF ZIRCONIUM AND TITANIUM IN ZIRCONIUM ORES.

BY G. E. F. LUNDELL AND H. B. KNOWLES.[1]

Received May 10, 1920.

CONTENTS.

I. Introduction.

Zirconium ores may be expected to contain besides zirconium such elements as silicon, iron, aluminum, titanium, calcium, magnesium, sodium and potassium. In addition to these elements others such as thorium, cerium, tin, yttrium, uranium, manganese and phosphorus are often found,

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[1] Published by permission of the Director of the Bureau of Standards.

while tantalum, erbium, didymium, beryllium, scandium, lead, copper, bismuth, cobalt, zinc and lithium have been encountered. It is evident that an accurate determination of zirconium in mixtures so complex requires careful analytical procedures. When this Bureau was called upon to act as umpire in zirconium ore analyses during the war period, an extended study of the various published methods for this determination was made, and the cupferron method described in the following pages was finally adopted. Considerable difficulty was experienced at first in obtaining complete decomposition of zirconium ores, and this operation will, therefore, be discussed under a separate heading.

II. Decomposition of the Ore.

Various fluxes have been employed for this operation. Sodium carbonate has been recommended by Ferguson,[1] Brown,[2] and Wunder and Jeanneret.[3] Fusions with this reagent are usually tedious and often incomplete, even though the material has been ground to a very fine powder and well mixed with the flux.

Potassium hydrogen sulfate was employed by Dittrich and Pohl[4] and is specified in a method given by Johnstone.[5] This flux and the related one, potassium pyrosulfate, give good fusions of some ores like baddeleyite, and works very slowly and often incompletely on others, such as zircon.

Sodium hydrogen sulfate has been recommended by J. Lawrence Smith[6] as being far preferable to potassium pyrosulfate for the decomposition of emery. It may prove valuable in zirconium ore fusions.

Sodium peroxide has been recommended by Travers,[7] and also by Holladay.[8] Travers obtained excellent fusions by mixing one g. of the finely ground ore with 10 g. of sodium peroxide and fusing for a few minutes in a nickel crucible. Holladay recommends a sodium carbonate lining which is described as follows. "The sodium carbonate lining, which has for its object the prevention of attack of the crucible by sodium peroxide with consequent introduction of a large amount of nickel into the zirconium solution, is made by fusing sodium carbonate in the crucible at 1050–1100° and causing it to cool in an even layer on the bottom and sides. Several grams of peroxide are then melted in the crucible and allowed to solidify on the bottom, and the mixture of ore and peroxide is

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[1] J. D. Ferguson, *Eng. Mining J.*, 106, 793–794 (1918).

[2] Jas. Brown, THIS JOURNAL, 39, 2358–66 (1917).

[3] M. Wunder and B. Jeanneret, *Z. anal. Chem.*, 50, 733–5 (1911).

[4] M. Dittrich and R. Pohl, *Z. anorg. Chem.*, 43, 236–241 (1905).

[5] S. J. Johnstone, "The Rare Earth Industry." C. Lockwood & Son, 1915, p. 51.

[6] J. Lawrence Smith, *Compt. rend.*, 31, 48–50, 191–193 (1850); *Silliman's J.*, 10, 354–369 (1850).

[7] A. Travers, *Chimie et Industrie*, 2, 385–392 (1919).

[8] Private communication from J. A. Holladay, Electro Metallurgical Company, Niagara Falls, N. Y.

placed on top of this. The function of the layer of peroxide is to prevent particles of ore being caught in the carbonate lining and remaining unfused. Sodum carbonate does not melt at the comparatively low temperature required for the peroxide fusion and thus protects the crucible from attack."

Potassium hydrogen fluoride and also a recommended mixture of potassium pyrosulfate and potassium fluoride have been mentioned favorably. It seems quite possible that some zirconium may be volatilized as fluoride if the first named flux is used at high temperatures. Both fluxes require subsequent complete removal of all fluorine.

Borax has been used with success at the Bureau of Standards for the fusion of all zirconium ores as described under III. The flux does not cause any complications in the cupferron precipitation which is subsequently employed; if desirable, the boric acid can afterwards be easily removed by volatilization as methyl borate in the usual manner. Boric acid has not proven as satisfactory as borax.

III. The Bureau of Standards Method for the Determination of Zirconium and Titanium in Zirconium Ores.

A. Preliminary Remarks.

This method employs cupferron as a final precipitant and was adopted after a careful consideration of many possibilities. The following brief outline of the method indicates the manner in which the possible interfering elements are eliminated or provided for and will make clear the various steps in the method. After fusion of the ore with borax, solution of the melt in hydrochloric acid and evaporation to the appearance of fumes with sulfuric acid, the solution is cooled, diluted and digested in order to throw out, together with the impure silica, interfering quantities of phosphorus as zirconium phosphate. This insoluble matter is filtered off, ignited and treated with sulfuric and hydrofluoric acids to remove silicon. A sodium carbonate fusion of the non-volatile matter followed by a water extraction and filtration serves to remove the phosphorus. Zirconium and titanium in the water-insoluble are recovered by ignition, fusion with pyrosulfate, solution in acid and addition to the main solution.[1] Interfering quantities of such elements as calcium, magnesium, potassium, sodium, lithium, copper, cobalt, manganese, zinc and boron (introduced in the fusion) are next removed by an ammonium hydroxide precipitation followed by filtration. Solution of the ammonium hydroxide precipitate in acid, and treatment with hydrogen sulfide eliminates tin, lead, bismuth and any remaining copper. The filtrate from

[1] Tantalum when present, should come down with silica in the sulfuric acid treatment and subsequently resist solution of the carbonate melt. Traces of tantalum left in solution would afterwards be caught in the hydrogen sulfide precipitation in sulfuric acid solution.

the hydrogen sulfide precipitation is next treated with tartaric acid, ammonium hydroxide and hydrogen sulfide to throw out iron and any cobalt, manganese and zinc which may have escaped the ammonium hydroxide separation. The above operations leave in solution at this point zirconium, titanium, thorium, cerium (and any other rare earths), aluminum, beryllium, uranium, and possibly some phosphorus. After acidification with sulfuric acid, and boiling to expel hydrogen sulfide, the solution is cooled and treated with an aqueous solution of cupferron, whereby zirconium and titanium are quantitatively precipitated together with varying amounts of thorium, cerium and other rare earths; while aluminum, beryllium,[1] uranium, phosphorus, and the remainder of the rare earths remain in solution. The ignited and weighed cupferron precipitate is then fused with potassium pyrosulfate, dissolved in sulfuric acid, and the solution divided into 2 equal parts for the determination of titanium and the rare earths. The procedure for the determination of titanium depends on its amount; for small amounts Weller's[2] colorimetric method is used, while for large amounts, the aliquot is reduced to Ti_2O_3[3] in a Jones reductor containing ferric alum in the receiver and then oxidized to TiO_2 by a standard permanganate solution. The rare earths oxides are determined in the second aliquot by a preliminary hydrofluoric acid precipitation followed by an oxalate separation as recommended by Hillebrand.[4] Zirconium oxide is then calculated by difference.

The following discussion of 3 other methods which were seriously considered may be of interest.

1. The Substitution of Ammonium Hydroxide for Cupferron as the Final Precipitant.—This proceedure would possess the advantage of a complete precipitation of the rare earths (and therefore provide for their determination in the same sample), and the disadvantages of requiring complete removal of tartaric acid before precipitation, as well as complicating the analysis by throwing down aluminum, beryllium, uranium and phosphorus. In case the ore was originally decomposed by a sodium peroxide fusion, followed by boiling with water and filtering, the greater

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[1] Beryllium and scandium were not considered by the authors in a paper on "The Use of Cupferron in Quantitative Analysis" (*J. Ind. Eng. Chem.*, **12**, 344–350 (1920)). Subsequent quantitative tests made at this Bureau have demonstrated that beryllium when present alone or mixed with zirconium and titanium, is not thrown down by cupferron in sulfuric acid solution containing tartaric acid, and that scandium is partially precipitated.

[2] A. Weller, *Ber.*, **15**, 2593 (1882); W. F. Hillebrand, "The Analysis of Silicate and Carbonate Rocks," U. S. Geol. Surv., *Bull.* 700, pp. 155–162.

[3] F. Pisani, *Compt. rend.*, **59**, 298 (1864); H. D. Newton, *Am. J. Sci.* (4th Ser.), **25**, 130 (1908).

[4] W. F. Hillebrand, "The Analysis of Silicate and Carbonate Rocks," U. S. Geol. Surv., *Bull.* 700, pp. 176–177.

part of these elements would go into the water extract and thus be eliminated. Perhaps a solution by acid of the water-insoluble portion, followed by neutralization with sodium hydrogen carbonate and peroxidation as described by Noyes, Bray and Spear,[1] would give a reasonably complete separation. Two difficulties arise in this last procedure, namely, complete precipitation of titanium in the peroxidized solution is accomplished only by vigorous boiling for at least 15 minutes, and this operation results in a partial precipitation of uranium.

2. *Precipitation with Phenylhydrazine*[2] *in the Method as Given, after the Precipitation with Hydrogen Sulfide in Acid Solution.*—This procedure would possess the advantage that no ammonium tartrate—ammonium sulfide treatment to remove iron would be required; and would possess the disadvantage of giving a complex precipitate similar in composition to that given by ammonium hydroxide, with the difference, however, that some elements, such as cerium, would be incompletely precipitated.

3. *Direct Precipitation of Zirconium as Phosphate in a Sulfuric Acid Solution Containing Hydrogen Peroxide.*[3]—This procedure would undoubtedly require preliminary separations such as are employed in the Bureau method. In case the amount of iron were not excessive, the precipitation would finally be carried out in the filtrate from the hydrogen sulfide precipitation. This procedure appears to be most attractive, since it affords a direct determination of zirconium. The authors do not, however, regard this method, at present, as entirely satisfactory for the determination of large amounts of zirconium, since uncertainties are introduced on account of various factors, such as: (1) Incomplete data as to the interference of elements such as uranium; (2) the tendency of zirconium phosphate to hydrolyze upon washing; and (3) difficulties during ignition owing to decrepitation.

B. Procedure.

Fuse 4 g. of borax in a platinum crucible, cool and place on top of the fused mass a 0.3000 g. sample of ore which has been ground to approximately 100 mesh. Cover the crucible and fuse thoroughly over a Meker burner, stirring the melt occasionally with a short, stiff platinum rod or wire kept in the crucible. When the decomposition of the ore is complete,[4] remove the platinum rod and put it in the beaker used for the solu-

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[1] A. A. Noyes, W. C. Bray and E. B. Spear, *Technology Quarterly,* **21,** 36 (1908).

[2] E. T. Allen, This Journal, **25,** 421–444 (1903).

[3] W. F. Hillebrand, U. S. Geol. Surv., *Bull.* **700,** pp. 173–175; G. E. F. Lundell and H. B. Knowles, This Journal, **41,** 1801–1808 (1919).

[4] This operation does not ordinarily require more than half an hour. If determinations of other elements such as aluminum, calcium and magnesium are desired, the substitution of sodium peroxide as a fusion medium (see II) is desirable, since otherwise all boric acid must be expelled by a methyl alcohol-hydrochloric acid treatment after solution of the melt.

tion of the melt. As the melt cools, gently twirl the crucible in order to run the fusion up on the sides.

Dissolve the cooled melt in 150 cc. of 1 : 5 hydrochloric acid in a 250-cc. beaker by filling the crucible with acid, inverting in such a manner that one edge of the crucible rests on the crucible cover, which has been placed on the bottom of the beaker, thus allowing free circulation of the solvent, and then gently warming on the steam bath.

Transfer the solution to a platinum dish, add 20 cc. of 1 : 1 sulfuric acid, and evaporate till heavy fumes escape. Cool, dilute to 100 cc. with water, filter off the impure silica, wash with hot water, and reserve for subsequent treatment. Digest the filtrate and washings, preferably warm and overnight, to throw down, as zirconium phosphate, interfering amounts of phosphorus. If a precipitate appears, filter, wash with 5% ammonium nitrate solution, reserve the paper and residue and treat the filtrate and washings as described below.

Add approximately 5 g. of ammonium chloride and then ammonium hydroxide in slight excess. Boil the solution for one or two minutes, filter, wash with 2% ammonium nitrate solution and discard the filtrate.[1]

Dissolve the precipitate in 100 cc. of hot 5% sulfuric acid, wash thoroughly with hot water and reserve the filtrate and washings.

Ignite the filter paper, together with the reserved papers containing impure silica and zirconium phosphate, in the original platinum crucible. Moisten the ash with water, add one cc. of 1 : 1 sulfuric acid, 5 cc. of hydrofluoric acid and evaporate to complete expulsion of sulfuric acid. Fuse the residue with a small amount of sodium carbonate, digest the melt in water and filter off the insoluble residue. Wash the residue with hot water, ignite it in a platinum crucible, fuse with potassium pyrosulfate, dissolve the cooled fusion in hot 5% sulfuric acid and add the solution to the reserved solution. (The above steps serve to remove phosphoric acid and to recover any zirconium that accompanies the silica, or that has been precipitated by ammonium hydroxide as phosphate and subsequently resists solution in 5% sulfuric acid.)

Dilute or neutralize with ammonium hydroxide till the solution contains approximately 1% (by volume) of sulfuric acid, treat with hydrogen sulfide, and filter if the hydrogen sulfide group is indicated. If indicated, wash well with a 1% sulfuric acid solution saturated with hydrogen sulfide.[2] Keep the volume of the filtrate at approximately 200 cc. To the solution add tartaric acid in amount equal to 5 times the aggregate weight

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[1] If a determination of such elements as copper, manganese, zinc, calcium and magnesium is desired, a double precipitation should be performed, and the combined filtrates treated as in ordinary analysis. Where extreme accuracy is desired, due attention should be paid to the slight recoveries of copper, cobalt, zinc and manganese subsequently made.

[2] The treatment of the acid solution with hydrogen sulfide instead of proceeding

of the bases to be held in solution; when the acid has dissolved, make the solution ammoniacal and saturate with hydrogen sulfide. Filter through the equivalent of an S. and S. blue-ribbon No. 589 paper, wash with ammonium sulfide-ammonium chloride solution and refilter, on a new filter, if traces of iron sulfide are suspected in the filtrate.[1]

Carefully acidify to a total acidity of 10% sulfuric acid (by volume) in 400 cc., boil to expel hydrogen sulfide, filter if sulfides are indicated, and cool the solution to from 5 to 14°.

Precipitate with an excess of a cold 6% water solution of cupferron. An excess of the precipitant is indicated by the formation of a fine, white precipitate, which redissolves, instead of a curdy one which persists.[2] Filter after a 5-minute digestion, using a filter paper and platinum cone with gentle suction. Thoroughly wash the precipitate with cold 10% (by volume) hydrochloric acid.[3]

Carefully dry and ignite the paper and precipitate in a tared platinum crucible and finally ignite over a blast lamp or its equivalent.[4] Cool in a desiccator and weigh as oxides of zirconium, titanium and rare earths.[5]

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directly with an ammonium sulfide treatment is carried out for the following 2 reasons: (1) it serves to show up immediately all members of the hydrogen sulfide group; and (2) unless the iron is reduced before precipitation as sulfide, titanium will be in part thrown down also (A. Cathrein, *Z. Kryst. Min.*, 6, 243 (1882); 7, 250 (1883); W. M. Thornton, Jr., *Am. J. Sci.*, [IV] 37, 407–414 (1914). The sulfide precipitate may contain tin, copper, lead and bismuth, together with some platinum resulting from attack of the crucible during the various previous operations. If desired, these may be determined after the recovery and inclusion of the copper present in the filtrate from the ammonium hydroxide precipitation.

[1] All of the iron in the sample taken, together with any manganese, zinc and cobalt, which came down with the ammonium hydroxide precipitate, are caught at this point as sulfides. In case a determination of iron alone is desired, the simplest procedure would consist in solution of the sulfide in sulfuric acid, elimination of hydrogen sulfide reduction in a Jones reductor, and titration with permanganate.

[2] The color of the precipitate furnishes an excellent indication of the amount of titanium present, since zirconium precipitates are pure white while titanium precipitates are yellow. A brownish tint indicates iron or vanadium.

[3] Clear filtrates and washings indicate complete precipitation of zirconium and titanium, while cloudy or opalescent ones indicate the reverse. The latter have occasionally developed and no satisfactory explanation has been found. In these circumstances, recoveries must be made as follows. Evaporate the solution to a small volume, destroy the organic matter by treatment with nitric acid, and finally heat till fumes of sulfuric acid appear. Cool, dilute, filter off any silica resulting from attack of the glassware, and precipitate with cupferron in a 10% sulfuric acid solution as directed above.

[4] A correction for silica in the mixed oxides is not ordinarily necessary. In umpire work and in cases where a recovery has been obtained from the first cupferron filtrate, this correction should be made, paying due attention to adding sufficient sulfuric acid to prevent volatilization of zirconium and titanium fluorides and avoiding mechanical loss during the expulsion of the sulfuric acid.

[5] Although vanadium has not been reported as a constituent of zirconium ores, it may be worth while to call attention to the fact that vanadium is partly precipitated

Fuse the mixed oxides with potassium pyrosulfate, take up in 10% (by volume) sulfuric acid, dilute to exactly 100 cc. and divide into two 50-cc. portions.

Determination of Titanium in Portion I.—If the percentage of titanium is low, determine it colorimetrically by Weller's method;[1] when the percentage is high, reduce to titanium sesquioxide[2] in a Jones reductor containing ferric alum-phosphoric acid in the receiver and then oxidize to titanium dioxide by titration with standard permanganate solution.

Determination of Rare Earths in Portion II.—Determine the rare earths in this portion by Hillebrand's method[3] as follows. Precipitate the hydroxides with an excess of potassium hydroxide, decant the liquid, wash by decantation with water once or twice and then slightly on the filter. Wash the precipitate from the paper into a small platinum dish, treat with hydrofluoric acid, and evaporate nearly to dryness. Take up in 5 cc. of 5% (by volume) hydrofluoric acid. If no precipitate is visible, rare earths are absent. If a precipitate is present, collect it on a small filter held by a perforated platinum or rubber cone and wash it with from 5 to 10 cc. of the same acid. Wash the crude rare-earth fluorides into a small platinum dish, burn the paper in platinum, add the ash to the fluorides and evaporate to dryness with a little sulfuric acid. Dissolve the sulfates in dil. hydrochloric acid, precipitate the rare-earth hydroxides by ammonia, filter, redissolve in hydrochloric acid, evaporate the solution to dryness, and treat the residue with 5 cc. of boiling hot 5% oxalic acid. Filter after 15 minutes, collect the oxalates on a small filter, wash with not more than 20 cc. of cold 5% oxalic acid, ignite and weigh as rare-earth oxides, which are to be deducted from the weight of the cupferron precipitate.

The above procedure does not give an absolutely quantitative recovery of the rare earths. Experiments indicate a recovery by the method

by cupferron in a 10% sulfuric acid solution. In case vanadium is present in the ore, either of 2 procedures may be followed. 1. Substitution of a peroxide fusion of the ore for the recommended borax fusion, followed by a water extraction of the cold melt and filtration to eliminate vanadium at the start of the analysis. 2. Fusion with sodium carbonate of the weighed oxides obtained as above in the method, followed by water extraction and filtration to separate vanadium from zirconium, titanium and the rare earths. The determination of titanium and the rare earths would then be performed as directed in this method, on the ignited water-insoluble; while the determination of V_2O_5 would be carried out by acidifying the sodium carbonate filtrate with sulfuric acid, reducing to V_2O_3 in a Jones reductor containing ferric alum in the receiver, and then oxidizing to V_2O_5 by means of a standard permanganate solution.

[1] A. Weller, *Ber.*, **15**, 2593 (1882); W. F. Hillebrand, "The Analysis of Silicate and Carbonate Rocks," U. S. Geol Surv., *Bull.* **700**, pp. 155–162.

[2] F. Pisani, *Compt. rend.*, **59**, 298 (1864); H. D. Newton, *Am. J. Sci.* [IV] **25**, 130 (1908).

[3] W. F. Hillebrand, *loc. cit.*, pp. 176–177.

of approximately 85% of the rare earths present in residues containing 100 mg. of zirconia, 2 mg. of thoria and 2 mg. of ceria, the recovery of thoria being more complete than that of ceria.

Attempts which were made to omit the preliminary separation of the rare earths as fluorides were unsuccessful.

IV. Confirmatory Analyses.

The analyses listed in Table I were carried out by the Bureau Method on samples of diorite to which had been added various amounts of zirconium, titanium, thorium, cerium and phosphorus. All of the elements which might be present in zirconium ores were not added because researches by the authors and others[1] dealing with the use of cupferron in quantitative analysis had demonstrated that the ones added were most to be feared.

TABLE I.—ANALYSES.

	Weights taken in g. of:						Wt. of ignited cupferron precipitate.	Wts. found in g. of:		
Expt.	Rock.	ZrO_2.	TiO_2.[a]	ThO_2.	CeO_2.	P_2O_5.		ZrO_2.	TiO_2.	ThO_2–CeO_2.
1.....	0.0560	0.2096	0.0034	....	....	....	0.2129	0.2090	0.0039	....
2.....	0.0612	0.2151	0.0042	....	....	0.0100	0.2192	0.2149	0.0043	....
3.....	0.0607	0.2151	0.0042	0.0014	0.0013	....	0.2212	0.2152	0.0044	0.0016
4.....	0.0630	0.2151	0.0043	0.0054	0.0052	....	0.2235	0.2153	0.0043	0.0039
5.....	0.0621	0.2151	0.0042	0.0054	0.0052	0.0100	0.2234	0.2153	0.0043	0.0038

[a] Including a small amount of TiO_2 in the rock.

The results obtained show a gratifying accuracy for the method. It was expected that the values obtained for zirconium would be high in the analyses involving thoria and ceria on account of their probable incomplete recovery from the ignited cupferron precipitate. Thoria is more completely precipitated by cupferron than is ceria, and it is also more completely recovered by the fluoride-oxalate method. The rare-earth recoveries from the ignited cupferron precipitates in Expts. 3, 4 and 5 were therefore probably much better than the 85% obtained when equal parts of thoria and ceria were taken.

V. Summary.

1. Methods of decomposing zirconium ores are listed.

2. A cupferron method for the determination of zirconium and titanium in zirconium ores is given.

3. The method provides for the following elements which have been found in zirconium ores: zirconium, titanium, silicon, thorium, cerium, iron, aluminum, scandium, yttrium, erbium, didymium, beryllium, calcium, magnesium, sodium, potassium, lithium, uranium, phosphorus, tantalum, manganese, zinc, cobalt, tin, lead, copper and bismuth. It is also worthy of note that chromium and nickel do not interfere in a cupferron precipitation; that tungsten would not cause trouble since it is removed before

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[1] G. E. F. Lundell and H. B. Knowles, *J. Ind. Eng. Chem.*, 12, 344–350 (1920).

the final precipitation; and that vanadium would require special treatment. Since this element has not been reported in zirconium ores, and since its presence in significant amounts would be indicated at various stages of the analysis, it would cause no trouble.

The authors desire to express to Dr. W. F. Hillebrand of this Bureau their sincere appreciation of his aid and counsel.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE ROYAL POLYTECHNICAL INSTITUTE OF COPENHAGEN.]

STUDIES ON SOLUBILITY. II. THE SOLUBILITY RATIOS OF SALTS IN STRONG HOMOIONIC SOLVENTS.

BY J. N. BRÖNSTED.

Received May 24, 1920.

I. Influence of Hydration of the Solute.

In a recent paper[1] a treatment of solubility equilibria in salt solutions was given on the basis of the provisional hypothesis that the stoichiometric activity coefficient in a mixed salt solution is the same for any ion of the same type. It was shown that the general features of the solubility curves in the case of homoionic as well as heteroionic solvents could be accounted for by means of this hypothesis.

The provisional character of the hypothesis was emphasized by pointing out several factors capable of causing deviations from the requirements of the simple assumption. As the principal of these factors we can name the secondary electric effect, which, besides the primary Milner effect, may influence the potential of the ions, and which manifests itself in a way similar to that of incomplete dissociation. Furthermore, there is the hydration of the dissolved ions and finally the electrostriction effect introduced by several authors[2] in order to explain the salting-out effect of salt solutions.

As a start on a general discussion of the influence of these factors we may conveniently put the simpler case of considering not the shape of the solubility curve itself, but the ratio of solubilities or solubility products for salts of varying concentration in the same solvent. If the secondary electric forces exert a similar effect upon the activity coefficients, which presumably is the case when the ions of the solute possess similar molecular structure, deviations from a constant solubility ratio would be due chiefly to changes in the hydration of the dissolved ions. If, on the other hand, constant solubility ratios are actually found, using a solvent of considerably changing vapor pressure, we may be entitled to conclude

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[1] *Kgl. Danske Vidensk. Selsk. Mathemat.-fysiske Medd.*, 2, 10 (1919); THIS JOURNAL, 42, 761 (1920).

[2] Euler, *Z. physik. Chem.*, 31, 360 (1899); Geffeken, *ibid.*, 49, 257 (1904).

that the solutes concerned are uniformly hydrated as well as also equally acted upon by the secondary electric forces.

The influence of hydration of the solute can readily be accounted for thermodynamically in the following way. If the ions are hydrated in solution and the activity coefficients are, according to our hypothesis, the same for all ions, Equation 23 in the previous paper must be replaced by

$$c'_a c''_a f^2 = K \qquad (1)$$

where c'_a and c''_a are the concentrations, respectively, of the cation and anion in the anhydrous state, f the activity coefficient and K a constant peculiar to the saturating salt. If this salt be hydrated in the solid state also, we can write

$$c'_a c''_a f^2 \xi^{\nu} = K, \qquad (2)$$

where ξ indicates the activity of water in the solution and ν the number of molecules of water combined with one molecule of the solid salt.

Assuming the following equilibria to occur between the ions in the hydrated and anhydrous states,

$$K\,n'H_2O^+ \rightleftarrows K^+ + n'H_2O$$

$$A\,n''H_2O^- \rightleftarrows A^- + n''H_2O$$

and assuming the concentration of the anhydrous ions to be negligible when compared with the concentration of the hydrates, the mass action law gives

$$c'_a = \frac{k'}{\xi n'}\,c', \text{ and } c''_a = \frac{k''}{\xi n''}\,c'' \qquad (3)$$

where c' and c'' stand for the total (stoichiometric) concentration of the ions.

Introducing these expressions in (2) and putting $n' + n'' = n$ we obtain finally

$$c'c'' = k\,\frac{\xi^{n-\nu}}{f^2}. \qquad (4)$$

In this formula $k = K/k'k''$, and $n - \nu$ depends upon the nature of the solute only, while ξ and f are characteristic of the solvent. For the solubility ratio of 2 salts in the same solvent, therefore, we can write

$$\frac{(c'c'')_1}{(c'c'')_2} = \frac{k_1}{k_2}.\ \xi^{(n_1-\nu_1)-(n_2-\nu_2)}, \qquad (5)$$

while the ratio of solubilities of the same salt in two solvents is determined by

$$\frac{(c'c'')_{I}}{(c'c'')_{II}} = \frac{f_{II}^2}{f_I^2}\left(\frac{\xi_I}{\xi_{II}}\right) n - \nu. \qquad (6)$$

It is worth noticing that Equation 4 is also arrived at from the assumption of incomplete dissociation, n in that case indicating the total number of water molecules associated with one molecule of partly dissociated salt.

If $\nu > n$, *i. e.*, if the salt is more hydrated in the solid than in the dissolved state, increasing concentration of the solvent will tend to increase the solubility. This effect for the case $n = 0$ has been studied by H. Goldschmidt.[1] If $n > \nu$, the effect will be the opposite; increasing concentration will tend to diminish the solubility corresponding to the well known salting-out effect of salt solutions. This effect necessitates an increase in the activity of the less hydrated or anhydrous substance at constant stoichiometric concentration, a fact that has been recently pointed out by Bjerrum,[2] and used by him to explain the behavior of the hydrogen electrode according to this view.

We shall in the following, apply Equation 5 to the solubilities of salts in strong homoionic solvents. Consideration of this formula shows that—granting the validity of our hypothesis—2 salts will exhibit a constant solubility ratio either when dissolved in solvents having the same ξ, *i. e.*, the same vapor pressure, or when $n_1 - \nu_1 = n_2 - \nu_2$, *i. e.*, the difference in hydration of the two salts in the dissolved and solid states is the same. Materially differing values of the solubility product ratios as produced by different hydrations are to be expected only when dealing with solvents of very high concentration.

II. Experiments with Potassium Hydroxide as Solvent.

As already indicated in the previous article, potassium hydroxide possesses a marked power of reducing the solubility of other substances, a fact which is probably connected with a high degree of hydration of the hydroxyl ion. When using this solvent we are able to employ, therefore, salts as soluble as potassium chloride, bromide, and iodide as saturating salts, the solubility in strong solutions of potassium hydroxides being sufficiently diminished for the treatment of the solution in accordance with the above considerations.

Furthermore, on account of the great solubility of potassium hydroxide, very great alterations in the water activity can be obtained with this solvent, which, therefore, according to Equation 5, is especially fitted for an examination of degrees of hydration.

The results of a series of measurements on univalent potassium salts at 20° are given in Table I.

The figures in this table denote number of mols in one liter of solution. We see the solubilities of the 3 halides and of potassium chlorate steadily decreasing with rising concentration of potassium hydroxide. The solubility of potassium nitrate seems to keep constant in the most concentrated solutions, and with the iodate a slight increase is noted.

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[1] *Z. physik. Chem.*, 17, 145 (1895).

[2] *Medd. K. Vetenskapsakad. Nobelinst.*, 5, No. 16 (1919).

TABLE I.

Solubility of Salts in Potassium Hydroxide Solutions at $t = 20°$.

C_{KOH}.	KCl.	KBr.	KI.	KNO_3.	$KClO_3$.	KIO_3.
4.71	1.605	...	...	0.847	0.0924	0.0390
5.06	...	...	...	...	0.0882	0.0362
6.35	...	...	...	...	0.0609	0.0256
7.90	0.712	1.012	...	0.455	....	....
7.95	...	...	...	0.450	0.0445	0.0179
8.60	...	...	...	...	0.0410	....
9.41	0.405	0.693	1.72	0.364	0.0351	0.0144
10.95	0.273	0.515	1.23	0.298	0.0287	0.0130
11.10	0.253	0.451	1.176	...	....	0.0128
12.19	0.191	0.348	0.933	0.271	0.0254	0.0131
12.92	0.168	0.306	0.824	...	....	0.0135
13.84	0.138	0.247	...	...	....	....
14.02	0.136	0.246	0.672	0.241	0.0215	0.0154
14.85	0.121	0.214	...	0.232	0.0195	0.0194
15.02	0.118	0.210	0.558	0.233	0.0191	....

The solubility products P are calculated from these data, for instance for potassium chloride as $P = C_{KCl}(C_{KOH} + C_{KCl})$. The ratios of the products appear in the next table.

TABLE II.

Ratios of the Solubility Products of Salts in Potassium Hydroxide Solutions at $t = 20°$.

C_{KOH}.	$\frac{KBr}{KCl}$.	$\frac{KI}{KCl}$.	$\frac{KNO_3}{KCl}$.	$\frac{KNO_3}{KClO_3}$.	$\frac{KIO_3}{KClO_3}$.
4.71	....	....	0.457	10.6	2.39
5.06	....	....	....	....	2.42
6.35	....	....	....	....	2.40
7.90	1.67	....	0.622	....	....
7.95	....	....	....	10.6	2.49
9.41	1.76	4.76	0.898	10.8	2.44
10.95	1.77	4.92	1.100	10.6	2.22
11.10	1.82	4.96	....	....	....
12.19	1.83	5.15	1.42	10.9	1.94
12.92	1.84	5.14	....	....	....
13.84	1.80	....	....	....	....
14.02	1.83	5.15	1.81	11.5	1.40
14.85	1.80	....	1.93	12.1	1.02
15.02	1.80	4.89	2.00	12.4	....

Inspection of these figures shows that 4 of the 5 ratios actually do exhibit constant values over considerable ranges of concentrations.

Since all of the saturating salts are anhydrous in the solid state, Equation 5 can be written for this case

$$\frac{P_1}{P_2} = \frac{k_1}{k_2} \cdot \xi^{n_1 - n_2}. \qquad (7)$$

For the most dilute solutions of the solvent this ratio cannot be expected to give constant values in the case of the more soluble salts. As soon as the solubility is sufficiently diminished the ratio is found to be quite constant for the halides. Since the water activity ξ changes largely in this region of concentrations this result requires $n_1 = n_2$. All of the halides, therefore, are hydrated to the same extent in solution. As a consequence of Equation 7 and 8 a slight difference in the degree of hydration has a very marked influence upon the solubility ratio, and the test furnished by these experiments for equal hydration of the ions Cl^-, Br^- and I^- must be considered, therefore, as a rather rigid one. From the constancy of P_1/P_2 in the case of the halides we are furthermore justified in concluding that our hypothesis concerning the equality of the activity coefficient holds good for these systems, because it may be considered as highly improbable that this simple result could be given by a compensation of independent effects.

The figures given in the last 2 columns furnish the expected constant values only in the more dilute solutions, and for KNO_3/KCl the values change throughout the whole range of concentrations. According to the ideas stated above, we are led to attempt an explanation of these deviations by the assumption of differently hydrated ions. For these calculations the water activity ξ occurring in Equation 7 must be known.

The water activity is closely connected with the vapor pressure and can with sufficient exactness be put equal to this. From Dieterici's[1] measurements of the vapor pressure of potassium hydroxide solutions at 0°, the following expression can be derived,

$$p = 1.18 - 0.059\,M - \frac{0.2}{M} \tag{8}$$

where M is the molal concentration ($= C_{KOH}$ in Table II) and p is its vapor pressure. The expression holds good between $M = 5$ and $M = 15$, as shown by the figures in Table III.

TABLE III.

Activity of Water in KOH Solutions, Observed and Calculated by Means of Equation 8.

M.	Obs.	Cal.
4.52	0.85	0.85
6.55	0.75	0.75
10.2	0.56	0.55
14.0	0.336	0.334

We shall first consider the values of P_{KNO_3}/P_{KCl} exhibiting the greatest changes. If the increasing values of this ratio are to be interpreted as due to hydration, the chlorine ion must evidently contain more water combined with it than the nitrate ion. Calculation according to Equation 7 gives the following result:

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[1] *Wied. Ann. Physik*, 50, 47 (1893).

TABLE IV.

Ratio $P_{KNO_3}/P_{KCl} = P_1/P_2$, Water activity, and ξ, $n_1 - n_2$ in KOH Solutions of the Molal Concentration *M*.

M.	ξ.	P_1/P_2.	$n_2 - n_1$.
10.95	0.516	1.10	1.7
12.19	0.444	1.42	1.2
14.02	0.339	1.81	1.0
14.85	0.291	1.93	
15.02	0.282	2.00	1.0

In this table are considered only the stronger solutions of potassium hydroxide in which the solubility is sufficiently small. We see from these figures that the changes in P_1/P_2 are accounted for by assuming the chlorine ion to have combined with it one of two molecules of water more than the nitrate ion. That the number is not quite constant may be explained by the dehydrating power of the solvent, the measure of which is given by $1/\xi$. When this is the case, the assumption that the number of anhydrous ions is negligible in comparison with the number of hydrated ones of course does not hold true any longer and thus the calculation of $n_1 - n_2$ is uncertain. As the data do not, however, admit of more detailed calculations, we shall confine ourselves to emphasizing that only a small difference of one or two water molecules in the hydration of the two ions may suffice to explain the large change in the solubility ratios of the corresponding salts.

While the conclusion drawn from the constant solubility ratios must be considered as a rigorous one, as referred to above, other sources of deviations than diversities in the degrees of hydration may possibly be responsible for the deviations when dealing with systems furnishing varying solubility ratios as in the case of potassium chloride-potassium nitrate. As long as we are unacquainted with the true degrees of hydration of the ions it is difficult to decide whether or not secondary electric forces, etc., play a part in the phenomena observed.

From the constant values of the solubility ratio given in the last 2 columns of Table II we may argue, in analogy in the case of the halides, that the corresponding ions, NO_3^-, ClO_3^- and IO_3^- are equally hydrated and equally influenced electrically by the solvent at concentrations less than 10 *M*. The deviations appearing at higher concentrations may be explained by the dehydrating action of the solvent but are here looked upon as more likely due to the secondary electric influence which increases strongly in this region of concentrations. The action upon the three ions increases in the sequence ClO_3^-, NO_3^-, IO_3^-.

As a result of this investigation, we can affirm the necessity of dividing the series of salts here dealt with in 2 separate groups, namely, KCl, KBr, KI; and KNO_3, $KClO_3$, KIO_3—each comprehending salts of similar molecular structure. The salts in either of these groups exhibit similar behavior as solutes when compared together, thus permitting the inference that the salts belonging to the same group are hydrated to the same extent and equally acted upon by electric forces in the solvent within a very considerable domain of concentrations.

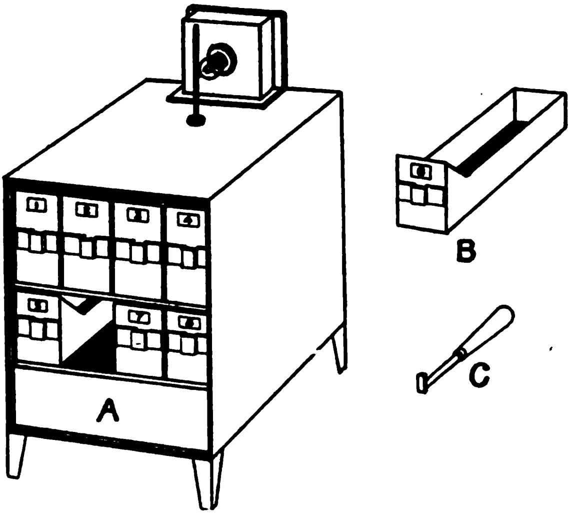
It may be added that the occurrence of constant solubility ratios in the case of easily soluble salts must be looked upon as an essential requirement for the carrying out of the thermodynamic calculations of affinities referred to in a previous paper.[1]

COPENHAGEN, DENMARK.

NOTES.

An Equipment for Drying Ovens.—The effective capacity of the ordinary drying oven can be increased from 5- to 10-fold by equipping it with metal drawers or trays as shown in the accompanying sketch. Each tray can hold a number of crucibles, small dishes or drying bottles, and because it is so easy to insert or withdraw one of the trays with its load without disturbing the others, the back part of the oven space is as available as the front. The supports of the trays are the wire mesh shelves of the oven; and to provide for the insertion of the thermometer in the usual way one tray should be made shorter than the others.

With the design as shown, the whole front of the oven is closed when all of the trays are in position. This is a decided advantage because with such an arrangement, opening the oven doors has little effect in decreasing the temperature, and since the withdrawal of one tray does not leave a large opening, and also because of the mass of hot metal of the remaining trays, the cooling is slight when objects are put into or taken out of the oven. The idea of keeping the front closed is carried still further by inserting a metal sheet at A to close the space below the first shelf.



The detail of a tray is shown at B. The bottoms are made of 12 mm. wire mesh to permit a free circulation of air throughout the interior of

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[1] *Medd. K. Vetenskapsakad. Nobelinst.*, 5, No. 25, 18 (1919).

the oven. A metal loop on the front engages the handle C with which they are lifted while hot.

This equipment has been in use for several years in the writer's laboratory and has proved its worth. In laboratories used by students its value is especially high because the rule, one tray to a student, can be followed and one student in inserting or removing his material need not interfere with the work of the others.

Since the trays rest on the original shelves of the oven, it takes but a minute to remove them all and again convert the oven interior into one large compartment.

Although this equipment increases the amount of metal subject to corrosion it cannot be said to increase the danger of contamination beyond what any increased use of the oven would involve. C. W. FOULK.

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Correction.—The figures for the ordinates of Fig. 5, in our article on "The Transference Numbers of Lithium Chloride, etc." in the June 1920 JOURNAL, have been printed one division too high in each case; for instance, the figure 0.270 should be 0.280. D. A. MACINNES,
JAMES A. BEATTIE.

[CONTRIBUTION FROM THE CHEMICAL INSTITUTE, SCIENCE COLLEGE, TOHOKU IMPERIAL UNIVERSITY.]

THE SUCCESSIVE STAGES OF THE HYDROLYSIS OF TRIACETIN.

BY EIICHI YAMASAKI.

Received March 22, 1920.

Introduction.

The various acetins, or glycerin esters of acetic acid, some of them, however, being still unknown, are as follows:

Triacetin

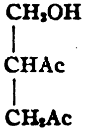
$$\begin{array}{l} CH_2Ac \\ | \\ CHAc \\ | \\ CH_2Ac \end{array}$$

(A)

Diacetin

$$\begin{array}{l} CH_2Ac \\ | \\ CHOH \\ | \\ CH_2Ac \end{array}$$

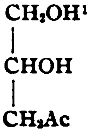
(B)



$$\begin{array}{l} CH_2OH \\ | \\ CHAc \\ | \\ CH_2Ac \end{array}$$

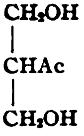
(C)

Monoacetin



$$\begin{array}{l} CH_2OH\text{[1]} \\ | \\ CHOH \\ | \\ CH_2Ac \end{array}$$

(D)



$$\begin{array}{l} CH_2OH \\ | \\ CHAc \\ | \\ CH_2OH \end{array}$$

(E)

If the ester A is hydrolyzed, the reaction will proceed successively by the following steps to glycerine, $C_3H_5(OH)_3$ (G)

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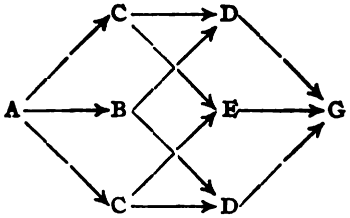
[1] Esters (C) and (D) have one asymmetric carbon atom, respectively. Hence both of them must have 3 modifications, *i. e.*, the racemic and the optically active antipodes.



(I)

Evidently such a reaction is very complex and its chemical kinetics almost hopelessly involved. However, according to the investigation of A. de Hemptine[1] and R. Löwenherz,[2] the esters of the same acid have one property in common, namely, the rate of hydrolysis is independent of the nature of the alcoholic radicals: that is, esters of primary, secondary and tertiary alcohols have the same velocity constant k of hydrolysis when the acid is the same. If this holds true in the case of the esters of polyvalent alcohol such as glycerin, the kinetics of the triacetin hydrolysis is simplified and can be ascertained by a suitable method.

Previous Investigations.

Geitel[3] prepared triacetin (A), diacetin (B) and monoacetin (D),[4] and studied their rates of decomposition with various reagents. He found that the hydrolysis of acetins with dil. hydrochloric acid takes place as follows.

1. Monoacetin (D) decomposes normally as a mono-molecular reaction.
2. The constants for diacetin, calculated as a reaction of the first order, do not show a sufficient concordance.
3. The velocity constants for triacetin increase steadily (results obtained at 40°).

He expressed these results by the following differential equations

$$\frac{dz}{dt} = k_1(e - z); \quad \frac{dy}{dt} = k_2(z - y); \quad \frac{dx}{dt} = k_3(y - x), \qquad (1)$$

where e is the initial concentration of triacetin; z, y and x are, respectively, the amounts of tri,- di- and monoacetin decomposed at the moment under consideration.

He transformed these Equations 1 into

$$\frac{dz}{dy} = n\frac{e - z}{z - y}; \quad \frac{dz}{dx} = n_1\frac{e - z}{y - x}; \quad \frac{dy}{dx} = n_2\frac{z - y}{y - x}, \qquad (2)$$

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[1] de Hemptine, *Z. physik. Chem.*, 13, 561 (1894).

[2] Löwenherz, *ibid.*, 15, 389 (1894).

[3] Geitel, *J. prakt. Chem.*, 55, 417 (1897); 57, 113 (1898).

[4] He gave only the chemical formulas $C_3H_5(OH)(Ac)_2$ and $C_3H_5(OH)_2Ac$. The above constitutional formulas are given according to the Beilstein. But the point is not important for this investigation.

when $n = k_1/k_2$, $n_1 = k_1/k_3$, and $n_2 = k_2/k_3$; and he integrated Equations 2 as follows:[1]

$$x = e - \frac{u}{(n-1)(n_1-1)} + \frac{n^2e^{(n-1)/n}}{(n-1)(n_1-n)}u^{1/n} - \frac{n_1u^{1/n_1}}{(n_1-1)(n_1-n)e^{1/n_1}}$$

$$y = e - \frac{u}{n-1} - \frac{n}{n-1}e^{(n-1)/n}u^{1/n}$$

$$z = e - u \qquad (3)$$

where u is the concentration of the triacetin at any moment.

Then, assuming that the regularity observed by Hemptine and Löwenherz, that the decomposition constants of the esters of a single acid are independent of the nature of the alcoholic radicals, also holds good in the case of the esters of polyvalent alcohols, he put

$$k_1 : k_2 : k_3 = 3 : 2 : 1. \qquad (4)$$

Introducing Relation 4 into Equations 3 and simplifying them by putting $e = 1$,

$$\begin{aligned} z &= 1 - u \\ y &= 1 + 2u - 3(\sqrt[3]{u})^2 \\ x &= 1 - u - 3\sqrt[3]{u} + 3(\sqrt[3]{u})^2 \\ x + y + z &= 3 - 3\sqrt[3]{u}. \end{aligned} \qquad (5)$$

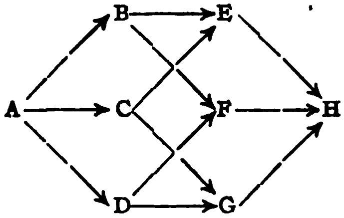
Consequently, if the function $u = f(t)$ were solved, x, y and z would be also obtained as known functions of t. So he gave the arbitrary value 0.05 to the constant k_1, and calculated u from Equations 3 and 4 between the limits

$$u = 1\ (= e) \quad \text{and} \quad u = 0;$$

that is, from the initial concentration (= 1) to the complete hydrolysis. From the value of u, he deduced the corresponding values of x, y and z by means of Equation 5 and expressed u, x, y and z graphically to explain the course of the reaction.

Unfortunately, he could not find the real value of the velocity constant k_1. Consequently, he could not make use of his experimental results to explain quantitatively the actual course of the reaction.

Recently Treub[2] made an interesting investigation of the successive hydrolysis of trilaurin with sulfuric acid. He gave the following reaction scheme



(II)

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[1] *Loc. cit.*

[2] Treub, *J. chim. phys.*, 16, 107 (1918); *Proc. Akad. Sci. Amsterdam*, 20, 343 (1917).

where A is trilaurin and H glycerin; B, C, and D are, respectively, dilaurin, and E, F and G monolaurin. When r, x and y are, respectively, the concentrations of tri-, di- and monolaurin, and s and z are the concentrations of glycerin and acetic acid, their relative concentrations, R, X, Y, S and Z are, respectively,

$$R = \frac{r}{a}, \quad X = \frac{x}{a}, \quad Y = \frac{y}{a}, \quad S = \frac{s}{a}, \quad Z = \frac{z}{3a}, \tag{6}$$

where a is the initial concentration of trilaurin. He also assumed that each radical of the ester is decomposed at the same rate, and gave the following differential equations,

$$-\frac{dr}{dt} = 3kr; \quad \frac{dx}{dt} = kr - 2kx; \quad \frac{dy}{dt} = 2kx - ky; \quad \frac{ds}{dt} = 3ky;$$

$$\frac{dz}{dt} = 3\left(\frac{dx}{dt} + 2\frac{dy}{dt} + \frac{ds}{dt}\right) = 3k(r + 2x + y)^1 \tag{7}$$

where k is the uniform value that the decomposition constants of the various esteric radicals are assumed to have, according to de Hemptine and Löwenherz. Equations 7 he transformed to

$$-\frac{dr}{3r} = \frac{dx}{r - 2x} = \frac{dy}{2x - y} = \frac{ds}{3y} = \frac{dz}{3(r + 2x + y)}. \tag{8}$$

After an ingenious mathematical treatment of the above equation, he found the relation

$$S = Z^3;$$

that is, the relative concentration of glycerin is always equal to the cube of the relative concentration of lauric acid throughout the course of the reactions, and this relation is quite independent of the progress of the reactions. He sought to confirm the above relation by the direct determination of the concentration of the lauric acid and glycerin produced by the hydrolysis of trilaurin.

Contrary to expectations, he could not obtain sufficient confirmation.[2] This can probably be attributed to the difficulty of a quantitative determination of glycerin.

Besides, he did not determine numerically the value of the velocity constant k and evaluate r, x, y, z and s as known functions of the time

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[1] dz/dt, the rate of the formation of the lauric acid is not directly given, as is the velocity of formation of the other components, in the original paper. But the above equation will be easily understood if we count the number of esteric radicals decomposed by the formation of x, y and s.

[2] He found actually that the relative concentration of glycerin is smaller than the cube of the concentration of its acid. Consequently, he assumed further that the velocity constants of the hydrolysis of the esters of primary and of secondary alcohols have *different* values and gave the following differential equation according to Scheme III (below), $-dr/dt = (p + 2)kr$; $dx_1/dt = kr - (p + 1)kx_1$; $dx_2/dt = pkx_2 - 2kx_1$; $dy_1/dt = pkx_1 + kx_2 - ky_1$; $dy_2/dt = 2kx_1 - pky_2$; $dS/dt = 2ky_1 + pky_2$, where k' is the

and of the initial concentration of trilaurin. Consequently, the present problem, the hydrolysis of the polyvalent ester is not yet in a way of settlement from the point of view of chemical kinetics.

The present writer has, however, evaluated the constant k of the reaction for triacetin numerically and has given the concentration of the components of the system under consideration as known functions of the time and of the initial concentration of triacetin. The results will be given in order.

Theoretical Part.

The successive hydrolysis of triacetin takes place according to the following equations.

$$C_3H_5(Ac)_3 \xrightarrow{k_1} C_3H_5(OH)(Ac)_2 + HAc,$$
$$C_3H_5(Ac)_2(OH) \xrightarrow{k_2} C_3H_5(OH)_2(Ac) + HAc,$$
$$C_3H_5(OH)_2(Ac) \xrightarrow{k_3} C_3H_5(OH)_3 + HAc.$$

Consequently, each reaction must be separately carried out as one of the first order, having, respectively, the velocity constants k_1, k_2 and k_3.

In the initial stage of the reaction (t = 0) acetic acid is formed only by

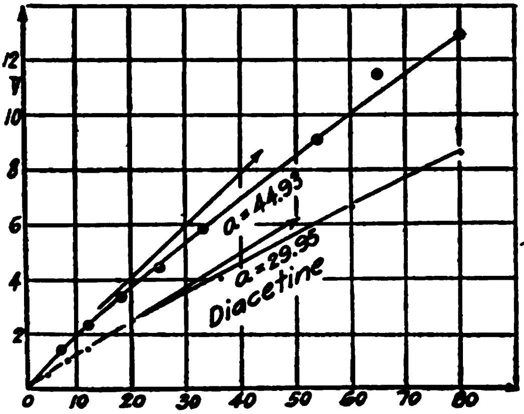


Fig. 1.

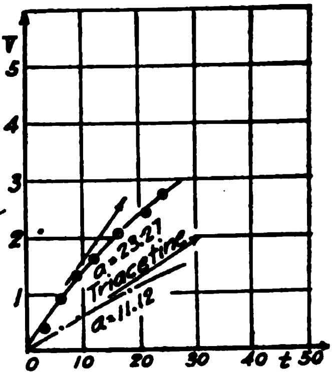
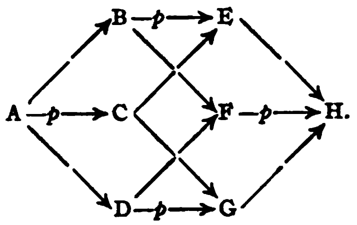


Fig. 2.

velocity constant of the ester of the secondary alcohol which is equal to kp, *i. e.*, $k'/k = p$.



(III)

By a skilful computation, he obtained the relation, $S < Z^2$, to explain his experimental results. But he did not definitely determine whether the constants k and k' actually differ or not in the polyvalent esters. Consequently the treatment must be said to be mere assumption.

the hydrolytic decomposition of triacetin. Hence, the velocity constant k_1 can be accurately determined, if the exact value of the initial velocity of the formation of acetic acid (C_A) is obtained. Then the relative initial velocity or the velocity constant k can be determined graphically, because, if C_A and C are the relative concentrations of acetic acid and triacetin, respectively,

$$\left(\frac{dC_A}{dt}\right)_{t=0} = \left(-\frac{dC}{dt}\right)_{t=0}.$$

and

$$\left(-\frac{d\,ln\,C}{dt}\right)_{t=0} = k_1.$$

Such a graphical method is not adapted for obtaining a very exact value of the velocity constant k_1, but the value of k_1 obtained by it is sufficiently accurate to verify the theory. Again returning to the data of Geitel's experiments, I drew the diagram (V, r, t) instead of (c, V, t), where V is the volume of barium hydroxide used to neutralize the acetic acid. From the initial tangents, the following are obtained,

$$\frac{1}{a}\left(\frac{dV}{dt}\right)_{t=0} = \frac{1}{V_\infty/3}\left(\frac{dV}{dt}\right)_{t=0} = k_1$$

for triacetin, and

$$\frac{1}{a'}\left(\frac{dV}{dt}\right)_{t=0} = \frac{1}{V_\infty/2}\left(\frac{dV}{dt}\right)_{t=0} = k_2,$$

for diacetin, where a denotes the initial concentration of triacetin and a' that of diacetin. Taking the mean value of the constants k_1 and k_2, respectively, from these two diagrams, we obtain

$$k_1 = 0.00638 \quad \text{and} \quad k_2 = 0.00423.$$

Now k_3 is the velocity constant of the hydrolysis of monoacetin, which is, of course, a monomolecular reaction. Hence, the constant k_3 can be easily determined from the equation,

$$k_3 = \frac{1}{t}\,ln\,\frac{V}{V_\infty},$$

I take the mean value of two series of experiments given by Geitel and obtain

$$k_3 = 0.002213.$$

If each alcoholic radical of acetin has an equal rate of hydrolysis as supposed, the following relation exists among them

$$1/3\,k_1 = 1/2\,k_2 = 1/1\,k_3 = k.$$

In agreement with this, the experimental values are found to be closely equal

$$\left.\begin{aligned} k_1/_3 &= 0.002127 \\ k_2/_2 &= 0.002115 \\ k_3/_1 &= 0.002213 \end{aligned}\right\}\ \text{mean } k = 0.002152.$$

This confirms the assumption made by Geitel and Treub that each alcoholic radical of the polyvalent esters has an equal rate of hydrolysis irrespective of whether the radical be primary or secondary.

Then the successive hydrolysis of triacetin given by Scheme I is simplified to

$$M_1 \longrightarrow M_2 \longrightarrow M_3 \longrightarrow M_4. \qquad \text{(IV)}$$

And the differential equations which express the progress of the reaction are given as follows:

$$\frac{dx_1}{dt} = k_1(a - x_1) = 3k(a - x_1)$$

$$\frac{dx_2}{dt} = k_2(x_1 - x_2) = 2k(x_1 - x_2)$$

$$\frac{dx_3}{dt} = k_3(x_2 - x_3) = k(x_2 - x_3) \qquad (10)$$

where a is the initial concentration of triacetin, and x_1, x_2 and x_3 are, respectively, the concentration of M_1, M_2 and M_3 decomposed at any time t. The above equations are integrated according to Rakowski[1] and C_0 is substituted for a as usual:

$$\begin{aligned} C_{M_1} &= C_0 e^{-kt} \\ C_{M_2} &= 3C_0(1 - e^{-kt})e^{-2kt} \\ C_{M_3} &= 3C_0(1 - e^{-kt})^2 e^{-kt} \\ C_{M_4} &= C_0(1 - e^{-kt})^3 \end{aligned} \qquad (11)$$

As the concentration of acetic acid C_A, formed by the reaction is expressed as follows,

$$C_A = C_{M_2} + 2C_{M_3} + 3C_{M_4}$$

it becomes

$$C_A = 3C_0(1 - e^{-kt}) \qquad (12)$$

from Equation 11.

When C_{M_4} and C_A are compared the following relation is easily found,

$$\left(\frac{C_A}{3C_0}\right)^3 = \left(\frac{C_{M_4}}{C_0}\right) \qquad (13)$$

Now both terms of Equation 13 express the relative concentrations of acetic acid and glycerin which were denoted as Z and S, respectively, by Treub. That is, $S = Z^3$, which is the relation deduced by him.

Experimental Part.

Unfortunately, the number of experimental results given by Geitel are few. In addition to this, the degree of hydrolysis of triacetin at 25° only amounts to 10%. Therefore, I prepared triacetin according to his method and undertook the hydrolysis with N hydrochloric acid at 35°. As a result, I obtained sufficient confirmation of the theory above enunciated.

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[1] Rakowski, *Z. physik. Chem.*, 57, 321 (1907).

Mode of Experiment.—Triacetin was dissolved to make a 0.25 N solution. 5, 10, 15 and 20 cc. of the solution were made up to 20 cc. in a thermostat at 35° and mixed with 10 cc. of 3 N hydrochloric acid of the same temperature. Two cc. of the solution was drawn off with a pipet from time to time and titrated with a 0.05 N solution of barium hydroxide.

The concentration of hydrochloric acid was determined by the volume of barium hydroxide solution used for the titration immediately after the reacting mixture had been prepared as above.

The initial concentration of the ester was determined from the concentration of the acetic acid obtained at $t = \infty$, *i. e.*, $(C_A/3)_{t=\infty} = C_0$. In order to determine the concentration of acetic acid, $(C_A)_{t=\infty}$ at the end of the reaction, 5 cc. of the same hydrochloric acid was mixed with the same volume of ester solution in a sealed tube. The solution in the tube was heated in a water bath for a long while until the titrations of the solution became constant, independent of the time of heating. The concentration of acetic acid $(C_A)_{t=\infty}$, corresponding to the former series of experiments, was determined by calculation from that of the latter experiment.

Explanation of the Experimental Results.—The concentrations of acetic acid C_A obtained from the reacting mixtures—namely, 4 different initial concentrations of esters—were divided by the corresponding concentrations of the acetic acid at infinite time. The series of relative concentrations of acetic acid (Z), are expressed by the ordinates of Fig. 3 and the corresponding times (in minutes) by the abscissas. As the concentration of the hydrochloric acid is constant and equal to 0.961, the respective curves must coincide with one another in spite of the fact that the initial concentrations of the ester C_0 differ, because

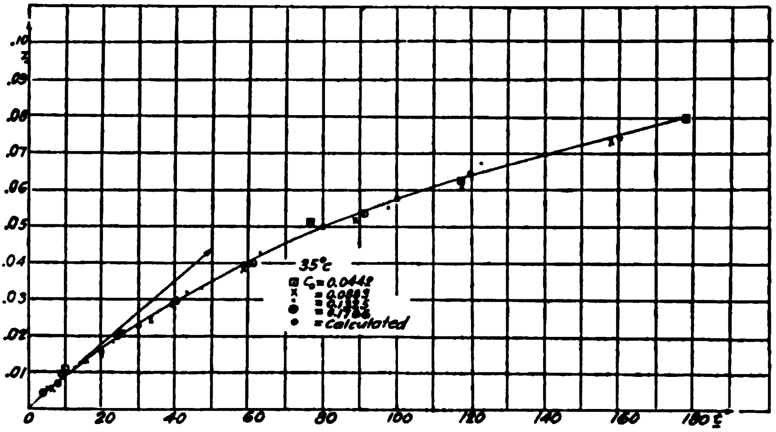

Fig. 3.

$$Z = \frac{C_A}{3C_0} = (1 - e^{-kt}) \qquad (14)$$

from Equation 12, and the right side of the above equation is quite independent of the value of C_0.

The results obtained in the 4 different series of experiments do indeed coincide sufficiently well to verify our expectations. The tangent line drawn at the starting point of the axes of the coördinates gives

$$\left(\frac{dZ}{dt}\right)_{t=0} = \frac{1}{3}\left(-\frac{d\,ln\,C}{dt}\right)_{t=0} = k. \qquad (15)$$

Consequently, k or 0.4343 $k = k' = 0.00373$ is determined graphically. Z, given in Fig. 3, is calculated back with this k' by Equation 14, and compared with the observed results to show their sufficient agreement.

Tables of Experimental Data.—The experimental data are summed up in the following tables, in which t is the interval of time in minutes; Z, the relative concentration of acetic acid; C_A(obs.), the concentration of acetic acid; C_A(calc.), that calculated from Equation 12; and C_{M_1}, C_{M_2}, and C_{M_3} are the concentrations of tri-, di-, and monoacetins at any time and C_{M_4}, the concentration of glycerin. The experimental conditions, with the exception of those for the initial concentration of triacetin, were exactly the same for all 4 series of results. That is, C_{HCl}, the concentration of hydrochloric acid, was 0.961 N and the temperature of the observation, 35°.

TABLE I.

$C_0 = 0.0442$.

t.	Z.	C_A(obs.).	C_A(calc.).	C_{M_1}.	C_{M_2}.	C_{M_3}	C_{M_4}.
10.00	0.104	0.0138	0.0108	0.0342	0.0092	0.0008	0.0000
25.18	0.202	0.0268	0.0256	0.0231	0.0167	0.0040	0.0003
47.00	0.332	0.0440	0.0424	0.0132	0.0196	0.0098	0.0016
76.37	0.513	0.0680	0.0637	0.0062	0.0172	0.0159	0.0049
116.94	0.629	0.0833	0.0842	0.0022	0.0113	0.0195	0.0113
177.17	0.800	0.1061	0.1036	0.0005	0.0049	0.0177	0.0211

TABLE II.

$C = 0.0883$.

t.	Z.	C_A(obs.).	C_A(calc.).	C_{M_1}.	C_{M_2}.	C_{M_3}.	C_{M_4}.
6.67	0.058	0.0154	0.0152	0.0744	0.0132	0.0009	0.0000
15.50	0.135	0.0357	0.0332	0.0593	0.0254	0.0036	0.0002
33.00	0.246	0.0652	0.0654	0.0377	0.0371	0.0122	0.0013
58.67	0.386	0.1024	0.1050	0.0195	0.0383	0.0251	0.0055
88.22	0.513	0.1359	0.1405	0.0091	0.0309	0.0350	0.0132
117.52	0.620	0.1642	0.1680	0.0043	0.0224	0.0389	0.0226
157.45	0.730	0.1934	0.1960	0.0015	0.0131	0.0376	0.0359
213.37	0.809	0.2143	0.2227	0.0004	0.0057	0.0299	0.0524
283.62	0.867	0.2300	0.2415	0.0001	0.0019	0.0193	0.0670

Table III.

$C = 0.1325.$

$t.$	$Z.$	C_A (obs.).	C_A (calc.).	$C_{M_1}.$	$C_{M_2}.$	$C_{M_3}.$	$C_{M_4}.$
5.00	0.059	0.0234	0.0167	0.1165	0.0153	0.0007	0.0000
12.20	0.117	0.0464	0.0397	0.0968	0.0322	0.0036	0.0001
23.00	0.181	0.0720	0.0713	0.0733	0.0479	0.0105	0.0008
43.00	0.320	0.1273	0.1225	0.0438	0.0587	0.0262	0.0038
63.00	0.431	0.1699	0.1662	0.0271	0.0563	0.0404	0.0097
90.75	0.550	0.2189	0.2151	0.0128	0.0453	0.0534	0.0210
121.17	0.674	0.2681	0.2574	0.0058	0.0321	0.0588	0.0359
162.33	0.761	0.3026	0.2992	0.0020	0.0184	0.0558	0.0564

Table IV.

$C = 0.1766.$

$t.$	$Z.$	C_A (obs.).	C_A (calc.).	$C_{M_1}.$	$C_{M_2}.$	$C_{M_3}.$	$C_{M_4}.$
4.00	0.045	0.0240	0.0180	0.1593	0.0168	0.0006	0.0000
9.33	0.090	0.0480	0.0406	0.1389	0.0348	0.0029	0.0000
25.00	0.197	0.1046	0, 1022	0.0927	0.0665	0.0159	0.0013
40.00	0.295	0.1565	0.1544	0.0630	0.0776	0.0318	0.0044
60.50	0.400	0.2119	0.2144	0.0371	0.0759	0.0517	0.0117
91.00	0.535	0.2838	0.2871	0.0169	0.0602	0.0713	0.0281

From these results, it is clearly seen that the concentration of acetic acid as observed agrees very well with that calculated. Or, in other words, the theory given above is sufficiently verified by experiment.

Graphical Representation of the Results and Explanation of the Diagrams.—The results given in the above tables are reproduced in the two figures, 4 and 5, in which the concentration of the components of the reacting system and the corresponding times are taken as the 2 axes. Then the courses of the successive hydrolysis of polyvalent esters having

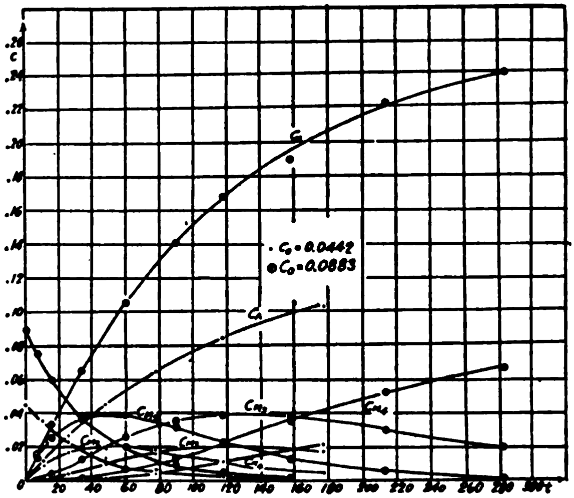

Fig. 4.

4 different components, *i. e.*, $M_1 \longrightarrow M_2 \longrightarrow M_3 \longrightarrow M_4$, are fully explained graphically.

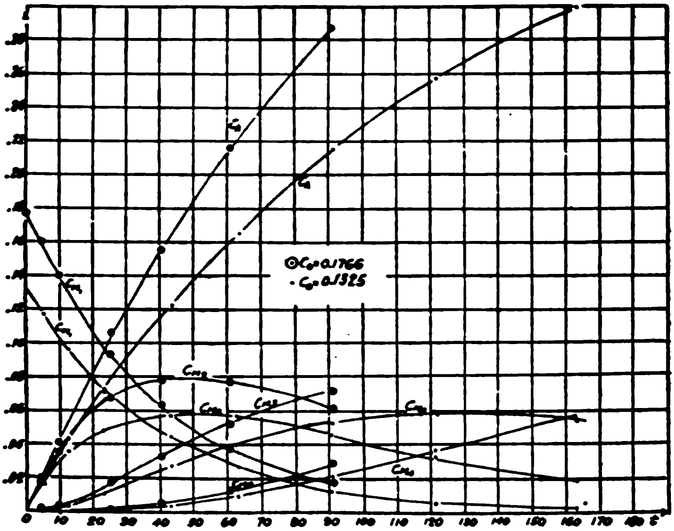

Fig. 5.

The intermediate component, M_2, has its maximum value at the time when

$$\frac{dC_{M_2}}{dt} = 3kC_0e^{-2kt}(3e^{-kt} - 2) = 0,^1 \quad i.\ e.,\ t_1 = \frac{1}{k}\ ln\ \frac{3}{2} \quad (16a)$$

and the substance M_3 has its maximum concentration at the time when

$$\frac{dC_{M_3}}{dt} = 3kC_0(1 - e^{-kt})(3e^{-kt} - 1)e^{-kt} = 0, \quad i.\ e.,\ t_2 = \frac{1}{k}\ ln\ 3. \quad (16b)$$

The numerical values (C_{M_2}) and (C_{M_3}) of their maximum concentrations are calculated by introducing the times t_1 and t_2 into Equation 13.

$$(C_{M_2}) = 3C_0(1 - e^{-ln\ 3/2})e^{-2\ ln\ 3/2} = 4/9\ C_0$$

and

$$(C_{M_3}) = 3C_0(1 - e^{-ln\ 3})^2e^{-ln\ 3} = 4/9\ C_0$$

i. e.,

$$(C_{M_2}) = (C_{M_3}) = 4/9\,C_0. \quad (17)$$

That is, the maximum concentrations of M_2 and M_3 are equal in numerical value, but the corresponding times, of course, differ.[2] The relations above enunciated are satisfied in the diagrams.

Further, the curve if C_{M_2} has one inflection point at

$$t'_1 = 1/k\ ln\ 9/4 \quad (18)$$

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[1] $e^{-2kt} = 0$ when $t = \infty$, the same for $e^{-kt} = 0$; and $1 - e^{-kt} = 0$ when $t = 0$. The times have no relation to the maximum values of C_{M_2} and C_{M_3}.

[2] Such a simple relation does not hold, of course, generally. Such results are due to the fact that the 3 constants have a simple ratio, $k_1 : k_2 : k_3 = 3 : 2 : 1$.

where

$$\frac{d^2C_{M_2}}{dt^2} = 3k^2C_0\,(4 - 9e^{-kt}) = 0.$$

And the curve of C_{M_3} has two inflexion points at t'_2 and t'_3, respectively,

$$t'_2 = 1/k\ ln\ \alpha, \quad \text{and} \quad t'_3 = 1/k\ ln\ \beta,$$

where

$$\frac{1}{\alpha} = \frac{4 + \sqrt{7}}{9}, \quad \text{and} \quad \frac{1}{\beta} = \frac{4 - \sqrt{7}}{9}$$

in which times,

$$\frac{d^2C_{M_3}}{dt^2} = 3k^2C_0\,e^{-kt}\,(9e^{-2kt} - 8e^{-kt} + 1) = 0.$$

Now, t'_1, is greater that t', and t'_3 greater than t_2, but t'_2 is less than t_2. The last time, t'_2, suggests that the nature of the increase of C_{M_2} and C_{M_3} is quite different up to their maximum concentrations. That is, dC_{M_2}/dt always decreases from $t = 0$ to $t = t'_1$, and the curve C_{M_2} is always concave to the t-axis till $t = t'_1$. But dC_{M_3}/dt increases at first till it reaches t'_2, then it begins to decrease steadily to the second inflection point t'_3. The curve C_{M_3} is convex to the axis t in the initial stage up to t'_2, then it becomes concave to the same axis till t increases up to t'_3.

Now, when we investigate the curve C_{M_4}

$$dC_{M_4}/dt = 3kC_0\,(1 - e^{-kt})2e^{-kt} = kC_{M_3}.$$

The curve C_{M_4} has no maximum, but has one inflexion point at the time when the curve C_{M_3} has them aximum concentration, *i. e.*, $t_2 = 1/k\ ln\ 3$.

Lastly consider the curve C_A,

$$dC_A/dt = 3C_0e^{-kt} = k(3C_0 - C_A).$$

But the value $3C_0$ is the concentration of acetic acid at $t = \infty$. Consequently

$$dC_A/dt = k(C_{A\infty} - C_A). \tag{19}$$

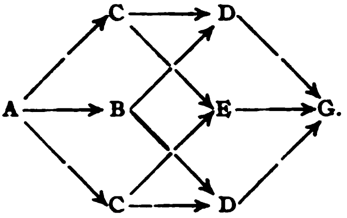
That is, the curve must be a logarithmic one which has neither a maximum nor an inflexion point. Furthermore, the rate dC_A/dt is the same as that of the chemical reaction,

$$A_1 = 3A_2$$

where C_A corresponds to the concentration of A_2.

Conclusion.

The hydrolysis of the ester formed by a polyvalent alcohol and a monobasic acid, such as triacetin, takes place according to the simple rule that each ester radical has an equal rate of hydrolysis. Consequently, their rates are simply expressed in the same way as those of the successive reactions $M_1 \longrightarrow M_2 \longrightarrow M_3 \longrightarrow M_4$, which have, respectively, the velocity constants $3k$, $2k$ and k, though the actual reactions would be carried out according to the following scheme,



Consequently an explanation in detail of the results of experiment would give a clear idea of the course of the successive chemical reactions.

Appendix.

1. For the sake of comparison, the results obtained at 40° by Geitel for triacetin are calculated by the same method and are given in Table V.

TABLE V.

Temperature 40°. $k' = 0.00253$.

$C_0 = 0.2000$.

t.	Z.	C_A (obs.).	C_A (calc.).	C_{M_1}.	C_{M_2}.	C_{M_3}.	C_{M_4}.
12	0.0720	0.0432	0.0407	0.1621	0.0355	0.0026	0.0000
24	0.1381	0.0829	0.0778	0.1315	0.0590	0.0088	0.0004
36	0.1937	0.1162	0.1136	0.1066	0.0746	0.0174	0.0014
60	0.3059	0.1835	0.1769	0.0701	0.0880	0.0368	0.0051
84	0.4060	0.2436	0.2323	0.0461	0.0873	0.0551	0.0116
120	0.5249	0.2149	0.3021	0.0246	0.0746	0.0755	0.0255

As can be seen from the above table, the concentration C_A as observed shows sufficient agreement with that calculated.

2. Now, diacetin (B) decomposes according to the scheme $M_1 \longrightarrow M_2 \longrightarrow M$, respectively, the velocity constants being $2k$ and k. Then the concentrations of the components in the system are expressed as known functions of the initial concentration of diacetins and the time

$$\begin{aligned} C_{M_1} &= C_0 e^{-2kt} \\ C_{M_2} &= 2C_0 e^{-kt}(1 - e^{-kt}) \qquad . \qquad (20) \\ C_{M_3} &= C_0 (1 - e^{-kt})^2. \end{aligned}$$

The data at 25° obtained by Geitel are calculated according to the above equation and given in Table VI.

TABLE VI.

Temp. 25°. $C_{HCl} = 0.05$. $C_0 = 0.05$. $k' = 0.000836$.

t.	Z.	C_A (obs.).	C_A (calc.).	C_{M_1}.	C_{M_2}.	C_{M_3}.
7	0.0164	0.00164	0.00150	0.0485	0.00148	0.00001
12	0.0264	0.00264	0.00250	0.0475	0.00244	0.00003
18	0.0375	0.00375	0.00380	0.0463	0.00366	0.00007
25	0.0515	0.00515	0.00519	0.0449	0.00493	0.00013
33	0.0653	0.00653	0.00691	0.0434	0.00643	0.00024
54	0.1015	0.01015	0.01101	0.0396	0.00979	0.00061
65	0.1282	0.01282	0.01311	0.0378	0.01139	0.00086
80	0.1448	0.01448	0.01580	0.0354	0.01330	0.00125

These also show that the calculated values agree tolerably well with the observed.

3. The effect of temperature on the constant k', have been calculated from Geitel's experiment at 25° and 40°. According to this,

$$k' = 0.00253 \quad \text{at} \quad 40^{\circ}\,[1]$$
$$= 0.000936 \quad \text{at} \quad 25^{\circ}$$

Consequently, the temperature coefficient becomes 1.94; that is, the velocity of reaction is almost doubled for every successive 10° elevation of temperature.

SENDAI, JAPAN.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY.]

THE PREPARATION OF TRIMETHYL ARSINE AND TRIMETHYL ARSINE SELENIDE.[2]

BY R. R. RENSHAW AND G. E. HOLM.[3]

Received April 15, 1920.

Trimethyl Arsine.

Trimethyl arsine, $(CH_3)_3As$, has not previously been isolated in a pure condition. Its preparation seems to have been mentioned first by Cahours and Hofmann,[4] who state that it can be obtained by the action of potassium hydroxide on the double salt resulting from the interaction of arsenic trichloride and zinc methyl. In 1859 Cahours[5] claims to have prepared the compound by the dry distillation of the double salt of tetramethyl arsonium iodide and zinc iodide with potassium hydroxide. He described this arsine as a colorless liquid boiling under 100°. In a later publication[6] the author again mentions this preparation and subsequently[7] states that the pure compound boils at about 70°.

Hibbert, in 1906,[8] seems to have produced the compound by the action of arsenic tribromide on magnesium methyl iodide. He did not isolate the free arsine.

The authors have tried variations of 2 methods for the preparation of this substance: (1) the action of arsenic trichloride or bromide on magnesium methyl iodide and (2) the action of arsenic trichloride on zinc methyl. The latter method seems to be preferable.

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[1] The magnitude of the constant obtained from Geitel's results seems to be excessive, compared with that of my own results.

[2] Published by permission of the Director of the Chemical Warfare Service.

[3] The authors wish to express their appreciation for the generosity shown by Dr. E. Emmet Reid in whose laboratory the work was done.

[4] Cahours and Hofmann, *Compt. rend.*, 41, 831. *Abst. Jahr.*, 1855, 538.

[5] Cahours, *Ann.*, 112, 228 (1859).

[6] Cahours, *ibid.*, 122, 197 (1862).

[7] Cahours, *ibid.*, 337.

[8] Hibbert, *Ber.*, 39, 160 (1906).

The Action of Arsenic Trichloride on Magnesium Methyl Iodide.—The Grignard reagent was made from 12.2 g. of magnesium, 71 g. of methyl iodide and 125 cc. of ether. The distilling flask containing the reagents was fitted with a dropping funnel and a mechanical stirrer, and attached to a condenser and a receiver. It was immersed in a freezing bath of ice and salt, and 30 g. of arsenic trichloride was added slowly through the dropping funnel. A violent reaction took place, liberating much heat, and yellowish brown crystals gradually formed until at the end of the reaction the contents of the flask consisted of almost one solid mass. When all the chloride had been added, the ether was distilled off over a water bath. The uncondensed vapor passing through the receiver possessed a powerful odor resembling arsine rather than the trimethyl arsine. On redistilling the ether, 2 g. of a liquid was obtained boiling between 45° and 55°. The solid residue in the reaction flask was mixed with sufficient solid potassium hydroxide to unite with all the chlorine and iodine compounds produced in the process, and then subjected to dry distillation. There was obtained a small quantity of liquid which added to that from the ether distillate gave a total yield of approximately 5 g. On redistillation most of this passed over between 50° and 60°. It gave a very heavy precipitate with bromine, and was probably rich in trimethyl arsine, though at that time, following the indications in the literature, we thought that trimethyl arsine boiled materially higher.

While it is felt that the experiment is not wholly conclusive, it seems certain that at least one other volatile compound in addition to trimethyl arsine, having a stronger and more penetrating odor, was produced. This is in line with the results obtained by Auger and Billy,[1] who found that arsenic trichloride produced with magnesium ethyl iodide, primary and secondary derivatives as well as a tertiary.

The Action of Arsenic Tribromide on Magnesium Methyl Iodide.—Fifty g. of arsenic tribromide dissolved in ether was added to a Grignard reagent prepared from 12.3 g. of magnesium and 71 g. of methyl iodide. The reaction was less vigorous than in the case of the arsenic trichloride, and the solid material which formed dissolved on stirring. At the completion of the reaction the contents of the flask consisted of 2 layers, an upper greenish colored ether layer and a lower yellowish brown layer. The product was distilled over a water bath until no more material condensed. Here, as in the experiment with the trichloride, the odor indicated that lower alkylation products than the trimethyl derivative were produced. The distillate, however, contained considerable trimethyl arsine as indicated by the amount of the precipitate obtained by treating a portion of it with bromine.

It was decided to convert this crude product into the selenide and use

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[1] Auger and Billy, *Compt. rend.*, 139, 597 (1904).

the more certain zinc methyl method for the preparation of the pure trimethyl arsine. This was done by boiling up the ether solution with finely powdered selenium as described under the preparation of the selenide. Somewhat more than 10 g. of the trimethyl arsine selenide was obtained. This does not represent nearly all of the arsine formed, as there was considerable loss through oxidation and volatilization.

Preparation of Trimethyl Arsine by the Action of Arsenic Trichloride on Zinc Methyl.—The set up of the apparatus was as follows. A dropping funnel was inserted in a distilling flask containing a weighed amount of the zinc methyl. The side arm was connected to a second distilling flask and to the side arm of the latter was attached a U-tube containing enough arsenic trichloride to form a seal. The U-tube was connected to a large bottle through which carbon dioxide was continually passing. Fifty cc. of dry ether was added to the 45 g. of crude zinc methyl through the dropping funnel and the flask thoroughly cooled in an ice pack. Fifty g. of arsenic trichloride diluted with 50 cc. of ether was then slowly dropped into the flask with occasional shaking. Considerable heat was evolved in the reaction. At its completion the ether was poured off and the white solid formed dissolved in water and an excess of a strong alkali solution added. The mixture was then distilled on the water bath until no more condensation took place.

There was obtained about 20 cc. of liquid which boiled on redistillation between 38° and 51°. This was subjected to several fractional distillations. The larger portion of the product gradually worked into the fractions boiling below 38° and one boiling between 50° and 53°. From the latter there was finally obtained about 5 g. of a clear, colorless, highly refractive liquid with a sickening, garlicky odor, boiling between 50.7° and 51.7° at 747.5 mm. pressure.

It would seem from these results that ether and trimethyl arsine form a mixture which is fairly troublesome to separate by fractional distillation. Experiments were then run using xylene as a diluent. This gave very satisfactory results.

The process was carried out as in the foregoing except that xylene was used as a diluent. Thirty g. of zinc methyl and proportional molecular quantities of the other materials were used. On redistilling the crude distillate there was obtained 17.4 g. of a liquid boiling between 50° and 53°. This, on fractionation, gave the pure trimethyl arsine boiling at 51.9° to 52° at 736 mm. pressure.

The specific gravity was determined to be 1.124 at 22°.

The product was subjected to an indirect analysis by converting a sample of the constant boiling liquid into the selenide and determining its selenium content as described under the preparation of the compound.

Trimethyl Arsine Selenide.

Trimethyl arsine selenide, $(CH_3)_3AsSe$, does not appear to have been prepared previously, though the possibility of its formation is a natural inference on account of the similarity between trimethyl arsine and trimethyl phosphine which has been shown to form a selenide.

Five g. of very finely powdered selenium was added to the ether solution obtained in the preparation of trimethyl arsine by the Grignard method using arsenic tribromide. Small prism-like crystals began forming at once, and on standing a mass of crystals was obtained. The ether solution was cooled in ice and the ether poured off. The crystals were taken up with a few cc. of hot alcohol, filtered and then crystallized by cooling in an ice-salt mixture. Instead of the prism-like structure which the crystals had in an ether solution they now came down as long thin needles. The substance is markedly unstable in the presence of air, giving off an odor similar to that of trimethyl arsine, and quickly forming a brick-red deposit on the surface of the crystal. This reddish substance is somewhat soluble in alcohol and carbon disulfide and is likely amorphous selenium. The crystals, however, seem to be fairly stable when covered with alcohol or ether or when dissolved in water, especially if kept in the dark. When standing in the light, even when covered with alcohol, they gradually become red. On heating they begin to decompose appreciably at 100°, evolving condensible vapors believed to be trimethyl arsine and finally leaving a black residue of selenium.

Some dexterity was required in getting a colorless sample weighed for analysis. A concentrated solution of the substance in ether was carefully transferred to a weighing bottle through which hydrogen was being passed and which had been previously weighed full of hydrogen. The bottle was then stoppered with a cork which had been given a slight impregnation with wax and which was fitted with an inlet and an outlet tube. After cooling the bottle, the ether was poured off from the crystals which had formed, while at the same time hydrogen was passed into the flask. It was then dried to constant weight at room temperatures in a current of hydrogen, the crystals quickly dissolved in water and the selenium precipitated with standard silver nitrate solution. After standing overnight, the amount of silver selenide was determined gravimetrically and the excess of silver nitrate estimated volumetrically by the thiocyanate method.

Calc. for $C_3H_9As.Se$: Se, 39.76. Found: gravimetrically, Se, 40.00, 39.85. Found: volumetrically, Se, 39.48, 39.69.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY.]

THE PREPARATION OF ZINC METHYL.[1]

BY R. R. RENSHAW AND C. E. GREENLAW.[2]

Received April 15, 1920.

Apparently the greatest difficulty in the preparation of zinc alkyl compounds is in obtaining a highly active zinc-copper couple. A number of investigators have made recommendations for its preparation, but in the judgment of the writers, as matters stand, the accomplishment is an art rather than a science. In general, the inexperienced worker will at first find difficulty in preparing couples as active as those described by Lachman[3] and by Gladstone and Tribe.[4]

This difficulty, while not of great significance in the preparation of zinc ethyl, is serious when one attempts to prepare the methyl derivative, for the velocity of the reaction between methyl iodide and the zinc-copper couple is very much less than that with ethyl iodide; Gladstone and Tribe[4] estimate it as hundreds of times less.

A number of experiments were carried out under various heat treatments, using commercial zinc dust directly with copper oxide and also acid washed zinc dust with finely divided, precipitated copper. Couples were obtained which were fairly active with ethyl iodide, but none of them was as active as the products prepared later from 30-mesh zinc and precipitated copper, nor were they nearly as active as the couples prepared from zinc filings by Gladstone and Tribe.[4] In the absence of a catalyst they were all acted on very slowly by methyl iodide. At least a partial explanation of the greater activity of the granulated zinc couples is believed to lie in the greater porosity, which allows a better penetration of the iodide.

As might have been expected from the fine subdivision of the zinc in the zinc dust as compared with the filings, relatively more copper oxide than that used by Lachman was found to increase the activity.

Experiments were carried out with the idea of being able to define the conditions of heat treatment for the most active couple. This was done by placing the well-mixed material in a 25 mm. glass tube which was imbedded in a trough full of sand and heated over a combustion furnace, while a current of dry hydrogen was passed through the tube. The temperature of the sand throughout the length of the trough was difficult to maintain uniform. It appeared that the best temperature was about 400°, but without special apparatus, as for instance an auto-

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[1] Published by permission of the Director of the Chemical Warfare Service.

[2] The authors wish to express their appreciation for the generosity shown by Dr. E. Emmet Reid, in whose laboratory this work was done.

[3] Lachman, *Am. Chem. J.*, **24**, 31 (1900).

[4] Gladstone and Tribe, *J. Chem. Soc.*, **35**, 569 (1879).

clave heated to a constant temperature and fitted with a stirrer, it is believed that it is better to judge the desired heating by the appearance of the material. As the change in appearance of the material on heating is so characteristic it is believed that no one will have difficulty in preparing an active couple by using the following directions. The commercial 30-mesh zinc may be used directly if free from grease and not badly oxidized. Otherwise the zinc should be shaken up in a bottle in turn with dil. hydrochloric acid, water, alcohol and ether and then connected to a vacuum pump and the bottle placed in a hot air bath. This treatment is neither laborious nor long. The copper may be prepared by precipitating a 5% copper sulfate solution with zinc. Zinc dust works excellently. The copper is filtered, washed with water, a little alcohol and then with ether and dried by heating under a vacuum. Nine parts of the zinc are then thoroughly mixed with one part of copper and the mixture placed in a long combustion tube. The amount of material should be such as to fill the tube a little less than half full. Plugs of glass wool are placed at both ends to keep the material from rolling out. Dry hydrogen is then passed into the tube and when the air is replaced the tube is heated over the free flames of the combustion furnace and rotated rapidly. If the flames are of equal height, no trouble is experienced in having part of the material fuse while other portions are not sufficiently heated; as the tube becomes hot, the copper appears to separate out and become spongy. This gradually then works into the zinc, giving it a yellowish color and then a little more heat causes the zinc to form little pellets of a tarnished lead color. This is the stage at which to stop. Higher heating causes the pellets to sinter together and take on a reddish color. With care the whole contents of the tube may be converted into uniform, lead-colored pellets. The couple should be allowed to cool in hydrogen and bottled up if not to be used immediately. Batches of 200 g. may be prepared in this manner in 12 to 15 minutes.

The catalytic effect of a few substances was tested roughly. Early experience had confirmed the accelerating effect of dry ether, but small amount of this substance did not have the influence of either acetonitrile or methyl acetate.

The following experiments were carried out with a moderately inactive couple in order to make more pronounced the effect of the catalyst.

1. 2.5 cc. of ethyl iodide and 10 g. of couple when heated in a water bath at 60° under a reflux condenser ceased to return ethyl iodide in slightly over 14 minutes.

2. The same to which 2 drops of acetonitrile were added, ceased within 5.5 min.

3. The same with the addition of 2 drops of methyl acetate ceased within 4.5 minutes.

The Preparation of Zinc Methyl.—The set up of the apparatus was as follows. A short-necked 500 cc. flask containing 300 g. of couple was fitted with a cork bearing a dropping funnel and a 12 mm. glass tube bent at right angles just above the cork. This tube was surrounded by a Leibig's water jacket, and the other projecting end was fitted with a cork and inserted far into a distilling flask. The side tube of the latter was connected to a mercury seal by means of rubber tubing. The flask with its rubber tubing connection and a pinchcock, was weighed. After the air in the apparatus was displaced with carbon dioxide 110 g. of methyl iodide mixed with one cc. of methyl acetate was added to the couple through the dropping funnel. The apparatus was tilted so that the tube acted as a reflux condenser. It was found convenient to set up the apparatus in the late afternoon and allow it to stand overnight and then warm the flask on a water bath at 60° the next day. Usually condensation ceased by late afternoon, *i. e.*, after about 7 hours heating. When the reaction was complete the apparatus was tilted so that the tube acted as a condenser. The distilling flask was packed in ice and the reaction flask heated in an oil bath until zinc methyl no longer distilled off. Carbon dioxide was passed through the dropping funnel slowly during the distillation and more rapidly at the end, in order to drive the zinc methyl out of the apparatus, and also to fill the neck of the receiving flask with this inert gas. Finally the cork attached to the distilling flask was carefully moved down to the end of the tube while the carbon dioxide was passing through and the distilling flask disconnected and a cork fitted with a dropping funnel and previously weighed, was quickly inserted. After closing the pinchcock, the flask and its attachment were weighed and the amount of zinc methyl calculated. The zinc methyl was then directly treated with the desired reagent.

The records of a large number of runs gave weights of the crude zinc methyl obtained varying between 40 and 45 g. The theoretical yield would have been 42.1 g. The weighings were, however, rough and no corrections were made for the difference in weights of the carbon dioxide and the air. Then, too, probably small amounts of methyl iodide were present in some cases.

The literature does not seem to mention one important property of zinc methyl iodide, namely that at ordinary temperatures it dissociates to give enough zinc methyl to cause the vapor above it to inflame spontaneously when exposed to the air.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, BARNARD COLLEGE.]

THE PREPARATION OF *o*-NITROBENZOIC ACID.

BY MARIE REIMER AND ELIZABETH STEWART GATEWOOD.

Received April 24, 1920.

The object of the work described in this paper was the preparation of pure *o*-nitrobenzoic acid. The method was the oxidation with potassium permanganate of the mixture of *o*- and *p*-nitrotoluenes formed by the nitration of toluene and the separation of the *o*- and *p*-nitrobenzoic acids thus formed. The usual slow oxidation in dilute solution and the laborious separation of the 2 acids by fractional crystallization of their barium salts[1] which gave an impure *o*-acid, was replaced by more rapid oxidation in concentrated solution and the separation of the 2 acids by fractional distillation of their methyl esters under diminished pressure. Thus much time was saved and pure *o*-nitrobenzoic acid obtained.

After working out the procedure with the product from the nitration of toluene, it was possible to prepare in a few hours by the same method pure *o*-nitrobenzoic acid from any one of a number of samples of *o*-nitrotoluene of various grades of purity which had been obtained on the market. Some *p*-nitrotoluene was present in every sample even in those which distilled within 0.1°.

The Oxidation of the Mixed *o*- and *p*-Nitrotoluenes.

The usual method is oxidation in dil. alkaline solution with potassium permanganate. The reaction is slow and a great deal of time is required for evaporation of the large volume of solution. An attempt was made to carry out the oxidation in a very concentrated solution of permanganate, the flask being heated on the water bath and the contents agitated by an electrical stirrer fitted with a mercury seal to avoid loss of substance. The oxidation was rapid but the yields of acid extremely poor.

While these experiments were in progress the paper of Bigelow[2] on the oxidation of the nitrotoluenes appeared. Our results with mixed *o*- and *p*-nitrotoluenes agree substantially with his.

The procedure finally adopted for rapid oxidation was as follows. Forty g. of mixed nitrotoluenes, 400 cc. of water and 25 cc. of 10% solution of sodium hydroxide were put into a 2-liter flask fitted with a return condenser and an inlet tube for steam. Forty-six g. of solid potassium permanganate, half the calculated quantity, were added, the flask heated on the water bath and steam passed in until the reaction was well started. The heat of reaction was then sufficient to keep the mixture boiling rapidly. At the end of an hour the rest of the permanganate was added. As soon as the boiling caused by the heat of reaction ceased, steam was again passed into the solution and this continued until the permanganate was

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[1] Monnet, Reverdin, Noelting, *Ber.*, 12, 443 (1879).

[2] Bigelow, THIS JOURNAL, 41, 1559 (1919).

entirely decolorized. The time for the oxidation was about 2 hours. The oxides of manganese were then filtered out by suction and washed repeatedly with boiling water. The combined filtrates were cooled and filtered through a folded filter paper. The unoxidized oil was held back completely by the filter paper and could be run out, dried and weighed. The yield of oxidation product could then be calculated from the amount of oil oxidized. The separation of the oil by filtration is an immense saving of time over the usual method of distillation with steam.

In no case was it found possible to oxidize all the oil, even when a large excess of permanganate was used, a fact noted by the early investigators. The incomplete reaction and low yield of product are due, as pointed out by Bigelow,[1] to the reduction of some of the permanganate by the oxides of manganese formed during the reaction and to the rapid and complete oxidation of some of the nitrobenzoic acids by the excess of permanganate. For this reason oxidation in concentrated solution gives a low yield of product, from 50 to 60% being obtained by following the above directions, while slow oxidation in very dilute solution gave yields as high as 87%. As it is possible, however, by the method described to obtain fair yields in less than $^1/_4$ the time required for oxidation in dilute solution the procedure is to be recommended.

The Partial Separation of *p*-Nitrobenzoic Acid from the Oxidation Mixture.

Although both the nitrobenzoic acids are soluble in water, the *p*-acid is far less soluble than the *ortho*. It was found that if the filtrates from the oxidation mixture were evaporated so that there was about 900 cc. of liquid for each 30 g. of oil oxidized, practically pure *p*-nitrobenzoic acid was precipitated on acidification of the cooled solution. If the solution were more concentrated, some *o*-acid separated with the *para* and was subsequently lost on crystallization of the latter acid from boiling water.

The filtrates from the precipitation were exactly neutralized with sodium carbonate, since *o*-nitrobenzoic acid is slightly volatile with water vapor, and evaporated to a small volume. From the cooled solution, hydrochloric acid precipitated a mixture of *o*- and *p*-nitrobenzoic acids melting at about 120–140°. The filtrate was extracted with ether, the ether evaporated, and the residue added to the precipitated mixed acids.

The Separation of *o*-Nitrobenzoic Acid from the Mixture of Acids.

The crude mixed acids were dried, dissolved in 10 times their weight of methyl alcohol that had been saturated with hydrochloric acid, and boiled for 2 hours. The alcohol was then completely distilled off, and the residue cooled in a freezing mixture. Crystals of *p*-nitro ester separa-

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[1] *Loc. cit.*

ted and were filtered out by suction. The oil remaining, consisting of *o*-nitro ester in which some *p*-nitro ester was dissolved, was washed with dil. sodium carbonate solution, extracted with ether, the solution dried, the ether distilled off, and the residue repeatedly fractioned under diminished pressure. The boiling points of the purified products were, 160° (14 mm.), 162° (16 mm.), 167° (21 mm.). Fractions of slightly higher boiling point, on cooling, usually deposited a few crystals of *p*-ester. These were filtered out and the liquid fractioned until it had a constant boiling point.

The methyl ester of *o*-nitrobenzoic acid is a pale yellow mobile liquid. In spite of a constant boiling point it may still contain traces of *p*-ester. It is possible to get rid of this by saponification in an alcoholic solution of definite concentration. For each g. of ester, one g. of potassium hydroxide in 16 cc. of cold absolute alcohol was used. In less than a minute, shining crystals of the potassium salt of the *o*-acid began to form. The mixture was allowed to stand an hour, and the mass of pearly crystals then filtered out by suction and washed with a small quantity of cold absolute alcohol. More than 90% of the acid separated out as the potassium salt. From the concentrated aqueous solution of this salt, hydrochloric acid precipitated pure *o*-nitrobenzoic acid as a snow-white solid, melting at 147–147.5°. The filtrate from the separation of the potassium salt gave an acid of considerably lower melting point.

The melting points of *o*-nitrobenzoic acid given in the literature are 140°,[1] 141°,[2] 145°,[3] 147°.[4] The cause of this wide variation in melting points is, undoubtedly, admixture of *p*-nitrobenzoic acid. The effect of various amounts of *p*-acid on the melting point of the *o*-acid, is shown in the following table:

p-Nitro-benzoic acid with *o*-acid. %	° C. at which substance begins to soften. °	° C. at which substance melts. °
20	127	138–142
15	131	139–144
10	132	139–144
5	135	140–145
0 (pure *o*-acid)	145	147–147.5
100 (pure *p*-acid)	...	239–240

Mixtures with 20% and with 15% of *p*-acid are almost completely melted at 140°. Thus a very impure *o*-acid gives a fair melting point. It is not possible to purify this acid by repeated crystallization, as much of the very soluble *o*-acid remains in the filtrate, the percentage of *p*-acid

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[1] Greiss, *Ann.*, 166, 132 (1873).

[2] Beilstein and Kuhlberg, *ibid.*, 163, 135 (1872).

[3] Monnet, Reverdin, Noelting, *loc. cit.*

[4] Windmrnn, *Ann.*, 193, 221 (1878).

increasing with each crystallization. By far the most rapid method of obtaining perfectly pure *o*-acid is by way of its methyl ester.

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[CONTRIBUTION FROM THE OIL, FAT AND WAX LABORATORY, BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE.]

MENTHOL AND PHENYLHYDRAZINE DERIVATIVES OF THE HIGHER FATTY ACIDS.

BY D. H. BRAUNS.

Received May 1, 1920.

The separation of the higher fatty acids, or their determination when several are present together is a matter of very considerable difficulty. In the hope of securing a simple and reliable method of separation or determination of these acids, the preparation and properties of their menthyl esters and their phenylhydrazids have been studied. Although in neither case was the hope of a quantitative identification realized, the compounds are of sufficient interest to merit description.

The menthol esters of lauric, myristic, palmitic, stearic, and arachidic acids were prepared by heating the acid chlorides with menthol. The acid chlorides were obtained by the action of phosphorus pentachloride and thionyl chloride on the fatty acids. It was found that the reaction with thionyl chloride was not only more nearly quantitative but also yielded a product freer from impurities. However, since even the thionyl chloride did not give a quantitative yield of the acid chlorides, it was not possible to utilize the optical rotation of these methyl esters for the estimation of the above mentioned acids in mixtures when only 2 of them were present.

The phenylhydrazine derivatives of several of these fatty acids were prepared by heating the acids with an excess of phenylhydrazine. Derivatives of palmitic, stearic, and arachidic acids were prepared and their solubilities in alcohol, which was found to be the most suitable solvent from which to crystallize them, was studied. It was found that they were only slightly soluble in cold alcohol and that with the increase of the molecular weight the solubility decreased, as was to be expected. However, there was not enough difference in their respective solubilities to enable the compounds to be utilized in the separation of these acids from each other by fractional crystallization.

Experimental Part.

Menthyl Laurate, $C_{22}H_{42}O_2$.—Equal weights of pure lauric acid and phosphorus pentachloride were heated on the steam bath. When the reaction was completed, the phosphorus oxychloride was removed by heating the mixture under 15 mm. pressure to 150°. Then the pressure was reduced to 5 mm. and the acid chloride was distilled. The lauric acid chloride was heated with an excess of menthol until the evolution of hydrochloric acid ceased. The reaction product was dissolved in ether, washed with dil. sodium hydroxide solution and water, and dried over potassium carbonate. The menthyl laurate was further purified by fractional distillation under diminished pressure. From 10 g. of lauric acid, 6.3 g. or a 37% yield of the pure ester, was obtained. Menthyl laurate is a liquid at ordinary temperatures; d_4^{20} 0.8915; $[\alpha]_D^{20} = -46.07$; $[M]_D^{20} = -155.9$. Analysis by combustion gave the following results.

Subs., 0.1866; CO_2, 0.5341; H_2O, 0.2077.
Calc. for $C_{22}H_{42}O_2$: C, 78.03; H, 12.51. Found: C, 78.06; H, 12.45.

Menthyl Myristate, $C_{24}H_{46}O_2$.—This compound was prepared in the same manner as the corresponding lauric acid derivative. A second preparation was made from myristic acid chloride which was obtained by the action of thionyl chloride on myristic acid according to F. P. Hilditch.[1] This method of obtaining the acid chlorides was found to be much more satisfactory than the customary procedure with phosphorus pentachloride. Although Hilditch described this compound as melting at 32°, it was impossible to obtain a melting point above 21–22° in spite of repeated purification by fractional distillation under diminished pressure. Ten g. of myristic acid gave 7 g. of pure ester which is equivalent to a yield of 48%; d_4^{20}, 0.882; $[\alpha]_D^{20} = -42.33$; $[M]_D^{20} = -155.1$.

Subs., 0.2097; CO_2, 0.6055; H_2O, 0.2370.
Calc. for $C_{24}H_{46}O_2$: C, 78.61; H, 12.66. Found: C, 78.76; H, 12.65.

Menthyl Palmitate, $C_{26}H_{50}O_2$.—This compound was obtained in the same manner as described above, except that it could not be distilled under diminished pressure, but had to be purified by repeated crystallization from absolute alcohol. The purified derivative was found to melt at 32°. It is very soluble in alcohol. It separates from alcohol in the form of illy defined soft crystals; d_4^{20} 0.8848; $[\alpha]_D^{20} = -39.10$; $[M]_D^{20} = -154.2$. It should be observed that the melted compound was employed in determining the specific rotation.

Subs., 0.1653; CO_2, 0.4821; H_2O, 0.1895.
Calc. for $C_{26}H_{50}O_2$: C, 79.11; H, 12.73. Found: C, 79.53; H, 12.73.

Menthyl Stearate, $C_{28}H_{54}O_2$.—This substance was prepared and purified in the same manner as the palmitic ester. Three preparations were made, starting each time with 10 g. of stearic acid for making the acid chloride. The ester was found to melt at 38° to 39°, which is in agreement with that found by E. Beckman.[2] This compound, which is very soluble in alcohol, separates in aggregates of very small crystals not well defined. Ten g. of the acid gave 3 g. of pure ester, which is a

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[1] Hilditch, *J. Chem. Soc.*, 101, 192 (1912).

[2] *J. prakt. Chem.*, [2] 55, 17 (1847).

yield of 20%; d_4^{45} 0.8665; $[\alpha]_D^{45} = -36.60$; $[M]_D^{45} = -154.6$. Analysis gave the following results.

Subs., 0.2483; CO_2, 0.7238; H_2O, 0.2839.
Calc. for $C_{28}H_{54}O_2$: C, 79.54; H, 12.88. Found: C, 79.50; H, 12.73.

Menthyl Arachidate, $C_{30}H_{58}O_2$.—This substance was prepared from arachidic acid chloride obtained by both the phosphorus pentachloride and thionyl chloride methods. After repeated recrystallization from alcohol, a melting point of 55° was obtained. From 10 g. of acid, 3 g. of purified ester was obtained; d_4^{55} 0.8566; $[\alpha]_D^{55} = -30.63$; $[M]_D^{55} = -138.0$. Analysis gave the following results.

Subs., 0.1906, 0.2049; CO_2, 0.5639, 0.6051; H_2O, 0.2218, 0.2392.
Calc. for $C_{30}H_{58}O_2$: C, 79.92; H, 12.98. Found: C, 80.69, 80.54; H, 13.02, 13.06.

The analysis as well as the low result obtained for the rotation indicate that in spite of repeated recrystallizations from alcohol, the compound was not quite pure. This compound crystallizes in illy defined soft thin prisms.

It should be observed that all the figures given for the rotation in this paper were determined directly with the molten derivatives, while Hilditch, who previously prepared those of myristic, palmitic, and stearic acids, measured the rotations in chloroform and alcoholic solutions, with the result that he obtained slightly higher values. It is interesting to note that with the exception of the menthyl arachidate, these compounds gave an average molecular rotation of —155 which is in close agreement with the average value —157, found by L. Tchugaeff[1] for the corresponding derivatives of the lower members of this series of acids extending from acetic acid to caprylic acid.

Palmitic Phenylhydrazide, $C_{16}H_{31}O.HNNHC_6H_5$, was obtained by heating palmitic acid with an excess of phenylhydrazine until the mixture began to boil, according to the method of Strache and Iritzer,[2] who described the corresponding stearyl compound. After the reaction was completed, alcohol was added and the mixture was allowed to cool. The crystals from this solution were further purified by recrystallization from alcohol until the constant melting point 105° was obtained. A yield of 25% of the purified compound was obtained.

Subs., 0.1419; CO_2, 0.3958; H_2O, 0.1379.
Calc. for $C_{22}H_{38}N_2O$: C, 76.23; H, 11.06. Found: C, 76.07; H, 10.87.

It is readily soluble in hot 95% alcohol and sparingly soluble in cold alcohol. From alcohol it separates in aggregates of extremely small soft crystals. This compound was found to be quite soluble in chloroform and ether.

Stearic Phenylhydrazid, $C_{18}H_{35}O.HNNHC_6H_5$, was obtained by heating 2 g. of stearic acid with 1.5 cc. of phenylhydrazine to 140° for 20

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[1] Tchugaeff, *Ber.*, 31, 360 (1898).

[2] Strache and Iritzer, *Monatsh.*, 14, 37 (1893).

minutes. After cooling somewhat, alcohol was added and the solution was allowed to stand until crystallization had taken place. After 2 recrystallizations the constant melting point of 110° to 111° was obtained. It was observed that Strache and Iritzer,[1] who previously described this compound, gave the melting point 105° to 107°. When crystallized from alcohol it crystallized in well defined small, thin, rectangular prisms. It is readily soluble in hot alcohol, but sparingly soluble in cold alcohol. 100 cc. of 95% alcohol at 29° dissolved 0.076 g. A yield of 18% of the pure derivative was obtained.

Subs., 0.1315; CO_2, 0.3706; H_2O, 0.1298.
Calc. for $C_{24}H_{42}N_2O$: C, 76.93; H, 11.04. Found: C, 76.71; H, 11.05.

Arachidic Phenylhydrazid, $C_{20}H_{39}O.HNNHC_6H_5$ was obtained in the same manner as the stearyl derivative starting with 2 g. of arachidic acid and 1.5 cc. of phenylhydrazine. The highest melting point obtained by recrystallization from alcohol was 108 to 109°. From alcohol it crystallizes in small illy defined thin prisms. It was found that 100 cc. of 95% alcohol at 27° dissolved 0.050 g. while at 40° 0.0530 g. was dissolved. A yield of 29% of the pure derivative was obtained.

Subs., 0.1384; CO_2, 0.3924; H_2O, 0.1409.
Calc. for $C_{26}H_{46}N_2O$: C, 77.54; H, 11.52. Found: C, 77.33; H, 11.39.

Summary.

The menthyl esters of lauric, myristic, palmitic, stearic, and arachidic acids have been prepared and their optical rotations have been determined.

Also the phenylhydrazine derivatives of palmitic, stearic, and arachidic acids have been made and studied.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH.]

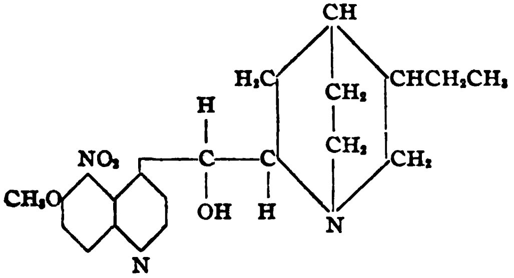
SYNTHESES IN THE CINCHONA SERIES.

IV.[2] NITRO- AND AMINO-DERIVATIVES OF THE DIHYDRO ALKALOIDS.

BY WALTER A. JACOBS AND MICHAEL HEIDELBERGER.

Received May 4, 1920.

In the preparation of 5-nitro-dihydro-quinine



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[1] *Loc. cit.*

[2] Cf. THIS JOURNAL, 41, 817, 2090, 2131 (1919).

and 5-amino-dihydro-quinine according to German patent No. 283,537, difficulties were encountered which had to be overcome before the amino compound could be obtained readily enough to serve as a starting point for certain synthetic work which we had contemplated. In the first place, nitro-dihydro-quinine is described as resulting from the nitration of dihydro-quinine sulfate by the use of a nitric-sulfuric acid mixture, with no reference to the exact proportions employed. A study of the reaction showed that the formation of nitro-dihydro-quinine was complicated by the production of a nitro-dihydro-quinine sulfonic acid. Although this did not occur when the sulfate was added to a mixture of equal volumes of nitric and sulfuric acids, the tendency toward sulfonation increased as the proportion of sulfuric acid to nitric acid was increased, with consequent diminution of the yield of nitro-dihydro-quinine. It was then found that a quantitative conversion of dihydro-quinine into the nitro base could easily be realized with fuming nitric acid, and this was finally adopted as the most satisfactory reagent since it is less viscous and dissolves the alkaloid more rapidly than the mixture of equal parts of sulfuric and nitric acids, and also yields a less highly colored product.

Experiments with nitro-dihydro-quinine sulfonic acid explained its occurrence, since it was shown that this substance is formed both by nitration of dihydro-quinine sulfonic acid and by sulfonation of nitro-dihydro-quinine. In the latter case, it is sufficient to allow a solution of the nitro base in conc. sulfuric acid to stand at room temperature, a result in no way surprising, since the dihydro alkaloids have been found to yield sulfonic acids readily under the same conditions.[1] Since the nitro acid may be obtained from dihydro-quinine sulfonic acid, the sulfonic acid group occupies the same position in both of these acids, but according to Schmid's[2] experiments with cinchotine sulfonic acid, it is not situated in the quinoline nucleus. The lability of the sulfonic acid group toward boiling hydrochloric acid and its stability in boiling alkaline solution as demonstrated by Schmid for dihydro-quinine sulfonic acid, are properties retained by the nitro acid.

By following the method for the reduction of nitro-dihydro-quinine given in the patent we obtained but poor yields of the amino alkaloid, and it was necessary to modify the method considerably before a smooth conversion of the nitro alkaloid into the amino compound was afforded. In extending the work, the methods outlined were successfully applied to ethyl-dihydro-cupreine (optochin), dihydro-quinidine, ethyl-dihydro-cupreidine,[3] and dihydro-quinane,[4] resulting in the synthesis of the corre-

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[1] Hesse, *Ann.*, **241**, 283 (1887); Skraup, *Monatsh.*, **18**, 414 (1897).

[2] Schmid, *ibid.*, **22**, 803 (1901).

[3] THIS JOURNAL, **41**, 830 (1919).

[4] See following paper.

sponding nitro and amino derivatives. Like 5-amino-quinoline, the amino alkaloids form orange-red, non-fluorescent solutions in dilute acids and in addition give the thalleoquinine reaction. This reaction is not given by the nitro compounds.

Experimental Part.

5-Nitro-dihydro-quinine.—Although this substance was prepared by the use of a nitration mixture consisting of equal parts of conc. nitric and sulfuric acids as in the preparation of dinitro-quinine by Rennie,[1] fuming nitric acid was found to give the most satisfactory results with dihydro-quinine and was, therefore, employed in the other cases described below.

Fifty g. of anhydrous dihydro-quinine sulfate were added in small portions to 200 cc. of fuming nitric acid (sp. gr. 1.52), with turbining, and keeping the temperature at 0°. The salt dissolved rapidly, and after addition of the full amount the clear solution was allowed to stand for 15 minutes at 0° and then poured on to ice. After dilution to about 4 liters the solution was treated with 25% aqueous sodium hydroxide until most of the nitric acid was neutralized and the alkaloid still remained dissolved as the nitrate. The solution was then vigorously stirred and the base quickly precipitated by the rapid addition of ammonia in excess. If the precipitation is too slow, or if the solution is not sufficiently dilute, a gummy mass of what is presumably the mono nitrate separates and is difficult to transform into an easily filterable form. The pale yellow, partially crystalline precipitate is filtered off, washed well with water, and dissolved in dil. hydrochloric acid. After adding an equal volume of alcohol, warming, and making alkaline with ammonia, the nitro-dihydro-quinine separates rapidly as lustrous yellow plates. After washing with 50% alcohol the yield is 90%.

For final purification the base was dissolved in 50% alcohol by the addition of sufficient acetic acid, and, after warming again, precipitated with ammonia, forming lustrous, pale yellow, hexagonal scales which decompose at 220–2° with preliminary darkening and softening, and not at 209–12° as given in the patent. The nitro compound is appreciably soluble in methyl or ethyl alcohol, acetone or benzene, more readily so in the hot solvents. It is easily soluble in chloroform and dil. acids and very sparingly in ether. It does not give the thalleoquinine test, and on exposure to sunlight turns a purplish brown. $[\alpha]_D^{25°} = -200.0°$ in chloroform; $c = 1.350$.

Subs., 0.1293: 12.91 cc. N (25.0°, 760 mm.).
Calc. for $C_{20}H_{25}O_4N_3$: N, 11.32. Found: 11.42.

5-Nitro-dihydro-quinine Sulfonic Acid.—(*A*). From nitro-dihydro-quinine. This substance was obtained as the main product of the reaction when the nitration of dihydro-quinine was attempted with a mixture

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[1] Rennie, *J. Chem. Soc.*, 39, 470 (1881).

of sulfuric acid and the theoretical amount of conc. nitric acid. It was then found that the compound results either from the nitration of dihydro-quinine sulfonic acid, or by allowing a solution of nitro-dihydro-quinine in conc. sulfuric acid to stand at ordinary temperature, just as in the formation of dihydro-quinine sulfonic acid.

Five g. of nitro-dihydro-quinine were dissolved in 25 cc. of conc. sulfuric acid and allowed to stand for 24 hours. After pouring on to ice and diluting, the greenish yellow solution was partly neutralized with sodium hydroxide and finally made neutral to Congo red with sodium acetate solution. On rubbing the acid separates as yellow needles which were washed with water. It was recrystallized by dissolving in dil. alkali, warming, and reacidifying with acetic acid, a transitory turbidity appearing at the neutral point. The acid separates as flat, glistening, yellow needles which rapidly turn green on exposure to sunlight. It chars when heated above 260° but does not melt below 285°, and is practically insoluble in the usual solvents except boiling 50% alcohol. It dissolves in dil. hydrochloric and nitric acids but less readily in dilute sulfuric acid. The addition of strong sodium hydroxide or sodium chloride solution to the solution of the acid in dil. sodium hydroxide salts out the sodium salt as a gummy precipitate. Like dihydro-quinine sulfonic acid, the nitro acid is relatively stable in alkaline solution but on boiling with 20% hydrochloric acid the sulfonic group is quantitatively eliminated with the formation of nitro-dihydro-quinine. This property was, therefore, employed for the sulfur determination. The position occupied by the sulfonic acid group was not determined, although it was shown to be the same as that occupied by the sulfo group in dihydro-quinine sulfonic acid, since this yielded the same nitro compound. $[\alpha]_D^{25°} = -133.0°$ in 0.5 N NaOH; $c = 1.000$.

Subs., 0.1240: 10.6 cc. N (28.0°, 759 mm.). Subs., 0.1509: $BaSO_4$, 0.0751.
Calc. for $C_{20}H_{25}O_7N_3S$: N, 9.31; S, 7.10. Found: N, 9.69; S, 6.84.

(*B*). From dihydro-quinine sulfonic acid. Dihydro-quinine sulfonic acid was obtained by allowing a solution of 10 g. of anhydrous dihydro-quinine sulfate in 50 cc. of conc. sulfuric acid to stand for 24 hours. After dilution with water and partial neutralization with sodium hydroxide solution, the mixture was neutralized to Congo red with sodium acetate, causing the separation of 8.7 g. of the sulfonic acid as lustrous, colorless rhombs, often grouped as serrated aggregates. This was added in small portions to 30 cc. of fuming nitric acid (sp. gr. 1.52) kept at 0°. After 15 minutes' standing at 0°, the mixture was poured on to ice and the acid isolated as previously described. After recrystallization 8.7 g. of slightly greenish yellow, flat, glistening needles were obtained, identical in all respects with the acid obtained from nitro-dihydro-quinine. $[\alpha]_D^{27°} = -129.6°$ in 0.5 N NaOH; $c = 1.012$.

Subs., 0.1201: 10.0 cc. N (23.5°, 759 mm.). Subs., 0.2005: $BaSO_4$, 0.1052.
Calc. for $C_{20}H_{25}O_7N_3S$: N, 9.31; S, 7.10. Found: N, 9.58; S, 7.21.

Hydrolysis of Nitro-dihydro-quinine Sulfonic Acid to Nitro-dihydro-quinine.—2 g. of the sulfonic acid dissolved in 25 cc. of 1 : 1 hydrochloric acid were boiled for one hour. An equal volume of alcohol was added and the solution made alkaline with ammonia. The crystalline precipitate was recrystallized as previously described, forming lustrous, pale yellow, hexagonal scales which decomposed at 220–2° and proved identical with the 5-nitro-dihydro-quinine prepared by the direct method.

Subs., 0.1312: 13.2 cc. N (24.0°, 758 mm.).
Calc., N, 11.32. Found: 11.54.

5-Amino-dihydro-quinine.—On repeating the directions given in German patent 283,537 for the reduction of nitro-dihydro-quinine, it was found that when the reaction mixture was made alkaline before extracting the amino compound with ether, it rapidly turned deep green owing to oxidation, showing that decomposition had occurred. In consequence, the yield of amino-dihydro-quinine was poor, only 5.8 g. being recovered from 18 g. of the nitro compound. A number of experiments finally led to the following satisfactory method, which was then applied to the reduction of the other nitro cinchona derivatives described below.

18.5 g. of nitro-dihydro-quinine were dissolved in 185 cc. of conc. hydrochloric acid with chilling and stirring, the alkaloid being slowly added in order to diminish the tendency to form a gum. After chilling the solution to 0°, 45 g. of stannous chloride were added. On removing the beaker from the freezing mixture and stirring, the temperature rose as the reaction proceeded, but was not allowed to exceed 35°. A thick, partially crystalline, yellow paste of the tin salt separated, and after standing for 15 minutes, the mass was dissolved in water and ice added. The deep orange-red solution was then treated with an excess of 25% sodium hydroxide solution, no trace of green coloration being evident. The amorphous amino compound was shaken out with about one liter of ether, the yellow solution depositing most of the substance as yellow needles on standing. On concentration the mother liquor yielded the remainder, the total being 15 g. Recrystallized from hot benzene, in which it is fairly easily soluble at the boiling point, it separates as rosets of thickly matted, minute, yellow, microscopic needles which melt at 220–1° with slight preliminary softening. Giemsa and Halberkann[1] give 217–8° as the melting point, while in German patent 283,537 it is given as 208–12°. The base is very readily soluble in chloroform, quite easily in methyl or ethyl alcohol, less so in acetone, and very sparingly in ether or cold benzene. It gradually turns a brownish purple on exposure to sunlight. It dissolves in dilute acids with an orange-red color

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[1] *Ber.*, **52**, 922 (1919).

and gives the thalleoquinine reaction, and, as we shall describe more fully in a subsequent communication, it couples smoothly with diazo compounds to form well defined amino-azo dyes. $[\alpha]_D^{21°} = -17.7°$ in absolute alcohol; $c = 1.020$.

Subs., 0.1187: 12.85 cc. N (20.0°, 749 mm.).
Calc. for $C_{20}H_{27}O_2N_3$: N, 12.31. Found: 12.44.

5-Nitro-ethyl-dihydro-cupreine (5-Nitro-optochin).—20 g. of anhydrous ethyl-dihydro-cupreine sulfate (from a solution of the chloride with ammonium sulfate) were nitrated as in the case of dihydro-quinine sulfate. The base, precipitated from the diluted reaction mixture with ammonia, first separated amorphous and then partly crystallized. It was recrystallized by dissolving in 50% alcohol with the aid of acetic acid and reprecipitated by the addition of ammonia to the warm solution. The base separated in excellent yield as lustrous, pale yellow, hexagonal platelets which melted and decomposed at 225–6° with preliminary darkening and softening after another recrystallization from toluene. It is rather difficultly soluble in cold alcohol or acetone but readily on boiling, and is more easily soluble in cold methyl alcohol or chloroform. A concentrated neutralized solution of the nitro alkaloid in hydrochloric acid deposits pale yellow, delicate needles of the hydrochloride. $[\alpha]_D^{22.5°} = -198.2°$ in chloroform; $c = 0.515$.

Subs., 0.1267: 12.15 cc. N (23.5°, 760 mm.).
Calc. for $C_{21}H_{27}O_4N_3$: N, 10.91. Found: 11.04.

5-Amino-ethyl-dihydro-cupreine (5-Amino-optochin).—18.5 g. of the nitro compound, treated as in the case of nitro-dihydro-quinine, yielded 14 g. of the amino alkaloid after recrystallizing from dil. alcohol with the aid of boneblack. Recrystallized from 85% alcohol, the base separates as minute, lemon-yellow platelets which melt with slow decomposition at 214–5° with slight preliminary softening and darkening. It is very readily soluble in chloroform, quite easily in methyl and ethyl alcohols and less readily in acetone, forming yellow solutions. It dissolves in hot benzene, separating in gelatinous form on cooling. The solution in dil. hydrochloric acid is orange in color, and gives the thalleoquinine reaction. $[\alpha]_D^{24.5°}$ is $-15.9°$ in absolute alcohol, $c = 1.034$, while Giemsa and Halberkann[1] give $[\alpha]_D^{20} = -13.2°$ and the melting point as 211–2°.

Subs., 0.1225: 12.55 cc. N (23.0°, 770 mm.).
Calc. for $C_{21}H_{29}O_2N_3$: N, 11.83. Found: 11.97.

5a-Nitro-dihydro-quinidine.—46.5 g. of anhydrous dihydro-quinidine sulfate were nitrated as in the previous cases, the final precipitation of the free base being carried out rapidly with ammonia from the highly diluted reaction mixture. If the precipitation is too slow, or if the solution is too concentrated the substance separates largely as a gum consisting of the

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[1] *Loc. cit.*, pp. 922–3.

nitrate of the base. It is advisable even when precipitation is properly accomplished to grind the filtered and washed base with dil. ammonia and to filter and wash again. The yield of amorphous base was 43 g. and was sufficiently pure for reduction to the amino alkaloid.

On dissolving the dried base in hot ethyl acetate and allowing to cool rapidly it separates as a jelly, but when the concentrated solution is kept warm and rubbed, the nitro compound separates slowly as yellow rhombs. The same phenomena occur in 50% alcohol, since crystallization is slow, and in order to avoid contamination with amorphous material the solutions must be kept warm. The crystalline base is readily soluble in alcohol, chloroform, acetone and ethyl acetate, less easily in benzene and very sparingly in ether. It melts and decomposes at about 208–9° with preliminary darkening and softening, and does not give the thalleoquinine test. $[\alpha]_{D}^{23} = +326.5°$ in absolute alcohol; $c = 0.668$.

Subs., 0.1082: CO_2, 0.2579; H_2O, 0.0647. Subs., 0.1307: N, 13.2 cc. (23.0°, 765 mm.).

Calc. for $C_{20}H_{25}O_4N_3$: C, 64.65; H, 6.79; N, 11.32. Found: C, 65.00; H, 6.69; N, 11.72.

The Nitrate.—This salt was obtained in one experiment in which the insufficiently diluted reaction mixture from the nitration of dihydroquinidine sulfate had been precipitated with ammonia, the precipitate consisting mostly of the nitrate. Although flocculent at first, it sintered to a gum which prevented filtration, but was collected and dissolved in 95% alcohol, the salt separating as pale yellow rhombs, which were again crystallized from alcohol. The air-dry salt contains solvent approximately equivalent to 2 molecules of water of crystallization, and like the anhydrous salt intumesces at 142–5°. It is slowly but fairly readily soluble in water with a bright yellow color and dissolves readily in methyl and ethyl alcohols, acetone and chloroform, and only sparingly in hot benzene. $]\alpha[_{D}^{22}$ of the anhydrous salt is +232.8° in water; $c = 0.896$.

Air-dry: Subs., 0.6727: loss, 0.0570, *in vacuo* at 80° over H_2SO_4.
Calc. for $C_{20}H_{25}O_4N_3.HNO_3.2H_2O$: H_2O, 7.66. Found: 8.47.
Anhydrous: Subs., 0.1112: N, 12.0 cc. (22.0°, 763 mm.).
Calc. for $C_{20}H_{25}O_4N_3.HNO_3$: N, 12.90. Found: 12.54.

5-Amino-dihydro-quinidine.—18.5 g. of the dried, amorphous nitro alkaloid yielded 11.5 g. of the amino compound. The substance separates slowly from the ethereal extract as olive-yellow rhombs. Recrystallized from 95% alcohol, it forms minute, rhombic platelets which, when rapidly heated to 235°, then slowly, darken and decompose at 238–42°. The base is somewhat less soluble in cold alcohol than in methyl alcohol, forming yellow solutions, and is more easily soluble in hot chloroform than in hot acetone. It gives the thalleoquinine reaction and dissolves in dil. hydrochloric acid with an orange-red color which appears orange-brown in thin layers. $[\alpha]_{D}^{20}$ is +115.5° in absolute alcohol; $c = 0.870$.

Subs., 0.1230: N, 13.05 cc. (24.5°, 768 mm.).

Calc. for $C_{20}H_{27}O_2N_3$: N, 12.31. Found: 12.30.

5-Nitro-ethyl-dihydro-cupreidine.—5 g. of ethyl-dihydro-cupreidine[1] were slowly added to 25 cc. of fuming nitric acid (sp. gr. 1.52), keeping the temperature below 0°. Five cc. of conc. sulfuric acid were then added, and after standing for 20 minutes in the cold the mixture was poured into 1500 cc. of water. The nitro base was precipitated with ammonia and shaken out with ether, which, on concentration, yielded 4–5 g. of the crystalline nitro compound. Recrystallized as in previous examples from 50% alcohol, it separates as rosets and plumes of minute, narrow, pale yellow, glistening platelets which melt and decompose at 220–1° with preliminary darkening and softening. It is quite soluble in alcohol, acetone, benzene, and ether, and very readily so in chloroform. $[\alpha]_D^{22}$ is $+322.4°$ in absolute alcohol; $c = 0.951$.

Subs., 0.1082: CO_2, 0.2593; H_2O, 0.0688. Subs., 0.1194: 11.3 cc. N (22.0°, 758 mm.).

Calc. for $C_{21}H_{27}O_4N_3$: C, 65.41; H, 7.07; N, 10.91. Found: C, 65.36; H, 7.12; N, 10.92.

5-Amino-ethyl-dihydro-cupreidine.—The nitro compound was reduced as in previous examples, but an entirely pure product was not obtained. The ethereal solution of the amino alkaloid left a crystalline residue on evaporation, which was recrystallized first from 85% alcohol, then from not too little toluene, separating on cooling as rosets of minute, lemon-yellow needles which melt at 216–7° with slight preliminary darkening and show $[\alpha]_D^{26.5} = -69.4°$ in dry chloroform; $c = 1.017$, $[\alpha]_D^{26.5} = +91.6°$ in absolute alcohol, $c = 0.524$. The base is rather difficultly soluble in alcohol, more easily in methyl alcohol, and fairly readily in dry chloroform, especially on warming. It is sparingly soluble in cold toluene, readily at the boiling point, separating in gelatinous form on cooling unless the solution is seeded and permitted to crystallize while still warm. It gives the thalleo-quinine reaction.

Subs., 0.1166: CO_2. 0.3007; H_2O, 0.0834. Subs., 0.1309: 14.0 cc. N (23.5°, 770 mm.).

Calc. for $C_{21}H_{29}O_2N_3$: C, 70.93; H, 8.23; N, 11.83. Found: C, 70.33; H, 8.00; N, 12.48.

5-Nitro-dihydro-quinane.—Dihydro-quinane trihydrate[2] was nitrated in the same way as was ethyl-dihydro-cupreidine. The partially crystalline nitro compound was shaken out with ether, which was dried and the solution then concentrated. The residue was taken up in 85% alcohol and diluted with water until the initial turbidity just redissolved. On rubbing and cautiously adding further small amounts of water, the hydrated nitro compound separated in a yield equal to that of the dihydro-quinane used. Recrystallized from 50% alcohol it forms radia-

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[1] THIS JOURNAL, 41, 830 (1919).

[2] See following paper.

ting masses of pale yellow, delicate needles which retain 3.5 molecules of water of crystallization when dried to constant weight in a desiccator over water. When dried in the air, water is lost and the substance sinters to a gum. The hydrate begins to soften above 60° and melts to a turbid liquid at 67.5–9°. It dissolves readily in alcohol, acetone, or chloroform, and rather less easily in ether. It does not give the thalleoquinine test. $[\alpha]_D^{22}$ is $+80.2°$ in 95% alcohol; $c = 1.059$.

Air-dry: Subs., 0.4842: loss, 0.0717 *in vacuo* at 80° over H_2SO_4. Subs., 0.1218: 10.8 cc. N (23.5°, 757 mm.).

Calc. for $C_{20}H_{25}O_3N_3.3.5H_2O$: H_2O, 15.07; N, 10.04. Found: H_2O, 14.80; N, 10.17.

An attempt to reduce this substance failed owing to the insolubility of its tin double salt.

Summary.

Improved methods are given for the preparation of 5-nitro- and 5-amino-dihydro-quinine, and it is shown that under the usual conditions of nitration with nitric and sulfuric acids sulfonation also occurs, and 5-nitro-dihydro-quinine sulfonic acid is formed as a by-product. The extension of the methods of nitration and reduction to ethyl-dihydro-cupreine (optochin), dihydro-quinidine and ethyl-dihydro-cupreidine led to the formation of the nitro and amino derivatives of these alkaloids, and descriptions of these new substances are given. 5-Nitro-dihydro-quinane (see next paper) is also described.

NEW YORK, N. Y.

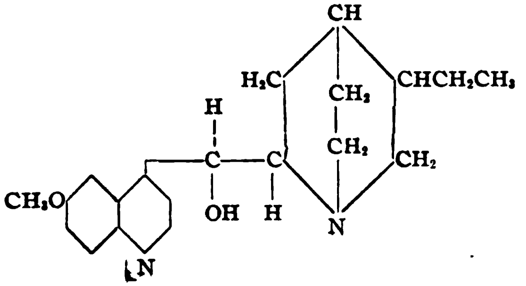
[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH.]

SYNTHESES IN THE CINCHONA SERIES. V. DIHYDRO-DESOXY-QUININE AND DIHYDRO-DESOXY-QUINIDINE AND THEIR DERIVATIVES.

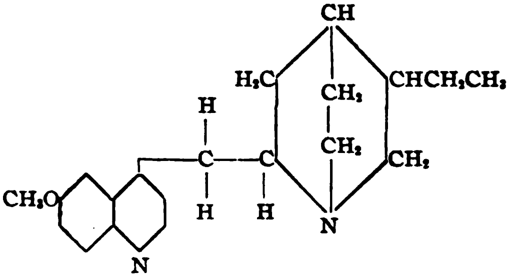
BY MICHAEL HEIDELBERGER AND WALTER A. JACOBS.

Received May 4, 1920.

As a part of our studies on the cinchona alkaloids it became of interest to examine the biological properties of the so-called "desoxy" compounds, in which the secondary alcoholic group of the parent bases

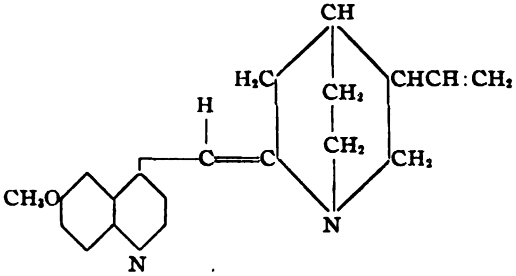


has been replaced by the hydrogen atom.

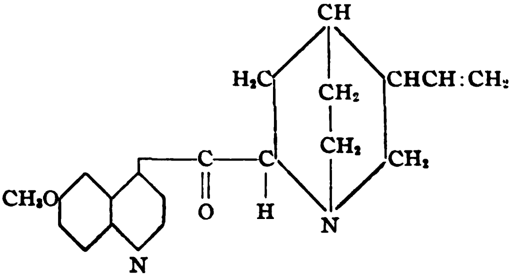


While several of these modified alkaloids have been prepared and studied chemically by Koenigs[1] and Rabe[2] and their co-workers, we are unaware of any previous publications on the desoxy compounds of dihydro-quinine and dihydro-quinidine or their immediate derivatives.

In reporting this work we have adopted a slight modification of the terminology hitherto used in this series, a modification which we believe will avoid the use of unwieldy combinations and take care of any further expansion in this field. Using as a basis Koenigs' adoption of the term "quinene" for



and Rabe's use of the term "quininone" for



we have employed the suffix "-ane" to indicate "desoxy-." "Desoxy-quinine" and its stereoisomer would then become "quinane" and "quinidane," while the awkward dihydro-desoxy-quinine and dihydro-desoxy-

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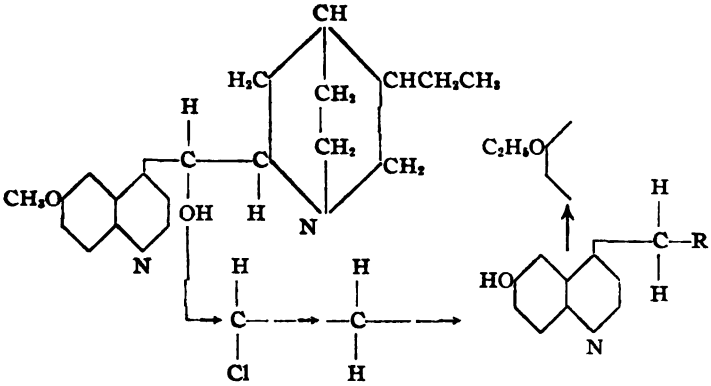
[1] Koenigs, *Ber.*, 28, 3147 (1895); 29, 372 (1896).

[2] Rabe, *Ann.*, 373, 107 (1910).

quinidine become dihydro-quinane and dihydro-quinidane. Similarly, the terms "cinchonane" and "dihydro-cupreane" seem preferable to desoxy-cinchonine and dihydro-desoxy-cupreine.

Adopting this terminology then, the following series was studied, dihydro-quinine ⟶ chloro-dihydro-quinine ⟶ dihydro-quinane ⟶ dihydro-cupreane ⟶ ethyl-dihydro-cupreane; or, graphically.



While it would no doubt have been possible to complete the corresponding series starting with the dextrorotatory dihydro-quinidine, we have carried our chemical studies with the entire group only as far as was necessary to establish the fact that these compounds are less bactericidal for the pneumococcus than the corresponding parent alkaloids.

The methods used for the preparation of the chloro- compounds and the "quinanes" were essentially those employed by Koenigs and Rabe for the corresponding non-hydrogenated derivatives, with the exception that the "quinanes" were isolated directly from the reaction mixture as the picrates. The demethylation of dihydro-quinane and dihydro-quinidane was accomplished by boiling with hydrobromic acid (sp. gr. 1.49).[1]

With the exception of ethyl-dihydro-cupreane all of the new bases crystallized fairly readily, and were further characterized by the preparation of crystalline mono-acid and di-acid salts. Dihydro-quinane and its stereoisomer could be crystallized, however, only in the form of hydrates, a property already noted by Koenigs in the case of quinane and quinidane. The 2 phenolic alkaloids, dihydro-cupreane and dihydro-cupreidane showed themselves entirely analogous in their properties to dihydro-cupreine and dihydro-cupreidine.

A. Derivatives of Dihydro-Quinine.

Chloro-dihydro-quinine.—133 g. of anhydrous dihydro-quinine dihydrochloride were worked up into a smooth, thin paste with dry chloroform and poured into a suspension of 200 g. of phosphorus pentachloride

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[1] Cf. This Journal, 41, 821 (1919).

in dry chloroform, checking the first evolution of heat by immersion in a freezing mixture. A voluminous, pale yellow precipitate formed, and there was a steady evolution of hydrogen chloride as the mixture came up to room temperature. During the next 4 or 5 days the mixture was heated in a water bath at 45–55° with frequent shaking, and was then cooled and treated with ice until no further evolution of heat was apparent. The base was precipitated from the aqueous layer by means of sodium hydroxide, taken up with ether, dried over sodium sulfate, and the solvent distilled off. The crystalline residue was taken up in boiling benzene and the solution treated with several volumes of ligroin (b. p. 80–90°), the chloro-dihydro-quinine separating on seeding as cream-colored rhombs. The yield was 67 g. Recrystallized first from dil. alcohol, then from ligroin, it forms large rhombic aggregates which melt slowly at 143–4° with slight preliminary softening. The substance dissolves readily in alcohol, acetone, chloroform, or benzene, less readily in ether, and is very sparingly soluble in cold ligroin but fairly readily so at the boiling point. It gives a pale yellow, non-fluorescent solution in dil. sulfuric acid. $[\alpha]_D^{21.5}$ is +42.1° in absolute alcohol; $c = 1.365$.

Subs., 0.1869: 13.4 cc. N (22.0°, 757 mm.).
Subs., 0.1534: (Carius) AgCl, 0.0635.
Calc. for $C_{20}H_{25}ON_2Cl$: N, 8.13; Cl, 10.28. Found: N, 8.27; Cl, 10.24.

The Hydrochloride.—A solution of the base in dil. hydrochloric acid was neutralized to litmus and treated with sodium chloride until the initial turbidity just redissolved on shaking. The salt gradually separated, and was recrystallized from 50% alcohol, separating on seeding and letting stand in the ice-box as aggregates of narrow plates which are anhydrous and dissolve rather sparingly in cold water or alcohol, more easily on heating. The aqueous solution is colorless, but turns a pale yellow when excess acid is added. The hydrochloride begins to darken and decomposes at 230°, melting with decomposition at 232–3°. $[\alpha]_D^{20.5}$ is —2.9° in water; $c = 1.197$.

Subs., 0.1387: 8.8 cc. N (20.0°, 760 mm.).
Subs., 0.1700: 8.89 cc. $AgNO_3$ sol. (1 cc. = 0.001794 g. Cl).
Calc. for $C_{20}H_{25}ON_2Cl.HCl$: N, 7.35; Cl^-, 9.31. Found: N, 7.40; Cl^-, 9.38.

Dihydro-quinane (Dihydro-desoxy-quinine). — Chloro-dihydro-quinine was reduced with iron filings and dil. sulfuric acid according to the method of Rabe *et al.*[1] for the formation of similar desoxy compounds. Instead of extracting the base from the dried precipitate of iron hydroxides, we found it less time-consuming to filter, dilute the solution with an equal volume of water, and precipitate the alkaloid with an excess of 4% sodium picrate solution, making sure that the reaction remained acid to Congo red. The picrate, which filters readily, was washed with 1%

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[1] *Ann.*, 373, 107 (1910).

sulfuric acid, ground to a thin paste with water, the mixture diluted, and then made strongly alkaline with sodium hydroxide. The base was shaken out with ether, the latter dried over sodium hydroxide, and concentrated. The residue, taken up in acetone and precipitated with water, crystallized on rubbing, owing to the formation of the *trihydrate*, the yield being 85% of the amount of chloro compound used. Recrystallized twice by dissolving in acetone, diluting with water to incipient turbidity, and rubbing, the trihydrate separated as silky needles which were brought to equilibrium for analysis in a desiccator containing only a beaker of water. When exposed to the air the crystals gradually lose their water, forming the oily, anhydrous base which could not be crystallized from dry solvents. The trihydrate dissolves readily in the usual organic solvents. A solution in dil. sulfuric acid shows a strong bluish fluorescence and is also relatively stable to permanganate. The base also gives a typical thalleoquinine test. $[\alpha]^{24}_{\mathrm{D}}$ of the trihydrate is —77.5° in absolute alcohol; $c = 1.244$.

Subs., 0.4048: loss, 0.0606 *in vacuo* at 100° over H_2SO_4.

Subs., 0.1142: CO_2, 0.2761; H, 0.0889.

Subs., 0.1181: 8.4 cc. N (23.0°, 764 mm.).

Subs., 0.1613: (Kjeldahl) 12.45 cc. 0.0714 *N* HCl.

Calc. for $C_{20}H_{26}ON_2.3H_2O$: C, 65.88; H, 8.86; N, 7.69; H_2O, 14.83. Found: C, 65.94; H, 8.71; N, 8.25; 7.72, H_2O, 14.97.

The Hydrochloride.—Dihydro-quinane was neutralized in alcoholic solution with hydrochloric acid, concentrated to dryness *in vacuo*, and the residue again taken down to dryness *in vacuo* after the addition of absolute alcohol. On adding dry acetone the salt soon crystallized as delicate needles which are anhydrous when air dried and melt at 179–80°. $[\alpha[^{22.5}_{\mathrm{D}}$ is —6.8° in water; $c = 1.034$. It dissolves readily in water, alcohol, chloroform, or methyl alcohol, and only difficultly in the cold in dry acetone or benzene, more easily on warming.

Subs., 0.1237: 9.0 cc. N (22.5°, 753 mm.).

Subs., 0.1293: 7.40 cc. $AgNO_3$ sol. (1 cc. = 0.00176 g. Cl).

Calc. for $C_{20}H_{26}ON_2.HCl$: N, 8.08; Cl, 10.22. Found: N, 8.33; Cl, 10.07.

The Dihydrochloride.—The base was treated with a slight excess of absolute alcoholic hydrochloric acid and then with dry acetone to initial turbidity. The salt crystallized on seeding with a test portion which was precipitated with dry acetone, decanted off, and let stand under dry acetone. Recrystallized by dissolving in absolute alcohol, adding a few drops of dry alcoholic hydrochloric acid, then about two volumes of dry acetone, followed by dry ether to incipient turbidity, the salt separated on seeding as faintly yellow, radiating masses of hair-like, felted needles which come to equilibrium in the air with solvent equivalent to 1.5 molecules of water of crystallization. When rapidly heated to 155°, then slowly, the salt softens to a jelly at 158–62°, gradually swelling and evolving gas, and becoming entirely fluid at about 210°. It dissolves readily in alcohol or chloroform, and very easily in water, yielding a non-fluorescent solution. When treated with a slight excess of hydrobromic acid (sp. gr. 1.49), then with acetone to incipient turbidity, a dihydrobromide separates on standing as long, delicate needles.

Air dry: Subs., 0.5360: loss, 0.0380 *in vacuo* at room temp. over H_2SO_4.
Calc. for $C_{20}H_{26}ON_2.2HCl. 1.5H_2O$: H_2O, 6.59. Found: 7.09.
Anhydrous: Subs., 0.1241: 8.05 cc. N (24.0°, 753 mm.).
Subs., 0.1232: 12.95 cc. $AgNO_3$ sol. (1 cc. = 0.00176 g. Cl).
Calc. for $C_{20}H_{26}ON_2.2HCl$: N, 7.31; Cl, 18.50. Found: N, 7.39; Cl, 18.50.

Dihydro-quinane Methiodide.—After several hours the solution of the components in dry acetone was diluted with water, the salt separating slowly on rubbing and letting the solution stand. Recrystallized from 25% alcohol it separates on seeding as faintly yellow, glistening platelets and prisms which contain one molecule of water of crystallization and dissolve with difficulty in cold water and very easily on boiling. The anhydrous substance begins to sinter above 110°, forms a pale yellow jelly at 119–24°, and is completely fluid at about 145°. $[\alpha]_D^{21}$ is —7.4° in absolute alcohol; $c = 1.145$. It dissolves very easily in dry chloroform, somewhat less readily in dry methyl or ethyl alcohol, and is almost insoluble in dry acetone.

Air dry: Subs., 0.7350: loss, 0.0286 *in vacuo* at 100° over H_2SO_4.
Calc. for $C_{21}H_{29}ON_2I.H_2O$: H_2O, 3.83. Found: 3.89.
Anhydrous: Subs., 0.1486: 8.1 cc. N (23.5°, 762 mm.).
Subs., 0.1104: 4.85 cc. $AgNO_3$ sol. (1 cc. = 0.00642 g. I).
Calc. for $C_{21}H_{29}ON_2I$: N, 6.20; I, 28.07. Found: N, 6.29; I, 28.22.

Dihydro-cupreane (Dihydro-desoxy-cupreine).—25 g. of dihydroquinane trihydrate were boiled with 100 cc. of hydrobromic acid (sp. gr. 1.49) until the temperature reached 125°, after which an air condenser was attached and the boiling continued for 3 hours.[1] The solution was then concentrated *in vacuo*, taken up in about 1.5 liters of water, and treated with 10% sodium hydroxide solution until all but a little gummy material had dissolved. This was redissolved in dil. hydrochloric acid and again made alkaline with sodium hydroxide, whereupon it all redissolved. The combined solutions were treated with boneblack and filtered to remove an almost negligible turbidity, and the filtrate treated with ammonium chloride solution. The resulting precipitate, and an additional portion obtained by shaking out the filtrate with chloroform, were dried and boiled with dry acetone, crystallization soon being complete. The yield was 15.8 g. Recrystallized from ethyl acetate, it separates on seeding as minute, delicate needles which melt at 191–1.5° to a yellow liquid filled with bubbles. It is very slightly soluble, with a faint yellow color, in boiling water, but dissolves readily in methyl or ethyl alcohol, or chloro-

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[1] *Loc. cit.*

form. It is sparingly soluble in cold benzene, but dissolves on warming. The base separates from methyl ethyl ketone as crusts of minute, thin, narrow platelets. $[\alpha]_D^{21}$ is —77.1° in absolute alcohol; $c = 0.973$. Like dihydro-cupreine and dihydro-cupreidine[1] it couples readily in alkaline solution with diazotized aromatic amines and does not give the thalleo-quinine reaction.

Subs., 0.1123: CO_2, 0.3165; H_2O, 0.0800.

Subs., 0.1175: 10.0 cc. N (28.0°, 748 mm.).

Calc. for $C_{19}H_{24}ON_2$: C, 76.97; H, 8.17; N, 9.46. Found: C, 76.86; H, 7.97; N, 9.50.

The Hydrochloride.—Dihydro-cupreane was dissolved in a little absolute alcohol and neutralized to wet litmus with absolute alcoholic hydrochloric acid. The salt soon crystallizes if water has been excluded. Recrystallized from absolute alcohol, filtering the cooled solution from a slight turbidity, it separates on standing in the cold as thin, glistening platelets which melt at about 210° with slight decomposition. $[\alpha]_D^{23} = +1.5°$ in water, $c = 0.999$. It dissolves readily in water with a greenish yellow color, the solution giving a brown color with ferric chloride and becoming almost colorless with an excess of hydrochloric acid. It also dissolves readily in dry methyl alcohol without color, changing to yellow on adding water. It is very difficultly soluble in boiling dry acetone or chloroform.

Subs., 0.1229: 9.1 cc. N (26.0°, 764 mm.).

Subs., 0.1227: 7.4 cc. $AgNO_3$ sol. (1 cc. = 0.00176 g. Cl).

Calc. for $C_{19}H_{24}ON_2.HCl$: N, 8.42; Cl, 10.66. Found: N, 8.50; Cl, 10.62.

The Dihydrobromide.—In another preparation of dihydro-cupreane the hydrobromic acid solution was concentrated as far as possible *in vacuo*, finally in a boiling water bath, taken up in a small volume of absolute alcohol, and allowed to stand overnight in the cold. The crude salt was recrystallized from 20% aqueous hydrobromic acid, after seeding with a test portion. It forms delicate, radiating needles which contain one molecule of water of crystallization and dissolve readily in water. The anhydrous salt slowly liquefies to a yellow fluid filled with bubbles at 225–7°. It dissolves in dry methyl alcohol, less readily in absolute alcohol, and very difficultly in boiling dry acetone or chloroform.

Air dry: Subs., 0.7651: loss, 0.0266 *in vacuo* at room temp. over H_2SO_4.

Calc. for $C_{19}H_{24}ON_2.2HBr.H_2O$: H_2O, 3.78. Found: 3.48.

Subs., 0.1239: 10.85 cc. $AgNO_3$ sol. (1 cc. = 0.00396 g. Br).

Calc. for $C_{19}H_{24}ON_2.2HBr$: Br, 34.89. Found: 34.70.

Dihydro-cupreane Methiodide.—The salt separated from chloroform solution. Recrystallized twice from absolute alcohol it forms thin, nacreous, faintly yellow platelets which dissolve in the cold in water, 50% alcohol, or methyl alcohol, and only sparingly in absolute alcohol but more

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[1] Cf. This Journal, 41, 827 (1919).

easily on boiling. It is difficultly soluble in boiling dry acetone, chloroform, or benzene. $[\alpha]_D^{22}$ is —37.6° in 50% alcohol, c = 1.050. When rapidly heated to 160°, then slowly, it melts to a jelly at 160–5° and becomes completely fluid at 165–7°.

Subs., 0.1452: AgI, 0.0766.
Calc. for $C_{20}H_{27}ON_2I$: I, 28.97. Found: 28.52.

Ethyl-dihydro-cupreane (Dihydro-cupreane Ethyl Ether) Hydrochloride.—Equimolecular amounts of dihydro-cupreane, 50% aqueous potassium hydroxide, and washed diethyl sulfate were allowed to stand in the cold in absolute alcoholic solution for 10 days.[1] The mixture was then treated with water and sodium hydroxide, shaken out with ether, and this dried over potassium hydroxide and concentrated. As the free base showed no tendency to crystallize it was neutralized to wet litmus with absolute alcoholic hydrochloric acid, treated with several volumes of dry ether, and seeded with crystals obtained from a similar test portion on long standing. The hydrochloride forms delicate needles which melt at 185–6° and dissolve readily in water, methyl or ethyl alcohol, acetone, or chloroform. The yield was poor. $[\alpha]_D^{23}$ is —9.0° in water, c = 0.722. It gives the thalleoquinine test, and fluorences strongly in aqueous solution on addition of a drop of dil. sulfuric acid.

Subs., 0.1193: 8.4 cc. N (22.5°, 753 mm.).
Subs., 0.1158: 6.28 cc. $AgNO_3$ sol. (1 cc. = 0.00176 g. Cl).
Calc. for $C_{21}H_{28}ON_2.HCl$: N, 7.77; Cl, 9.83. Found: N, 8.06; Cl, 9.55.

Bromo-dihydro-cupreine Dihydrobromide.—8 g. of chloro-dihydroquinine were demethylated in the same way as was dihydro-quinane. During the concentration of the hydrobromic acid solution *in vacuo* the dihydrobromide crystallized and was filtered off after cooling and the concentration continued, an additional amount being obtained from the residue on taking up in water and seeding. The total yield was 10.6 g. Recrystallized from water containing a little hydrobromic acid it separates as glistening, cream-colored plates containing one molecule of water of crystallization. Analysis showed that the chlorine of the chloro-dihydro quinine had been substituted by bromine. The salt dissolves in water with a pale yellow color, and after neutralization with sodium hydroxide gives a pale brown color with ferric chloride. $[\alpha]_D^{24}$ of the anhydrous salt is —69.1° in water, c = 1.005. When rapidly heated to 195°, then slowly, the yellowish anhydrous salt turns a deeper yellow and melts with gas evolution at 196–7°. It is soluble in absolute alcohol, especially on warming, and is almost insoluble in boiling dry acetone or chloroform.

Air dry: Subs., 0.5990: loss, 0.0201 *in vacuo* at room temp. over H_2SO_4.
Calc. for $C_{19}H_{23}ON_2Br.2HBr.H_2O$: H_2O, 3.25. Found: 3.36.
Anhydrous: Subs., 0.1367: 6.6 cc. N (26.0°, 752 mm.).
Subs., 0.1423: 10.71 cc. $AgNO_3$ sol. (1 cc. = 0.00396 g. Br).
Calc. for $C_{19}H_{23}ON_2Br.2HBr$: N, 5.22; Br^-, 29.76. Found: N, 5.45; Br^-, 29.81.

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[1] Cf. Ger. pat 254,712; THIS JOURNAL, 41, 830 (1919).

The free base was found to be quite unstable. It is precipitated from aqueous solution by sodium carbonate or bicarbonate as pale yellow, amorphous flocks, but on extracting with chloroform red decomposition products are rapidly formed, and while crystals could be obtained by taking up in dry acetone the residue from the evaporation of the chloroform *in vacuo*, satisfactory analytical values could not be realized. It was also noted that the product contained ionizable halogen. Solution of the dihydrobromide in excess alkali resulted in the rapid development of an orange color, and the base recovered on adding ammonium chloride was found to be halogen-free.

B. Derivatives of Dihydro-quinidine.

Chloro-dihydro-quinidine.—133 g. of dihydro-quinidine dihydrochloride (anhydrous) were dissolved in about 10 volumes of dry chloroform and converted into chloro-dihydro-quinidine exactly as in the case of the dihydro-quinine derivative. The crude base was dissolved in several volumes of hot ligroin, filtered with the aid of boneblack from a small amount of insoluble material, and seeded while still warm with crystals obtained by dissolving a test portion in ligroin and letting stand. 44.6 g. of the crystalline base were obtained by keeping the solution warm until most of the base had crystallized and then allowing to cool slowly to room temperature. The filtrate was treated with absolute alcohol and neutralized to litmus with alcoholic hydrochloric acid, an additional 21 g. of the hydrochloride separating in this way as delicate, voluminous needles. Recrystallized twice from ligroin as above, the base forms hard, compact, cream-colored aggregates of minute plates which melt at 93.5–5° with preliminary softening and show $[\alpha]_D^{22}$ +20.0° in absolute alcohol, $c = 0.600$. It gives the thalleoquinine reaction and is very easily soluble in alcohol, acetone, chloroform, benzene, or ether.

Subs., 0.1280: 9.4 cc. N (24.0°, 770 mm.).
Subs., 0.1742: (Carius) AgCl, 0.0717.
Calc. for $C_{20}H_{25}ON_2Cl$: N, 8.13; Cl, 10.28. Found: N, 8.55; Cl, 10.18.

The Hydrochloride.—The base was dissolved in a little absolute alcohol and neutralized to wet litmus with dry alcoholic hydrochloric acid. The salt which separated was recrystallized from absolute alcohol, forming sheaves and rosets of delicate needles. After drying *in vacuo* $[\alpha]_D^{25}$ was +39.7° in water; $c = 0.795$. The salt turns yellow and softens above 205° and blackens and melts at 208–9°. It is quite soluble in cold water and dissolves readily in dry methyl alcohol, less easily in dry alcohol or chloroform, and only with difficulty in boiling dry acetone.

Subs., 0.1191: 6.25 cc. $AgNO_3$ sol. (1 cc. = 0.00176 g. Cl).
Calc. for $C_{20}H_{25}ON_2Cl.HCl$: Cl^-, 9.31. Found: 9.24.

Dihydro-quinidane (Dihydro-desoxy-quinidine).—40 g. of chlorodihydro-quinidine were reduced to dihydro-quinidane and isolated exactly as in the case of the corresponding quinine derivatives. The oily base was dissolved in alcohol, diluted with water to incipient turbidity, and seeded with crystals obtained from a test portion dissolved in a little ligroin and allowed to evaporate spontaneously. The dihydrate separated as glistening rhombs, the amount being increased by the cautious addition of small quantities of water. The yield was 28.7 g. Recrystallized twice from 60% alcohol the dihydrate separates as rhombs and prisms which show $[\alpha]_D^{22.5} = +167.3°$ in absolute alcohol, $c = 1.124$, and melt at 81–3° with marked preliminary softening to a turbid liquid which clears at 88°. It dissolves readily in alcohol, acetone, chloroform, or benzene, less easily in ether, exhibits a marked purplish fluorescence in dil. sulfuric acid solution, and gives the thalleoquinine test. The anhydrous alkaloid melts at 68.5–70° with preliminary softening.

Air dry: Subs., 0.4798: loss, 0.0496 *in vacuo* at room temp. over H_2SO_4.
Subs., 0.1242: CO_2, 0.3159; H_2O, 0.0980.
Subs., 0.1255: 9.6 cc. N (23.0°, 760 mm.).
Subs., 0.1554: (Kjeldahl) 9.05 cc. 0.1 N HCl.
Calc. for $C_{20}H_{28}ON_2.2H_2O$: C, 69.31; H, 8.73; N, 8.09; H_2O, 10.40. Found: C, 69.37; H, 8.83; N, 8.82, 8.17; H_2O, 10.33.

The Hydrobromide.—The dihydrate was suspended in a little 50% alcohol and neutralized hot with 40% aqueous hydrobromic acid. The salt separated on chilling and rubbing and was recrystallized twice from 50% alcohol, separating as prismatic needles containing one molecule of water of crystallization, dissolving rather sparingly in cold water but readily in cold alcohol, and showing $[\alpha]_D^{24} = +64.5°$ in water, $c = 1.063$. The anhydrous salt melts slowly at 151–2° with very slight gas evolution and dissolves readily in methyl or ethyl alcohol, acetone, or chloroform and difficultly in cold benzene but easily on warming.

Subs., 0.4948: loss, 0.0222 *in vacuo* at 80° over H_2SO_4.
Calc. for $C_{20}H_{26}ON_2.HBr.H_2O$: H_2O, 4.40. Found: 4.49.
Anhydrous: Subs., 0.1177: 7.5 cc. N (26.0°, 756 mm.).
Subs., 0.1048: 5.45 cc. $AgNO_3$ sol. (1 cc. = 0.00396 g. Br).
Calc. for $C_{20}H_{26}ON_2.HBr$: N, 7.16; Br, 20.42. Found: N, 7.24; Br, 20.59.

The Dihydrobromide.—Dihydro-quinidane dihydrate was dissolved in absolute alcohol and treated with hydrobromic acid (sp. gr. 1.49) until acid to wet Congo red paper. Dry ether was then added to incipient turbidity and the solution seeded with crystals obtained by precipitating a test portion with dry ether and taking up the product in dry acetone. The collected salt was suspended in a little boiling absolute alcohol containing a few drops of hydrobromic acid and treated on the water bath with small portions of 95% alcohol until clear. The dihydrobromide separated slowly on cooling and seeding as faintly yellow, glistening rhombs which were white when powdered and contained no solvent of crystallization. It begins to turn yellow above 180°, softens at about

210°, and is completely fluid, with slow gas evolution, at about 225°. The salt dissolves readily in water and very difficultly in boiling dry acetone or chloroform.

Subs., 0.1051: 8.91 cc. $AgNO_3$ sol. (1 cc. = 0.00396 g. Br).
Calc. for $C_{20}H_{26}ON_2.2HBr$: Br, 33.86. Found: 33.59.

Dihydro-quinidane Methiodide.—The salt separates in quantitative yield from a solution of the components in dry acetone. Recrystallized twice from absolute alcohol it forms faintly yellow, warty masses of short needles which dissolve appreciably in cold water, readily on heating. When rapidly heated to 160°, then slowly, it melts at 163–4° with slight preliminary softening to a yellow liquid. It dissolves readily in methyl alcohol or chloroform.

Subs., 0.1020: 4.47 cc. $AgNO_3$ sol. (1 cc. = 0.00629 g. I).
Calc. for $C_{21}H_{29}ON_2I$: I, 28.07. Found: 27.57.

Dihydro-cupreidane (Dihydro-desoxy-cupreidine).—25 g. of dihydroquinidane were demethylated as in the case of the quinine analog. The residue from the concentration *in vacuo* crystallized on standing overnight, and was dissolved in much water, the solution made alkaline and then treated with saturated ammonium chloride solution. The gummy alkaloid was filtered off, dried, and combined with a further amount obtained by extracting the filtrate with ether. A crystalline product was rapidly formed on rubbing with dry acetone, the yield being 16.1 g. after washing with dry acetone. Recrystallized from toluene, in which it is quite soluble at the boiling point, but sparingly so at even a few degrees less, it forms a crust of cream-colored rosets of microcrystals which melt slowly at 183–3.5° to a straw-colored liquid. $[\alpha]_D^{24}$ is +183.7° in absolute alcohol, $c = 0.991$. It dissolves readily in methyl or ethyl alcohol or chloroform, and very difficultly in boiling benzene. In its chemical reactions it behaves like its stereoisomer, dihydrocupreane.

Subs., 0.1033: CO_2, 0.2912; H_2O, 0.0762.
Subs., 0.1428: 11.75 cc. N (23.5°, 764 mm.).
Calc. for $C_{19}H_{24}ON_2$: C, 76.97; H, 8.17; N, 9.46. Found: C, 76.88; H, 8.25; N, 9.52.

The Hydrochloride.—The base was dissolved in a slight excess of *N* hydrochloric acid, neutralized, and the solution treated with saturated sodium chloride solution. It soon solidified, and the collected salt was recrystallized from water, separating on seeding as short, slightly brownish, glistening needles which contain 2 molecules of water of crystallization when air dry, but appear to separate with more water, as the air dry salt first dissolves freely in water and then quickly crystallizes again. The solution gives a brownish color with ferric chloride. The anhydrous salt gradually softens to a jelly at 125–45°, and forms a yellow fluid at about 200°. It dissolves readily in dry methyl or ethyl alcohol or chloroform, the colorless solutions in the first two turning yellow on adding water. $[\alpha]_D^{22}$ of the anhydrous salt is +76.8° in water, $c = 0.436$.

Air dry: Subs., 0.5424: loss, 0.0547 *in vacuo* at 100° over H_2SO_4.
Calc. for $C_{19}H_{24}ON_2.HCl.2H_2O$: H_2O, 9.77. Found: 10.08.
Anhydrous: Subs., 0.1244: 9.2 cc. N (22.5°, 763 mm.).
Subs., 0.1530: 9.18 cc. $AgNO_3$ sol. (1 cc. = 0.00176 g. Cl).
Calc. for $C_{19}H_{24}ON_2.HCl$: N, 8.42; Cl. 10.66. Found: N, 8.57; Cl, 10.56.

The Dihydrobromide.—The salt separates from a small volume of chilled, dil. hydrobromic acid as faintly yellow aggregates of hexagonal plates containing 2 molecules of water of crystallization and dissolving quite readily in water at room temperature, less easily at 0°. The anhydrous salt softens and turns yellow above 140°, forming a jelly by the time 175° is reached and becoming completely fluid at about 205°. It forms a gum under dry methyl or ethyl alcohol, dissolving on shaking, and also gums under dry chloroform but does not dissolve completely.

Air dry: Subs., 0.5211: loss, 0.0414 *in vacuo* at room temp. over H_2SO_4.
Calc. for $C_{19}H_{24}ON_2.2HBr.2H_2O$: H_2O, 7.29. Found: 7.95.
Anhydrous: Subs., 0.1225: 10.68 cc. $AgNO_3$ sol. (1 cc. = 0.00396 g. Br).
Calc. for $C_{19}H_{24}ON_2.2HBr$: Br, 34.89. Found: 34.54.

Dihydrocupreidane Methiodide.—The salt soon separated from a solution of the components in absolute alcohol. Recrystallized from 25% alcohol it forms short, slightly brownish, prismatic rods which contain no water of crystallization and are difficultly soluble in cold water but readily on heating. It is quite soluble in methyl alcohol or 50% alcohol and almost insoluble in boiling dry acetone or chloroform. $[\alpha]_D^{23}$ is +95.0° in 50% alcohol, $c = 1.105$.

Subs., 0.1369: 6.25 cc. $AgNO_3$ sol. (1 cc. = 0.00629 g. I).
Calc. for $C_{20}H_{27}ON_2I$: I, 28.97. Found: 28.71.

Bromo-dihydro-cupreidine Dihydrobromide.—Chloro-dihydro-quinidine hydrochloride was demethylated as in the case of chloro-dihydro-quinine. In less than 2 hours the dihydrobromide separated from the boiling solution and the mixture was accordingly cooled and the salt filtered off, an additional amount being recovered on concentrating the filtrate to small bulk. Recrystallized from water containing a little hydrobromic acid it separates as sheaves of pale yellow, delicate needles which are anhydrous and decompose at about 255–6° with slight preliminary softening and darkening. $[\alpha]_D^{24}$ is —47.7° in water, $c = 1.141$. A neutralized aqueous solution gives a brown color with ferric chloride. The salt is sparingly soluble in boiling absolute alcohol, but dissolves somewhat more readily in boiling dry methyl alcohol, and behaves in the same way as its stereoisomer with carbonates and alkalies, the free base being equally unstable.

Subs., 0.1620: 7.40 cc. N (23.0°, 755 mm.).
Subs., 0.1200: 9.0 cc. $AgNO_3$ sol. (1 cc. = 0.00396 g. Br).
Calc. for $C_{19}H_{23}ON_2Br.2HBr$: N, 5.22; Br^-, 29.76. Found: N, 5.23; Br^-, 29.70.

If a warm, fairly concentrated solution in water is nearly neutralized with sodium hydroxide, the monohydrobromide separates on rubbing as diamond shaped, microscopic platelets.

C. Derivatives of Quinidine.

Chloroquinidine Hydrochloride.—Chloroquinidine, prepared essentially according to Comstock and Koenigs,[1] was neutralized in dil. alcohol with hydrochloric acid. The solution, after boiling with boneblack and filtering, was concentrated to dryness *in vacuo* and the residue taken up in boiling absolute alcohol. The hydrochloride was deposited on cooling and was recrystallized from absolute alcohol, with the addition of a little dry ether to the cooled solution. The salt forms woolly, cream-colored needles which show $[\alpha]_D^{25} = +47.7°$ in water, $c = 1.017$. When rapidly heated to 195°, then slowly, it gradually melts and decomposes from 199–206°. It dissolves readily in water with a faint yellow color, and also dissolves easily in dry methyl alcohol, less readily in dry chloroform, and is practically insoluble in dry acetone.

Subs., 0.1278: 8.4 cc. N (29.0°, 752 mm.).
Subs., 0.1216: 6.26 cc. $AgNO_3$ sol. (1 cc. = 0.00181 g. Cl).
Calc. for $C_{20}H_{23}ON_2Cl.HCl$: N, 7.39; Cl^-, 9.35. Found: N, 7.35; Cl^-, 9.33.

Quinidane (Desoxy-quinidine) Hydrochloride.—Quinidane (desoxyquinidine[2]) was dissolved in a little absolute alcohol, treated with a molecular equivalent of conc. hydrochloric acid, and then with 6–8 volumes of dry ether. The hydrochloride crystallized on rubbing, and was dissolved in warm 95% alcohol, and the solution treated with 6–8 volumes of dry ether and filtered rapidly from the slight precipitate which carried considerable colored impurity with it. The salt separated slowly on seeding as aggregates of minute crystals which retained solvent equivalent to one molecule of water of crystallization on air drying. The anhydrous salt shows $[\alpha]_D^{30} = +81.9°$ in water $c = 1.313°$, and sinters and gradually melts above 125°, forming a yellow liquid at about 145°. It dissolves readily in water, methyl or ethyl alcohol, or chloroform, sparingly in cold, dry acetone, although fairly easily on boiling, and is very difficultly soluble in boiling benzene.

Air dry: Subs., 0.6065: loss, 0.0322 *in vacuo* at 80° over H_2SO_4.
Calc. for $C_{20}H_{24}ON_2.HCl.H_2O$: H_2O, 4.97. Found: 5.31.
Anhydrous: Subs., 0.1575: 11.4 cc. N (25.5°, 759 mm.).
Subs., 0.1196: 6.96 cc. $AgNO_3$ sol. (1 cc. = 0.00181 g. Cl).
Calc. for $C_{20}H_{24}ON_2.HCl$: N, 8.13; Cl, 10.28. Found: N, 8.27; Cl, 10.54.

Quinene Dihydrochloride.—Crude quinene, prepared and isolated according to Comstock and Koenigs,[3] was dissolved in absolute alcohol, treated with an excess of absolute alcoholic hydrochloric acid, and the

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[1] *Ber.*, 18, 1223 (1885).

[2] Koenigs, *Ber.*, 28, 3147 (1895); Rabe, *et al.*, *Ann.*, 373, 107 (1910).

[3] *Ber.*, 17, 1988 (1884).

dihydrochloride precipitated with dry ether. Recrystallized from absolute alcohol it forms sheaves and rosets of delicate, lemon-yellow needles which retain solvent equivalent to one molecule of water of crystallization when air-dry. The anhydrous salt shows $[\alpha]_D^{24.5} = +18.4°$ in water, $c = 1.060$, and gradually sinters and darkens when heated, melting to a dark red-brown liquid at 180–5°. It dissolves readily in water or methyl alcohol, less easily in absolute alcohol or dry chloroform, and is practically insoluble in dry acetone.

Air dry: Subs., 0.6382: loss, 0.0267 *in vacuo* at room temperature over H_2SO_4.
Calc. for $C_{20}H_{22}ON_2.2HCl.H_2O$: H_2O, 4.54. Found: 4.18.
Anhydrous: Subs., 0.1329: 8.8 cc. N (25.0°, 756 mm.).
Subs., 0.1297: 13.85 cc. $AgNO_3$ sol. (1 cc. = 0.00176 g. Cl).
Calc. for $C_{20}H_{22}ON_2.2HCl$: N, 7.39; Cl, 18.69. Found: N, 7.55; Cl, 18.81.

Summary.

The so-called "desoxy" derivatives of dihydro-quinine and dihydro-quinidine are described, together with certain of their salts, homologs, and the alkaloidal derivatives encountered in their preparation. It is proposed that the substitution of the suffix "ane" for the prefix "desoxy" would simplify the terminology of this group of substances. The series dihydro-quinine ⟶ chlorodihydro-quinine ⟶ dihydro-quinane ⟶ dihydro-cupreane ⟶ ethyl-dihydro-cupreane, resulting in the preparation of an analog of ethyl-dihydro-cupreine (optochin) was prepared and studied.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PARKE, DAVIS AND CO.]

DERIVATIVES OF TRIHALOGEN TERTIARY-BUTYL ALCOHOLS.

III. THE BENZOIC ACID ESTER OF TRICHLORO-TERTIARY-BUTYL ALCOHOL OR CHLORETONE BENZOIC ACID ESTER.

BY T. B. ALDRICH.

Received May 12, 1920.

Under the title, "Benzoyloxyisobuttersäure trichlorid," Willgerodt and Dürr[1] have described an oil which they obtained through the interaction of trichloro-tertiary-butyl alcohol on benzoyl chloride in molecular quantities. They state

> "On heating the mixture there is a rapid evolution of hydrochloric acid gas. The liquid, boiling at 270–290°, obtained by fractionation is then dissolved in ether and shaken with an aqueous solution of sodium carbonate. After drying the ethereal solution, the ether is evaporated, and the yellowish oil remaining is distilled. The principal part of the ester distils between 275–280°, but on standing in the receptacle deposits crystals of benzoic acid which are removed by filtration. The oil thus obtained and further purified has finally a B. P. of 282° and is yellow in color. Chlorine determination: Theoretical 37.8%. Found 37.6%."

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[1] Willgerodt and Dürr, *J. prakt. Chem. N. F.*, 39, 286 (1889).

Having prepared a number of esters of trichloro- and tribromo-tertiary-butyl alcohol acetyl chloretone,[1] acetyl brometone,[2] propionic and butyric esters of brometone[3], and having obtained a *crystalline* benzoic ester of brometone (this work is unpublished) it occurred to me to repeat the work of Willgerodt and Dürr, especially since they reported their product as an oil, and compare it chemically, physically and pharmacologically with the other esters and especially with the corresponding benzoic acid ester of tribromo-tertiary-butyl alcohol. The product I obtained by carrying out this synthesis, differs so markedly from that obtained by the authors cited that I consider it imperative to publish the results of my investigation.

In carrying out the synthesis according to the very brief directions given at the beginning of this paper by Willgerodt and Dürr, the author finds that, during distillation under ordinary pressure, decomposition products are formed, consisting in part of benzoic acid, which may be recognized by its general appearance, solubility, odor, melting point, etc. Hydrogen chloride is also given off when the temperature is high. No doubt the product obtained by Willgerodt and Dürr is a mixture of benzoic acid, a small amount of the ester, the principal portion having been decomposed by the high temperature, and possibly some chloretone and other substances such as chlorine decomposition products. That benzoic acid is present is evidenced by the authors themselves who state "the distillate deposits crystals of benzoic acid on standing." Indeed the method employed by the authors for purification would naturally lead to a mixture of various products rather than to a single product, since no attempt was made to remove the uncombined chloretone and benzoyl chloride that presumably did not enter into the reaction.

According to the method to be given shortly, any excess of chloretone or benzoyl chloride is removed by thorough washing and heating the product with alkali, which decomposes the ester very slowly, and then with water before any attempt is made to purify the ester.

That the chlorine determinations made by Willgerodt and Dürr agree so closely with the theoretical value, suggests the presence of bodies with high chlorine content mixed with other bodies containing little or no chlorine.

Although distillation *under ordinary pressure*, as practiced by Willgerodt and Dürr, leads to decomposition of the ester, distillation *under reduced pressure* can be carried out, as shown later, with very little, if any, decomposition.

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[1] This Journal, 37, 2720 (1915).

[2] *Ibid.*, 38, 2740 (1916).

[3] *Ibid.*, 40, 1948 (1918).

Experimental.

Molecular quantities of chloretone, dehydrated over calcium chloride in a desiccator, and benzoyl chloride are heated on the steam bath for several hours, or until hydrogen chloride ceases to be given off to any extent. The reaction is practically ended in about 6 hours, although the product may be heated longer without injury.

As soon as the reaction is fairly complete, water is added, and the ester thereby thrown out in the form of an oil which solidifies when cooled in ice water. As the oil solidifies, it is best to agitate the contents of the flask to prevent the ester from forming a hard cake which is difficult to remove. When the ester has solidified, the supernatant liquid is decanted as completely as possible, an excess of caustic soda solution (5–10%) is added, and the vessel is heated on the steam bath for about half an hour. By this procedure, any chloretone or benzoyl chloride which remains will be decomposed, or rendered soluble in water. At the end of this time, the flask is cooled as before, and its contents poured into a mortar and ground to a fine powder. It is then transferred to a suction filter and washed a number of times with cold water. It dissolves readily, in alcohol, from which it is obtained in the form of white monoclinic crystals. If the reaction is carried out carefully the yield is excellent.

Chlorine determinations (Carius) carried out with a product which melted between 34–35° after several recrystallizations from moderately strong alcohol, gave the following results.

Subs., 0.2242, 0.2629: AgCl, 0.3426, 0.4027.
Calc. for $C_{11}H_{11}O_2Cl_3$: 37.83. Found: 37.80, 37.89.

The ester is readily soluble in strong alcohol, acetone, chloroform, ether, glacial acetic acid, benzene, etc., but very sparingly soluble in water. It may be recrystallized to advantage from alcohol, from which it may be precipitated by water.

Distillation.—(*a*) *Under normal pressure.* Twenty-three g. of the purified ester was distilled under ordinary pressure. Three fractions were obtained: (1) 170–200° (few cc.) (neglected) distillate colorless; (2) 200–250° (small portion); (3) 250–270° (greater portion). The residue was dark reddish in color, decomposition having taken place, since vapors were given off during the distillation. To the third fraction a little alcohol was added, and the solution was placed in a vacuum desiccator. Crystals formed after standing, m. p. about 112°. This would point possibly to benzoic acid, m. p. 120°.

Distillation.—(*b*) *Under reduced pressure.* Thirty-five g. of the purified ester was distilled under a pressure of 148 mm. Four fractions were obtained: (1) 190–220° (few cc.) slight coloration in distillation flask, distillate clear and colorless; (2) 220–225° (about 5 cc.) color increasing in flask, fumes noted in receiver, distillate colorless; (3) 225–

230° (about 5 cc.) color increasing slightly in flask, distillate colorless; (4) 230–235° (about 20 cc.) dark residue (small in amount) left in flask, distillate colorless.

All the fractions on cooling in ice water solidified to a mass of crystals, and, after recrystallization from alcohol, all gave the same m. p., 34.5 to 35°, the melting point of the original ester. There was a yield of 29 g. of purified product which shows very little decomposition. In this state the ester apparently boils under the above pressure without decomposition at from 220–235°. The volume of the several fractions was estimated.

The ester is very slowly volatile with steam, but does not decompose. It passes over as an oil which solidifies on cooling, especially when rubbed with a rod or when inoculated with a crystal of the substance.

Unlike chloretone, brometone, and the acetic esters, it is practically non-volatile in the air at ordinary temperature, as well as at incubator temperature (37°). The loss even after several days is very slight.

When boiled with water for 18 hours or with 10% sulfuric acid for several hours, very little decomposition occurred. The supernatant liquid gave a slight test for chloride, but in both instances practically all of the ester remained as an oil which solidified when cooled and melted between 34 and 35°.

However, when the ester is refluxed with 10% sodium hydroxide solution, it decomposes slowly, and chlorides may be recognized in the supernatant liquid. This resistance of the ester to the action of moderately strong alkali, as intimated previously, is utilized in its preparation to separate it from chloretone and benzoyl chloride, both of which are decomposed very quickly by this reagent, especially when heated with it. If the boiling with alkali is not continued too long, a portion of the ester remains undecomposed.

When *acetyl chloretone* is boiled with an excess of conc. nitric acid, saponification commences immediately and the presence of chloretone may be demonstrated in a few minutes if water is added; when acetyl, propionyl or butyryl brometone is treated in the same way saponification takes place also, but the brometone itself is decomposed to a certain extent as shown by the evolution of bromine vapors. When, however, the benzoic acid ester is treated similarly, the halogen complex apparently is not changed.

With water or 10% sulfuric acid in a sealed tube under pressure at a temperature of 160–170° for several hours the greater part of the ester is found undecomposed in the form of an oil, which, when cooled in ice water, solidifies, and after recrystallization, melts between 35° and 36°.

One fact stands out prominently: the benzoic ester is characterized by great relative stability, greater even than the other esters thus far studied. It also differs in toxicity, being $^1/_8$ as toxic as the acetic ester of brometone, and about $^1/_{10}$ as toxic as the corresponding acetic ester of chloretone. As far as observed, the benzoic ester does not produce convulsions, which is at variance with the observations of Wolffenstein, Lowey and Bachstex relative to analogous esters.[1] Perhaps owing to the insolubility of the ester, the properties referred to do not develop, but this is hardly to be expected since the other esters are also practically insoluble.

The following pharmacological facts relative to the ester were furnished by my associate, Mr. L. W. Rowe.

"When melted and mixed with olive oil and injected intraperitoneally into guinea pigs, its M. L. D. was found to be about 1.5 g. per kg. body weight.

"Experiments upon dogs indicate that the compound has very slight physiological action, even when given in very large doses. One dog when given 0.5 g. per kg. in capsule per stomach showed slight muscular incoördination $1^1/_2$ hours later. No other effect.

"Another dog given twice the above dose (one g. per kg.) in the same way exhibited slight incoördination and uneasiness. This dog was killed 4 days later and an examination of the stomach showed that no irritating action of a serious nature had taken place.

"A dog was given one g. per kg. by intraperitoneal injection. A slight sedative effect was observed in about 20 minutes. Marked diuresis and purgation resulted in about 30 minutes after injection. Slight nausea was observed about 2 hours after injection. Dog was very sick and died 20 hours after being dosed. Autopsy showed marked inflammation of the intestines and bladder, showing that the irritation caused by the material injected must have been largely responsible for the purgation and urination.

"Five g. of the melted sample was injected subcutaneously into a dog. No general effect was observed. Several days later the skin sloughed off at the site of injection showing that the material was very irritating and was not properly absorbed.

"That irritation is produced when the ester is injected intraperitoneally or subcutaneously is not necessarily indicative of irritant properties inherent in the substance itself; but is probably, in part at least, caused by its non-absorption, just as with any other similarly introduced foreign material.

"The insolubility of the compound as well as the fact that it is apparently not broken up in the body into soluble constituents renders it difficult to study its pharmacological action."

Summary.

The benzoyl ester of chloretone, $C_6H_5CO.OC\text{-}C_3H_6Cl_3$, is prepared by

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[1] Wolffenstein, Lowey and Bachstex, *Ber.*, 48, 2035–43 (1916).

heating molecular quantities of benzoyl chloride and anhydrous chloretone on the steam bath until hydrogen chloride ceases to be given off. The ester is a solid which melted between 34–35° and not an oil as claimed by Willgerodt and Dürr, and may be distilled under reduced pressure without decomposition. It is not readily saponified, and in this respect is much more stable than the other esters previously studied. Boiling with conc. nitric acid does not decompose it as is the case with the aliphatic esters of both chloretone and brometone. Pharmacological tests would indicate that it possesses less hypnotic or anesthetic properties and is less toxic than the esters studies thus far.

DETROIT, MICH

[CONTRIBUTION FROM THE NORTH CAROLINA DEPARTMENT OF AGRICULTURE.]

COCKLE-BUR OIL. A NEW SEED OIL.

BY LELAND B. RHODES.

Received May 22, 1920.

The purpose of the investigation was to prepare cockle-bur oil and determine some of its physical and chemical constants, also to determine some of the properties of the kernels.

The burs for examination were gathered in the vicinity of Raleigh, N. C., during October, 1919, and until the middle of November. They were of the variety sometimes known as the clot-bur (*Xanthium Echinatum*), a coarse asteracious weed having rough leaves and prickly bur-like heads. The seed has the property that one-half germinates one year and the other half the succeeding year. The burs were cut in half by a trimming board; by a quick sharp movement the burs are not mashed and the kernels come out readily. After cutting, the burs were placed in a box and shaken vigorously. The hulls were then taken out, leaving the kernels on the bottom. The kernels as thus obtained were placed in a mortar and gently pounded and rubbed to remove the black shucks. By blowing into the mortar the shucks were removed, leaving the kernels.

In order to determine the per cent. yield of the kernels, the most luxuriant plants were harvested and the kernels separated by hand from a 500 g. sample of burs. 30.69% by weight was recovered.

TABLE I.—PROPERTIES OF THE KERNELS.

	1. %.	2. %.
Moisture (by heating)	6.85	6.95
Moisture (by vacuum)	7.22	7.23
Crude protein	40.34	40.53
Crude fiber (A. O. A. C. method)	2.58	2.47
Oil (Soxhlet) extracted with ethyl ether	29.89	29.78
Oil (Soxhlet) extracted with petroleum ether	29.80	...
Ash	5.42	5.41

The oil was obtained by subjecting the ground kernels to very heavy pressure in the cold between steel plates, after which it was allowed to settle for 2 or 3 days, and then filtered through filter paper with suction. It is light yellow, sparkling, has a pleasant odor and an agreeable and nutty taste, but the taste is not marked. A sample was kept 6 months and no rancidity was observed, but all samples were stored in a dark cool place.

TABLE II.—PROPERTIES OF COCKLE-BUR OIL.

Sp. gr. at 15.5°	0.9251
Refractive index at 15.5°	1.4773
Zeiss butyro. at 20.0°	1.4771
Refractometer at 40.0°	1.4691
Solidification point	—18.0°
Iodine number (Hanus)	140.8
Saponification number	190.2
Reichert-Meissl number	0.233
Hehner number	89.7
Acetyl value	10.6
Melting point of the fatty acids	+ 19.0°

A drying test was also made on the oil. The oil was dropped on a pane of glass inclined at an angle of 30° from the horizontal, down which it ran leaving a film of graduated thickness. The glass was placed in a well-lighted place, not in direct sunlight, but indoors, and exposed to the air during the test. Average room temperature, 22°. The oil was completely dried in 5 days. Pure raw linseed oil under like conditions required 4 days to reach the same degree of dryness.

In considering the oil for commercial value it was thought that the volume of the crude burs for unit weight should be obtained as well as the toxicity of the meal. A one liter measure packed tightly with the burs was found to weigh 160.3 g. Thus one liter will yield 49.19 g. of kernels. The meal was found to be highly toxic. A small quantity of meal or press cake fed to guinea pigs killed them in one day.

With sulfuric acid cockle-bur oil gives, first, a bright yellow color, changing to brownish yellow, which alters to purple and finally to green.

Summary.

The physical and chemical characteristics of a sample of cold-pressed cockle-bur oil have been determined, and also some of the properties of the unpressed kernels. The oil is a drying oil, with an iodine number of 140.8, saponification number 190.2. The kernels contain 29.89% oil and 40.34% crude protein.

RALEIGH, N. C.

[Contribution from the Phytochemical Laboratory, Bureau of Chemistry, U. S. Department of Agriculture.]

THE ODOROUS CONSTITUENTS OF APPLES. EMANATION OF ACETALDEHYDE FROM THE RIPE FRUIT.

By Frederick B. Power and Victor K. Chesnut.

Received May 24, 1920.

The fact that many ripe fruits possess characteristic odors is well known, but it is somewhat remarkable that so little information has been recorded respecting the chemical nature of the substances to which these odorous properties are due. This deficiency of knowledge may, however, be attributed to the extremely small proportion in which such constituents are usually present, to their more or less complex character, and to the consequent difficulties attending their separation or identification. The respective odorous substances have commonly been regarded as esters, and a number of artificially prepared compounds of this class have indeed been given names which indicate their resemblance in odor to certain fruits, such as "apple oil" for amyl valerate, "pear oil" for amyl acetate, and "pineapple oil" for ethyl butyrate. The so-called artificial fruit essences are, however, usually composed of a mixture of substances, without any consideration of their actual occurrence in the fruits whose flavors they are supposed to represent. An actual identification of the principal flavoring constituent of an edible fruit appears to have been first accomplished by Clemens Kleber,[1] who has shown by exact analytical data that ripe bananas contain amyl acetate, and, so far as known to us, this has remained to the present time the only recorded instance in which the chemical identity of a natural fruit flavor has been determined.

Although amyl valerate is designated in most chemical text-books as "apple oil," there appears to be no evidence that this compound has ever actually been found in the apple. So far as can be ascertained from a survey of chemical literature the only published references to the odorous constituents of apples are contained in 2 brief communications by C. Thomae,[2] who has noted that when fresh apple parings are mixed with water and distilled in a current of steam a little solid substance passes over, while occasionally some oil drops are formed which soon for the most part solidify. By extracting the distillate with ether a solid mass was obtained, which on the addition of a little alcohol became crystalline. After separating the crystals by filtration the liquid yielded a yellowish oil which had the odor of apples. Other experiments were made by extracting fresh apple parings with ether, whereby wax-like substances and some drops of yellowish oil were obtained. The author does not state the quantity of material employed, and no product of the investigation was further characterized or identified.

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[1] *Am. Perfumer*, 7, 235 (1913).

[2] *J. prakt. Chem.*, 84, 247 (1911); 87, 142 (1913).

Experimental.

The material employed in the present research was generously provided by Mr. L. C. Corbett, in charge of horticultural and pomological investigations of the Bureau of Plant Industry, and consisted of fruit grown on the experimental farm at Arlington, Va. To him and all others of the above-mentioned Bureau of the Department of Agriculture who so kindly placed at our disposal the facilities for preparing and distilling the material our warmest thanks may here be expressed.

Part I. Examination of Ben Davis Apples.

The variety of apple first examined was that known as the Ben Davis, as this was available in considerable quantity, and as the odorous constituents appear to be contained chiefly in the outer skin or rind of the fruit, only the parings were employed. The apples had been stored in a cellar without refrigeration, and at the time of distillation, in the latter part of October, had developed considerable odor. They were pared by means of a machine, which was so adjusted as to completely remove the rind with only a very small portion of the white substance of the apple, and without removing the core, so that any admixture of seeds was carefully excluded. In order to avoid any possibility of fermentation or loss of volatile substances the fresh parings were brought immediately into a still, and, without any further addition of water, subjected to distillation in a current of steam. The total amount of parings employed from the above-mentioned variety of apples was about 161 kg., representing approximately 805 kg. of the entire fruit. The amount of aqueous distillate collected was 163 liters. This distillate was somewhat opalescent, and the first portions separated some oily drops, but on keeping for a few days it became perfectly clear, with the separation of a little solid material on the sides of the glass vessels containing it. The liquid possessed in a high degree the pleasant, characteristic odor of fresh, ripe apples, and even the first portions of the distillate were perfectly neutral to test-paper. After decanting the aqueous liquid, the above-mentioned solid material was dissolved by means of ether, the ethereal solution dried with anhydrous sodium sulfate, and the solvent evaporated. A small amount (0.04 g.) of a colorless, flocculent substance was thus obtained, which was soluble in hot alcohol, but separated for the most part on cooling. When collected on a filter, and dried on a porous plate, it formed thin, satiny laminae, which were not altered by contact with either conc. nitric or sulfuric acid. The substance melted quite sharply at 63° and was probably slightly impure triacontane, $C_{30}H_{62}$, which is stated to melt at 65.6°.

Concentration of the Distillate. Identification of Furfural and Acetaldehyde.

A large portion of the original aqueous distillate, amounting to 106 liters and representing 107 kg. of apple parings, was repeatedly cohobated in a current of steam, whereby the odorous substances were eventually concentrated in a volume of about one liter, the nearly odorless liquids remaining from this treatment being reserved for further examination. The concentrated distillate, which was practically neutral and contained some globules of colorless oil floating on the surface, was first subjected to some special tests. It gave no coloration with ferric chloride, indicating the absence of phenolic substances, but rapidly reduced an ammoniacal solution of silver oxide in the cold, producing a metallic mirror, and also gave an immediate red coloration with sensitized Schiff's reagent,[1] which was evidence of the presence of an aldehyde. A few drops of the liquid gave with aniline and hydrochloric acid the bright red coloration characteristic of furfural, the latter having doubtless been produced in the process of distillation. When tested for formaldehyde by means of phenylhydrazine hydrochloride[2] a perfectly negative result was obtained. On the other hand the distillate gave the specific reaction for acetaldehyde, which consists in adding to a little of the liquid in a test-tube one or two drops of a solution of dimethylamine (33%) and subsequently about 5 drops of a freshly prepared 1% aqueous solution of sodium nitroprusside, when a beautiful indigo-blue color is produced, soon changing to brown or yellow. Rimini[3] has shown that the reaction for acetaldehyde as obtained by Simon[4] with trimethylamine was due to the presence in the latter of dimethylamine, and that it is given by all secondary bases of the aliphatic series or by ring compounds which have completely lost their aromatic character by hydrogenation. We have found that the above-mentioned blue coloration is readily obtained with a solution of one part by weight of acetaldehyde in 10,000 parts of water, but that it is not produced by formaldehyde, the higher fatty aldehydes, such as *n*-heptylic aldehyde, or by aliphatic terpene aldehydes, such as citral, which gives only a reddish color. Further confirmation of the presence of acetaldehyde, and evidence of its occurrence as an emanation from ripe apples, will subsequently be described.

Hydrolysis of the Esters Contained in the Concentrated Distillate. Identification of Amyl Alcohol and Formic and Caprylic Acids.

The previously mentioned concentrated distillate, amounting to about one liter, was brought into a flask provided with an inverted condenser, 25 g. of pure sodium hydroxide added, and the mixture kept in active ebullition for 2 hours. During this operation the liquid acquired a deep yellow color and a small amount of material separated, which evidently

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[1] Mulliken, "Identification of Pure Organic Compounds," Vol. I, p. 15 (1905).

[2] *Z. Nahr. Genussm.*, 5, 353 (1902) and *J. Assoc. Official Agr. Chemists, Methods of Analysis*, 1916, p. 147.

[3] *Annali Farmacoterapia e Ch.*, 1898, p. 249; *Chem. Centr.*, 1898, Bd. II, p. 277.

[4] *Compt. rend.*, 125, 1105 (1897); *J. Chem. Soc.*, 74, II, 315 (1898).

consisted of the so-called aldehyde resin. After cooling, the contents of the flask were distilled in a current of steam, and about 300 cc. of liquid was collected. This liquid, which gave no reaction for aldehyde, possessed a pleasant odor,[1] and after a short time an appreciable amount of yellowish, oily drops separated on the surface. It was extracted 5 times with pure, aldehyde-free ether, and the neutral aqueous liquid then reserved in order to test for the presence of methyl alcohol, as subsequently described.

The above-mentioned ethereal liquids were united, dried with anhydrous sodium sulfate, and the greater part of the ether removed by distillation, the residual liquid being then brought into a small, tared flask and allowed to evaporate spontaneously until the odor of ether had disappeared. A yellowish, oily liquid was thus obtained, which had a distinct odor of amyl alcohol, and produced the characteristic irritating effect of the latter on the throat when inhaled. The amount of this liquid was 0.7063 g., which represented 0.00065% of the weight of apple parings employed. It was brought into a strong flask provided with a tightly-fitting glass stopper, 25 cc. of a chromic acid mixture[2] added, and the whole heated for 15 minutes on a water bath at a temperature of about 90° with occasional agitation. The flask was then cooled, the contents diluted with water, transferred to a separatory funnel, and the acid liquid extracted 5 times with pure, aldehyde-free ether. The united ethereal liquids, after being washed with a little water, were extracted 4 times successively with 25 cc. of a 5% solution of barium hydroxide. The total alkaline liquid was treated with carbon dioxide for the removal of the excess of baryta, and, after filtration, the neutral liquid was concentrated to a small volume. On the addition of silver nitrate a small amount of a nearly colorless precipitate was obtained, which was collected, washed, and dried on a porous tile over sulfuric acid.

Subs., 0.0358: Ag, 0.0185.
Calc. for $AgC_5H_9O_2$: Ag, 51.7. Found: 51.6.

The acid obtained by the oxidation of the above-described hydrolytic product was thus found to be valeric acid, and its formation established the presence of amyl alcohol in the apple distillate.

After extracting the above-mentioned ethereal liquid with baryta it was washed with a little water, dried with anhydrous sodium sulfate, and the ether allowed to evaporate. A small amount of an oily liquid was thus obtained, which was mixed with water and distilled in a current of

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[1] It is known that acetaldehyde when heated with a caustic alkali is chiefly converted into the so-called aldehyde resin, and that small amounts of formic and acetic acids are also produced, together with some odorous substances which may be extracted from the distilled liquid by means of ether. The formation of these products has been duly considered when necessary in the present investigation in order to exclude any incorrect deductions.

[2] *J. prakt. Chem.*, 45, 599 (1892).

steam. The first portion of the distillate separated some drops of a fragrant oil, and, assuming it to be an ester, the entire distillate was subjected to hydrolysis with sodium hydroxide and further examined in the manner previously described. The oily product was thus found to consist of amyl valerate, which had been formed together with free valeric acid by the oxidation of the amyl alcohol.

The yellow, strongly alkaline liquid remaining from the hydrolysis and subsequent distillation of the concentrated apple distillate was filtered in order to remove the small amount of aldehyde resin, which, when washed and dried, amounted to 0.63 g. The liquid was then acidified with sulfuric acid and distilled in a current of steam. About 2 liters of distillate was collected, the first portions of which had a pronounced odor and acid reaction, and separated a few oily drops. The entire distillate was made alkaline with barium hydroxide, concentrated, filtered, and the excess of baryta removed by carbon dioxide. The clear, filtered solution of barium salt was found to contain a considerable amount of formate, which was removed by treatment in the cold with a 4% solution of potassium permanganate, a current of carbon dioxide being meanwhile passed through the liquid. After removing the slight excess of permanganate by a gentle heat, and filtering to separate the manganese dioxide, the colorless, neutral liquid was concentrated. It then gave with silver nitrate a small amount of a nearly white precipitate, which was collected, washed, and dried on a porous tile over sulfuric acid.

Subs., 0.0449: Ag, 0.0192.
Calc. for $AgC_8H_{15}O_2$: Ag, 43.0. Found: 42.8.

This result is thus seen to indicate the presence of caprylic acid, of which further evidence was subsequently obtained. The filtrate from this salt gave no further precipitate with silver nitrate, and no additional amount of a definite silver salt could be obtained from it by concentration. The residue from its evaporation, however, when heated with absolute alcohol and a little conc. sulfuric acid, developed a fruity odor, which was evidence of the presence of small amounts of the lower fatty acids. In addition to the above-mentioned formic and caprylic acids, as obtained in the process of hydrolysis, the identification of other acids in the original distillate will subsequently be described.

It was previously noted that after hydrolysis of the concentrated apple distillate the subsequent distillate from the alkaline liquid was first extracted with ether and then reserved in order to test it for methyl alcohol. This was conducted by first saturating the liquid with common salt, filtering, extracting with light petroleum (b. p. 30–55°), and distilling the salt solution. After repeated concentration of this distillate it was tested according to the method of Denigès,[1] as elaborated by von Fellen-

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[1] "Recherche de traces de méthanal en présence d'éthanal par la fuchsine bisulfitée," *Compt. rend.*, 150, 529 (1910).

berg,[1] which depends upon the oxidation of methyl alcohol in strongly acid solution to formaldehyde. A reaction was obtained which showed quite definitely the presence of traces of methyl alcohol, and it was ascertained by control experiments that this was not contained in the ether which had previously been employed for extracting the liquid examined. This result was, moreover, confirmed by some special experiments, to be described later, which completely established the occurrence of small amounts of both methyl and ethyl alcohols in apple parings.

Examination of the Aqueous Liquids Remaining from the Concentration of the Original Distillate. Identification of Formic, Acetic, Caproic and Caprylic Acids.

The large quantity of nearly odorless liquid remaining from the cohobation of 106 liters of the original distillate, together with that obtained by the subsequent concentration of 57 liters of distillate, as later described, was made alkaline with sodium hydroxide and evaporated to a volume of about one liter. It was then acidified with sulfuric acid and distilled in a current of steam. About 5 liters of distillate was collected, the first portions of which were turbid, had a strongly acid reaction, and separated some oily drops. The entire amount of distillate, which had an odor resembling that of the higher fatty acids, was made alkaline with barium hydroxide and evaporated to a small volume. After filtration the excess of baryta was removed by carbon dioxide, and the liquid again filtered and concentrated. It was found to contain a large amount of formic acid, which was removed by treatment with a cold 4% solution of potassium permanganate, a current of carbon dioxide being meanwhile passed through the liquid. After the separation of the manganese dioxide by gently heating and filtering, the colorless, neutral solution was concentrated. By the subsequent addition of silver nitrate a number of silver salts were obtained, which gave the following figures on analysis.

Fraction I. Subs., 0.0139: Ag, 0.0059.
Calc. for $AgC_8H_{15}O_2$: Ag, 43.0. Found: 42.4.

This result indicates the presence of a small amount of caprylic acid, which had been found in larger proportion in the products obtained from the concentrated distillate after hydrolysis.

Fraction II. Subs., 0.0370: Ag, 0.0177.
" III. Subs., 0.0457: Ag, 0.0223. Subs., 0.0394: Ag, 0.0192.
Calc. for $AgC_6H_{11}O_2$: Ag, 48.4. Found: II, 47.8; III, 48.8, 48.7.

These fractions evidently represented salts of caproic acid, and they all developed the characteristic fatty odor on ignition.

The filtrate from the preceding fractions yielded successively the following additional silver salts.

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[1] *Biochem. Z.*, 85, 45 (1918).

Fraction IV. Subs., 0.0464: Ag, 0.0284.
" V. Subs., 0.0540: Ag, 0.0342.
" VI. Subs., 0.0489: Ag, 0.0312.
" VII. Subs., 0.0519: Ag, 0.0335.
" VIII. Subs., 0.0632: Ag, 0.0407.
Calc. for $AgC_2H_3O_2$: Ag, 64.6. Found: IV, 61.2; V, 63.3; VI, 63.8; VII, 64.5; VIII, 64.4.

It may be concluded from the above results that the volatile acids of the Ben Davis apple are chiefly formic, acetic and caproic acids, with a very small amount of caprylic acid. There was no evidence of the presence of valeric acid.

Extraction and Characters of the Essential Oil.

In order to ascertain the general characters of the combined volatile constituents of the apple a portion of the original distillate amounting to 57 liters, which represented 54 kg. of the parings, was repeatedly cohobated in a current of steam until the odorous substances were finally contained in a volume of about 8 liters. The practically odorless liquids remaining in the large distilling flasks were mixed with those obtained by the cohobation of a larger quantity of the original distillate, and the whole examined as already described.

The above-mentioned concentrated distillate was extracted 4 times successively with specially purified ether, which was free from aldehyde. The united ethereal liquids were dried with anhydrous sodium sulfate, and the ether removed for the most part by distillation, after which the liquid was brought into a small, tared flask, and the remainder of the ether allowed to evaporate spontaneously. The amount of volatile product so obtained was 1.905 g., thus representing 0.0035% of the apple parings or about 0.0007% of the entire fruit.

The essential oil was a yellow, somewhat viscid liquid, which gradually became darker on keeping, and possessed in a high degree the pleasant, characteristic odor of fresh apples. When cooled slightly below the ordinary room temperature it formed a soft, concrete mass, due to the separation of minute, acicular crystals, which evidently consisted of the previously mentioned paraffin hydrocarbon. A few drops of the oil, when shaken with a little water, gave all the above-noted reactions for acetaldehyde, and it also gave a decided reaction for furfural with aniline and hydrochloric acid.

The concentrated aqueous distillate which had been extracted with ether for the removal of the essential oil was made alkaline with sodium hydroxide and evaporated. It was then acidified with sulfuric acid and distilled in a current of steam. The faintly acid distillate was made alkaline with baryta, concentrated, and the excess of baryta removed by carbon dioxide. After filtration and concentration the liquid was found to contain an appreciable amount of formate, which was removed by oxidation with a 4% solution of potassium permanganate in a current of carbon dioxide. The small amount of colorless solution eventually obtained gave on the addition of silver nitrate only a slight precipitate, which was too small for examination, but on concentrating the filtrate therefrom a very small amount of a silver salt was deposited, which was collected, washed with water, dried and analyzed.

Subs., 0.0156: Ag, 0.0101.
Calc. for $AgC_2H_3O_2$: Ag, 64.6. Found: 64.7.

The distillate from which the essential oil had been removed was thus found to contain only formic and acetic acids.

Part II. Examination of Springdale Apples.

Occurrence of Traces of Methyl and Ethyl Alcohols.

It was noted in connection with the examination of Ben Davis apples that traces of methyl alcohol were found in the distillate. In order to confirm this observation it was deemed desirable to conduct a special experiment in which there could be no possibility of error, although the purified ether used for the previous extraction of the distillate had been carefully tested and found to be free from methyl alcohol. The variety of apples available for this purpose was that known as Springdale, and they were examined in the latter part of January.

A quantity of fresh parings from the apple, amounting to about 7.5 kg., was immediately distilled in large glass flasks by means of a current of steam, and about 5 liters of distillate were collected. The first portions of the distillate, which had a fragrant odor and contained some drops of oil, had a faintly acid reaction and responded to the tests for acetaldehyde. The entire amount of distilled liquid was repeatedly cohobated until the odorous or more volatile constituents were finally contained in a volume of about 500 cc. To this liquid, contained in a flask provided with an inverted condenser, 10 g. of sodium hydroxide was added, and the mixture kept in active ebullition for 2 hours. It had then acquired a deep yellow color with the separation of a small amount of aldehyde resin. After cooling, the alkaline mixture was distilled, and 20 cc. of distillate collected. This liquid, which had a pleasant odor, was saturated with common salt, and then extracted with light petroleum for the purpose of removing any higher alcohols. The salt solution was subsequently distilled, and this distillate subjected to further repeated distillations until finally 1.5 cc. was collected, the receiver being cooled with ice. A small portion (0.1 cc.) of this liquid when oxidized with potassium permanganate in strongly acid solution developed a distinct odor of formaldehyde, and when further treated according to the method of Denigès[1] a decided reaction for this

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[1] *Loc. cit.*

aldehyde was obtained. As the last-mentioned substance was not contained in the original apple distillate, the presence of minute amounts of methyl alcohol was definitely established. It could naturally not be determined whether this alcohol was contained in the original distillate as such or in the form of an ester, and it may possibly have been produced during the distillation of the apple parings by the hydrolysis of a methyl ester of pectin.[1]

The remainder of the above-mentioned 1.5 cc. of concentrated distillate was tested for the presence of ethyl alcohol by means of the iodoform reaction, when distinct crystals of this substance were obtained.

The occurrence of ethyl alcohol in fruits and other parts of plants which have not undergone fermentation has previously been recorded by several observers.[2] Moreover, Gutzeit,[3] by the distillation of several umbelliferous fruits, obtained both methyl and ethyl alcohols, which may have existed in the form of esters, and methyl alcohol or its esters was likewise found by Lieben[4] in the products of distillation of meadow grass and the leaves of trees. It has, furthermore been noted by A. Gautier[5] that he obtained 0.8 g. of ethyl alcohol from 300 g. of so-called *pommes gelées*, an expression which refers to a condition of some apples known as "water-core," but the fruit employed by us was of perfectly normal appearance.

Other Constituents of Springdale Apples.

All the aqueous liquids remaining from the concentration of the original distillate, together with the liquid remaining after the hydrolysis and distillation of the concentrated portion, were made alkaline with sodium hydroxide and evaporated to a small volume. The acids were then liberated by means of sulfuric acid and converted into barium salts in the manner previously described. As a considerable amount of formic acid was found to be present, this was first removed by oxidation with potassium permanganate, and by subsequent precipitation with silver nitrate the following fractions of silver salt were obtained, the first of which became slightly reduced on drying.

Fraction I. Subs., 0.0342: Ag, 0.0168. Found: Ag, 49.1.
" II. Subs., 0.0245: Ag, 0.0149. Found: Ag, 60.8.
" III. Subs., 0.0509: Ag, 0.0317. Found: Ag, 62.3.

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[1] Compare Tschirch, *Arch. Pharm.*, **252**, 538 (1914); von Fellenberg, *Biochem. Z.*, **85**, 45 (1918).

[2] Lechartier and Bellamy, *Compt. rend.*, **69**, 356, 466 (1869); Pasteur, *ibid.*, **75**, 1054 (1872); Müntz, *ibid.*, **86**, 49 (1878); Berthelot, *ibid.*, **128**, 1366 (1899).

[3] *Ann.*, **177**, 344, 372, 382 (1875).

[4] *Monatsh.*, **19**, 333 (1898). Compare also Miller, Univ. Wisconsin, *Bull.* 991 (1919).

[5] *Bull. soc. chim.*, **25**, 433 (1876).

These results indicated the acids to be chiefly formic and acetic, with a small amount of caproic acid.

On allowing the previously mentioned light petroleum extract to evaporate spontaneously in a suitable flask a very small amount of substance was obtained which possessed a pleasant odor. This was oxidized with 10 cc. of a chromic acid mixture and further treated in the manner previously described. The amount of barium salt eventually obtained was too small for analysis, but a portion of it on the addition of dil. sulfuric acid gave a pronounced odor of valeric acid, and the remainder when heated with absolute alcohol and a few drops of sulfuric acid developed the characteristic odor of ethyl valerate. There could thus be no doubt respecting the occurrence of amyl alcohol or its esters in Springdale apples.

Part III. Examination of Crab Apples.

As crab apples possess a particularly fragrant odor, and were available to us in considerable quantities, it was deemed of interest to compare their odorous constituents with those of the previously examined Ben Davis apple. The variety employed for this purpose consisted of the cultivated yellow fruit known as the "Golden Beauty."

The operations of paring the apples and conducting the distillation were precisely the same as those described in the first part of this paper. The amount of parings employed was 77 kg., which represented about 257 kg. of the entire fruit, and the total amount of distillate collected was 76 liters.

The distillate, which had a fragrant, apple-like odor, was somewhat opalescent, but on keeping for a few days the liquid became clear and an oily film separated on the surface. Even the first portions of the distillate were perfectly neutral to test-paper. It seemed desirable in this investigation to compare the yield and characters of the essential oil with those of the analogous product obtained from Ben Davis apples, and the total amount of distillate was, therefore, cohobated in a current of steam until the odorous constituents were concentrated in a volume of 10 liters. The first portions of this concentrated liquid were practically neutral and contained a considerable amount of acetaldehyde, but gave no reaction for furfural. On extracting the entire concentrated distillate with 4 successive portions of ether which was free from aldehyde, and removing the solvent, first by distillation and finally by spontaneous evaporation, there was obtained 3.3579 g. of a pale yellow oil. This represented 0.0043% of the apple parings or about 0.0013% of the entire fruit.

The essential oil from crab apples possessed the same general character as that obtained from Ben Davis apples, and no material difference in odor could be observed, although the yield of oil from the former was somewhat larger. The presence of both furfural and acetaldehyde was established by special tests.

After extracting the concentrated distillate with ether it was made alkaline with sodium hydroxide and distilled from a sand bath, the portion passing over below 97° being collected. This distillate consisted chiefly of ether with a small aqueous layer. After separating the latter and washing the ether several times with water the aqueous liquids were united, saturated with common salt, extracted with light petroleum (b. p. 30–55°), and distilled. On concentrating this distillate, and testing in the previously described manner the small portion which was first collected, a decided reaction for methyl alcohol was obtained. As the ether originally employed for extracting the aqueous distillate, when similarly tested, gave a perfectly negative result, the presence of minute amounts of methyl alcohol or its ester in the crab apple was definitely determined.

The above-mentioned, aqueous, alkaline liquid, from which the portion boiling below 97° had been removed, was acidified with sulfuric acid and distilled in a current of steam until the distillate was practically neutral. The volatile acids were subsequently converted into barium salts, and as the latter were found to contain a considerable amount of formic acid, this was removed in the previously described manner by means of potassium permanganate. After finally concentrating the neutral solution it yielded with silver nitrate the following fractions of silver salt, which were analyzed.

Fraction I. Subs., 0.0329: Ag, 0.0208.
" II. Subs., 0.0497: Ag, 0.0317.
" III. Subs., 0.0439: Ag, 0.0282.
Calc. for $AgC_2H_3O_2$: Ag, 64.6. Found: I, 63.2; II, 63.8; III, 64.2.

The concentrated distillate from crab apples, after extraction of the essential oil, was thus found to contain chiefly formic and acetic acids, with a very small proportion of an acid of higher molecular weight.

Examination of the Aqueous Liquids Remaining from the Cohobation of the Original Distillate. Identification of Formic, Acetic, and Caproic Acids.

The large amount of nearly odorless liquid remaining from the cohobation of 76 liters of the original crab apple distillate was made alkaline with sodium hydroxide and evaporated to a comparatively small bulk. It was then acidified with sulfuric acid, and subjected to distillation in a current of steam. The first portion of the distillate was strongly acid, had an odor of the higher fatty acids, and separated an oily film on the surface. After converting the entire amount of volatile acid into a barium salt, the latter was found to contain a considerable proportion of formate, and this was, therefore, removed by treatment with potassium permanganate in the manner previously described. The concentrated, neutral solution eventually obtained yielded with silver nitrate several successive fractions of silver salt, which were collected, dried, and analyzed.

Fraction I. Subs., 0.0205: Ag, 0.0099.
" II. Subs., 0.0284: Ag, 0.0138.
" III. Subs., 0.0439: Ag, 0.0215.
Calc. for $AgC_6H_{11}O_2$: Ag, 48.4. Found: I, 48.3; II, 48.6; III, 48.9.

All the above fractions evidently consisted of nearly pure silver caproate.

By concentrating the filtrate and washings from the above-mentioned precipitates several additional fractions of silver salt were obtained.

Fraction.	Subs.	Ag. Found. G.	%.
IV	0.0353	0.0178	50.4
V	0.1212	0.0616	50.8
VI	0.0530	0.0273	51.5
VII	0.0634	0.0329	51.9
VIII	0.0805	0.0477	59.3
IX	0.0724	0.0457	63.1
X	0.0764	0.0487	63.7
XI	0.0334	0.0215	64.4

Calc. for $AgC_2H_3O_2$: 64.6.

In view of the composition of the first 3 fractions, and the gradual increase in percentage of silver, it may be considered that Fractions IV to X consisted of mixtures of silver caproate and acetate, especially as the last fraction was evidently nearly pure acetate. The rather close agreement of Fractions VI and VII with silver valerate, which requires 51.7% Ag, is regarded merely as a coincidence, for the odor developed by all the salts on ignition was similar to that produced by caproic acid, and throughout the investigation there was otherwise no evidence of the presence of valeric acid.

The above results have thus shown the volatile acids of the crab apple to be the same as those of the Ben Davis apple, consisting chiefly of formic, acetic, and caproic acids, and, as will be indicated later, a very small amount of caprylic acid is also undoubtedly present.

Separation of the Aldehyde from the Distillate of Crab Apples, and its Further Identification as Acetaldehyde.

In the preceding examination of the apple distillates the presence of a notable quantity of acetaldehyde was observed, but its identification was effected only by the described qualitative tests, which included, however, the characteristic reaction with dimethylamine and sodium nitroprusside. Inasmuch as the plan of the previously described investigation necessitated the treatment of the concentrated distillate with a caustic alkali, in order to effect the hydrolysis of the esters, and as this resulted in the destruction of the aldehyde, it was deemed desirable to conduct some special experiments whereby the identity of the aldehydic constituent could be further confirmed. It was also considered important to ascertain that the acetaldehyde was not accompanied by a higher homolog, since some of these compounds possess highly odorous properties, and incidentally the alcoholic constituent of the crab apple esters has also been determined.

For the above-mentioned purpose 17.24 kg. of fresh crab apple parings were brought immediately into a still, and the material subjected to distillation in a current of steam. The first portion of the distillate, being concentrated, was set aside, and the distillation then continued so long as any odorous substances passed over. The weaker distillate was subsequently concentrated by repeated cohobation, until finally the concentrated distillate amounted to about 500 cc. This liquid was saturated with sodium hydrogen sulfite, and the mixture set aside for several days, after which it was extracted 5 times successively with pure, aldehyde-free ether. The examination of these ethereal liquids will subsequently be described. The sulfite solution was made alkaline with sodium carbonate and distilled in a current of steam until about 500 cc. of distillate was obtained. The first portion of the distillate possessed an odor which was chiefly that of acetaldehyde, but also reminding somewhat of a higher aldehyde, and the total distillate was slightly opalescent. It yielded in a high degree all the previously described aldehyde reactions, including that characteristic of acetaldehyde. A special test for formaldehyde with phenylhydrazine hydrochloride gave a perfectly negative result, thus confirming the previous observations regarding the absence of this compound in the apple distillate.

The distillate containing the aldehyde was treated with an alkaline solution of potassium permanganate until the red color was permanent, after which it was filtered, the excess of permanganate removed by the addition of a solution of ferrous sulfate in dil. sulfuric acid, and the mixture distilled in steam. The entire acid distillate, which had a very slight odor, was made alkaline with barium hydroxide, and the liquid filtered and concentrated. On the subsequent addition of a few drops of solution of silver nitrate a slight blackish precipitate was produced, which was removed by filtration, after which by fractional precipitation a series of perfectly white silver salts was obtained. These were dried over sulfuric acid and analyzed.

Fraction.	Subs. G.	Ag. Found. G.	%.
I	0.0486	0.0311	64.0
II	0.0374	0.0240	64.2
III	0.0558	0.0359	64.3
IV	0.0485	0.0312	64.3
V	0.0822	0.0527	64.1

Calc. for $AgC_2H_3O_2$: 64.6.

These results indicate that the aldehyde obtained from the crab apple was nearly pure acetaldehyde, with possibly a trace of a higher homolog.

The total amount of silver salt obtained was 0.6493 g., which would correspond to 0.1711 g. of acetaldehyde, or about 0.001% of the weight of apple parings employed. Inasmuch as the yield of essential oil, which naturally would contain but little of the aldehyde, was 0.0043%, the proportion of the latter in the original apple distillate was relatively large.

Hydrolysis of the Esters. Identification of Amyl Alcohol.

As previously mentioned, the concentrated crab apple distillate after saturation with sodium hydrogen sulfite was extracted several times with ether in order to remove the non-aldehydic substances. The united ethereal liquids, which gave no reaction for aldehyde, were washed with a little water, dried with anhydrous sodium sulfate, and the greater part of the ether removed by distillation. The liquid was then brought into a small, tared flask and the remainder of the ether allowed to evaporate spontaneously, when there was obtained 0.2677 g. of a yellowish oil which had an intense, and, when diluted, pleasant apple-like odor. This represented 0.0015% of the weight of apple parings. The oily product was mixed with 200 cc. of water, 10 g. of sodium hydroxide added, and the mixture heated for 2 hours in a flask provided with an inverted condenser. It was then allowed to cool and distilled in a current of steam. The first portion of the distillate separated some oily drops and had the odor of amyl alcohol. The entire distillate was extracted 5 times with pure, aldehyde-free ether, the united ethereal liquids dried with anhydrous sodium sulfate, and the greater part of the ether removed by distillation, the remainder being then allowed to evaporate spontaneously in a flask provided with a glass stopper. To this residue, consisting of a few drops of yellowish oily liquid, 10 cc. of the previously mentioned chromic acid mixture was added, and the whole heated on a water bath, with occasional agitation, for about 15 minutes. It was then cooled, diluted with water, and extracted 5 times with pure ether. The united ethereal liquids were washed with a little water, and then extracted 4 times successively with a 5% solution of barium hydroxide in portions of 25 cc. each. These alkaline liquids were saturated with carbon dioxide to remove the excess of baryta, and the filtered solution concentrated. On the subsequent addition of silver nitrate a very small amount of a nearly white precipitate was obtained, which was collected, washed with a little water and dried.

Subs., 0.0196: Ag, 0.0100.
Calc. for $AgC_5H_9O_2$: Ag, 51.7. Found: 51.0.

This result showed that the salt was silver valerate, and it afforded evidence that the crab apple, like ordinary apples, contains amyl alcohol in the form of esters.

No further amount of silver salt could be obtained from the above-mentioned solution, but the evaporated mother-liquor on the addition of dil. sulfuric acid developed the odor of valeric acid. The ethereal liquid from which the valeric acid had been extracted by means of baryta was washed with water, dried with anhydrous sodium sulfate, and the ether removed, but it yielded a scarcely perceptible residue.

Acids Obtained by the Hydrolysis of the Esters.

The strongly alkaline liquid remaining after the hydrolysis of the esters and subsequent distillation was acidified with sulfuric acid and again distilled in a current of steam. The first portion of distillate was opalescent, and a very small amount of solid substance separated in the condenser, but it was gradually carried over and probably consisted of caprylic acid, which melts at 16.5°. The entire amount of volatile acid so obtained was converted into a barium salt, and the concentrated solution of the latter yielded with silver nitrate a perfectly white silver salt, which was analyzed.

Subs., 0.0975: Ag, 0.0459.
Calc. for $AgC_6H_{11}O_2$: Ag, 48.4.
Calc. for $AgC_8H_{15}O_2$: Ag, 43.0. Found: 47.1.

This result indicated the salt to consist of a mixture of silver caproate and caprylate, the former largely predominating.

Acids Remaining in the Original Distillate after Cohobation.

The large volume of aqueous liquid remaining from the concentration of the original distillate by cohobation was made alkaline with sodium hydroxide and evaporated. It was then acidified with sulfuric acid and distilled in a current of steam, the volatile acids being subsequently converted into a barium salt. As the solution of the latter was found to contain a considerable amount of formic acid, this was removed by means of potassium permanganate in the manner previously described. The filtered and concentrated neutral liquid eventually obtained gave with silver nitrate a small precipitate, which was collected, dried, and analyzed.

Fraction I. Subs., 0.0450: Ag, 0.0224. Found: Ag. 49.8.

This salt evidently consisted chiefly of silver caproate, which requires 48.4% Ag, together with a little acetate. By the evaporation of the mother-liquor two other portions of salt were successively obtained and analyzed.

Fraction II. Subs., 0.0635: Ag, 0.0384.
" III. Subs., 0.0516: Ag, 0.0328.
Calc. for $AgC_2H_3O_2$: Ag, 64.6. Found: I, 60.5; II, 63.6.

From the above results it may be concluded that the aqueous liquid remaining after cohobation of the original distillate contained chiefly formic and acetic acids with a small proportion of caproic acid.

Part IV. Emanation of Acetaldehyde from Ripe Apples.

The occurrence of acetaldehyde among the products of distillation of odorous substances has frequently been observed in recent years, and it has indeed been stated[1] that it is probably never entirely absent in any essential oil, although on account of its ready solubility in water, as well as its great volatility, it is mostly contained in the water of the distillate from which the oil has been separated. It has, however, hitherto been assumed that the lower aliphatic aldehydes are first produced in the process of distillation, and that they do not exist as such in the plant.[2] Semmler[3] has particularly noted that from the standpoint of vegetable physiology acetaldehyde would gain in importance if it could be proved that it occurs ready formed in the plant. Inasmuch as the present authors had found that considerable amounts of acetaldehyde are contained in the distillate from ripe apples, it was deemed of special interest to ascertain whether this compound could be detected in the odorous emanation from the fruit, and the experiments in this direction have been completely successful.

In the month of December a quantity of sound red apples of the variety known as "Nero" was brought into a large copper vessel, provided with a tightly fitting cover and a small opening both at the top and the bottom, so that a current of air could be slowly aspirated through it. In this experiment 215 apples were used, which weighed 31.85 kg. The air which entered the vessel at the top was first passed through an alkaline solution of potassium permanganate and then through conc. sulfuric acid. At the bottom the exit tube was first connected with a small inclined glass apparatus consisting of a series of bulbs and containing a saturated solution of sodium hydrogen sulfite. To this bulb apparatus an empty gas washing bottle was attached and to the latter a similar bottle containing a saturated solution of sodium hydrogen sulfite, the whole being then connected through an intervening empty flask with a filter pump, by means of which the air was continuously drawn through the entire system. This operation was allowed to proceed uninterruptedly for 7 or 8 days, when the absorbing apparatus was detached, and the liquid through which the air had passed was then found to possess a pleasant apple-like odor. The entire amount of sulfite solution contained in the bulb apparatus and gas washing bottle was about 300 cc. It was made alkaline with sodium carbonate and distilled, the first distillate of about 50 cc. being then again distilled and 5 cc. of liquid collected, the receptacle having been cooled with ice. The concentrated distillate so obtained had the characteristic odor of acetaldehyde, immediately reduced an ammoniacal solution of silver oxide in the cold, and gave within a few seconds a deep pink coloration with Schiff's reagent. It also gave with dimethyl-

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[1] Gildemeister and Hoffmann, "Die aetherischen Oele," second edition, Bd. II, p. 480.

[2] *Ibid.*, Bd. I, p. 422.

[3] Semmler, "Die aetherischen Oele," Bd. I, p. 568, 1906.

amine[1] and sodium nitroprusside the deep indigo-blue color which is characteristic of acetaldehyde.

The above-described operation was subsequently conducted with several other varieties of apples, which were loosely packed in a large conical glass percolator, but otherwise the conditions were the same.

The second experiment was made early in January, and 60 "Paragon" apples were used, which weighed 9.37 kg. For the third experiment, begun in the middle of January, a green variety of apple known as the "Keeper" was employed, and 57 of them weighed 9.18 kg. A final experiment was made early in February with crab apples, which were of the same kind and quality as those used for the previously described chemical examination of this fruit. This variety of apple being small in size the number used was 150, which weighed 9.6 kg.

In all the above-mentioned experiments the aldehyde was liberated from its bisulfite compound, and in the subsequent tests for its identification the same decisive results were always obtained. The interesting fact has thus been established that the odorous emanations from the apple during its period of vital activity contain acetaldehyde, and it follows that the occurrence of this compound in a distillate from the fruit does not depend upon any chemical changes in the process of distillation.

Summary.

The results of the present investigation, for which several varieties of apples were employed, may be briefly summarized as follows.

1. The odorous constituents of apples have been found to consist essentially of the amyl esters of formic, acetic, and caproic acids, with a very small amount of the caprylic ester and a considerable proportion of acetaldehyde. In considering the relative amounts of the respective alcohol and acids it seems probable that the latter are also present to some extent in the free state.

2. It has been shown that acetaldehyde is a product of the vital activities of the fruit, and that it occurs in the exhalations of ripe apples. This observation is deemed of considerable biological importance, especially as it has hitherto been assumed that the lower aliphatic aldehydes are first formed during the process of steam distillation. It is, for example, quite probable that the exhalation of acetaldehyde may prove to be one of the factors involved in the production of so-called "apple-scald," an affection to which some apples are subject when stored without free circulation of air.[2]

3. The aqueous distillate from fresh apple parings has been found to

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[1] As several works of reference designate the use of trimethylamine in the specific test for acetaldehyde, the fact may again be noted that the reaction is not obtained with this reagent, unless it may by chance contain some dimethylamine.

[2] Compare Brooks, Cooley and Fisher, *J. Agr. Res.*, **18**, 211–240 (1919).

contain, in addition to the above-mentioned substances, exceedingly small amounts of methyl and ethyl alcohols and also a small amount of furfural. Inasmuch as the last compound is doubtless produced by chemical changes in the material during its distillation, it can not be regarded as one of the odorous constituents of the apple.

4. The essential oil, as extracted by means of ether from a concentrated distillate of either ordinary apple parings or those of the crab apple, is at ordinary temperatures a yellowish, somewhat viscid liquid, becoming much darker on keeping. When slightly cooled it forms a concrete mass, due to the separation of small acicular crystals, which consist of a paraffin hydrocarbon. It possesses in a high degree the characteristic, fragrant odor of fresh apples. Besides the esters mentioned, it has been found to contain, by specific tests, small amounts of acetaldehyde and furfural. The yield of oil from the parings of the Ben Davis apple was 0.0035%, and that from the more odorous crab apple 0.0043%, which corresponds to about 0.0007 and 0.0013% respectively of the entire ripe fruit.

5. Although amyl valerate is generally designated in chemical literature as "apple oil," it is quite certain that this compound has never been identified as a constituent of apples, and in the course of this investigation no evidence could be obtained of its presence. On the other hand it has been shown that the characteristic, fragrant odor of ripe apples is due to a mixture of the previously enumerated substances, which may exist in varying proportions in the numerous varieties of the fruit, thus giving rise to slight differences of odor.

WASHINGTON, D. C.

NEW BOOKS.

Practical Physiological Chemistry. A Book Designed for Use in Courses in Practical Physiological Chemistry in Schools of Medicine and of Science. 6th edition, revised and enlarged. By PHILIP B. HAWK, M.S., PH.D., Prof. of Physiological Chemistry and Toxicology in the Jefferson Medical College of Philadelphia. P. Blakiston's Son & Co., Philadelphia, 1918. xiv + 661 pp., 185 figs. and 6 plates. 16 X 24 cm. $3.50 net.

Despite the fact that the general plan of this book was adversely criticized when it first appeared more than 10 years ago, it has probably found more widespread use as a laboratory manual and text of physiological chemistry than any other book. The reason for this is not hard to find. Although this book contains more exercises and quantitative methods than it would be possible to utilize in an extended course in physiological chemistry, it allows the instructor such a wide choice in the selection of the exercises he might desire to employ as to fit almost any need. As a handbook of quantitative methods in physiological and pathological chemistry the book is most valuable, since nearly all the methods which the laboratory worker has occasion to use may be found in this handy volume. The frequent editions have kept these quantitative procedures thoroughly up to date.

The present edition contains a new chapter on acidosis which gives an excellent presentation of current views and methods on this subject. The discussion on gastric analysis is likewise most excellent, particularly of the fractional methods of analysis developed in Hawk's own laboratory. Considering the fact that the tube developed for use in fractional gastric analysis is a modification of a tube originally employed for securing duodenal contents, it is to be regretted that no mention is made of this latter fluid. The book also contains a very good chapter dealing with the comparatively recent subject of chemical blood analysis, although this is not quite as authoritative as the chapter on gastric analysis.

The printing of the more important laboratory procedures in bold faced type, as in the previous edition, is a great advantage to the laboratory worker. The book is well printed and is comparatively free from typographical errors. VICTOR C. MYERS.

A Glossary of the Mining and Mineral Industry. By ALBERT H. FAY, Mining Engineer. Published as Bulletin 95 of the Bureau of Mines, U. S. Department of the Interior, 1920. Supplied by the Superintendent of Documents, Government Printing Office, Washington, D. C. Pp. 754. 15 × 23 cm. Paper covers. $0.75.

This Bulletin is a very successful attempt to supply a comparatively complete glossary of scientific, technical and popular words and phrases used in mining and the mineral industries, and, less completely in such allied fields as coking, quarrying, oil, geology, chemistry, ceramics, glass making, building constructon and power plants. The number of terms listed is stated to be 30,000 and the definitions 20,000. It contains in addition to terms in the English language used in limited localities, "over 2,000 Latin-American mining terms" and many obsolete words and phrases.

It is distinctly a popular dictionary. All extraneous information is, as a rule, carefully eliminated, and highly technical explanations are rigorously avoided, as can be seen by the following typical examples.

Air jig. An apparatus for separating ores without water, by intermittent puffs of air. (Lawver).

Cinta. 1. (Sp.) A surveyor's tape. 2. (Mex.) A layer or band of mineral in a vein. 3. (Colom.) Pay dirt in placers. (Halse.)

Lid. 1. (Eng.) A flat piece of wood placed between the end of a prop or stempel and the rock. (Raymond.) 2. (Forest of Dean.) The roof of an ironstone working. (Gresley.) 3. (Scot.) The cover or flap of a valve. (Barrowman.) 4. A cross-beam on an upright prop. (Standard.)

Porcelain Lace. A decorative material formed by soaking lace in porcelain slip and firing it. The threads of the fabric are consumed, leaving the pattern in a fine lace-like porcelainware. (Standard.)

Nitrite. A salt of nitrous acid. (Standard.)

The language of the definitions is simple and colloquial enough to be understood by the elementary student and the untrained worker, and exact enough to be valuable to the superintendent and the engineer. Very frequently the origin of a term is indicated, information which should be invaluable to lexicographers and etymologists of the future. It is particularly interesting to note the variety of terms which are not popularly used in the United States. Vocabularies in use in the British Isles, Australia, South Africa, and India are fully represented.

About 140 books, journals, reports, glossaries and other sources of information are cited as references, and modern great dictionaries have been freely quoted. As a rule each definition is preceded by the locality in which the word originated, where this is known and useful, and followed by a reference to the authority, in choosing which the compiler has exercised all necessary judgment. A strict alphabetical arrangement has been followed. There is an avoidance of unnecessary cross-referencing which is wholly praiseworthy.

The only adverse criticism to the book which perhaps should be made has to do with its completeness. It is undoubtedly almost impossible, humanly speaking, to produce a work of this kind which shall include all of the terms ever used in the language and literature relating to a chosen field, and every compiler must draw an arbitrary line between the pertinent terms which he must include and the irrelevant words which should be omitted. But it seems to the reviewer that in this glossary some subjects have been unwisely slighted. A rather obvious example is that of metallurgy. To test the matter, about 55 terms were picked entirely at random from 3 standard text-books on metallurgy. These terms were then looked up in the glossary, when it was found that 30 of the 55 were not defined. These 30 terms, however, included a number relating to metallography, a subject which might perhaps be assumed to be outside of the scope of the Glossary, although it would seem that this subject is as closely related to the mining industries as is pottery, for example,

The chemistry of some of the definitions is not wholly satisfying, as for example,

> **Oxidation.** A chemical union with oxygen, (Raymond);

and

> **Mass Action.** Chemical action as affected by the masses of the reacting substances. (Webster.)

Water is not defined as a chemical substance.

In general the paper, printing and typography are what one usually finds in a Government publication. The wisdom of issuing a volume of 750 pages of thin paper with only a paper cover seems doubtful. A better binding should at least be available for those who might desire it. There are few typographical errors, and most of these are of such a nature as to be entirely obvious. WILLIS A. BOUGHTON.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

THE THIRD LAW OF THERMODYNAMICS AND THE ENTROPY OF SOLUTIONS AND OF LIQUIDS.

BY GILBERT N. LEWIS AND G. E. GIBSON.

Received April 9, 1920.

The third law of thermodynamics, as stated by Nernst, requires that the change in entropy accompanying any process, involving only solid and liquid substances, approaches zero as the absolute zero of temperature is approached. Planck[1] has shown, however, the necessity of modifying this statement when processes of solution are concerned. He pointed out the convenience of so choosing the arbitrary zero of entropy that the entropy of every elementary substance is zero at the absolute zero. With this convention, he states the third law as follows: the entropy of any pure substance is zero at the absolute zero.

In a recent article,[2] by comparing the results of equilibrium measurements with those obtained from the study of specific heats at low temperatures, we have brought forward a good deal of evidence for the validity of the third law, but the cases there cited involved only pure crystalline substances. Indeed there have been no experiments published hitherto which give any information regarding the thermal properties of solutions

[1] Planck, "Thermodynamik," 3rd Ed. 1911, p. 279.

[2] Lewis and Gibson, THIS JOURNAL, 39, 2554 (1917).

at low temperatures. There are, however, certain considerations of an *a priori* character which seem to us to justify the conclusion that some and perhaps all solutions are to be excluded in the statement of the third law.

When 2 liquids like benzene and toluene are mixed, they form approximately what is known as a perfect solution; that is, one in which there is no heat of mixing, and in which the vapor pressures or fugacities obey Raoult's law. The increase in entropy in producing one mol of the mixture from the 2 pure constituents is given by the equation

$$\Delta S = -N_2 R \ln N_2 - N_2 R \ln N_2 \qquad (1)$$

where N_2 is the mol fraction of the first and N_2 of the second constituent. For an equimolal mixture where $N_1 = N_2 = 0.5$,

$$\Delta S = R \ln 2 = 1.4 \text{ cal. per degree.}$$

In such a case as this we find also that the heat capacity of the mixture is about equal to the sum of the heat capacities of the pure constituents, and, therefore, ΔS must be nearly independent of the temperature. For we have the thermodynamic relation

$$\frac{d(\Delta S)}{dT} = \frac{\Delta C_p}{T} \qquad (2)$$

where ΔC_p is the difference between the heat capacity of the solution and the heat capacity of the pure substances from which it was formed.

If now the solution and the 2 pure liquids can be cooled to very low temperatures without crystallization, as indeed can be done with many liquids owing to the phenomenon of supercooling, then if the solution continues to behave as a perfect solution (that is if ΔC_p remains zero), ΔS will remain constant and equal to $R \ln 2$ down to the absolute zero. However, we know that many solutions which are nearly perfect at higher temperatures diverge in a pronounced manner from the behavior of the perfect solution at lower temperatures, and it is possible that at low temperatures the heat capacity of the mixture might become greater than that of its pure constituents, so as to reduce ΔS to a small value or even to zero at the absolute zero.

Nevertheless it would seem hardly likely that this phenomenon could occur in such a way as to reduce ΔS to zero in the limit for all types of solutions.[1] Thus with a mixture of 2 almost identical organic isomers we should expect ΔC_p to be nearly zero, and, therefore, ΔS to be nearly constant over a wide range of temperature. This reasonable surmise becomes a conviction when we consider the extreme case of a mixture of two isotopes. Here we have substances which are so nearly identical in prop-

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[1] Planck indeed assumes that for all solutions Equation 1 holds at the absolute zero. There seems to be no evidence at present to support this assumption, and we shall, therefore, content ourselves with the proof that ΔS in a process of solution is not in general equal to zero at the absolute zero.

erties that as yet no way has been found for bringing about their separation. We even find isotopes which have not only the same atomic number but also the same atomic weight. It seems hardly conceivable that 2 such isotopes would suffer any measurable change in heat capacity on mixing, and, therefore, we must conclude that in such a case the entropy change on mixing remains essentially constant down to the absolute zero.[1]

We may, therefore, conclude that at the absolute zero there is in general a difference in entropy between a solution and the pure substances of which it is composed. In other words, if we assign zero entropy to the pure substances we cannot take the entropy of the solution as zero.

The Entropy of Pure Liquids.

The conclusion we have just reached, concerning the entropy of solutions, immediately raises a doubt as to the validity of the third law when applied to supercooled liquids or glasses, even when composed of a single constituent. The distinction between a pure liquid and a solution is in some measure artificial. Thus water is probably composed of several molecular species, including simple molecules, various types of associated molecules, together with hydrogen and hydroxide ions. Yet water is regarded as a pure substance, since at ordinary temperatures the establishment of equilibrium between these various types of molecules is so rapid that water, in the condition in which we know it, can be formed instantly from a single molecular species. This might not be the case, however, if we could cool water to a very low temperature where the several molecular species could behave as independent constituents of a mixture.

Just such a state of affairs is known in the case of sulfur. Liquid sulfur at high temperatures has entirely reproducible properties, but at lower temperatures it behaves like a mixture of 2 substances, S_λ and S_μ, which are only slowly transformable into one another. By rapid cooling, and treatment with carbon disulfide, it is possible to ascertain the amounts of the 2 species, since one is soluble and the other insoluble in this solvent. Insofar as the 2 species are not transformed into one another, they act as entirely independent substances. Thus when crystalline sulfur melts it produces pure liquid S_λ and the addition of S_μ lowers the melting point

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[1] In fact one such solution has already been thoroughly investigated. Ordinary lead is known to be a mixture of isotopes, and yet its specific heat at low temperatures follows quantitatively the course that would be predicted from the behavior of other metals. It is true, in this case we are dealing with a solid solution or mixed crystal, but all that we have said hitherto applies equally well to solid and to liquid solutions. In order to give an idea of the numerical magnitude of the change in heat capacity on the mixing of equivalent amounts of 2 isotopes, which would be necessary in order to make $\Delta S = 0$ at the absolute zero, we may point out that in the case of lead at the point where $C_p = 3$ for the average of the pure isotopes, C_p for the mixture would have to be 3.8 cal. per degree.

just as any other solute would. Therefore, if S_λ and S_μ are mixed there must be a definite increase in entropy.

This liquid mixture is readily supercooled by sudden chilling. If we should study this material at low temperatures and also pure S_λ and S_μ in the supercooled liquid state we should undoubtedly find at least a part of this entropy change persisting down to the absolute zero. If then we assign zero entropy to the supercooled S_λ and S_μ we cannot assume zero entropy for the mixture. But this mixture would ordinarily be classed as a pure substance, and is in fact composed of a single element. These conditions which happen to have been observed in the case of sulfur may exist in many other liquids and glasses.

Even if a substance contain but a single molecular species, if it is in an "amorphous" state or in the state of a supercooled liquid, there seems at present no reason, theoretical or experimental, which forces us to believe that such a substance falls within the scope of the third law.

A Restatement of the Third Law of Thermodynamics.

When we turn to the consideration of crystalline solids we not only find numerous cases in which the third law has been verified experimentally, but we also see some *a priori* reasons for the existence of such a law, even though these reasons cannot at present be stated with all the lucidity that might be desired.

Since entropy is a quantity defined for the purpose of giving mathematical expression to the second law of thermodynamics, and since that law, from the standpoint of statistical mechanics, is essentially a consequence of the law of probability, it is natural to look for a relation between the entropy of a substance in a given state and the probability of the particular arrangement of molecules which determines that state. Essays in this direction by Boltzmann and more recently by Planck, important and suggestive as they have been, have not sufficed to show just what this relationship is. Nevertheless, it seems to us that if the entropy of a given state be regarded as in some sense a measure of the randomness of that state, the condition of a perfect crystal of a pure substance at the absolute zero is unique. In a solution there is a random distribution of several types of molecules. Even in a pure liquid or glass there is some randomness of arrangement. In any substance at a finite temperature there is a random distribution of energy among the individual molecules. But in the pure crystal at the absolute zero no randomness remains, for when the positions and the properties of a few molecules are fixed, the positions and properties of all other molecules are completely determined; thus when a few elements of the crystalline structure are known we may build up the whole crystal by a process of repetition.

It is this lack of any sort of randomness that we believe to be the theoretical basis for the conclusion that the entropy of a perfect crystal of a pure substance vanishes at the absolute zero.

We, therefore, state the third law of thermodynamics as follows: *if the entropy of each element in some crystalline form be taken as zero at the absolute zero, the entropy of any pure crystal at the absolute zero is zero, and the entropy of any other substance is greater than zero.*

It seems likely, however, that the difference between the entropy of a pure substance in a crystalline state and in an amorphous state may, in many cases, prove to be very small.

BERKELEY, CALIF.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

ENTROPY CHANGES AT LOW TEMPERATURES. I. FORMIC ACID AND UREA. A TEST OF THE THIRD LAW OF THERMODYNAMICS.

BY G. E. GIBSON, W. M. LATIMER AND G. S. PARKS.

Received April 9, 1920.

The third law of thermodynamics, which states that the entropy of all pure crystalline substances at zero absolute temperature is zero,[1] offers a ready method for the determination of the free energy of compounds which cannot conveniently be investigated by determination of equilibrium or electromotive force. This is in general true of organic compounds. If the specific heats of a compound and of its elements at various temperatures are known, ΔS, the entropy of formation of the compound from its elements may be calculated. It is necessary then to know only the heat of formation ΔH in order to obtain the free energy ΔF from the relationship

$$\Delta F = \Delta H - T\Delta S \qquad (1)$$

The only organic compounds for which specific heat measurements at low temperatures have been made are benzene and oxalic acid, investigated by Nernst.[2] Calculation of the free energy of these compounds by the method indicated above, offers no check on the validity of the Third Law, since the free energies of these compounds have not been determined by other methods. From the equilibrium between water, carbon monoxide and formic acid, Branch[3] has calculated the free energy of formation of formic acid from its elements to be

$$\Delta F_{298} = -85{,}200 \text{ cal.}$$

From the work of Lewis and Burrows[4] on the equilibrium between am-

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[1] The exact statement of the third law has been discussed in the preceding paper by Lewis and Gibson.

[2] Nernst, *Ann. Physik,* [4] 36, 395 (1911).

[3] Branch, THIS JOURNAL, 37, 2316 (1915).

[4] Lewis and Burrows, *ibid.*, 34, 1575 (1912).

monia, carbon dioxide, water and urea the free energy of formation of urea may be calculated to be

$$\Delta F_{298} = -48{,}992 \text{ cal.}$$

The object of this investigation, then, is to determine the specific heat of formic acid and urea over the range of temperature from the boiling point of liquid air to 25°, and to compare the free energy calculated from these measurements with the values given above.

Experimental.

In principle the method of Eucken and Nernst[1] was employed in the measurements of the specific heats. A measured amount of heat was supplied by an electric current to the substance contained in a copper calorimeter, which was suspended in a vaccum in a silvered glass tube in order to diminish the conduction and radiation of heat to and from the surroundings. A thermocouple in the center of the calorimeter measured the rise in temperature.

The Calorimeter.—The poor thermal conductivity of the substances dealt with necessitated a calorimeter which gave uniform heating and rapid distribution of heat. After experimenting with several types of copper and glass calorimeters, a cylindrical copper calorimeter, of approximately 3.8 cm. diameter and 11.5 cm. length, with walls 0.05 cm. thick, was adopted. A heating coil of silk-wound Therlo wire, of 90 ohms resistance, was wound on a thin copper cylinder (2.2 × 10 cm.) which slipped through a circular slit in the bottom of the calorimeter, and fitted tightly in the annular space between 2 thin concentric copper cylinders, the upper ends of which were soldered together, while their lower ends were soldered to the edges of the circular slit in the bottom of the calorimeter. Heat could thus be supplied from the inside of the calorimeter without the troublesome sealing of insulated copper wires through copper walls, and with the added advantage of being able to slip the heating coil in and out. Copper vanes running from the sheath enclosing the heating coil gave rapid distribution of the heat throughout the calorimeter. The thermocouple was inserted through a small vertical copper tube 6 cm. long which was soldered through the center of the top of the calorimeter. The calorimeter was filled through an opening in the top which was then closed by means of solder. Hydrogen was introduced with the substance to aid in thermal distribution, and all joints were made gas-tight. The weight of the calorimeter varied from 73 to 97 g., and its heat capacity from 15 to 20% of that of the substance under investigation.

Heat Insulation.—While the method of heat insulation was essentially that employed by Eastman and Rodebush[2] of this laboratory, it differed

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[1] Nernst, *Ann. Physik,* [4] 36, 395 (1911).

[2] Eastman and Rodebush, THIS JOURNAL, 40, 489 (1918).

somewhat in detail. The calorimeter was suspended by a silk thread from a lead block in the lower portion of a silvered tube, approximately 5.5 × 70 cm. The block was supported by a constriction in the tube, and its under and upper sides covered with a polished copper sheet. A few centimeters above the block a copper baffle was sprung into place, to cut down radiation to the block from above. The silvered tube extended to the bottom of a long Dewar vessel which was filled with the cooling mixture to well above the copper baffle. Radiation was further decreased by surrounding the calorimeter by a screen of thin polished copper foil insulated by fine glass points. Although some conduction of heat along the thermocouple and fine heating wires was unavoidable, this effect was reduced to a minimum by bringing the bundle of 8 insulated wires into good thermal contact with the lead block, and winding in helical form the portion, over 10 cm. long, between the block and the calorimeter. The Kraus[1] arrangement of double mercury vapor pumps, supported by a small oil pump, gave the necessary high vacuum. The connection between the top of the silvered tube and the vacuum line was made either by a large ground glass joint or a seal of de Khotinsky cement. The character of the electrical discharge produced in the tube by a small spark coil indicated the quality of the vacuum.

Measurements.—Heat was supplied to the calorimeter by means of an electric current from a battery of 14 Edison cells. The fall in potential across the terminals of the heating coil could be measured with an accuracy of at least 0.1% by means of a calibrated voltmeter. The current of 0.13 to 0.15 ampere was measured by a Leeds and Northrup potentiometer and a standard ohm. In runs above 150° K. the current was remarkably steady, but below this temperature there was a uniform decrease in current during each run, owing to the change in resistance of the fine copper leads during heating. This variation, about 0.5% in magnitude, was corrected for by averaging the readings taken at intervals of 30 seconds. As the voltmeter was in parallel with the heating coil in the calorimeter, it was also necessary to correct for the current passing through the voltmeter. It is believed that the error in the final value for the current through the heating coil was never more than 0.1%. The time for heating was 300 to 600 seconds, and this interval was measured with a stop-watch with an accuracy of 0.1% or better. Thus the maximum error in the amount of heat delivered to the calorimeter during any run should not exceed 0.3%; the average error was probably much less.

For the temperature measurements a single element copper-constantan thermocouple, calibrated from the 4-element couple of Eastman and Rodebush,[2] was used. Measurements of its e. m. f. were made with a

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[1] Kraus, This Journal, 39, 2183 (1917).

[2] Eastman and Rodebush, *ibid.*, 40, 489 (1918).

modified White potentiometer[1] by which temperature differences could be measured accurately to 0.001° at 273° K. and 0.003° at 100° K. The increase in temperature during a run was from 3° to 6°. The temperature, T, and the rate of change of e. m. f. with change of temperature, dE/dT, were obtained from curves plotted for values calculated from the equation of Eastman and Rodebush:

$$E = 1/426{,}840 - 0.74097\, T^{1.837} - 17.45\, T.$$

Experimental Procedure.—The substances studied were extremely poor conductors of heat. Owing to this fact it was found that after each addition of heat to the contents of the calorimeter a period of 40 to 50 minutes elapsed before thermal equilibrium was complete. At the end of this time the temperature of the calorimeter became constant, provided that the difference between the calorimeter and its surroundings was not greater than 5° or 6° at 90° K., or than 0.5° at 270° K. Otherwise there existed a heating or cooling rate, the magnitude of which depended upon this temperature difference and upon the absolute temperature of the bath. In order to arrive at an accurate value for this rate, measurements of the temperature of the calorimeter were continued at minute intervals for 70 to 90 minutes after the cessation of the heating current. With these data a correction for the heating or cooling of the calorimeter during the period of the run was made, and the true temperature rise in the calorimeter, due to the heat added, could be computed within at least 1%. In about $^1/_6$ of the runs the final temperature was constant. In general the correction averaged 3 or 4% of the total increase, although in a few cases it rose as high as 8 or 10%.

Clearly, if the correction for temperature difference during a run is so large, it becomes very important to maintain the surroundings at a fairly constant temperature which does not differ very much from that of the calorimeter itself. After considerable experimentation it was found that by regulating the amount of liquid air in the long Dewar tube successful runs could be made with liquid air as a cooling agent between 85° and 140° K. By boiling liquid air under reduced pressure, a bath temperature of about 71° to 75° K. could be obtained and maintained for several hours. Temperatures between 170° and 250° K. could be obtained easily by means of a mixture of solid carbon dioxide and acetone, while a mixture of ice and salt proved suitable between 255° K. and room temperature.

Pure formic acid and urea purchased in the open market were used. Without further purification of the formic acid its specific heat was found to rise abnormally with temperature in the interval beginning 18° below the melting point. Following Schlesinger,[2] the acid was twice distilled over boron sesquioxide at 20° C. and 6 mm. pressure in a glass apparatus

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[1] Randall, Bichowsky and Rodebush, THIS JOURNAL, 38, 1266 (1916).

[2] Schlesinger and Coleman, *ibid.*, 38, 271 (1916).

free from rubber connections, and then twice recrystallized *in vacuo*. Even when so purified the specific heat was found to be abnormally high, a few degrees below the freezing point.

Specific Heats.

TABLE I.—FORMIC ACID.

Temperature. ° K.	C_p per g.	C_p per g. atom.
71.0	0.157	1.45
73.3	0.163	1.50
76.6	0.163	1.50
77.7	0.165	1.52
82.0	0.168	1.55
86.0	0.174	1.60
89.0	0.174	1.60
90.0	0.179	1.66
90.3	0.182	1.68
94.0	0.188	1.73
176.3	0.270	2.48
180.0	0.273	2.51
184.5	0.282	2.59
196.0	0.292	2.69
205.0	0.297	2.73
237.0	0.328	3.02
243.2	0.339	3.12
248.0	0.348	3.20
250.5	0.344	3.17
253.0	0.352	3.24
257.0	0.353	3.25
270.0	0.372	3.42
275.0	0.459	4.22
286.0	0.506 (liquid)	4.66 (liquid)
288.0	0.517 (liquid)	4.77 (liquid)
291.5	0.510 (liquid)	4.69 (liquid)

Experimental Results.—The results of the measurements made are shown in Tables I and II. As a typical example of the way in which the values given were obtained, the data for one of the runs with formic acid are given in detail.

Voltage at terminals of heating coil, 12.66 volts.
Current, 0.1177 ampere.
Time, 310.4 seconds.
Total heat supplied, 12.66 × 0.1177 × 310.4 × 0.2391 = 112.09 cal.
Initial potentiometer reading....... 5786.88 microvolts.
Final potentiometer reading........ 5696.00 microvolts.
Difference.......................... 90.88 microvolts.
Average T, corresponding to average potentiometer reading, 82° K.

$$\text{Corresponding } \frac{dE}{dT}, \text{ 17.97 microvolts.}$$

Heat capacity of calorimeter, at 82° K. 3.76 cal.

$$\text{Heat supplied to calorimeter........} \quad 3.76 \times \frac{90.88}{17.97} = 19.00 \text{ cal.}$$

Heat supplied to formic acid........	112.09 — 19.00 = 93.09 cal.
Weight of formic acid..............	109.66 g.
C_p of formic acid per g.............	$\frac{93.09}{109.66} \times \frac{17.97}{90.88} = 0.168$ cal./deg.
C_p per mol........................	7.73 cal./deg.
C_p per mean gram atom............	1.546 cal./deg.

The heat capacity of the calorimeter, as determined experimentally, was on the average 2% higher than that calculated for the same mass of pure copper from the values given by Nernst and Lindemann.[1]

TABLE II.—UREA.

Temperature. ° K.	C_p per g.	C_p per g. atom.
86.4	0.239	1.79
90.0	0.235	1.76
90.0	0.244	1.83
90.3	0.243	1.82
96.5	0.252	1.89
97.0	0.244	1.83
104.0	0.249	1.87
107.5	0.259	1.94
128.1	0.285	2.13
198.5	0.343	2.57
199.6	0.340	2.55
201.4	0.338	2.54
204.7	0.345	2.59
204.7	0.346	2.59
208.2	0.344	2.58
223.9	0.377	2.83
244.2	0.382	2.87
274.0	0.428	3.21
275.0	0.425	3.19
277.5	0.430	3.22
295.5	0.463	3.47
298.0	0.459	3.44
300.3	0.460	3.45

The specific heats of liquid formic acid agree with the following values given by Landolt and Börnstein: 18° to 56°, 0.522 cal.; 57°, 0.515 cal.; 17° to 82°, 0.532 cal. per degree per g. In the value given for the solid, formic acid seems to have been confused with lauric acid. The value 0.321 cal. for urea is certainly in error.

Calculation of Entropy and Free Energy.

Formic Acid.—Assuming the entropy at absolute zero to be zero, the entropy at 298° K. is given by the equation

$$S_{298} = \int_0^{298} \frac{dQ}{T}. \qquad (3)$$

Thus for formic acid we may write

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[1] Nernst and Lindemann, *Z. Elektrochem.*, 17, 817 (1911).

$$S_{298} = \int_{0}^{281.5} \frac{C_p\,(\text{solid})\;dT}{T} + \frac{\Delta H\ \text{fusion}}{281.5} + \int_{281.5}^{298} \frac{C_p\,(\text{liquid})\;dT}{T}. \quad (4)$$

The values of the integrals may readily be obtained by plotting C_p as ordinates against *ln* T as abscissas, the entropy then being the area under the curve. If, as in the present case, the curve is not known at lower temperature, some interpolation formula must be used. It has been shown from existing data for many substances which crystallize in the regular system that

$$C_v = f\,(T/\theta), \quad (5)$$

where T is the absolute temperature, θ is a characteristic constant for each substance and f is the same function for different substances. Likewise, Lewis and Gibson[1] suggest for all other solids

$$C_v = f\,(T^n/\theta^n), \quad (6)$$

where f is the same function as before, and n is less than unity.

The latter formula agrees well with the values for formic acid and has been employed in the entropy calculations. To obtain the values of C_v, corresponding to the experimental C_p, use is made of the thermodynamic equation

$$C_p - C_v = T\beta^2 V/41.8\alpha \quad (7)$$

where v is the molecular volume and α and β are respectively the coefficients of cubical compressibility and thermal expansion. Although α and β have not been determined for solid formic acid, a good estimate may be obtained by comparing values of similar substances. $C_p - C_v$ is thus calculated to be 0.4 cal. per atom at 270° K. from the estimated values $\beta = 7.0 \times 10^{-4}$ and $\alpha = 30 \times 10^{-6}$. The difference at 71° K. may be obtained from the equation of Lindemann and Magnus,[2]

$$C_p - C_v = aT^{3/2}, \quad (8)$$

to be 0.05 cal. per atom.

For a detailed description of the method of calculating entropies from Equation 6, reference is made to the paper of Lewis and Gibson.[3] Adopting their notation we obtain for solid formic acid

$$n = 0.350 \qquad \theta = 270 \qquad \log 281.5/\theta' = 0.0063$$

$$S_{v281.5} = 4.72 \text{ per atom.}$$

Adding the value of $S_p - S_v = 0.14$, which was obtained from the area between the C_p and C_v curves, we have $S_{p281.5} = 4.86$ per atom or 24.30 per mol. For the heat of fusion we shall adopt Berthelot's[4] value, 2420 cal. at 281.5° K. The corresponding entropy of fusion is 8.60.

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[1] Lewis and Gibson, THIS JOURNAL, 39, 2555 (1917).

[2] Lindemann and Magnus, *Z. Elektrochem.*, 16, 269 (1910).

[3] Lewis and Gibson, *loc. cit.*

[4] *Compt. rend.*, 78, 716 (1874).

Taking 4.72 as the mean specific heat per atom of liquid formic acid, we obtain for the liquid

$$\Delta S = (\log 298 - \log 281.5) \times 4.72 \times 2.3 \times 5 = 1.30$$

and

$$S_{298} \text{ liquid} = 24.30 + 8.60 + 1.30 = 34.2$$

Thomsen[1] obtained for the heat of combustion of formic acid 69,400 cal. calculated for the vapor at 18° C. Figuring the heat of vaporization at 18° to be 6300 cal. the heat of combustion of the liquid becomes 63,100 cal. Berthelot[2] gives 61,700 cal. Although the difference, 1400 cal., leads to some uncertainty, we shall accept the mean value 62,400 cal. For the heat content of the products of combustion we shall use the values

$$H_2O = 68{,}275 \text{ cal.}^3 \text{ and } CO_2{}^4 = 94{,}250 \text{ cal.}$$

Then for the reaction

$$H_2 + O_2 + C = HCOOH\ (l) \qquad (1)$$

$$\Delta H_{298} = -100{,}100 \text{ cal.}$$

For the entropies of hydrogen, oxygen and carbon, Lewis and Gibson[5] have calculated 15.9 ± 1, 24.1 ± 1 and 1.3, respectively.

$$\Delta S_{298} = 34.2 - 31.8 - 48.2 - 1.3 = -47.1.$$

Hence $\Delta F_{298} = -100.100 + 298 \times 47.1 = -86.070$ cal., a difference of 870 cal. from the value obtained by Branch[6] by means of equilibria measurement.

Since S_{298} for water (16.8), and carbon monoxide (45.55), are also given by Lewis and Gibson, we may calculate ΔF_{298} for the reaction

$$H_2O + CO = HCOOH.$$

Using the value for heat of formation[7] of carbon monoxide as —26,140 cal. and water as given above,

$$\Delta H_{298} = 100{,}100 - (-68{,}275 - 26{,}140) = -5685 \text{ cal.}$$

$$\Delta S_{298} = 34.2 - 16.8 - 45.55 = -28.15$$

$$\Delta F_{298} = -5685 + 298 \times 28.15 = 2705 \text{ cal.,}$$

a difference of 1275 cal. from the value obtained by Branch.

Considering the uncertainty of the heats of combustion and some of the values used in calculating the entropies of the elements, the agreement of the free energies obtained by the 2 different methods is very satisfactory and certainly well within the experimental error. If, in place of the mean

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[1] Thomsen, "Thermochemistry." Longmans, Green and Co., 1908, p. 373.

[2] Berthelot, *Ann. chim. phys.*, [6] **28**, 126 (1893).

[3] Lewis and Randall, This Journal, **36**, 1969 (1914).

[4] Lewis and Randall, *ibid.*, **37**, 488 (1915).

[5] Lewis and Gibson, *loc. cit.*

[6] Branch, *loc. cit.*

[7] Lewis and Randall, This Journal, **37**, 458 (1915).

value for the heat of combustion, we had taken Thomsen's value, 63,100 cal., we find for the formation from the elements

$$\Delta F^\circ_{298} = -85{,}370 \text{ cal.},$$

a difference of 170 cal. from Branch, and for the formation from water and carbon monoxide

$$\Delta F^\circ_{298} = 3415 \text{ cal.},$$

a difference of 575 cal.

Urea.—The C_p curve for urea is flatter than that for formic acid and hence a greater portion of its entropy lies below liquid air temperatures. For this reason experimental errors in C_p and doubtful approximations in the value of $C_p - C_v$ lead to rather large uncertainties in the entropy as calculated by the "*n* formula." It is hoped that these uncertainties may shortly be cleared up by measurements at liquid hydrogen temperatures. From the data given in Table II we calculate $S_{298} = 41.0 \pm 2$ entropy units, using

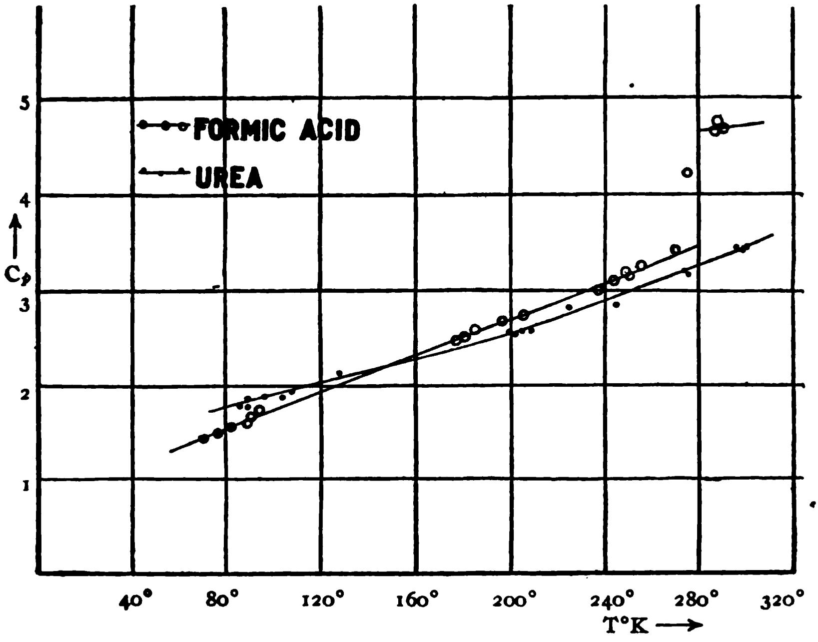

Fig. 1.—Specific heat of formic acid and urea (per gram atom).

$$n = 0.345 \qquad \theta = 245.$$

The Lewis and Gibson values for the entropies of the elements of urea are: C, 1.3; O, 24.1 ± 1; N, 22.8 ± 1; H, 15.9 ± 1. Thus for the reaction

$$C + 0.5O_2 + N_2 + 2H_2 = CON_2H_4(s)$$

$$\Delta S_{298} = 41.0 - (1.3 + 24.1 + 45.6 + 63.6) = -93.6 \pm 9.$$

For the heat of combustion of urea Berthelot[1] gives 151,600 cal. and Stohmann[2] 152,300 cal. The deviation from its mean value 151,950 is 350 cal. Using the values for the heats of formation of water and carbon dioxide given above, the heat of formation of urea from its elements is

$$\Delta H_{298} = 151{,}950 - 2 \times 68{,}275 - 94{,}250 = -78{,}850 \text{ cal.},$$

and the free energy of formation of urea from its elements is

$$\Delta F_{298} = -78{,}850 + 298 \times 93.6 = -50{,}960 \pm 3350 \text{ cal.}$$

Lewis and Burrows[3] found from measurements of equilibrium for the reaction

$$2NH_3(g) + CO_2(g) = CON_2H_4(s) + H_2O(l);\ \Delta F = -1772 \text{ cal.}$$

This gives for the free energy of formation of urea from its elements

$$\Delta F_{298} = -48{,}992 \text{ cal.},$$

using for the free energy of formation of $NH_3(g)$, $CO_2(g)$ and $H_2O(l)$ the respective values —4740 cal., —94,360 cal. and —56,620 cal.

Summary.

The specific heats of formic acid and urea have been measured over the temperature range 75° K. to 298° K., and their entropies and free energies have been calculated.

The values for the free energies agree within the experimental error with values calculated from equilibrium data. A check upon the validity of the third law of thermodynamics as applied to organic compounds has thus been obtained.

BERKELEY, CALIF.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

ENTROPY CHANGES AT LOW TEMPERATURES. II. ETHYL AND PROPYL ALCOHOLS AND THEIR EQUAL MOLAL MIXTURE.

BY G. E. GIBSON, G. S. PARKS AND W. M. LATIMER.

Received April 9, 1920.

In a previous paper[4] Lewis and Gibson have discussed the applicability of the third law of thermodynamics to processes of solution. They conclude that the entropy of a solution should always exceed at the absolute zero the sum of the entropies of the pure crystalline constituents. They also suggest that the transition from a pure crystalline substance to the same substance in the form of glass may be accompanied by an increase in entropy. The object of the present investigation is to obtain additional experimental data suitable for testing these conclusions.

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[1] Berthelot and Petit, *Ann. chim. phys.*, [6] **20**, 113 (1889).

[2] Stohmann and Langbein, *J. prakt. Chem.*, **44**, 380 (1891).

[3] Lewis and Burrows, THIS JOURNAL, **34**, 993 (1912).

[4] Lewis and Gibson, *ibid.*, **42**, 1529 (1920).

Ethyl alcohol and propyl alcohol were selected for this purpose because they both supercool readily to form glasses. Moreover, due to their close chemical relationship, they are very similar as regards internal pressure and dielectric constant, and for this reason a mixture of these 2 liquids may be assumed to conform to Raoult's law with fair exactness.[1] Hence, for the process of mixing $^1/_2$ mol. of ethyl alcohol with $^1/_2$ mol. of propyl alcohol to produce one mol. of mixture, the entropy change is approximately $\Delta S_{298} = R \ln 2 = +1.37$ cal. per degree abs.

The question then is whether this positive entropy change persists down to the absolute zero in accordance with the argument of Lewis and Gibson, or whether it decreases with decrease of temperature and becomes zero in the limit. It was impossible for us to follow experimentally the behavior of the substances concerned down very near to the absolute zero, but it is exceedingly probable that between room temperature and the boiling point of liquid air any tendency toward change in the magnitude of the quantity ΔS for the process under consideration would become manifest. The specific heats of pure ethyl alcohol, pure propyl alcohol, and of the equimolal mixture (all in the liquid or vitreous condition) were, therefore, determined over the above range of temperature, and from these data the entropy changes in question have been calculated.

In the course of the experiments it was found that pure ethyl alcohol crystallized very readily. The heat of fusion and the specific heats of the crystalline form were, therefore, also determined. From these data the entropy change for the transition from the crystalline to the vitreous form has been calculated.

Applying the third law of thermodynamics to the same data, together with the heat of formation of ethyl alcohol, the free energy of formation at 25° C. has been calculated.

Experimental.

The experimental procedure was essentially the same as that employed in the investigation of the specific heats of formic acid and urea, and has been discussed in the preceding paper.

The ethyl alcohol and propyl alcohol used were pure commercial products. They gave no test for aldehydes. The ethyl alcohol as taken from the bottle had a specific gravity corresponding to 99.6% and was used in determining the heat of fusion, the specific heats of the glass, and the specific heats of the crystalline form between 120° and 145° K. A sample of this alcohol was distilled over metallic sodium and used for the determination of the specific heats of the crystalline form from 88° to 115° K, and of the liquid at and above 195° K. The propyl alcohol had a mean

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[1] As a matter of fact, Bose in his measurements finds that ΔH for the above process is —5.8 cal. at 273.4° K. and —6.9 cal. at 294.6° K. This small heat of mixing would indicate that no great error is made in the above assumption that the mixture conforms to Raoult's law and that $\Delta H = 0$. Bose, *Göttingen Ges. Nachr.* 1906, 333.

boiling temperature of 97° C. with a boiling range of approximately 1°. This liquid was fractionally distilled over anhydrous potassium carbonate, and the middle portion, about $^1/_2$ of the total, was used for these determinations.

It is believed that the error in most of the results which follow does not exceed 1%, or at most 1.5%. The region where the values are least concordant is in the range from 100° to 125° K. in the cases of the propyl alcohol and mixed alcohol glasses. At these temperatures it is rather hard to maintain the surroundings of the calorimeter at reasonably constant temperature over the required period of time. Moreover, the glasses begin to soften and become jelly-like, and their thermal conductivity is probably lowest at this stage. The error in the values obtained in this region may be as high as 4 or 5% in some cases. For this reason, the runs which from the nature of the determination are regarded as least reliable, are marked with an X.

Specific Heats.

TABLE I.—ETHYL ALCOHOL: GLASS.

Temperature. ° K.	C_p per g.	C_p per g. atom.
85.9	0.266	1.361
87.0	0.268	1.371
91.0	0.283	1.448
92.0	0.289	1.479
92.4	0.296	1.515
94.6	0.313	1.602
96.3	0.370	1.893

TABLE II.—ETHYL ALCOHOL: LIQUID.

Temperature. ° K.	C_p per g.	C_p per atom.	T. ° K.	C_p per g.	C_p per g. atom.
196.2	0.456	2.332	201.4	0.459	2.349
196.3	0.461	2.359	205.4	0.462	2.363
198.2	0.463	2.369	262.7	0.524	2.680
199.0	0.455	2.329	267.2	0.527	2.696
199.2	0.456	2.332	267.9	0.527	2.696
...	...	...	271.4	0.531	2.717

TABLE III.—ETHYL ALCOHOL, PROPYL ALCOHOL, EQUIMOLAL MIXTURE: GLASS AND LIQUID.

Temperature. ° K.	C_p per g.	T. ° K.	C_p per g.
78.5	0.234	117.3	0.472
85.2	0.242	195.9	0.448
86.4	0.249	196.8	0.448
86.9	0.250	197.0	0.452
88.4	0.256	199.4	0.447
91.8	0.264	200.3	0.445
92.2	0.275	200.5	0.454
92.7	0.278	261.7	0.513
94.2	0.301	265.8	0.521
97.9	0.400	269.2	0.525
98.0	0.393	269.4	0.524
103.7	0.468x	273.1	0.524
103.8	0.482	273.2	0.528
110.8	0.476	...	...

TABLE IV.—PROPYL ALCOHOL: GLASS AND LIQUID.

Temperature. ° K.	C_p per g.	C_p per atom.	T. ° K.	C_p per g.	C_p per g. atom.
77.0	0.223	1.115	196.8	0.440	2.202
82.9	0.234	1.171	197.7	0.442	2.211
87.1	0.244	1.221	199.0	0.446	2.232
87.2	0.246	1.231	199.3	0.447	2.237
88.4	0.247	1.236	199.6	0.445	2.228
88.7	0.248	1.239	200.8	0.446	2.232
89.5	0.247	1.236	206.0	0.451	2.258
89.7	0.251	1.256	210.7	0.447	2.237
92.8	0.269	1.346	214.4	0.453	2.267
93.4	0.273	1.366	219.0	0.461	2.307
95.0	0.287	1.436	222.8	0.456	2.281
96.0	0.293	1.466	227.0	0.458	2.293
98.2	0.346	1.731	231.1	0.459	2.298
98.3	0.353	1.767	235.2	0.466	2.333
100.2	0.411	2.058	235.9	0.469	2.348
102.7	0.428x	2.141x	239.0	0.470	2.353
103.2	0.458	2.292	240.1	0.476	2.383
104.8	0.437x	2.188x	243.8	0.476	2.382
108.9	0.450	2.251	247.8	0.487	2.439
109.9	0.464	2.321	252.1	0.489	2.447
115.0	0.453	2.268	256.2	0.492	2.463
115.8	0.481x	2.408	258.8	0.502	2.512
121.7	0.437	2.188	261.5	0.504	2.522
123.8	0.455x	2.278x	264.5	0.511	2.557
165.7	0.429	2.147	267.5	0.513	2.568
177.0	0.431	2.156	274.6	0.522	2.612
187.4	0.440	2.201	...	...	...

TABLE V.—ETHYL ALCOHOL: CRYSTALLINE.

Temperature. ° K.	C_p per g.	C_p per atom.	T. ° K.	C_p per g.	C_p per g. atom.
88.0	0.240	1.228	113.8	0.284	1.455
88.7	0.243	1.244	121.8	0.299	1.530
89.8	0.243	1.245	126.2	0.305	1.560
92.3	0.246	1.260	129.5	0.308	1.577
94.9	0.250	1.277	131.4	0.315	1.613
100.9	0.257	1.317	136.0	0.329	1.682
106.3	0.275	1.407	136.6	0.329	1.684
106.7	0.270	1.384	141.4	0.366	1.872
112.6	0.282	1.441	...	...	...

Heat of Fusion of Ethyl Alcohol at the Melting Point 156.2° K.

First determination...... 24.4 cal. per g.
Second determination.... 23.7 cal. per g.
Mean result............ 24.0 cal. per g. or 123 cal. per g. atom.

Discussion of the Entropy of the Mixture.

At the temperature of solid carbon dioxide or above, the specific heats of the substances under consideration are varying but slightly, and over intervals of 10° or 15° conform closely to a straight line relationship. Hence, if we average the temperatures for a number of neighboring runs and also the corresponding specific heats, we obtain mean values in which the accidental errors have been cancelled or minimized to a large extent. Thus the runs between 195° and 202° K. were averaged for each of the alcohols with the following result.

	Temperature. ° K.	C_p per g.
Ethyl alcohol	198.4	0.4583 cal.
Propyl alcohol	198.9	0.4443 cal.
Equimolal mixture	198.3	0.4492 cal.

The mean temperatures thus obtained are not identical, but, since the curve for propyl alcohol shows that dC_p/dT per g. is 0.0005 at these temperatures, we may compute C_p for propyl alcohol at 198.3°, which is the temperature of the mean result for the mixture. Undoubtedly ethyl alcohol has practically the same temperature coefficient, so we can correct in its case in similar fashion.

In this manner Table VI was constructed by averaging the runs in the intervals 195–202° K. and 261–275° K. Since the value for C_p in the case of the glasses at liquid air temperatures is changing with extreme rapidity, the specific heats in this region were plotted against temperature for each substance, a smooth curve was drawn, and the values for C_p at 86° and at 90° were then obtained from this curve. The product of C_p per g. and the molecular weight gives the molecular heat capacity which is the quantity that primarily interests us in the present discussion.

TABLE VI.—MOLECULAR HEAT CAPACITIES.

Temperature. ° K.	C_2H_5OH.	C_3H_7OH.	Equimolal mixture.	Mean.
268.7	24.39	30.96	27.72	27.67
198.3	21.10	26.67	23.83	23.89
90.0	12.80	15.17	13.90	13.98
86.0	12.15	14.47	13.21	13.31

The second, third and fourth columns of the above table contain the molecular heat capacities of ethyl alcohol, propyl alcohol, and of the equimolal mixture, respectively. The values in the fifth column are the mean of those in the second and third. From the data it appears that the molecular heat capacity of the mixture is approximately the mean of the values for the pure alcohols, a result which Bose[1] found to be also true at 276.9° and at 296.3°K. for these same substances. This fact indicates that the entropy change involved in the formation of the equimolal mixture persists without appreciable diminution down to 86° K. Furthermore, there is nothing which indicates that the quantity ΔS would decrease at any point below this temperature, and hence it seems reasonable to conclude that the entropy of the equimolal mixture is greater than zero at the absolute zero in agreement with the argument of Lewis and Gibson.

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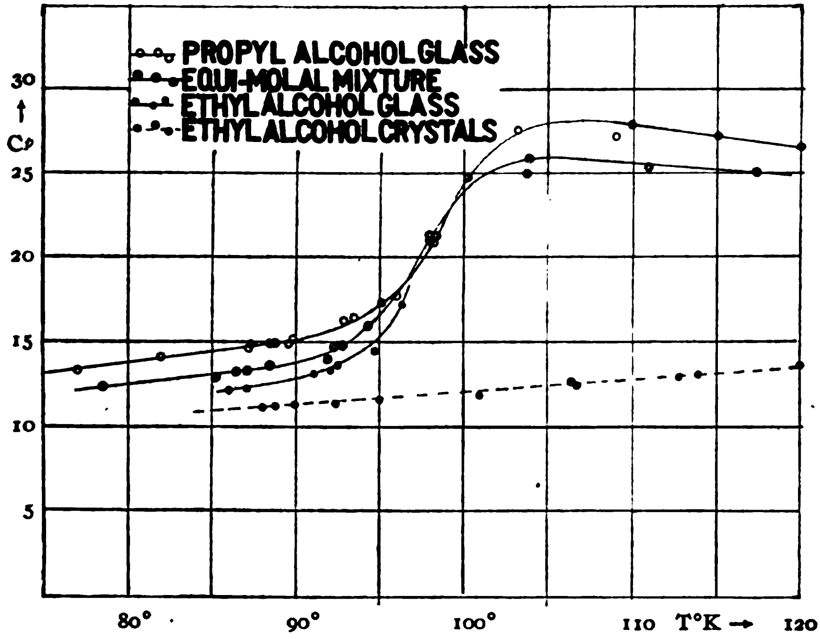
[1] Bose, *Göttingen Ges. Nachr.* 1906, 298.

The Entropy Difference between the Two Forms of Ethyl Alcohol.

When a sample of propyl alcohol or of the equimolal mixture was cooled in liquid air, it became more and more viscous. At 125° K. the substance reached a jelly-like consistency; on further decrease in temperature the liquid underwent a noticeable contraction and solidified to a hard, transparent glass. Pure ethyl alcohol, if rapidly cooled, exhibited the same behavior but with slow cooling crystallized completely.

The specific heats of propyl alcohol and of the mixture show some remarkable changes in the course of this temperature decrease. In the neighborhood of 130° K. they begin to increase as the temperature is lowered, reaching a maximum at 105–110° K.[1] With a further decrease the solid glass is formed and the heat capacity changes very greatly, falling off in the interval 90–100° K. to about $^1/_2$ of its value in the liquid state. In the case of the ethyl alcohol glass the data are not so complete, owing to the greater difficulty in preventing crystallization. Sufficient determinations, however, have been made to indicate that super-cooled ethyl alcohol is analogous to super-cooled propyl alcohol, and hence we may draw the 2 specific heat curves parallel for these substances.

For crystalline ethyl alcohol C_p was plotted against log T between 78° and 156.5° K., the melting point of the substance. In like manner the



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[1] It is thought that the high specific heats in this region may be due to a great increase in the amount of association within the super-cooled liquid; this is the usual explanation for the anomalous behavior of water from —5° to 15° C.

curve for super-cooled ethyl alcohol was drawn over the same temperature range. The area between the 2 curves is then a measure of the difference between the increase of entropy of the glass and the increase of entropy of the crystalline form over the interval 78–156.5°. This difference, obtained by graphical integration, amounts to 0.50 cal. per degree per mean g. atom. At 78° K. C_p for the glass is approximately 12% greater than C_p for the crystals, but at lower temperatures the 2 curves probably approach much closer to one another. Thus White's[1] data for the silicates and Koref's[2] for crystalline and amorphous betol show that at a considerable distance below the melting point the specific heat of the glass exceeds that of the solid by only 1 or 2%. However, for the present argument we will assume that below 78° the difference of 12% in the specific heats of the two forms is maintained practically down to 0° K. For crystalline alcohol the entropy increase, calculated by means of the "*n* formula" of Lewis and Gibson, is 1.32 for the interval 0–78° K. Hence, on the assumption of 12% difference in C_p, the entropy of the glass exceeds that of the crystalline form by $1.32 \times 0.12 = 0.16$ cal. per degree. If then we assume that the entropy for both forms is zero at the absolute zero, the entropy change for the process, liquid alcohol ⟶ crystalline alcohol, becomes $\Delta S_{156.5} = -(0.50 + 0.16) = -0.66$ cal. per degree per g. atom, while when calculated from the heat of fusion

$$\Delta S_{156.5} = \frac{223}{156.5} = -0.78 \text{ cal./deg.}$$

This discrepancy of 0.12 entropy units per mean g. atom (or 20 calories at 156.5°) could be accounted for if we assume simultaneously an error of $2^1/_2$% in the determination of the heat of fusion and a 9% error in the specific heats of the glass over the temperature interval 95–156.5°. While errors of this magnitude seem improbable, the assumptions made and the absence of data at and just above the temperature of liquid hydrogen hardly justify us in concluding that the entropy of the glass is really different from that of the crystalline form at the absolute zero.

Calculation of the Free Energy of Ethyl Alcohol.

Assuming the entropy at the absolute zero to be zero, the entropy at 298° K. is given by the equation

$$S_{298} = \int_0^{298} \frac{dQ}{T}. \qquad (1)$$

Then for pure ethyl alcohol we may write

$$S_{298} = \int_0^{156.5} \frac{C_p\,(\text{solid})\,dT}{T} + \frac{\Delta H\,(\text{fusion})}{156.5} + \int_{156.5}^{298} \frac{C_p\,(\text{liquid})\,dT}{T}. \qquad (2)$$

The values of the integrals may be obtained by plotting C_p as ordinates

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[1] White, *Am. J. Sci.*, 47, 1 (1919).

[2] Nernst, Koref and Lindeman, *Sitzb. Akad.*, 1910, 247.

against $ln\ T$ as abscissas, the entropy then being the area under the curve. As in the present case, the curve is not known below 85° K., some extrapolation formula becomes necessary. Lewis and Gibson[1] suggest for all solids

$$Cv = f\,(T^n/\theta^n) \qquad (3)$$

where T is the absolute temperature, θ and n are characteristic constants for each substance, and f is the same function for different substances. For elements crystallizing in the regular system n is unity; for all other substances it is less than unity.

Applying the methods of Lewis and Gibson, we obtain for crystalline ethyl alcohol $n = 0.315$, $\theta = 473°$, $\log 156.5/\theta' = -0.15$ and $S_{156.5} = 2.35$ per g. atom. The entropy of fusion is equal to 123/156.2 or 0.79 per g. atom. The increase of entropy per atom for liquid ethyl alcohol between 156.2° and 298° was obtained graphically by plotting C_p against the corresponding logarithm of the temperature. The values of C_p found experimentally at ice and at carbon dioxide temperatures were used and between these points the curve was drawn parallel to the curve for propyl alcohol. The values of Bose were used between 275° and 298° K. The integral $\int_{156.2}^{298} C_p\, d\, ln\ T$ was found to be 1.59 per g. atom. Hence for ethyl alcohol

$$S_{298} = 9(2.35 + 0.79 + 1.59) = 42.6 \text{ per mol.}$$

For the heat of combustion of liquid ethyl alcohol, Landolt-Börnstein give 3 values: 326,100 cal. (Berthelot), 326,700 (Atwater and Snell), and 326,900 (Atwater and Snell). We shall take the mean value 326,600 cal. For the heat content of the products of combustion we shall use the values

$$H_2O = -68{,}275 \text{ cal.}^2 \text{ and } CO_2 = -94{,}250 \text{ cal.}^3$$

Then for the reaction

$$3H_2 + 0.5O_2 + 2C = C_2H_5OH$$
$$\Delta H_{298} = -66{,}700 \text{ cal.}$$

For the entropies of hydrogen, oxygen and carbon, Lewis and Gibson have calculated 15.9, 24.1 and 1.3, respectively. With these values,

$$\Delta S_{298} = 42.6 - 95.4 - 24.1 - 2.6 = -79.5.$$

Hence, using the relationship $\Delta F = \Delta H - T\Delta S$, we obtain

$$\Delta F_{298} = -66{,}700 + (298)(79.5) = -43{,}000 \text{ cal.}$$

Summary.

Specific heat data for ethyl alcohol, propyl alcohol, and for an equimolal mixture, all in the liquid or supercooled condition, have been obtained

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[1] Lewis and Gibson, *loc. cit.*

[2] Lewis and Randall, THIS JOURNAL, **36**, 1969 (1914).

[3] Lewis and Randall, *ibid.*, **37**, 488 (1915).

over a wide range of temperature. The specific heat and heat of fusion of crystalline ethyl alcohol have also been measured.

From an examination of the data, it appears probable that the entropy of the equimolal mixture is not zero at the absolute zero.

With the assumption of the applicability of the third law to the process C_2H_5OH (super-cooled) ⟶ C_2H_5OH (crystalline), $\Delta S_{156.2}$ has been calculated in two ways. The difference (per gram atom) between the results obtained is 0.12 cal. per degree, or 20 calories at 156.2° K.

By means of the third law of thermodynamics the free energy of pure ethyl alcohol has been calculated. $F_{298}° = —43{,}000$ cal.

BERKELEY, CALIF.

[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY, HARVARD UNIVERSITY.]

THE MELTING POINTS AND THERMOELECTRIC BEHAVIOR OF LEAD ISOTOPES.

BY THEODORE W. RICHARDS AND NORRIS F. HALL.

Received April 17, 1920.

Among the properties of the isotopes of lead, the melting points stand out as of especial interest. Since the molecular volumes of these substances are essentially equal,[1] the question as to whether or not the melting points are likewise equal, compels attention.

Thermocouples were used for this measurement, not only because they could be used with small amounts of material but also because they are essentially suited to "differential" estimation. W. P. White's papers[2] on this topic afforded many useful suggestions.

The thermo elements employed were 4 in number, 3 single elements and one of 4 junctions. The difficulty with work at high temperatures is the breaking down or the increasing conductivity of most insulating materials even below the melting point of lead. Through the kindness of Professor Harvey N. Davis and Dr. F. Wheeler Loomis, asbestos-insulated copper and nickel wire were available for the construction of the elements. This combination has thermoelectric advantages. The thermoelectric effect (about 23 microvolts per degree at 327°) is much higher than that of noble-metal elements, although not so high as copper-constantan; moreover, both sorts of wire are generally very free from the inhomogeneity often met with in alloys, and both metals are sufficiently resistant to oxidation under ordinary conditions.

The use of copper here as well as for connections to the rest of the measuring apparatus diminishes the danger of parasitic effects to a minimum.

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[1] See T. W. Richards and Charles Wadsworth, 3rd, THIS JOURNAL, 38, 221, 1658 (1916).

[2] W. P. White, *ibid.*, 36, 1856–1885, 2011–2020 (1914).

The asbestos insulation, which had an inflammable binder, was removed from a few millimeters at the ends of the wires, and the ends were twisted together. They were then soldered with a minimum amount of silver solder, using borax as a flux.

The junctions were insulated from each other by a thin glaze of lead borate prepared from litharge and boric anhydride in a nickel crucible in the proportion represented by $Pb_3B_2O_6$. For convenience in introducing into the glass tube the several separately insulated elements were twisted together and the whole glazed so as to form a single bead. The single element used to measure the bath temperature was simply enclosed in a glass tube. All the "cold ends" were contained in a single glass tube under paraffin. The free ends were, after several windings, soldered firmly to thin copper strips which made contacts through strong clamps.[1]

The furnace consisted of 2 tall glass beakers of which the smaller was wound with a commercial resistance wire wrapped in asbestos and placed in the larger beaker. The beakers thus nested were set in the center of a fiber pail, of which the bottom had been covered with magnesia and asbestos, the whole being packed in this mixture. Around the top of the beakers a smooth covering was made of plaster of Paris. The heavy tempering oil placed in the inner beaker and used for the bath needed renewal from time to time; it carbonized and evaporated but never burned, and its odor while unpleasant was not unbearable. The viscous oil was rapidly stirred with a brass stirrer and the bath was covered with a block of asbestos nearly 3 cm. thick. After the stirrer, the melting point apparatus, the thermo-couples and a mercury thermometer had all been inserted through the cover all the holes were luted with a paste made of magnesia, asbestos threads and oil. The whole furnace was thickly surrounded and covered with wool felt. The rapidity of stirring was such that no difficulty whatever was found in keeping the temperature of the 2 samples of lead the same within 0.1° while the furnace was rising in temperature at the rate of 10° per minute, or in keeping the furnace temperature constant within 0.05° for hours at a time with proper regulation of heating current. The alternating 110-volt lighting circuit was used as a source of heat, but on account of fluctuating voltage needed frequent regulation if constant temperature was desired. The heat insulation was satisfactory; cooling curves could be taken with the heating current broken completely. Nevertheless, in order that greater accuracy might be obtained a small current was usually passed through the heating coil to delay the cooling.

The Electrical Measuring System and Connections.

A 20,000 ohms resistance Wolff potentiometer was employed, instead of an apparatus of lower resistance, because it was somewhat more

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[1] W. P. White, *loc. cit.*, p. 1861.

convenient (especially in that it simplified the standard cell connections) and because even with it, the galvanometer gave all the sensitiveness desirable. The floated battery arrangement described by White[1] was used to keep the battery voltage constant, and with about 19,800 ohms in series with the 2 cells, gave variations so small that it was seldom necessary to change the resistance by as much as 0.1 ohm, in making a balance against the standard of which the voltage was assumed to be $1.0183 + 0.00004\ (t^\circ - 20^\circ)$. Three single-knife switches connected the 3 single elements with the potentiometer galvanometer circuit, which was provided with an eliminating switch and a switch for making direct connection with the standard cell. The whole battery circuit was shielded and the shield carried into the eliminating switch. Another switch made connection with the differential element, and at the same time cut out the potentiometer. A suitable protective resistance for the galvanometer was an integral part of the potentiometer.

The galvanometer was a Leeds and Northrup wall type with a mirror. The lamp signal, focussed sharply on a translucent scale, was easily read to tenths of a millimeter. The deflection was nearly 2 mm. per microvolt, so that it was easy to read hundredths of a degree with the single elements and thousandths of a degree with the multiple element. All the measuring apparatus was on a single shielded table, under which, but separate from it, was a box with the switches of the lighting and heating circuits and the slide resistors for the latter.

The entire measuring system was shielded by a complete equipotential shield, as advocated by White. After the hope that the insulation of oil and glass would prevent leakage from the heating current had proved illusory, the shield was extended into the furnace itself by the device of silver-plating the several parts of the entire melting apparatus, winding their tops with tin-foil and then continuing the winding with thin copper foil. This was wound spirally around the sheaf of connecting wires, forming a continuous flexible protective sheath, and connected into the shield, which quite eliminated trouble from electrical leakage unless the heating current switches were handled simultaneously with some part of the measuring system.

Parasitics were detected and allowed for by means of a suitable eliminating switch. Early in the day's work they were large and often quite variable, but always seemed to become fairly constant and of rather small value about noon when the room and furnace temperatures had reached approximate equilibrium. In the final measurements, they were always tested immediately before and after the experimental crisis and all trials in which they varied enough to cause appreciable error were rejected.

[1] W. P. White, "Constant Battery," *Phys. Rev.*, 23, 447 (1906).

The two sorts of lead were contained in identical sealed cylinders of Pyrex glass from which the air was exhausted before melting the lead. Each vessel was provided with a smaller co-axial cylindrical glass sheath for the thermo-elements, which thus extended into the center of the cylindrical mass of lead.

The 2 kinds of lead were prepared as follows. Ordinary lead, in the form of acetate, was dissolved, filtered, and precipitated as nitrate from concentrated solution, and then recrystallized (with centrifuging) 6 times as nitrate from concentrated solution. The purified crystals were then dissolved in warm water in a quartz dish, about 10% of pure nitric acid was added, and the lead was precipitated electrolytically as dioxide in order to eliminate possible traces of silver. The lead dioxide was washed repeatedly, dried on the steam bath, and heated to redness in order to reduce it, at least partially, to litharge and expel any included nitrogen compounds. The orange-red mixture of oxides was then cautiously heated in an unglazed porcelain crucible with potassium cyanide of high purity, until it was reduced to metallic lead, which was next melted in small "alundum" crucibles and poured into a carefully cleaned steel die kindly loaned by Professor P. W. Bridgman. This die, containing the lead, was heated to about 250°, the melting point of soft solder, in a blast flame, and then transferred to a press, where the lead was extruded in the form of wire about 1 mm. in diameter, of which the first 3 meters were rejected. The remainder of the wire, cut into pieces about 5 mm. long with a clean knife on a glass plate, was introduced into one of the cylindrical lead containers.

The other specimen of lead—the Australian radioactive sample—was treated in the same way, except that the raw material was not the acetate, but rather in metallic form. This was dissolved in nitric acid, evaporated to dryness, taken up with water, filtered, evaporated, recrystallized 6 times, electrolyzed, and after ignition reduced by cyanide as described above.

Samples of each kind of lead were tested spectrographically before and after extrusion through the die, through the kindness of Professor G. P. Baxter. All the samples showed a trace of silver, and the extruded ordinary lead a very small trace of copper. This sample also showed an intensification of one of the lines which appeared in all the lead samples ($\lambda = 3048$); but such intensification is usually not significant, depending rather upon the vagaries of the arc-spark, than upon differences of material. Evidently neither of the samples was perfectly pure—evidently, too, the ordinary lead was somewhat less pure than the other. The maximum impurity probably amounted to not more than 5 parts in one hundred thousand.

Measurements.

After preliminary trials the method of measurement adopted was as follows. The temperature of the bath was raised rapidly until (with the potentiometer set at the value corresponding approximately to the melting point) the spot of light from the galvanometer was at the extreme low-temperature side of the indicator scale. Resistance was now thrown into the heating circuit until the passage of the spot of light toward the center of the scale was sufficiently slow. Readings of E. M. F. were taken every 15 seconds through the melting interval, the heating being so regulated as to maintain a constant temperature gradient between the bath and the charge to be measured. The cooling curve was taken similarly. Marked super-cooling from one to two degrees was the rule, but after this marked depression the temperature rose again to a constant level which was maintained for a long time. This maximum temperature was taken as the freezing point. The battery voltage was balanced against the standard cell before and after every trial with satisfactory outcome. Corrections for parasitics and galvanometer drift (if any) were made in the immediate neighborhood of the critical portion of the melting and freezing interval. The super-cooling was greater in the radioactive lead than in ordinary lead, probably because of the slightly less purity of the latter.

In the first experiments using single elements, the difference between the melting points of the two isotopes did not greatly exceed the probable error of experiment. In the more sensitive subsequent "differential" experiments, the temperatures of the samples travelled nearly together, differing only ±0.05° during wide variations of the furnace temperature above and below the melting point; but they did not remain together in the immediate neighborhood of the melting point. On heating, a difference in temperature became manifest about 0.5° below the true melting point in the sense that the temperature of the radioactive sample rose more rapidly. Evidently the ordinary lead began to melt at a lower temperature. After reaching the melting point, the difference diminished to less than 0.1°, and afterwards diminished only very slowly until one of the samples melted.

On cooling, as already stated, the ordinary lead crystallized first; but after the radioactive isotope had crystallized, its maximum rose about 0.05° above that of the other. During most of the cooling the radioactive sample showed a temperature about 0.05° above the other. When the heating or cooling was properly regulated and extremely slow it was possible to extend greatly the interval of constancy and to diminish the small unavoidable constant error which tended to increase the apparent difference due to the fact that the ordinary lead was always in a more advanced state either of melting or of freezing than the radioactive.

There seems to be no question then that the radioactive lead showed the higher melting point by about 0.05° or 0.06°—a difference of only one ten-thousandth of the absolute melting temperature of lead. Part of the difference is unquestionably due to slight impurity in the ordinary lead, as shown by the spectroscope and also by a slight obliquity of the melting curve even under the best conditions of heat supply. Possibly all of the difference may be due to this cause. Certainly there is no difference between the melting points at all comparable with the difference between the atomic weights, which was almost 0.5%.

The Australian radioactive specimen used in this test had an atomic weight of about 206.4, whereas pure uranium lead probably has an atomic weight very near 206. Accordingly the Australian specimen may be supposed to consist of a solid solution of uranium lead and one or more isotopes of higher atomic weight. Ordinary lead being the most probable admixture, we may assume the specimen to consist of about one part of common lead to three parts of the isotope believed to owe its origin to uranium. But ordinary lead also is probably an isotopic mixture. That two chance mixtures of isotopes in different proportions should assume essentially the same melting point is extremely unlikely, if their melting points were different, or if the addition of one isotope caused any appreciable effect on the melting point of another. Hence from the results just recounted, it is fairly safe to conclude that isotopes must be wholly soluble in one another, in perfectly consolute solid solution, and that all have the same melting point, as indeed one would expect. Separation by freezing is obviously impossible.

Time was lacking for the preparation of yet purer specimens, which would have given a more conclusive verdict.

The Thermoelectric Behavior of Isotopes.

The apparatus being at hand, a test of the thermoelectric behavior of the 2 isotopic forms of lead was worth while. Two precisely similar wires of ordinary lead were connected with the galvanometer terminals, and the other ends were joined by wire made of the radioactive lead—one junction being introduced into an ice bath and the other heated gradually to melting in a flame. No deflection in the galvanometer was observed in any of several repetitions of this test, although one ten-millionth of a volt could have been detected. Evidently, then, there is no difference in thermoelectric power between these two kinds of lead. Presumably this behavior is characteristic of the behavior of isotopes in general.

It was intended also to compare their electrical conductivity, but the time needed to prepare the wires with sufficient care as to exact constancy of cross section was lacking. Later this test was accomplished by Professor P. W. Bridgman upon the same samples with more carefully drawn wire. He has described these experiments in another place.[1] He found no difference (beyond the range of experimental error) in the conductivity of the 2 kinds of lead nor in the effect of pressure or temperature upon their conductivity.

We are glad to acknowledge our indebtedness to the Carnegie Institution of Washington for much of the apparatus used in this research.

Summary.

In this paper experiments are described which show that the difference in the melting points of 2 specimens of lead differing 0.8 in atomic weight is, if appreciable, not over 0.05°. From this outcome, it is fairly safe to assume that the kinds of lead not only have very nearly the same melting point but also (since the sample consisting chiefly of the lighter isotope doubtless contained ordinary lead) they mix (or rather mutually dissolve) without affecting the melting point.

The Seebeck thermoelectric effect produced at a junction of the two kinds of lead is also shown to be nil.

CAMBRIDGE, MASS.

THE ACTIVITIES OF THE IONS IN AQUEOUS SOLUTIONS OF SOME "STRONG" ELECTROLYTES.

BY FREDERICK H. GETMAN.

Received May 3, 1920.

In a recent number of THIS JOURNAL, Noyes and MacInnes[2] gave an interesting summary of a series of investigations which have been carried out under their direction with a view to determining the activity of several electrolytes which are known to be largely ionized in solution.

The appearance of this paper has made it seem worth while to the author to publish a brief account of some studies made by him along similar lines which not only confirm the experimental results of Noyes and MacInnes but also furnish additional evidence in support of the validity of the formula developed by MacInnes[3] for the calculation of the electromotive force developed at a liquid junction.

The term "activity," which was first introduced by Lewis[4] to express the effective concentration of a dissolved substance may be defined as the quantity which must be introduced into the mass action equation to express correctly the effect of concentration in determining the equilibrium.

Apparently the first to derive activity coefficients from measurements

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[1] Bridgman, *Proc. Nat. Acad. Sci.*, 5, 351–3 (1919).

[2] THIS JOURNAL, 42, 239 (1920).

[3] *Ibid.*, 37, 2301 (1915).

[4] *Proc. Am. Acad. Arts Sci.*, 43, 259 (1907); *Z. physik. Chem.*, 61, 129 (1908).

of electromotive force was Linhart,[1] who, by making use of a method recommended by Lewis, calculated the so-called "thermodynamic" degree of dissociation of potassium chloride from existing experimental data. Shortly afterward he published the results of similar calculations on hydrochloric acid[2] and at a later date, employing the silver-silver chloride electrode, he determined the activity coefficients of hydrochloric acid in extremely dilute solutions.[3]

In the present investigation 3 typical uni-univalent electrolytes, hydrochloric acid, sodium chloride, and potassium chloride, were studied in both dilute and concentrated solutions, making use of cells involving transference as indicated in the following scheme.

$$\mathrm{Hg} - \mathrm{HgCl} - \mathrm{MCl}(c_1) \,\|\, \mathrm{MCl}(c_2) - \mathrm{HgCl} - \mathrm{Hg}$$

After correcting the observed electromotive forces for liquid potentials at the junctions of the 2 solutions, the activity coefficients were calculated in the usual manner. All measurements were made at a temperature of 25°.

Preparation of Materials and Solutions.

The mercury used was first sprayed through a column of 5% nitric acid 60 cm. in length and then further purified by distillation in a current of air at diminished pressure as recommended by Hulett.[4]

The calomel employed was prepared from pure mercury by dissolving in distilled nitric acid and precipitating with pure hydrochloric acid according to the directions of Loomis and Acree.[5]

The potassium chloride was obtained from a high-grade sample by 5 recrystallizations. The well-drained crystals were first dried at 110° and then heated to incipient fusion, after which they were pulverized in a mortar and preserved in a desiccator over phosphorus pentoxide. The purified salt, when tested spectroscopically, failed to reveal the presence of any sodium.

The sodium chloride used was prepared by 2 successive precipitations of a saturated solution of a good commercial sample of salt with hydrogen chloride followed by washing and thorough draining of the resulting crystals. The remaining treatment was similar to that employed in the preparation of pure potassium chloride. The hydrochloric acid used was obtained by redistillation of a good grade of commercial acid.

The water used in the purification of the above substances, as well as that employed in making up all solutions, was obtained by the usual procedure in the preparation of so-called "conductivity" water.

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[1] THIS JOURNAL, 39, 618 (1917).

[2] *Ibid.*, 39, 2601 (1917).

[3] *Ibid.*, 41, 1175 (1919).

[4] *Phys. Rev.*, 21, 388 (1905).

[5] *Am. Chem. J.*, 46, 596 (1911).

Solutions of the 2 salts were made up by direct weighing of the solutes and diluting to the mark in calibrated flasks, while solutions of the acid were standardized by precipitating with silver nitrate and weighing as silver chloride. The more dilute solutions were prepared by dilution from a solution of known concentration.

Cells.

Two different types of cells were used: (*a*) cells similar to those described by Gibbons and Getman[1] and (*b*) cells which were essentially the same as those employed by MacInnes and Parker[2] in their study of potassium chloride concentration cells. The latter type of cell proved to be very satisfactory provided care was taken when assembling to separate the mouths of the siphon tubes in the intermediate vessel as far as possible. The statement of MacInnes and Parker, that the "time change," which is apparently always present where a liquid junction is involved, was "less than 1 millivolt per hour" was more than corroborated; in fact, in a large number of cases the change in 24 hours did not exceed 0.1 millivolt when the boundary remained unchanged.

Method of Procedure.

In setting up the different cells studied in this investigation, the concentration of the electrolyte on one side was varied over a wide range, while that on the other side was maintained uniformly at 0.1 molar concentration. In the preparation of the electrodes, attention was paid to the precautions pointed out by Loomis and Acree[3] and also by Ellis[4] and special care was taken to compare the electrodes with each other at frequent intervals. Not only were similar electrodes intercompared, but the electromotive forces of the following combinations were also measured.

(*a*) $\mathrm{Hg} — \mathrm{HgCl} — 0.1\ N\ \mathrm{KCl}\ \|\ 0.1\ N\ \mathrm{NaCl} — \mathrm{HgCl} — \mathrm{Hg}$,

(*b*) $\mathrm{Hg} — \mathrm{HgCl} — 0.1\ N\ \mathrm{KCl}\ \|\ 0.1\ N\ \mathrm{HCl} — \mathrm{HgCl} — \mathrm{Hg}$,

and compared with the values calculated by means of the formula of Lewis and Sargent[5] for the electromotive force at the junction of 2 uni-univalent electrolytes having an ion in common. The measured electromotive forces were as follows. (*a*) 0.00469 volt and (*b*) 0.02838 volt, while the calculated values were 0.00434 volt and 0.02840 volt, respectively.[6] The maximum values of the electromotive force were taken in each case as a correct measure of the free energy attending the transfer of the solute from one concentration to the other. All measurements were made with a Leeds and Northrup potentiometer in conjunction with

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[1] This Journal, 36, 1645 (1914).

[2] *Ibid.*, 37, 1455 (1915).

[3] *Loc. cit.*

[4] This Journal, 38, 745 (1916).

[5] *Ibid.*, 31, 363 (1909).

[6] See also Lewis, Brighton and Sebastian, *Ibid.*, 39, 2255 (1917).

a sensitive galvanometer and a Weston standard cell, the latter having been recently certified by the Bureau of Standards.

Experimental Data.

Before giving the summarized data of the entire series of observations, it may be of interest to give a typical series of measurements of the electromotive force, E, of a single combination extending over a period of 5 days.

TABLE I.—OBSERVED VALUES OF THE E. M. F. OF THE CELL.
Hg-HgCl-0.1 N KCl || 0.0298 N KCl-HgCl-Hg.

Date.	E.	Date.	E.
Dec. 10, 10.25 A.M.	—0.02796	Dec. 12, 4.50 P.M.	—0.02791
4.05 P.M.	—0.02793	13, 12.00 M.	—0.02790
11, 11.00 A.M.	—0.02792	4.55 P.M.	—0.02794
5.00 P.M.	—0.02791	15, 11.00 A.M.	—0.02785
12, 12.20 P.M.	—0.02796	Mean	—0.02792

Average deviation from the mean, 0.02 millivolt.

The negative sign prefixed to the electromotive force indicates that the current tends to flow from left to right through the cell, this convention being in accord with the scheme adopted by Abegg, Auerbach and Luther.[1]

A complete summary of the measurements of potassium chloride cells is given in Table II.

TABLE II.—SUMMARY OF E. M. F. DATA ON KCL CELLS.

I. C.	II. E_t.	III. E_l.	IV. E.	V. Δ.
0.001	—0.11101	+0.00089	—0.11190	0.17
0.005	—0.07240	+0.00058	—0.07298	0.08
0.010	—0.05438	+0.00044	—0.05482	0.15
0.01499	—0.04430	+0.00036	—0.04466	0.04
0.0298	—0.02792	+0.00023	—0.02815	0.02
0.03994	—0.02108	+0.00017	—0.02125	0.05
0.049	—0.01700	+0.00014	—0.01714	0.01
0.0800	—0.00523	+0.00004	—0.00527	0.03
0.100	0.00000	0.00000	0.00000	0.00
0.1599	+0.01059	—0.00008	+0.01067	0.09
0.490	+0.03526	—0.00028	+0.03454	0.20
1.000	+0.05241	—0.00042	+0.05283	0.05
1.4988	+0.06269	—0.00051	+0.06320	....
2.9985	+0.08077	—0.00065	+0.08142	....

Throughout the series the 0.1 N calomel electrode formed one-half of each cell; the concentration of the solution in the other half of each cell, expressed in mols per liter, had the respective values given in Col. I of the table. Col. II gives the observed electromotive force, E_t, while Col. III gives the value of the liquid junction potential, E_l, as calculated by the MacInnes formula,[2]

$$E_l = E_t\,(1 - {}^1/_2n_c),$$

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[1] "Messungen elektromotorischer Kräfte galvanischer Ketten," 1911, p. 114.

[2] *Loc. cit.*

where n_c is the transference number of the cation to which, in the case of potassium chloride, the value 0.496 has been assigned. It is of course quite improbable that the value of the transference number remains constant throughout the entire range of concentration included in the table, but it may be assumed to undergo little change up to 0.2 molar concentration. Column IV of the table contains the electrode potential, E, *i. e.*, the observed electromotive force of the cell minus the electromotive force developed at the liquid junction. The last column of the table contains the average deviation from the mean, Δ, of each series of measurements expressed in millivolts. The values of E were plotted as ordinates against the logarithms of the concentrations as abscissas and a smooth curve was then drawn through the resulting points. From this curve the activity coefficients at round concentrations were calculated as shown in Table III. In calculating the activity coefficients it has been assumed that at 0.001 molar concentration the numerical values of the activity coefficient and the conductance viscosity ratio are equal. The table also contains the conductance viscosity ratios, $\Lambda\eta/\Lambda_0\eta_0$, corresponding to the different activity coefficients.

TABLE III.—ACTIVITY COEFFICIENTS AND CONDUCTANCE-VISCOSITY RATIOS FOR POTASSIUM CHLORIDE.

I. C.	II. E.	III. a.	IV. $\Lambda\eta/\Lambda_0\eta_0$.
0.001	—0.11190	0.979	0.979
0.005	—0.07039	0.938	0.956
0.01	—0.05410	0.907	0.941
0.02	—0.03782	0.855	0.922
0.03	—0.02829	0.826	0.914
0.04	—0.02153	0.805	0.898
0.05	—0.01629	0.790	0.889
0.06	—0.01200	0.778	0.882
0.07	—0.00838	0.768	0.876
0.08	—0.00524	0.759	0.871
0.09	—0.00248	0.753	0.866
0.10	0.00000	0.745	0.860
0.20	+0.01629	0.703	0.827
0.50	+0.03782	0.650	0.779
1.00	+0.05410	0.613	0.742
2.00	+0.07039	0.577	...
3.00	+0.07991	0.557	...

The data of the preceding table are represented graphically in Fig. 1, together with the activity data determined by Noyes[1] and Harned.[2]

The corresponding data for sodium chloride and hydrochloric acid are contained in Tables IV and V, only the values at rounded concentrations being given.

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[1] *Loc. cit.*

[2] THIS JOURNAL, 38, 1990 (1916).

Table IV.—Activity Coefficients and Conductance-Viscosity Ratios for Sodium Chloride.

I. C.	II. E.	III. α.	IV. $\Lambda\eta/\Lambda_0\eta_0$.
0.001	—0.11200	0.976	0.976
0.005	—0.07023	0.932	0.954
0.01	—0.05403	0.897	0.936
0.02	—0.03777	0.845	0.914
0.03	—0.02825	0.815	0.898
0.04	—0.02150	0.795	0.886
0.05	—0.01626	0.780	0.877
0.06	—0.01198	0.767	0.871
0.07	—0.00837	0.758	0.865
0.08	—0.00524	0.749	0.860
0.09	—0.00247	0.742	0.855
0.10	0.00000	0.735	0.848
0.20	+0.01626	0.692	0.816
0.50	+0.03776	0.639	0.772
1.00	+0.05403	0.602	0.738
2.00	+0.07029	0.567	...
3.00	+0.07981	0.548	...

Table V.—Activity Coefficients and Conductance-Viscosity Ratios for Hydrochloric Acid.

I. C.	II. E.	III. α.	IV. $\Lambda\eta/\Lambda_0\eta_0$.
0.001	—0.11130	0.990	0.990
0.005	—0.07278	0.965	0.981
0.01	—0.05595	0.929	0.972
0.02	—0.03910	0.895	0.964
0.03	—0.02925	0.876	0.957
0.04	—0.02226	0.862	0.952
0.05	—0.01684	0.852	0.948
0.06	—0.01241	0.844	0.944
0.07	—0.00867	0.836	0.940
0.08	—0.00542	0.831	0.936
0.09	—0.00256	0.825	0.931
0.10	0.00000	0.821	0.925
0.20	+0.01684	0.791	0.909
0.50	+0.04000	0.776	0.890
1.00	+0.05900	0.829	0.845

The transference numbers used in calculating the electromotive forces at the junctions of the different solutions were taken from Noyes and Falk's compilation of transference data;[1] the values of n_c employed in the calculations were as follows: KCl, 0.496; NaCl, 0.396; HCl, 0.833 for all concentration below 0.2 molar, and 0.845 for the higher concentrations. The data contained in Tables IV and V are represented graphically in Fig. 1, together with Linhart's values for dil. hydrochloric acid.

Since the error in the measured values of the electromotive force of the

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[1] This Journal, 33, 1449 (1911).

different cells may reasonably be assumed to be less than 0.0003 volt, it follows that the values of the activity coefficients given in the foregoing tables are probably accurate to within 1%. The agreement between the foregoing values and those obtained by Jahn,[1] Harned,[2] Linhart,[3]

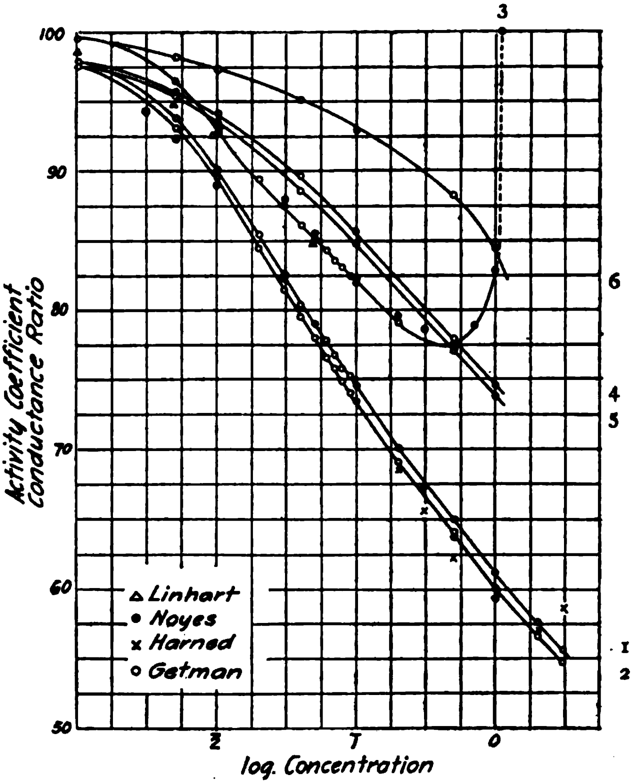

Fig. 1.—Curve 1, activity coefficients of KCl; Curve 2, activity coefficients of NaCl; Curve 3, activity coefficients of HCl; Curve 4, conductance-viscosity ratios of KCl; Curve 5, conductance-viscosity ratios of NaCl; Curve 6, conductance-viscosity ratios of HCl.

MacInnes and Parker,[3] Ellis[2] and Noyes and Ellis[4] is, in general, quite satisfactory; the average deviation from the mean values recently published by Noyes and MacInnes for potassium chloride and hydrochloric acid is approximately 5%.

The results of this investigation may be briefly summarized as follows.

(1) It is apparent in the case of each of the substances studied, that the rate of decrease in the activity coefficient with increasing concentration,

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[1] *Z. physik. Chem.*, 33, 559 (1900).

[2] *Loc. cit.*

[3] THIS JOURNAL, 41, 1178 (1919).

[4] T *Ibid.*, 39, 2532 (1917).

is greater than the corresponding decrease in the conductance-viscosity ratio.

(2) The differences between the activity coefficients of the chlorides of potassium and sodium, at the same concentrations, are very slight, whereas the corresponding values of the activity coefficients of hydrochloric acid differ appreciably from those of either of the above 2 salts.

(3) The activity coefficient curve of hydrochloric acid passes through a well-defined minimum in the neighborhood of 0.5 molar concentration and thereafter increases rapidly with the concentration. Inspection of Fig. 1 reveals the fact that a similar, though much less clearly defined, minimum was found by Harned to exist in the activity coefficient curve of potassium chloride at approximately 2 molar concentration. The present investigation, however, failed to confirm the existence of this minimum.

Discussion of Results.

The foregoing results furnish confirmatory evidence of the conclusion which has been reached in several recent investigations, that the conductance-viscosity ratio does not afford a trustworthy measure of the activity of the ions of "strong" electrolytes. Furthermore, the marked increase in the activity coefficient of hydrochloric acid, which occurs beyond 0.5 molar concentration, proves conclusively that this quantity cannot be proportional to the degree of ionization.

Recent investigations by Chow[1] on potassium hydroxide and by MacInnes and Beattie[2] on lithium chloride, have revealed the fact that a minimum occurs in the activity coefficient curves of each of these substances at the same concentration as that observed with hydrochloric acid. Inspection of the following table shows that a similar minimum occurs in the molar freezing point depression of solutions of hydrochloric acid, lithium chloride and potassium hydroxide in the neighborhood of 0.2 molar concentration, whereas no such minimum occurs in the freezing point depressions of the chlorides of sodium and potassium.

TABLE VI.—MOLAR FREEZING-POINT DEPRESSIONS.

Concentration.	Molar Freezing-Point Depression. Δ/C.				
C.	KCl.	NaCl.	HCl.	LiCl.	KOH.
0.005	3.648	3.629	3.700	3.612	3.706
0.01	3.610	3.600	3.669	3.598	3.684
0.02	3.564	3.568	3.637	3.582	3.655*
0.05	3.502	3.516	3.591	3.563	3.61*
0.10	3.451	3.478	3.555	3.546	3.56*
0.20	3.394	3.424	3.56*	3.525	3.51*
0.30	3.359	3.396	3.60*	3.57*	3.50*
0.40	3.334	3.375	...	3.65*	3.51*
0.50	3.314	3.358	3.66	3.73*	3.53*

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[1] THIS JOURNAL, 42, 488 (1920).

[2] *Ibid.*, 42, 1117 (1920).

With the exception of the values marked with an asterisk, the data contained in the foregoing table have been compiled from the valuable summary of freezing-point data published by Noyes and Falk;[1] the values marked with an asterisk were taken from the tables published by Jones.[2]

The hypothesis advanced by Jones and the author[3] in explanation of this minimum in the freezing-point curve of a large number of electrolytes was that a certain portion of the solvent was removed from functioning as such owing to solvation of the dissolved substance. Should solvation tend to occur in solutions of hydrochloric acid, it is apparent that in a cell such as that indicated by the following scheme,

$$\mathrm{Hg} - \mathrm{HgCl} - 0.1\,N\,\mathrm{HCl} \,||\, 1.0\,N\,\mathrm{HCl} - \mathrm{HgCl} - \mathrm{Hg},$$

the removal of an increasing amount of water from the rôle of solvent, with increasing concentration, would tend to cause an increase in the observed values of the electromotive force above those calculated by the Nernst equation, and therefore a corresponding increase in the values of the activity coefficient would occur. If the minima are due to solvation, we might reasonably expect a shift in the direction of increasing concentration as the temperature is raised. Such is actually found to be the case; the minima in the freezing-point curves occur at 0.2 molar concentration while those in the activity curves, based on measurements of electromotive force at 25°, occur at 0.5 molar concentration. While it is not claimed that the existence of similar minima in the 2 sets of curves is to be ascribed to solvation, or to any other common cause, it is suggested that such an explanation is not without the range of probability.

The author hopes to continue the investigation of this question in the near future.

STAMFORD, CONN.

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSIOLOGICAL CHEMISTRY, MARQUETTE SCHOOL OF MEDICINE.]

A STUDY OF A DECOLORIZING CARBON.

BY JOSEPH C. BOCK.

Received May 6, 1920.

The use of finely divided carbon to decolorize solutions is universal. There are, however, comparatively few attempts recorded in the literature to use it for the removal of substances other than coloring matters. While working on the removal from blood of residual proteins (after heat coagulation) we tried a charcoal of vegetable origin. While this was found to remove proteins quantitatively, it also caused a lowering of the non-protein nitrogen. As there are numerous occasions where decolor-

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[1] THIS JOURNAL, 32, 1011 (1910).

[2] "Hydrates in Aqueous Solution," *Carnegie Inst. Publication* 60.

[3] *Z. physik. Chem.*, 46, 286 (1903).

izing carbons are used in laboratory procedures, it was thought of interest to find out to what extent the decolorizing carbon removes nitrogenous and other constitutents from biological fluids. Urine was used in the majority of these experiments.

The carbon used in the present investigation was a vegetable carbon called "Norit." It is obtained from the manufacturer as a finely divided, intensely black powder, perfectly dry and of very low ash content. In most of the experiments it was used in this form, no attempt being made to utilize the finer particles only, although the investigations of A. B. Bradley[1] show a higher efficiency for the more finely divided (124-mesh sieve) carbon. Other conditions being equal, the material having the higher carbon content should give the better result. We compared the ash contents of Norit with that of animal charcoal (Merck, U. S. P.), assuming that the latter is very commonly used in the laboratory. One set of determinations was made on carbon which had been treated with dil. hydrochloric acid, filtered with suction, washed with water, treated with dil. alkali and then washed to a neutral reaction. Table I shows the analytical results obtained.

Table I.

Composition of Decolorizing Charcoal, in Percentages.

		Norit.		Animal charcoal.	
		As purchased.	Washed.	As purchased.	Washed.
Ash	1	4.87	2.20	73.35	17.16
	2	5.40	2.17	73.13	17.01
	3	...	...	73.65	16.95
	Aver.	5.13	2.18	73.34	17.04
Difference as carbon		94.77	97.82	26.66	82.96

The procedure used in most of the experiments was as follows. A measured quantity of urine (100–200 cc.) was shaken with a weighed amount, usually 5%, of Norit, and then filtered. The shaking need not be very prolonged nor especially vigorous, as long as a good mixing and an even distribution of the substance throughout the liquid are accomplished.

The results are presented in the following tables. It will be seen from Table II that the total nitrogen is considerably decreased, the loss amount-

Table II.

Effect of Norit on Urine.

100 Cc. of Urine Treated with 5 G. of Norit.

Untreated urine.	Treated.	Loss. %.
	Total Nitrogen. G.	
13.265	10.773	18.8
4.900	4.162	15.0
9.576	8.232	12.9
7.140	6.066	15.0
5.894	4.858	15.8

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[1] A. B. Bradley, *J. Soc. Chem. Ind.*, 38, 396 (1919).

TABLE II (*continued*).

Untreated urine.	Treated.	Loss. %.
	Ammonia Nitrogen. G.	
0.6126	0.3199	4.59
0.4880	0.4550	0.67
0.5450	0.3560	3.47
0.3530	0.3050	1.57
	Urea Nitrogen. G.	
4.368	4.004	8.35
4.630	4.250	8.20
7.490	6.650	11.21

ing to about 15%, the decrease in ammonia and urea nitrogen being proportional.

A much larger decrease will be noted in the creatinine results, the loss amounting to from 50 to 90%.

TABLE III.

Effect of Norit on Urine.

100 Cc. of Urine Treated with 5 G. of Norit.

Untreated urine.	Treated.	Loss. %.
	Creatinine. G.	
1.154	0.437	62.13
1.300	0.610	53.07
0.850	0.095	88.82
0.855	0.170	80.11
1.501	0.600	60.03
1.470	0.558	62.04
1.316	0.210	84.04
0.675	0.055	91.85
	Uric Acid. G.	
0.655	Trace	...
0.520	Trace	...
0.122	Trace	...
0.557	0.018	...
0.375	None	...
0.313	None	...

Uric acid is almost quantitatively removed. In the cases where "trace" is reported, the color[1] in a liquid column of about 120 mm. or over was a faint blue. Where "none" is reported the color was that of the "blank" determination.

As indicated in Table IV, phosphates are decreased in amounts varying from 12 to 39%, whereas only a small percentage of chlorides is removed.

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[1] The Benedict-Hitchcock method was used for the determination of uric acid, *J. Biol. Chem.*, 20, 619 (1915).

TABLE IV.

Effect of Norit on Urine.

100 Cc. of Urine Treated with 5 G. of Norit.

Untreated urine.	Treated.	Loss. %.
	Phosphates. G. P_2O_5.	
0.960	0.716	25.41
1.345	0.965	28.25
1.470	0.970	34.01
3.170	2.760	12.93
2.950	2.520	14.58
1.780	1.090	38.76
	Chlorides. G. NaCl.	
4.85	4.75	2.06
9.90	9.90	0.00
7.00	6.90	1.42
9.60	9.40	2.08
7.00	6.60	5.71
12.20	12.10	0.81

The decrease in glucose, Table V, is comparatively small where sugar-containing urines are concerned. If, however, pure solutions containing small amounts of glucose are treated with Norit, the removal of sugar may amount to over 25%.

TABLE V.

Effect of Norit on Urine and Pure Sugar Solution.

Untreated urine.	Treated with 5% norit.	Loss. %.
	Glucose. Per cent.	
3.30	3.12	5.45
1.98	1.94	2.02
1.77	1.77	0.00
3.57	3.54	0.84
1.97	1.95	1.01
1.79	1.74	2.79
3.07	3.03	1.30
Pure glucose sol.		
0.41	0.32	21.95
0.30	0.22	26.66
0.37	0.30	23.33
0.77	0.64	16.88

It should be mentioned in this connection that lactose is removed to about the same extent from milk as glucose is from urine. The milk was diluted with water, acidified and heated. Norit was then added and the mixture filtered. Perfectly clear filtrates were obtained which showed, however, a considerable decrease in lactose as compared with samples with which another method of protein removal was employed.

The effects of adding various amounts of carbon are shown in Table VI. The loss is proportional to the amount of Norit used in all cases except that of uric acid. It is, however, impossible to obtain colorless filtrates with 3% and in cases of deeply colored urines with 4% additions of Norit.

TABLE VI.

Effect of Various Amounts of Norit on Urine.

	Untreated urine.	100 cc. treated with 3% Norit.	4% Norit.	5% Norit.
Total N	7.140	6.328	6.202	6.066
Uric acid	0.375	Trace	None	None
Creatinine	0.850	0.286	0.172	0.095

In all cases, we used the carbon as obtained from the manufacturer. A comparison between effectiveness of such material and washed Norit is shown in Table VII. The differences in the results are rather small, but are, of course, in favor of the purified product.

TABLE VII.

Comparison of the Effect of Commercial and Washed Norit on Urine.

	Total nitrogen.	Uric acid.	Creatinine.	Phosphates.	Chlorides.	Glucose.
Untreated urine	8.008	0.313	0.764	1.13	8.55	1.98
Treated with com'l Norit	7.280	None	0.139	0.98	8.40	1.94
Treated with washed Norit	7.056	None	0.123	0.96	8.55	1.94

A short attempt was also made to test the behavior of Norit toward bacteria. Bouillon cultures of 2 organisms were shaken with Norit for a few seconds, then allowed to stand for 3 or 4 minutes. While sterilization was by no means complete, there was a very marked decrease in bacterial count. It may be possible, as has been claimed by one European observer, to effect complete sterilization in this way. The matter will be further investigated.

Summary.

(1) Norit removes, from urine, ammonia-nitrogen, chlorides and glucose slightly; urea, total nitrogen and phosphates considerably; creatinine very largely, and uric acid completely.

(2) Adsorption from solution by solids is specific and selective. This unfortunately means only that we are as yet ignorant of relations which undoubtedly do exist between the degree of adsorption, on the one hand, and the physical and chemical properties of adsorbent and adsorbed substance on the other.

(3) Freundlich's simple adsorption formula holds good for the two cases of total nitrogen and creatinine, given in Table VI. In the case of pure glucose, Table V, the experimental errors in determining such small quantities of glucose are necessarily too large to test the adsorption formula. Nevertheless, Tests 1, 2 and 4 in this series indicate that the formula holds, as has already been established by Herzog and others.

(4) When several solutes are present in a solution, each one of them is adsorbed less than when they are present separately. This is well shown

in Table V, where the amount of glucose adsorbed, when present alone in quantities of 2 to 3% would be much larger than 0.05%, since 0.09% is adsorbed at an initial concentration of 0.46%.

We wish to express our thanks to Mr. W. Leitch, of Joseph Bakers, Ltd., White Plains, N. Y., for his help in procuring the Norit. We also wish to thank Mr. Robert Whymper, Bermondsey, London, S. E., for his kind and valued advice.

MILWAUKEE, WISCONSIN.

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF ILLINOIS.]

DETERMINATION OF THE ELECTROLYTIC POTENTIAL AND OVERVOLTAGE OF ARSENIC.

BY VINCENT B. MARQUIS.

Received May 18, 1920.

1. Electrolytic Potential.

The electrolytic potential of arsenic, or the potential between an arsenic electrode and a solution normal with respect to arsenious ions, has never been accurately determined because of the difficulty of determining the arsenious ion concentrations. In aqueous solution arsenious salts are strongly hydrolyzed and the metal ion concentration cannot be determined by conductivity measurements because of the presence of the acid which is formed by the hydrolysis. The conductivity of arsenious trichloride and hydrochloric acid solutions were measured by Zawidzki[1] with results as shown in the following table, in which V is the number of liters containing one mol and Λ the equivalent conductivity.

V.	Λ. $HCl + As(OH)_3$. 1/ohm.	Λ'. HCl. 1/ohm.	$\Lambda' - \Lambda$. 1/ohm.
16	366.3	368.5	+2.2
32	374.2	375.3	+1.0
64	379.6	379.2	—0.6

These results show clearly why conductivity measurements do not help in the determination of arsenious ion concentration. The ability of arsenious chloride to form arsenious cations has, however, been demonstrated by Kahlenberg and Lincoln[2] by measuring the conductivity of solutions of arsenious chloride in ethyl aceto-acetate and nitrobenzene.

The potential between an arsenic electrode and a normal solution of arsenious chloride was measured by B. Neumann[3] and found to be 0.550 volt. From this value it has been estimated by Abegg that the electrolytic potential of arsenic is +0.27 volt, using the scale in which hydro-

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[1] Zawidzki, *Ber.*, 36, 1434 (1903).

[2] Kahlenberg and Lincoln, *J. Phys. Chem.*, 3, 28 (1899).

[3] Neumann, *Z. physik. Chem.*, 14, 220 (1894).

gen is zero and potassium negative. From the same figures Wilsmore[1] estimates that the electrolytic potential is "less than —0.293 volt," taking potassium as positive.

In order to obviate the difficulty of finding the arsenious ion concentration it was decided to employ the method used by Roderburg for tungsten and also by Rideal for uranium. For the measurement of the electrolytic potential of uranium Rideal used a solution of uranium tetrachloride in ethyl alcohol. The salt is not rapidly hydrolyzed in cold solution and the metal ion concentration can be determined by conductivity measurements. The relation between the electrolytic potential in aqueous and alcoholic solutions is expressed by the following equation:

$$EP_w - EP_a = \frac{RT}{nF} \log \frac{P_w}{P_a}$$

in which EP_w and EP_a are the electrolytic potentials in water and alcohol, respectively, and P_w and P_a the solution pressures of the metal in each solution. According to Carrara and Agostini,[2] the value for the fraction P_w/P_a is the same for all metals and for copper and cadmium $EP_w - EP_a = 0.11$ volt. According to Roderburg the value for copper is 0.071 volt, and this value is also used by Rideal.

In the work described below dry arsenious chloride was dissolved in dry alcohol and the potential between this solution and an arsenic electrode was measured. The degree of ionization of the salt was determined by conductivity measurements and the electrolytic potential calculated by means of the Nernst equation.

In taking up this work the first thing to be determined was whether or not arsenious chloride is hydrolyzed by dry absolute alcohol. If such hydrolysis does take place, then it is clear that during the process the conductivity of the solution will gradually increase on account of the hydrochloric acid which is formed. The conductivity of a solution containing 0.0807 g. of arsenic trichloride in 50 cc. of alcohol was measured at different time intervals with results as shown in the following table. The temperature of the solution was 20°.

Time (after making the solution). Min.	Resistance. Ohms.
1	74.3
2	74.6
3	74.9
4	75.5
6	76.2
9	76.9
14	77.3
24	77.5
54	77.7

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[1] Wilsmore, *Z. physik. Chem.*, 35, 318 (1900).

[2] Carrara and Agostini, *Z. Elektrochem.*, 11, 385 (1905).

It will be seen from this table that the resistance instead of decreasing, as might be expected, slightly increased. This is explained by the fact that arsenious chloride forms an addition product with alcohol.[1] These results show that the change in arsenious ion concentration is slight and the solution quickly comes to equilibrium. The type of conductivity cell used permitted the exclusion of air so that no moisture was taken up by the solution during the experiment.

In order to determine the degree of ionization of arsenious chloride it was necessary to measure the conductivity of several solutions of increasing dilution so that the value of λ_∞, the molecular conductivity at infinite dilution, could be obtained by extrapolation. The conductivity measurements were made by the Kohlrausch method. The arsenic trichloride used was prepared by heating 40 parts of arsenious oxide with 100 parts of sulfuric acid to 100° and adding small pieces of fused sodium chloride. The arsenic trichloride was distilled off and redistilled from conc. sulfuric acid in order to make sure that it was dry. The absolute alcohol used was redistilled over calcium oxide. Its conductivity was 1.56×10^{-6}. The results are shown in the following table and are plotted in Fig. 1 according to the method suggested by Kohlrausch, where values of λ_1 are plotted as ordinates and $1/\sqrt[3]{\phi}$ (ϕ = volume in cc. in which one mol is dissolved) as abscissas. The values of λ shown below were corrected for the conductivity of the alcohol and give the average of several sets of readings in which both arsenious chloride prepared as described above and a sample furnished by E. H. Sargent Co. were used. There was good agreement between the readings obtained from these 2 samples of arsenious chloride.

Resistance. Ohms.	λ. 1/ohms.	$1/\sqrt[3]{\phi}$.
36.8	53.5	0.0303
61.0	64.6	0.0240
98.7	79.4	0.0191
113.9	87.0	0.0177
331.0	118.3	0.0110
606.0	127.2	0.0085

Original solution = 5.0340 g. of $AsCl_3$ per liter.
Temperature, 21°.
Conductivity of alcohol = 1.56×10^{-6}.
Cell constant = 0.05477.

The value for λ_∞ obtained by plotting these points and extending the curve to the axis is 155.0×1/ohms.

In order to measure the electrode potential of arsenic in an alcoholic solution it was necessary to prepare an alcoholic auxiliary electrode. The electrode used by Roderburg and Rideal consisted of mercury in

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[1] Walden, *Z. physik. Chem.*, 43, 438 (1903).

contact with alcohol saturated with mercurous chloride and lithium chloride. According to Roderburg the potential of this electrode is +0.193 volt. The arsenic electrodes used were copper plated with arsenic. For their preparation a solution of 5 g. of arsenious oxide in 300 cc. of 33% hydrochloric acid was electrolyzed with a current density of 0.15 ampere per square decimeter. The deposit of arsenic was smooth, bright, and in good physical condition. The following system, Hg/HgCl and LiCl in alc./$AsCl_3$ in alc./As, had an e. m. f. of 0.153 volt. Therefore the electrode potential of the arsenic was +0.040 volt. The potential between an arsenic electrode and an aqueous solution of the same arsenious ion concentration is found by adding 0.071 to this value, which gives 0.111 volt. The solution contained 0.176 mol. of arsenious chloride per liter and it was found by conductivity measurement that λ = 32.0. Therefore, $\alpha = \lambda/\lambda_\infty = 32.0/155.0 = 0.206$ and the arsenious ion concentration was $0.176 \times 0.206 = 0.0363$. By substitution in the Nernst equation,

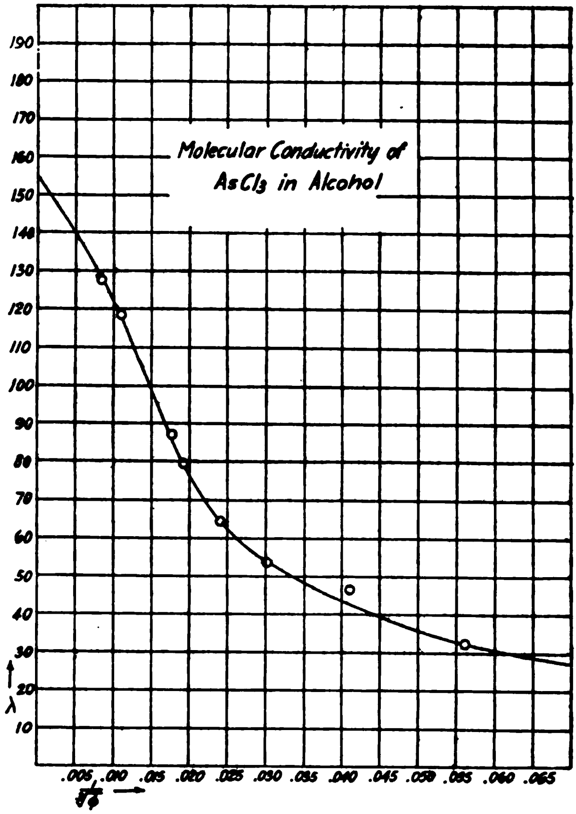

Fig. 1.

$$e = e_0 + \frac{RT}{nF} \log \frac{C}{C_0}$$

the value $e_0 = +0.138$ volt is obtained. Therefore, the electrolytic potential of arsenic is +0.138 volt, using the scale in which hydrogen is zero and potassium negative. The measurement was repeated with a different arsenic electrode and a solution which contained 0.0704 mol of arsenious chloride per liter. In this case λ was found to be 46.6 and α 0.301. The calculated value for e_0 was the same in this case as in the first determination, namely, +0.138 volt, thus placing arsenic between hydrogen and copper in the electromotive series.

2. Overvoltage.

The overvoltage of hydrogen on arsenic was determined by measuring the back e. m. f., or polarization, of a cell which consisted of a platinum anode, an arsenic cathode made as described above, and a *N* sulfuric acid electrolyte. The area of each electrode was one square centimeter. A gradually increasing e. m. f. was applied to these electrodes until a milliammeter indicated that current was just beginning to flow through the cell, showing that decomposition of the electrolyte had just begun. The polarization of the cell caused by this impressed e. m. f. was measured and by means of an auxiliary calomel electrode the anode and cathode polarizations, or overvoltages, were determined separately. Measurements were made by both the open and closed circuit methods. In the former the back e. m. f. is measured while the circuit furnishing the applied e. m. f. is open. It is necessary to make the readings very quickly because depolarization begins as soon as the circuit is broken. In the closed circuit method the arm of the auxiliary electrode vessel is drawn out at the end to a small tube which is bent up to a horizontal position and placed so that it almost touches the cathode. In this way the internal resistance of the electrolyte is largely eliminated and the potential between the cathode and the calomel electrode can be measured without breaking the main circuit. The value for the overvoltage of hydrogen on arsenic obtained by the open circuit method was 0.379 volt, while that by the closed circuit method was 0.478 volt.

This work was suggested by Dr. E. K. Rideal and carried out under his direction. The author wishes to take this opportunity to thank him for his many helpful suggestions and criticisms.

URBANA, ILL.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF KANSAS.]

THE LIQUID AMMONIA-SODIUM METHOD FOR THE DETERMINATION OF HALOGEN IN ORGANIC COMPOUNDS.

BY F. B. DAINS AND R. Q. BREWSTER.

Received May 27, 1920.

The liquid ammonia-sodium method for the determination of halogens in organic compounds was first published by Chablay.[1] This method had been independently developed in this laboratory, as the result of some observations by Dr. H. P. Cady, and was later published by Dains,[2] Vaughan and Janney. The process consists in dissolving 0.1 to 0.2 g. of substance, accurately weighed, in 30 to 50 cc. of liquid ammonia and

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[1] *Ann. chim. phys.*, [9] 1, 469–519 (1914).

[2] THIS JOURNAL, 40, 936 (1918).

treating the solution with small pieces of clean metallic sodium until the blue color formed in the solution persists for 1/2 hour. The ammonia is then allowed to evaporate and the residue of sodium halide is taken up in water and the halogen content determined by any of the ordinary methods;[1] gravimetric analyses give the most accurate results, especially if the solutions are highly colored. The chief advantage of this method is that it is quite rapid and much more convenient than the Carius method.

Recently C. W. Clifford[2] made an investigation of the accuracy of this method and reported the results of the analysis of 5 halogen-containing organic compounds.

The first, carbon tetrachloride, gave both qualitative and quantitative evidence of the formation of cyanides. The second, hexachloroethane, also showed the presence of cyanides but not in sufficient amount to interfere with the quantitative determination. The other 3 compounds, which were not named, were evidently cyanide-free.

In the summary of the article the statement is made, "Cyanide is formed in many cases by the treatment of organic compounds with sodium in liquid ammonia."

Since Chablay had not mentioned the cyanide formation and its presence had not been noted in the relatively large number of analyses made in this laboratory, it seemed advisable to follow up this interesting observation of Clifford and to ascertain under what conditions it would be formed in sufficiently large amounts to interfere with the halogen determination. Consequently, a study of the action of sodium in liquid ammonia was made on a series of substances representing various classes of organic compounds. The procedure was as follows.

Unweighed samples of about 0.5 to 1.0 g. of each of these substances were dissolved in about 50 cc. of liquid ammonia and small pieces of sodium were added until the permanence of the blue color in the solution showed that an excess of sodium was present. After evaporation of the ammonia the residue was dissolved in water and qualitative tests for cyanides were applied. The prussian-blue test was selected because of the ease with which it will detect very small quantities of cyanides. Throughout the entire list of qualitative tests made the formation of prussian blue was either very intense or nil. Some of the materials examined contained halogens while others were halogen-free. The following table of data shows the results obtained from the 123 substances examined.

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[1] THIS JOURNAL, 41, 1051 (1919).

[2] *Ibid.*, 41, 1051 (1919).

Formation of Cyanides on Treatment with Liquid Ammonia and Sodium.

Negative results were obtained with the following:

Aliphatic Series.

- Hydrocarbons
  - Gasoline
  - Amylene
- Alkyl Halides
  - Methyl iodide
  - Ethyl iodide
  - Propyl bromide (*iso*)
  - Propyl bromide (*normal*)
  - Propyl chloride (*normal*)
  - Butyl iodide (*normal*)
  - Ethylene dibromide
  - Iodoform
  - Hexachloro-ethane
  - Methylene iodide
- Alcohols
  - Methyl alcohol
  - Ethyl alcohol
  - Propyl alcohol (*normal*)
  - Propyl alcohol (*iso*)
  - Butyl alcohol (*normal*)
  - Amyl alcohol (*tert.*)
  - Allyl alcohol
  - Glycol
  - Glycerol
- Ethers
  - Diethyl ether
- Aldehydes and Ketones
  - Formaldehyde
  - Paraldehyde, $(CH_3CHO)_3$
  - Acetone
  - Butyrone, $(C_3H_7COC_3H_7)$
- Acids
  - Formic acid
  - Acetic acid
  - Monochloro-acetic acid
  - Monobromo-acetic acid
  - Trichloro-acetic acid
  - Oxalic acid
  - Lactic acid
  - Tartaric acid
  - Succinic acid
  - Alanine
- Esters
  - Ethyl formate
  - Ethyl chlorocarbonate
  - Ethyl acetate
  - Ethyl butyrate
  - Ethyl oxalate
  - Ethyl malonate
  - Ethyl acetoacetate
  - Ethyl nitrite
- Amines
  - Ethylamine hydrochloride
  - Methylamine hydrobromide
- Amides
  - Formamide
  - Acetamide
- Miscellaneous
  - Urea
  - *m*-Bromo-diphenyl-thiourea
  - *p*-Bromo-phenyl-allyl-thiourea
  - Urethane
  - Casein

Aromatic Series.

- Hydrocarbons
  - Benzene
  - Naphthalene
  - Toluene
  - Diphenyl
  - Pinene
- Halogen Compounds
  - Chlorobenzene
  - Bromobenzene
  - Phenyl iodide
  - Di-bromobenzene (1–4)
  - Benzyl chloride
  - Benzal chloride
  - *o*-Bromotoluene
- Azo Compounds
  - Azobenzene
  - Diazo-aminobenzene
  - Amino-azobenzene
- Aldehydes and Ketones
  - Benzaldehyde
  - Salicylic aldehyde
  - Anisic aldehyde
  - Quinone
  - Chloranil
  - Benzophenone

- Phenols, Alcohols, Ethers
  - Phenol
  - *p*-Bromophenol
  - Cresol
  - β-Naphthol
  - Benzyl alcohol
  - Benzyl ethyl ether
  - Phenetol
- Nitro Compounds
  - Nitrobenzene
  - *o*-Chloro-nitrobenzene
  - *p*-Bromo-nitrobenzene
  - *p*-Nitrotoluene
- Amino Compounds
  - Aniline
  - *p*-Bromo-aniline
  - Formanilide
  - Acetanilide
  - *p*-Bromo-acetanilide
  - *p*-Toluidine
  - β-Naphthylamine
  - Phenyl hydrazine
  - *p*-Phenylene-diamine hydrochloride
- Acids
  - Benzoic acid
  - *m*-Bromobenzoic acid
  - Salicylic acid
  - Sulfanilic acid
  - *o*-Toluic acid
  - Cinnamic acid
  - Dibromo-cinnamic acid
- Esters
  - Ethyl benzoate
  - Phenyl benzoate
  - Methyl salicylate
  - Phenyl salicylate
- Heterocylic Compounds
  - Pyridine
  - Quinoline
  - Isoquinoline
  - Antipyrine
  - Uric acid
  - Caffeine
  - Quinine sulfate

The following substances gave positive tests for cyanides.

- Chloroform
- Bromoform
- Carbon tetrachloride
- Chloral hydrate
- Bromal hydrate
- Ethylidene chloride
- Tetrachloro-ethylene
- Acetylene tetrachloride
- Methyl cyanide
- Benzyl cyanide
- Ethyl cyano-acetate

In the cases of chloroform, bromoform, carbon tetrachloride, chloral and bromal hydrates, the formation of cyanides may be easily explained by the assumption that the trivalent nitrogen has replaced 3 negative halogen atoms with the loss of hydrogen halide. It is well known that chloroform may be converted into potassium cyanide by treatment with ammonia and alkali even at ordinary temperatures.[1]

$$CHCl_3 + NH_3 + 4KOH = KCN + 3KCl + 4H_2O.$$

The presence of cyanides in the liquid ammonia solution of chloroform and sodium is hence to be expected. Bromoform, carbon tetrachloride, chloral hydrate and bromal hydrate resemble chloroform in this respect.

Methyl cyanide, benzyl cyanide and cyano-acetic ester evidently split off sodium cyanide directly.[2]

The formation of cyanides from ethylidene chloride, tetrachloro-ethylene, and acetylene tetrachloride is not so easily explained. Presumably

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[1] Richter-Spielmann, "Organic Chemistry," 1, 246 (1916).

[2] *Ber.*, 2, 319 (1869); *J. prakt. Chem.*, 22, 264 (1880); *Ann.*, 65, 269 (1848).

this is accounted for, first, by the loss of hydrogen chloride from the molecule,[1] followed by absorption of ammonia and further loss of hydrogen chloride, giving a cyanogen compound. In these special cases, therefore, a modified method of analysis must be used in order to separate the cyanides and halides. The method developed by Clifford has been found to be satisfactory.

Quantity of Cyanide Formed from Halogen Compounds.

It was considered of interest to determine whether the amount of sodium cyanide produced under the conditions of the analysis was at all near the quantity called for by the following equations.

$$CHCl_3 + NH_3 + 4Na = NaCN + 3NaCl + 2H_2$$

$$CCl_3CHO.H_2O + NH_3 + 4Na = NaCN + 3NaCl + \text{Unknown substances.}$$

Accurately weighed samples of chloroform, bromoform, iodoform and chloral hydrate were dissolved in liquid ammonia and treated with a slight excess of sodium. After the ammonia had evaporated the residue was dissolved in water and the quantity of cyanides formed determined by titration to faint turbidity with standardized silver nitrate solution in the weakly alkaline solution. The following table shows the percentage yield of sodium cyanide calculated for the theoretical yield according to the above equations.

YIELD OF CYANIDES.

Substance.	1. %.	2. %.	3. %.
Chloroform	48	31	33
Bromoform	30	36	24
Iodoform	0	0	0
Chloral hydrate	16.7	16.5	19.7

It is apparent that the quantity of sodium cyanide found is quite variable even under conditions which were believed to be very nearly the same. This statement was also made by Clifford, though no experimental evidence was given. The amount of cyanides formed might be increased or decreased by modifying the conditions of the analysis but no such effort was made.

Quantitative Analysis of Typical Organic Halogen Compounds.

The rather large list of qualitative experiments has shown that cyanides are formed to interfere in the analysis only in a few special cases. The following list of quantitative determinations is given to show the adaptability of the method to the various classes of organic compounds.

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[1] It has been shown by Chablay and also in this laboratory that the liquid ammonia-sodium solution behaves like alcoholic potash toward an alkyl halide, giving an unsaturated compound as one of the products.

Substance.	Halogen. Found. %.	Halogen. Calculated. %.
Isopropyl bromide	65.30	
	64.91	65.04
N-Butyl iodide	68.51	
	68.80	69.00
Monochloro-acetic acid	37.58	
	37.25	37.53
Chlorobenzene	31.50	
	31.35	31.53
Bromobenzene	50.70	
	50.89	50.93
p-Bromo-acetanilide	37.36	
	37.72	37.40
o-Chloro-nitrobenzene	22.80	
	22.42	22.52
p-Chloro-aniline	27.92	
	27.78	27.81
p-Bromophenol	46.50	
	46.37	46.25
m-Bromobenzoic acid	40.10	
	40.12	39.80
Benzyl chloride	27.85	28.03
m-Bromo-diphenyl-thiourea	25.85	
	25.96	26.03
2-*o*-Chloro-phenylamino-5-methyl-dihydro-thiazole	15.43	
	15.47	15.67

Attempts at the Quantitative Determination of the Cyanide Radical in Organic Compounds.

Since it was shown that the cyanogen radical was split off the organic molecule in liquid ammonia solution by treatment with sodium, it was hoped that this behavior could be made the basis for a quantitative determination of cyanides in such compounds. Hence, samples of methyl cyanide and benzyl cyanide were subjected to analysis by the general procedure as used in the case of halogen compounds. The sodium cyanide formed was determined by titration with standardized silver nitrate solution.

	Found. % CN.	Calculated. % CN.
Benzyl cyanide	20.25	
	19.50	22.2
Methyl cyanide	9.45	
	10.20	
	12.50	
	11.70	63.4

These results indicate that such a procedure could not be utilized for the quantitative determination of organic cyanides. Benzyl cyanide was converted very largely into sodium cyanide, but in the experiments with methyl cyanide this reaction was greatly decreased. In the latter case the chief product of the reaction seemed to be ethyl amine, resulting from the reduction of the methyl cyanide presumably, according to the following equation,

$$CH_3CN + 4NH_3 + 4Na = C_2H_5NH_2 + 4NaNH_2.$$

The behavior of alkyl halides and other substances with liquid ammonia alone and also in the presence of sodium, is being studied and further results will be published later.

Summary.

1. It has been shown that the reaction between liquid ammonia, sodium and organic compounds, leads to the formation of cyanides only in a few special cases whose nature has been discussed.

2. A list of quantitative determinations of halogen in various classes of organic compounds has been given which will supplement those formerly published by us and by Chablay.

3. Application of this method to the quantitative determination of cyanides in organic compounds met with no success.

LAWRENCE, KANSAS.

[CONTRIBUTION FROM THE PHYSICS LABORATORY, STATE UNIVERSITY OF IOWA.]

THE VAPOR PRESSURE CURVES OF SOLID AND LIQUID SELENIUM NEAR THE MELTING POINT.

BY L. E. DODD.

Object and Scope.

The object of this investigation has been to determine by the method of molecular flow the saturated vapor pressure of selenium in the vicinity of the melting point. This required the determination of both the sublimation curve of the crystalline solid and the vaporization curve of the liquid. Further, the aim has been to find from these data values for some of the physical constants of selenium near its melting point.

Molecular Flow of Gases and Knudsen's Equations.

Knudsen's[1] equations for resistance to molecular flow of gases are, for an aperture in a thin partition,

$$W_1 = \sqrt{2\pi}/A_1 \qquad (1)$$

and for a tube

$$W_2 = {}^3/_8\sqrt{\pi/2}\int^L O/A_2^2\,dl \qquad (2)$$

where l is length of tube, O is circumference, and A_2 cross-sectional area, which may be variable.

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[1] Knudsen, *Ann. Physik.*, 28, 75, 999 (1909).

For a combination of a thin partition with an aperture placed across a tube, and the tube, the total resistance is $W = W_1 + W_2$. If there is a steady flow of gas through this combination, such that the pressure where the gas enters the tube is p_2 and the pressure where it issues is p_1, the quantity flowing through in time t is given by

$$G = 1/W \,.\, (p_2 - p_1)\sqrt{\rho_1}\, t, \tag{3}$$

where G is weight of gas in grams, and ρ_1 the density at unit pressure and at the temperature of the apparatus. All quantities are in absolute units. ρ_1 can be obtained from the known density of the gas at unit pressure and 0°,

$$\rho_1 = (\rho_1)_0/(1 + at), \tag{4}$$

where a is the expansion coefficient and t the temperature. Knudsen verified (1), (2) and (3) experimentally with the gases hydrogen, oxygen and carbon dioxide.

Application of the Method of Molecular Flow to the Measurement of Saturated Vapor Pressures.

Knudsen[1] used the method of molecular flow to measure the vapor pressure of mercury at lower temperatures than are possible by other methods. For calculation of ρ_1 in this case he employed (4), which is applicable to any substance in the vapor state if the number of atoms per vapor molecule is known, since

$$(\rho_1)_0 = (1409.2 \times 10^{-12})/(2 \times 16)nA, \tag{4a}$$

where the number in the enumerator is the density of oxygen at unit pressure and 0°, n an integer expressing the number of atoms per molecule, and A the atomic weight. He made 2 standard determinations of mercury vapor pressure at 0° and 7°, respectively The vapor was condensed at the temperature of solid carbon dioxide, so that p_1 was negligible. For the other temperatures the vapor was condensed at 0°, and the standard value already found was used in this case for p_1.

Following up this application of the method Egerton,[2] at the suggestion of Nernst, applied it to determine the vapor pressure of metallic zinc and cadmium. To save time in these pressure measurements, Egerton decreased W in (1) by using, instead of one, several circular apertures in parallel in the same thin partition. He showed that the total resistance of a partition varies inversely as the number of apertures. Egerton used as many as 17 apertures in parallel with good results.

The present work was a continuation of some preliminary experiments by F. C. Brown, applying this method to selenium. As far as known to the present writer, this is the first application of the method to a substance with other than a monatomic vapor at the temperatures of the ex-

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[1] Knudsen, *Ann. Physik*, **29**, 179 (1909).

[2] Egerton, *Phil. Mag.*, **33**, 33 (1917).

periment. The preliminary results were spoiled by the lack of a high enough vacuum and by an important temperature difference inside and outside the vapor tube. In the present investigation selenium crystals of large size, as first produced by Brown[1] and furnished by him for this work, were used for the element in the solid state.

Apparatus.

The Egerton type of apparatus, which with some changes was used here, was a modification of that of Knudsen. Fig. 1 is a longitudinal section of the type of vapor tube employed for selenium. It consists of a glass tube set into a larger one by a ground joint. The whole apparatus may be called simply the "tube," made up of an "inside tube" and an "outside tube." The latter has near the top an arm through which the air is pumped out. A lower chamber is separated from the remaining space in this tube by a thin perforated partition of platinum. The substance being studied is placed below the partition and kept at a constant temperature in a suitable oven. The inner, or "condensation," tube is fitted with a stopper through which pass 2 narrower glass tubes, one acting as a nozzle for the inflow of a cooling fluid, such as water, the other for its outflow. The vapor molecules pass up through the partition to the inside tube, where they are condensed as a solid deposit.

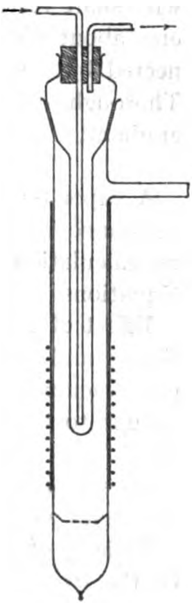

Fig. 1.

The vapor tube was inserted into a Freas oven through a hole drilled in the top, so that the tube projected into the oven space and was supported in place by its arm. The drilled hole was lined by a brass tube fitting it closely and providing a thermally conducting envelope. The platinum partition in the vapor tube extended one cm. or more below the roof of the oven chamber. Around the brass tube over this distance, the wire of an auxiliary heater was wound, to prevent condensation on the outside tube by maintaining a fairly uniform temperature up to the zone of deposit. Through the brass tube next to the ceiling of the oven chamber holes were drilled for a chimney effect, to give ready access of oven air to the vapor tube near the place of condensation.

A platinum resistance thermometer was hung in the oven chamber through a tube from above, so that the exposed helix of resistance wire was within about one cm. of the lower or vaporization chamber of the vapor tube when the latter was in place. A mercury thermometer also was passed through the wall of the oven chamber near the top, and its entire thread was always inside the oven. The bulb was within 2 cm.

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[1] Brown, *Phys. Rev.*, 5, 236 (1915). See also Brown and Sieg, *ibid.*, 28, 497 (1914).

of the glass wall of the vaporization chamber. This thermometer was read through the glass door of the oven, and an allowance of 0.5° was made for parallax at each reading. The 2 thermometers thus occupied very nearly the same relative positions. In the earlier work the mercury thermometer was used as a check on the resistance thermometer, which it was at first proposed to use for the temperature readings at one-minute intervals, but it was unexpectedly found that the mercury thermometer was more suited to the purpose, with the other as a check. Temperature readings were taken in this manner for the present data.

A small electric motor outside the oven operated a rotary fan, placed with shaft vertical near the floor of the oven chamber, and with a diameter about $^2/_3$ the width of the oven. Motor and fan were at first connected by a spiral spring belt, but later by a shaft with friction drive. Thorough stirring of the air insured freedom from serious temperature gradient.

Preliminary Standardization of Tubes.

A vapor tension tube such as described can be standardized with some substance whose vapor pressure is known, by applying Equation 3, or by calculation from measurements of the tube dimensions according to Equations 1 and 2.

Effect of Poor Vacuum on Tube Resistance.[1]—Comparison of Equations 1 and 2 with results by the first method showed, as expected, that a poor vacuum introduces serious error. The effect of an air pressure large enough to render inapplicable the Knudsen expressions is shown in Table I(*a*). The resistance with roughly constant air pressure in the tube increases rapidly with the temperature, due to the collisions of the mercury molecules with those of the air.

Validity of the Knudsen Equations with Good Vacuum Conditions.—Of the two methods for determining tube resistance the second is more accurate, as Egerton points out, unless with the first method the mean of quite a number of determinations should be taken. It is comparatively easy to make accurate measurements of the dimensions for calculation of W in the second method.

The first method, however, was used in a preliminary checking of Equations 1 and 2, with mercury as the standardizing material. Two tubes used earlier in the work were standardized in this wy. For Tube A the values of W given in Table I(*b*) were obtained with the Langmuir pump. The mean value for this tube was 40.4 absolute units. The diameter of the circular apertures in the platinum partition was very nearly 2 mm. This value of the area gives 40.0 units for W, leaving but 0.4 unit for W_2, for which 2 units would have been more nearly correct. This would require 38.4 units for W_1, or a diameter of 2.04 mm. for the apertures.

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[1] Dodd, *Phys. Rev.*, 11, 242 (1918).

Comparison of the diameter values for Tubes D, E, F, indicates that the diameters in Tubes A and B were likewise above 2 mm.

TABLE I.—VERIFICATION OF KNUDSEN'S EQUATIONS.

(*a*) Tube B, 6 apertures. Poor vacuum.

Temp. ° C.	*W*. abs. units.	Remarks. Determinations averaged.
87	227	12
97	294	3
106	329	3
120	629	2
129	771	3

(Approximate calculated value of *W* = 15 units.)

(*b*) Tube A, 2 apertures. Good vacuum.

Run No.	Temp. ° C.	*W* abs. units.
1	80	41.3
2	80	44.4
3	80	37.7
4	80	37.4
5	90	42.0
6	90	41.1
7	90	40.5
8	96	45.7
9	94	37.1
10	96	44.8
11	70.5	42.0
12	70	37.0
13	70	41.6
14	70	36.2
15	70	38.8
16	76	38.5
		Mean, 40.4

(Approximate calculated value of *W* = 40 units.)

That with good vacuum the effect of temperature on tube resistance is negligible was thus confirmed, and further, the value agreed with the Knudsen equations.

Calculation of Tube Resistances by Knudsen's Equations.

Calculation of W_1.—For the aperture measurements an enlarged photograph was made of the platinum partitions, with the glass broken away sufficiently to expose them. A millimeter scale was included in the photograph, for determining magnification. Measurements of diameters were made with Vernier calipers. The total aperture area for each tube was equal to *A* in Equation 1. Careful measurements of the individual apertures should have been carried out before the platinum partitions were sealed into the glass tubes. This was not done, as the holes were designed to be exactly 2 mm. diameter. Unfortunately, the method used in cutting them permitted slight departures from this specification.

Calculation of W_2.—The value of W_2 in (2) was determined for each tube from interior measurements of the dimensions. For the integrations a tube was regarded as divided conveniently into 4 parts, each part contributing its share of W_2. Thus, $W_2 = W_a + W_b + W_c + W_d$. In calculating W_2 it was necessary to decided what point should be taken as the upper limit, since the selenium condensed not only on the hemispherical end of the condensation tube, but to some degree spread up the sides. This upper limit of the part of the tube regarded as offering resistance to molecular flow was then taken as "the place of the deposit." The upper limit was in all cases put at one cm. from apex of condensation tube. This was done after a careful observation of the distribution of the condensed material, especially after the tube had been in continuous operation for an unusual length of time so that the thickness of the deposit was easily measured at various points with micrometer microscope, subsequent to breaking the deposit shell partially away from the glass.

Experimental Procedure.

The procedure in taking a measurement of vapor pressure was first to place the tube in the oven, at the same time starting the flow of tap water through the condensation tube. The pump system was not connected with the vapor tube until it had reached equilibrium temperature. At least 15 minutes, and usually more, was allowed for this, undoubtedly more than was necessary. The oil pump was then started and the pressure went down in 2 or 3 minutes to where the Gaede pump could be started. When this pump ceased to throw air up through the mercury at the revolving drum the time count by ordinary watch was begun. The apparatus was then allowed to run for 30 minutes, usually longer. Temperatures were read, as stated, at one-minute interval, and to 0.5°, and time was again read when air was let into the tube by disconnecting the short length of thick-walled rubber tubing between vapor tube and glass tubing connecting with Langmuir pump. The vapor tube was then removed from the oven, the inside tube removed from its place, and the selenium deposit scraped off on a previously weighed filter paper and weighed.

Data and Curves.

Data have been obtained for the vaporization curve of liquid selenium and the sublimation curve for the hexagonal crystals. Equation 3 was applied in the form

$$p = W.1/\sqrt{\rho_1}.G/t, \qquad (5)$$

where p_1 in Equation 3 has been neglected, since the vapor pressure of selenium at the condensation temperature must have been negligible compared with that near the melting point, some 200° higher. The condensation temperature was fairly constant at about 17°, and was that of the tap water used for cooling. For the temperature corresponding to a given pressure measurement, and determining the value of p_2, the mean of the one-minute readings was taken. This average temperature was regarded as equal to a constant temperature that would have given the same amount of condensed material. The mean value was subjected to 2 corrections, one for thermometer calibration, the other for difference in temperature inside and outside the vaporization chamber of the tube. Both the mercury and the resistance thermometers had been standardized at the boiling point of C. P. naphthalene (Bureau of Standards sample) and the freezing point of water. Calibration was carried out under the same conditions as prevailed when the thermometers were in use in the oven. Both corrections of the mean temperature for a pressure measurement were conveniently made from a total correction curve. Since each of the 2 corrections is represented by a linear relation the total correction is similarly represented.

The factor ρ_1 in Equation 5 was evaluated graphically. The constant in Equation 4, $(\rho_1)_0$, was found for selenium by putting $n = 2$, and the vapor pressure curves as here presented were plotted on this basis (see later discussion).

The data as thus treated are assembled in Table II, for the "F series" of the selenium crystals and the "E series" of the liquid, together with data for some check measurements. The 2 letters, E and F, indicate the vapor tube concerned in each case. The F series consisted of 11 successive measurements, or "runs," under best conditions, and the E series, with the exception of 2 runs omitted due to experimental conditions going wrong, of 30 successive measurements.

A plotting of the p and T values as thus computed is inadequate for locating the melting point with any precision, even if it indicated the presence of a change in slope in the general curve, for this change, as is well known, is slight. But there is found from the present data a decided difference in the characteristics of the 2 curves when log p is plotted with $1/T$. This form is suggested for short temperature ranges by the first latent heat equation, as shown later, if L is regarded as constant.

Egerton treated his data in this manner. His temperature range for zinc was 106° and for cadmium 134°. The lowest temperature in the first instance was 162° below the melting point, while in the second it was 182° below. His plotted results showed some departure from a straight line, as might be expected. Assuming Kirchhoff's equation, after a preliminary assumption of a value for C in Equation 11, he could find the constants A and B by applying the relation at 2 experimental temperatures. In Egerton's work there was a gap of 56° between the highest temperature and the melting point for zinc, and of 48° for cadmium, and the relation for p and T had to be assumed over this gap to solve

TABLE II.—VAPOR PRESSURE DATA.

(*a*) F series, hexagonal crystals of selenium.

Tube F, $W = 12.41$; thermometer J.

Run No.	Aver. temp., ° C.	Corr. temp., ° C.	T, ° abs.	Total time, secs.	G, g.	G/t, $\times 10^4$.	$1/\sqrt{p_1}$ $\times 10^{-4}$.	p bars.	$1/T$ $\times 10^3$.	log. p.
1...	205.3	193.6	466.6	3000	0.0300	0.1000	1.566	1.94	2.143	0.2378
2...	209.8	197.6	470.6	2760	0.0422	0.1525	1.573	2.98	2.124	0.4742
3...	212.6	200.3	473.3	2205	0.0396	0.1795	1.577	3.51	2.112	0.5453
4...	215.9	203.2	476.2	2370	0.0506	0.2130	1.582	4.18	2.099	0.6212
5...	217.1	204.4	477.4	2610	0.0666	0.2550	1.584	5.01	2.094	0.6998
6...	219.4	206.5	479.5	2445	0.0690	0.2825	1.588	5.57	2.085	0.7458
7...	222.0	208.9	481.9	2130	0.0690	0.3240	1.592	6.40	2.075	0.8062
8...	223.9	210.6	483.6	2025	0.0800	0.3950	1.594	7.81	2.067	0.8926
9...	225.9	212.5	485.5	2010	0.0956	0.4650	1.598	9.22	2.059	0.9647
10...	227.5	214.0	487.0	1830	0.0914	0.5000	1.600	9.92	2.053	0.9965
11...	229.1	215.5	488.5	2070	0.1140	0.5500	1.620	11.05	2.047	1.0433

(*b*) E series, liquid selenium.

Tube E, 6 apertures, $W = 11.46$, thermometer J.

No. Run.	Aver. of temp ° C.	Corr. temp. ° C.	T ° abs.	Total time, secs.	G. g.	G/t $\times 10^4$.	$1/\sqrt{p_1}$ $\times 10^{-4}$.	p bars.	$1/T$ $\times 10^3$.	log. p
1...	231.7	221.0	494.0	2055	0.1360	0.6618	1.611	12.22	2.024	1.0870
2...	229.8	219.0	492.0	2950	0.2086	0.7071	1.680	13.61	2.032	1.1338
3...	238.6	228.0	501.0	2520	0.2184	0.8666	1.623	16.12	1.996	1.2074
4...	237.4	226.8	499.8	2400	0.2430	1.0125	1.621	18.80	2.001	1.2741
5...	244.1	233.7	506.7	2430	0.3408	1.4024	1.632	26.22	1.973	1.4186
6...	248.3	238.0	511.0	2355	0.3984	1.6917	1.639	31.77	1.957	1.5020
7...	242.1	231.7	504.7	2210	0.2826	1.2787	1.629	23.87	1.981	1.3778
8...	241.7	231.2	504.2	2520	0.3000	1.1904	1.628	22.20	1.983	1.3463
9...	242.5	232.0	505.0	2400	0.3034	1.2640	1.630	23.61	1.980	1.3731
10...	240.1	229.6	502.6	2400	0.3000	1.2500	1.626	23.29	1.989	1.3672
11...	233.3	222.7	495.7	2355	0.2046	0.8687	1.614	16.06	2.017	1.2057
12...	232.9	222.2	495.2	2470	0.2130	0.8623	1.613	15.935	2.019	1.2022
13...	235.4	224.8	497.8	2400	0.2430	1.0125	1.618	18.68	2.009	1.2714
14...	234.7	224.0	497.0	2460	0.2360	0.9593	1.616	17.77	2.012	1.2497
15...	234.0	223.4	496.4	2400	0.2240	0.9333	1.615	17.27	2.014	1.2373
16...	238.3	227.7	500.7	2400	0.2536	1.0566	1.622	19.64	1.997	1.2931
17...	238.0	227.5	500.5	2370	0.2556	1.0784	1.622	20.05	1.998	1.3021
18...	236.0	225.5	498.5	2400	0.2424	1.0100	1.619	18.73	2.006	1.2725
19...	236.4	225.8	498.8	1930	0.1926	0.9979	1.619	18.51	2.005	1.2674
20...	235.4	224.8	497.8	2910	0.2936	1.0089	1.618	18.70	2.009	1.2718
21...	234.5	223.8	496.8	2430	0.2534	1.0427	1.616	19.31	2.013	1.2858
22...	237.2	226.6	499.6	2460	0.2866	1.1650	1.621	21.63	2.001	1.3350
23...	234.8	224.1	497.1	1830	0.1642	0.8972	1.617	16.62	2.012	1.2206
24...	233.9	223.2	496.2	2385	0.2116	0.8872	1.615	16.42	2.015	1.2154
25...	232.0	221.3	494.3	2400	0.2078	0.8658	1.612	15.99	2.023	1.2038
26...	232.6	222.0	495.0	2400	0.1952	0.8133	1.613	15.03	2.020	1.1769
27...	235.1	224.5	497.5	2430	0.2286	0.9407	1.617	17.43	2.010	1.2413
28...	234.5	223.9	496.9	2400	0.2160	0.9000	1.616	16.67	2.012	1.2219
29...	236.7	226.2	499.2	2430	0.2418	1.0197	1.620	18.92	2.003	1.2769
30...	238.7	228.2	501.1	2400	0.2964	1.2350	1.623	22.97	1.995	1.3611

(*c*) Check Measurements.

Tube	No. of apertures.	W	Run No.	Aver. temp. ° C.	Corr. temp. ° C.	Total time, secs.	G g.	G/t $\times 10^4$.	$1/\sqrt{p_1}$ $\times 10^{-4}$.	p bars.
E	7	11.46	Ea1	219.7	208.6	3600	0.1050	0.2916	1.591	5.31
D	7	10.87	Da1	228.1	214.0	2415	0.0966	0.4000	1.600	6.95
D	7	10.87	Da2	218.6	204.6	2190	0.0360	0.1643	1.585	2.83
C	2	36.74	C1	243.2	228.7	2600	0.0988	0.380	1.624	22.67
C	2	36.74	C2	243.0	228.5	2460	0.0820	0.333	1.624	19.87

for the pressure at the melting point. In the present work the range for the solid was roughly 25°, and for the liquid 15°, while the pressure measurements were carried to within 2 or 3° of the melting point in both parts of the experiment, so that dependence need not be placed to any appreciable extent on an extrapolated curve for computations at the melting point.

The log p and $1/T$ relations from the present data for selenium and for a diatomic vapor are at least approximately linear, and there is a decided difference in slope between the two curves. To the extent that the relations can be regarded as linear and constants found on this basis, the melting point can be located with precision. But since the data have been obtained so near the melting point, considerable precision in locating it is to be expected anyway, as the extrapolation is not extensive. Even if the results thus plotted are segments of curves that are not linear, their slopes, readily found graphically, cannot differ appreciably from the slopes of the true curves over the experimental temperature ranges, that is, in a limited region including the melting point.

TABLE III.

n.	f.	$(p)_n$ m. p. bars.	L_1. calories per gram.	L_2. calories per gram.	L_3. calories per gram.	$(dp/dT)_1$ bars per degree.	$(dp/dT)_2$ bars per degree.
2	. . .	12.68	135.5	83.9	219.4	0.57	1.05
4	0.707	8.95	67.7	42.0	109.7	0.40	0.74
6	0.577	7.31	45.1	28.0	73.1	0.33	0.60
8	0.500	6.34	33.9	20.9	54.8	0.28	0.52
10	0.447	5.66	27.1	16.8	43.9	0.25	0.46
12	0.408	5.17	22.6	14.0	36.6	0.23	0.42

Data for the log p and $1/T$ relations are given in Table III. For the F series the location of the mean straight line was quite easy. Even for the E series for the liquid, where the plotted points are more erratic than in the F series, there can be little doubt in locating the mean straight line when this is based on the points with lower values of mean temperature deviation during a run, or those where the deviation was less than 0.3%. These points were 16 in number, *viz.*, 5, 6, 8, 11, 13, 15–19, 22, 24–28. While temperature variation was not the only source of error more confidence was placed in those runs where this variation was not large. At any rate the points for the remaining runs group themselves well about the mean straight line as thus drawn, particularly points 4, 7, 9, 14. The points lying farthest removed from the line above it, with the single exception of 22, had larger temperature variation, *viz.*, 10, 13, 20, 29, 30. The points corresponding to the first 3 runs of the series may be neglected, as the required vacuum was slowly reached in all 3, due probably to gases coming off from the molten selenium. In the 4th run, however, the vacuum was not readable on the McLeod gage after 7 minutes. Vacuum conditions for the 6 runs of larger temperature variation were good, with the possible exception of 20, but even in this case they were obviously not poor enough to interfere with molecular flow. The mean straight line as determined from the 16 points of lower temperature deviation was, therefore, accepted.

The equations for the 2 lines are,

$$\text{F series: } \log p = -7644 \times 1/T + 16.692 \qquad (6)$$

$$\text{E series: } \log p = -4722 \times 1/T + 10.733 \qquad (7)$$

The values for y and x for the point of intersection give, respectively, $p_{\text{m. p.}}$ in abs. units, and the melting point itself on the absolute scale. As thus found, $p_{\text{m. p.}} = 12.7$ bars (0.00957 mm.), and melting point = 217.4°.

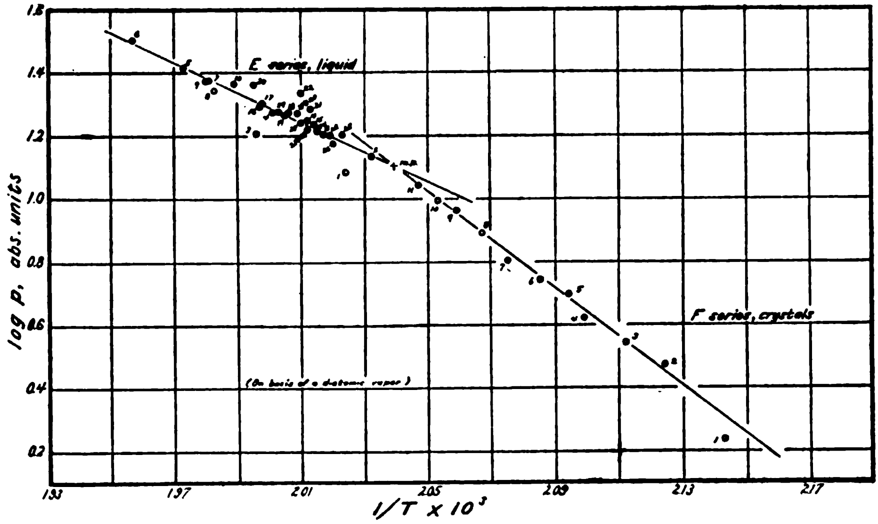

Fig. 2.

The exponential relations corresponding to Equations 6 and 7 are of the form

$$p = 10^{(b+m/T)} = c_1 \, 10^{c_2/T} \qquad (8)$$

where m is the slope and b the y-intercept of the log p and $1/T$ line whose equation is

$$\log p = m.1/T + b \qquad (9)$$

Equations 8 and 9, with the numerical values above, are empirical expressions for the temperatures of the present experiments, and on the basis of a diatomic vapor.

From the slopes of these 2 lines, Fig. 2, the slopes of the p and T curves may be found by

$$dp/dT = -2.3\,m/T^2 \times 10^{(b+m/T)} \text{ bars/degree} \qquad (10)$$

The values at the melting point were,

$$\text{for the solid, } dp/dT = 1.050 \text{ bars/degree}$$

$$\text{for the liquid, } dp/dT = 0.573 \text{ bar/degree}$$

The two p and T curves assembled in Fig. 3 were plotted from Equation 8. The triangles indicate points computed from the empirical expressions.

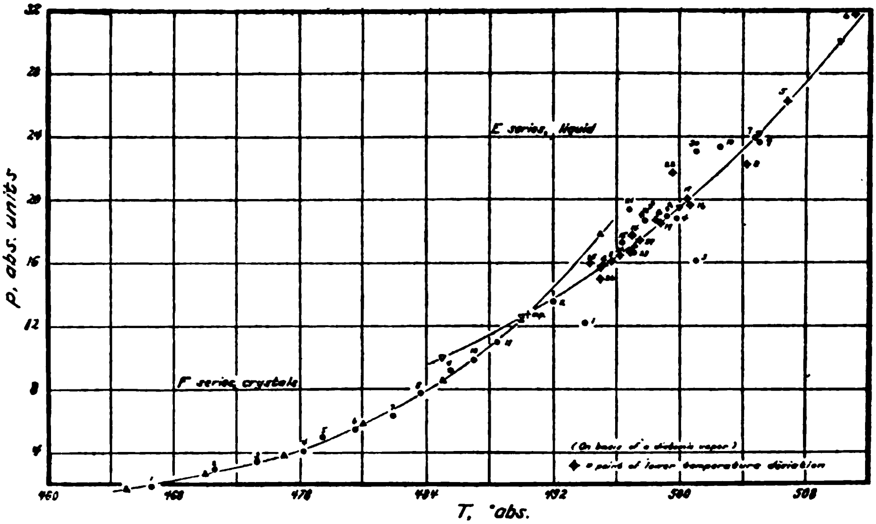

Fig. 3.

Five check values of pressure, with different tubes, are given with data in Table II(c). The 3 check values for the solid curve are all low for reasons known. Check measurements C_1 and C_2 were of most value, for they were obtained with a tube having but 2 apertures as contrasted with Tube E with 7 apertures. It was desired to make more check measurements with this tube at different temperatures, but unfortunately an accident during a third run destroyed the platinum partition. But the 2 measurements C_1 and C_2 are regarded as satisfactory. In addition there was the check on the method in the preliminary work with mercury already described.

Sources of Error.

There are various sources of error in the molecular flow method as here used, some of them of sufficient importance to be particularly guarded against.

To prevent serious temperature gradient in the oven a fan was operated as described. The temperature during a run was as constant as the thermostat of the oven gave. The average deviation from the mean for all 41 measurements of both series was 0.357%. The pressure value is affected by temperature variations in 2 ways, directly through ρ_1, and indirectly by giving an experimental value of G that does not correspond to the mean tube temperature and is likely to be too large, for the pressure of a saturated vapor rises more rapidly than the temperature. Error through ρ_1 can be neglected, since this factor is but slowly variable with temperature. As to the error through G, the indications are that it is small.

The important temperature correction for difference inside and outside the tube at the vaporization chamber was made for Tubes D, E, F, with C. P. tin and silver nitrate crystals as standardizing materials. These were used inside evacuated thin-walled glass Tubes as usual for melting point determinations. They were suspended one at a time in the central part of the vaporization chamber with the vapor tube in the oven as for a pressure measurement. The melting points of these substances were taken at 232 and 209°. In future work a thermocouple sealed into the vapor tube might be found useful and preferable.

The method of molecular flow requires a good vacuum, otherwise the tube resistance cannot be regarded as constant, as already shown. In the present work the vacuum soon reached a desirable degree, 0.00005 mm. or better, as indicated by the McLeod gage, which became useless for precise reading of the lower pressures obtained.

Another difficulty in this method is the uncertainty regarding when to begin the time count. Ideally the vacuum would reach the desired degree at the time zero, and the error will be least when this time is a minimum. Experience has shown that the Langmuir pump reduces the pressure in the vapor tube to a value permitting molecular flow in a brief interval, varying somewhat, possibly because of various amounts of adsorbed gases coming from the apparatus itself and so depending to some degree on the time of standing of the tube between runs. But, as a general rule, after 6 minutes, when the McLeod gage was usually read for the first time in a run, the pressure was less than 0.0002 mm., much below that necessary for molecular flow. In several cases noted, particularly E4, the vacuum was not readable after 7 minutes. But a study of the results shows no consistent variation with time of run.

For most precise measurement of aperture areas they should be perfectly circular, which was not completely realized. Since W_2 was in no case greater than 16% of W_1 any departure of the tube from the cylindrical has been neglected. Integration, however, was carried out for change in shape of cross-section. The distance the deposit spreads up the sides of the tube increases somewhat with temperature, but this slight increase was neglected, as was likewise any error in W_2 due to error in dimensional measurements. There may be some error in the resistance values due to locating the place of condensation in the manner already described, but no attempt has been made to correct for it. A test of the chemical balances showed an error of 0.3%, also neglected.

Adsorbed moisture gathered on the deposit between time of removal from condensation tube and time of weighing. Evidence of this was obtained on a humid day. For E3 the weight of the deposit had increased 0.91% in 1 hour, and 2.1% in 2 hours following the first weighing; E4 had increased 1.56% in 2 hours; E5, 0.41% in 2 hours; while E6, permitted to stand all night for a test weighing, showed no change in 11 hours. Evidently the humidity fell as the day advanced. E10, a run made 2 days afterward, showed an increase of 0.47% in over 2 hours following the first weighing, and E13, made later in the same day, showed a 0.41% increase in 11 hours. Usually the time elapsing from removal of tube from oven until the weighing, amounted to from 10 to 40 minutes. Measurements were not taken to determine this disturbance in all cases. It was noticeable that even with E3, where the adsorption rate appeared to be a maximum, the plotted point on the p and T diagram was low, due to other causes which more than offset error due to adsorption.

It was assumed that the outside tube was kept at the same temperature, at least up to a point opposite the place of deposit on the condensation tube. The precautions taken have been described.

The Kirchhoff Equation.

The Kirchhoff equation has the form

$$\log p = A - C \log T - B/T. \tag{11}$$

It may be derived from the Clapeyron-Clausius equation by integration after assuming a linear relation. By assuming certain constants for this relation there is obtained

$$\log p = k/2.3 - L_0/2.3R_1 . 1/T - (c - c_p)/R_1 . \log T \tag{12}$$

proposed by Hertz for mercury.

Knudsen found that this form applied to empirical results at higher temperatures, when extrapolated gave pressure values in good agreement with those obtained by him at lower temperatures by the molecular flow method. He used for mercury the value 0.847 for C in Equation 11, from experimental values of the specific heats. Egerton assumed for both zinc and cadmium the simpler value of 0.5 for this constant, based on theories of Boltzmann,[1] where both solid and vapor are monatomic.

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[1] Partington, "Thermodynamics," 1914, p. 17.

While admitting that this value cannot be true Egerton[1] justified it on the ground that it would make possible the simplest approximation for a comparison of results with different elements. But the specific heats of selenium have not been determined. Moreover, the vapor is probably not monatomic.

It is not necessary to regard the variability of L for short temperature ranges as in the present work. These ranges are not sufficient here to determine how strictly the Kirchhoff type applies to selenium. The present data do not conflict with that type.

It seems desirable to let the results stand for the present expressed by the simple exponential relation, which will suffice for a limited temperature range near the melting point, and to regard it as empirical, with the understanding that it is based on a diatomic vapor, although to the extent that it is exponential the number of atoms assumed per vapor molecule does not change the shape of the curves. That this simple relation may be taken to hold quite generally for temperatures considerably below the critical has been stated recently by Richards.[2]

The Three Latent Heats at the Melting Point.

From the empirical relation of Equation 10, $1/p.\mathrm{d}p/\mathrm{d}T.T^2 = -2.3m$, and from the latent heat equation (in the form $L = R/m.T^2/p.\mathrm{d}p/\mathrm{d}T$ the same quantity is equal to L/R_1 (see also Richards[3]). Equating

$$L = -2.3R_1m. \qquad (13)$$

Thus the latent heat is simply obtained from the slope of the log p and $1/T$ curve, by combining the theoretical latent heat equation with empirical results. The latent heat equation can then be used to find the latent heat at any temperature, provided the slope of the true log p and $1/T$ curve is known at that temperature. The actual relation between log p and $1/T$ can be regarded as linear over a limited segment of the true curve to the extent that the latent heat can be regarded as constant over the same limited temperature range. Obviously then, when Equation 13 is applied near the melting point the value of L is the value of L_0 in Equation 12. Now if the Kirchhoff equation (11) holds, the log p and $1/T$ curve can vary from a straight line only through the log T term. It follows from Equation 13 that the physical meaning of the variability of this term would be the variability with temperature not only of the difference in the specific heats but also of the latent heat. Otherwise m in Equations 10 and 13 and B in 11 would be identical. As it is, $m = -L/2.3R_1$, while $B = -L_0/2.3R_1$.

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[1] *Loc. cit.*, p. 43.

[2] Richards, *J. Franklin Inst.*, 187, 584–5 (1919).

[3] *Loc. cit.*

Treatment of Data on Basis of Different Numbers of Atoms Per Molecule of Vapor.

At 700° or 800° selenium vapor is apparently diatomic,[1] but that of itself probably tells little of conditions near the melting point. In the absence of direct density measurement of the vapor at the experimental temperatures, the 3 latent heats, the pressures, and the slopes have been computed at the melting point for 6 cases, depending on the number of atoms per molecule. See Table III.

Let n be number of atoms per vapor molecule. This enters the factor ρ_1 which by Equation 5 affects the pressure, while W is a constant of the apparatus and G and t are both experimental. Although ρ_1 depends also on temperature that is likewise experimental. Let $(\rho_1)_2$ be density at unit pressure for the data as already computed for a diatomic vapor. From Equation 4 by Avogadro's law, $1/\sqrt{(\rho_1)_n} = \sqrt{2/n}\,.\,1/\sqrt{(\rho_1)_2}$, and from Equation 3, $p_n = \sqrt{2/n}.p = f_p$, where p is pressure for a diatomic vapor and f is the conversion factor. For the melting point and $p_{m.p.}$, in Equation 8 $c_1 = 10^b$ and $c_2 = m$. The log p and $1/T$ relation remains linear if the initial relation with $n = 2$ is taken as linear, and the slope c_2 in Equation 8 is unchanged in the conversion, while the y-intercept is varied by an increment, log f. On this basis then the melting point does not depend on n; but $p_{m.p.}$, and the latent heats as computed from the vapor pressure data, do depend upon it. L changes only through R_1, and from the values of L already computed, $L_1 = 271/n$, and $L_3 = 438.8/n$. Also, $\mathrm{d}p/\mathrm{d}T = K'p$, so that $[(\mathrm{d}p/\mathrm{d}T)_1]_{m.p.} = 0.9451\ p$, and $[(\mathrm{d}p/\mathrm{d}T)_3]_{m.p.} = 0.0828\ p$. Pending a determination of the vapor density this treatment will serve for a simple approximation. The computed pressure values in Table III may be regarded as depending upon experiment rather than theory, since the Knudsen equations have been experimentally confirmed.

Summary.

1. By the method of molecular flow data for the sublimation curve for selenium crystals of the hexagonal system have been obtained over the approximate temperature range from 190° to 215°.

2. By the same method data for the vaporization curve for the liquid of vitreous, amorphous selenium have been obtained over the approximate temperature range from 220° to 235°.

3. The relation between vapor pressure and temperature for Se over the temperature ranges studied and on the basis of a diatomic vapor may be expressed by a simple exponential relation, $p = c_1e^{c_2/T}$, where T is absolute temperature.

4. On the basis of a diatomic vapor the results appear to locate the

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[1] See Roscoe and Schorlemmer, "Chemistry," 1, 469 (1911).

melting point at 217.4°, and give a pressure value at the melting point of 12.68 bars (0.00954 mm.), and slope values for the p and T curves at the melting point of 1.050 bars/degree (0.000767 mm./degree) for the crystals, and 0.573 bar/degree (0.000431 mm./degree) for the liquid.

5. The slope at the melting point was thus found to be greater for the solid than for the liquid, as required by thermodynamics, and as found for other substances. The difference between the 2 slopes is seen to be 0.477 bar/degree (0.000358 mm./degree) on the basis of a diatomic vapor.

6. From the first latent heat equation (Clapeyron) of thermodynamics, the 3 latent heats at the melting point were computed on the basis of a diatomic vapor as follows, for vaporization, 135.5; for sublimation, 219.4; and for fusion, 83.9 cals./g. Since the density of the vapor at the present experimental temperatures has not been determined, the 3 latent heats, the pressure at the melting point, and the slopes of the p and T curves at the melting point, have been computed on the basis of 4, 6, 8, 10, and 12 atoms per vapor molecule. The computed latent heat values vary inversely as these numbers.

7. The results are not out of harmony with the requirements of the Kirchhoff equation, based on thermodynamics, relating vapor pressure and temperature, but they do not give positive evidence that this equation is applicable to selenium, as would be expected from the limited temperature ranges even if that relation should apply.

8. As a preliminary to the present work the Knudsen equations for resistance to molecular flow have been further verified, with mercury as the standardizing material.

In conclusion, the writer wishes to express his thanks to the members of the Physics Department of the State University of Iowa for their interest. Particularly is he indebted to Dr. F. C. Brown, who suggested the problem, and under whose direction the research has been carried out, and also Dr. G. W. Stewart, who has contributed materially to its completion. His gratitude is also due the instrument makers, M. H. Teeuwen, and his successor, at the University, J. B. Dempster.

IOWA CITY, IOWA.

UNDAMPED OSCILLATIONS DERIVED FROM THE LAW OF MASS ACTION.

By Alfred J. Lotka.

Received June 2, 1920.

It was shown by the writer on a former occasion[1] that the course of a chemical reaction, as computed from the laws of chemical dynamics, may, in certain circumstances, assume an oscillatory character.

The case considered led, however, to damped oscillations fading off into equilibrium, not to a continued periodic process; and reflections of a general character on the kinetics of material transformations[2] seemed to make the occurrence of undamped oscillations, in the absence of geometrical causes (surface films, etc.), appear improbable, since it seemed to demand a very special numerical relation between the reaction constants. These, in nature, of course stand generally in no obvious relation.

It is, therefore, somewhat contrary to his first expectations that the writer now finds the conditions for undamped oscillations may occur in the absence of any geometrical causes in a homogeneous system.

A case which leads to such an effect is, for example, the following.

A substance S_0 is present in constant concentration. (This condition may be secured either by providing a large excess, or by using a saturated solution in the presence of undissolved substance. In the former case the system will be homogeneous, in the latter case it will not be. This circumstance has no bearing on the course of the reaction to be considered except insofar as it provides a constant concentration of the substance S_0. If the system is heterogeneous we shall assume, as on a former occasion, that the chemical changes taking place are slow as compared with diffusion effects so that these latter may be left out of account.) In this system let a substance S_1 be formed autocatalytically from the substance S_0. Since the concentration of S_0 is constant, the rate of formation of S_1 will, in the simplest case, be proportional to the quantity X_1 of S_1 actually present, so that we may write

$$\text{mass of } S_1 \text{ formed per unit of time}^3 = a_1X_1. \qquad (1)$$

Let another substance S_2 be formed from S_1 in mono-molecular reaction, so that we may write

$$\text{mass of } S_2 \text{ formed per unit of time} = cX_1. \qquad (2)$$

And furthermore let the substance S_2 also influence its own formation autocatalytically, so that

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[1] A. J. Lotka, *J. Phys. Chem.*, 14, 271 (1910); *Z. physik. Chem.*, 72, 508 (1910); 80, 159 (1912); see also Hirniak, *ibid.*, 75, 675 (1910); and compare also Lowry and John, *J. Chem. Soc.*, 97, 2634 (1910); Rakowski, *Z. physik. Chem.*, 57, 321 (1906).

[2] Lotka, *Phys. Rev.*, 24, 235 (1912); *Proc. Am. Acad.*, 55, 137 (1920); see, in particular, footnote 13 on page 145 of the latter reference.

[3] At constant volume; masses being, in that case, proportional to concentrations.

$$c = a_2X_2. \tag{3}$$

Likewise let S_2 decompose in molecular reaction, so that

$$\text{mass of } S_2 \text{ decomposed per unit of time} = b_2X_2. \tag{4}$$

If in the second reaction, S_2 alone is formed from S_1 then we have evidently

$$\frac{dX_1}{dt} = a_1X_1 - a_2X_1X_2 \tag{5}$$

since, in that case, the amount of S_1 decomposed is equal to the mass of S_2 formed.

We may, however, make the more general supposition that along with S_2 any other substances are formed in proportional amounts. In that case we may write

$$\frac{dX_1}{dt} = a_1X_1 - b_1X_1X_2 \tag{6}$$

where b_1 is in general different from (greater than) a_2.

On the other hand, as regards the substance S_2 we have

$$\frac{dX_2}{dt} = a_2X_1X_2 - b_2X_2. \tag{7}$$

The course of events in the system under consideration is now defined by Equations 6 and 7.

Dividing (7) by (6) we obtain

$$\frac{dX_2}{dX_1} = \frac{X_2(a_2X_1 - b_2)}{X_1(a_1 - b_1X_2)} \tag{8}$$

or

$$\left(\frac{a_1}{X_2} - b_1\right) dX_2 = \left(a_2 - \frac{b_2}{X_1}\right)dX_1. \tag{9}$$

Integrating,

$$b_2 \log X_1 - a_2X_1 + a_1 \log X_2 - b_1X_2 = K. \tag{10}$$

Let us put

$$X_1 = x_1 + b_2/a_2 = x_1 + p \tag{11}$$

$$X_2 = x_2 + a_1/b_1 = x_2 + q. \tag{12}$$

Then (10) becomes

$$b_2 \log (x_1 + p) - a_2x_1 + a_1 \log (x_2 + q) - b_1x_2 = K'. \tag{13}$$

Expanding the logarithms by Taylor's theorem certain terms are found to cancel out and we have

$$b_2\left(\log p - \frac{x_1^2}{2p^2} + \frac{x_1^3}{3p^3} - \ldots\right) + a_1\left(\log q - \frac{x_2^2}{2q^2} + \frac{x_2^3}{3q^3} - \ldots\right) = K'. \tag{14}$$

In the immediate neighborhood of the origin of x_1, x_2 this reduces to

$$\frac{b_2x_1^2}{p^2} + \frac{a_1x_2^2}{q^2} = 2(b_2 \log p + a_1 \log q - K'). \tag{15}$$

$$= \text{constant} \tag{16}$$

$$= r_2, \text{ say;} \tag{17}$$

from which it is seen that near the origin the integral curves (10) of (8) approach the elliptic form (17).

More generally the integral curves (10), or their equivalent (13), in the positive quadrant of X_1, X_2, are closed curves of some such form as indicated in Fig. 1.

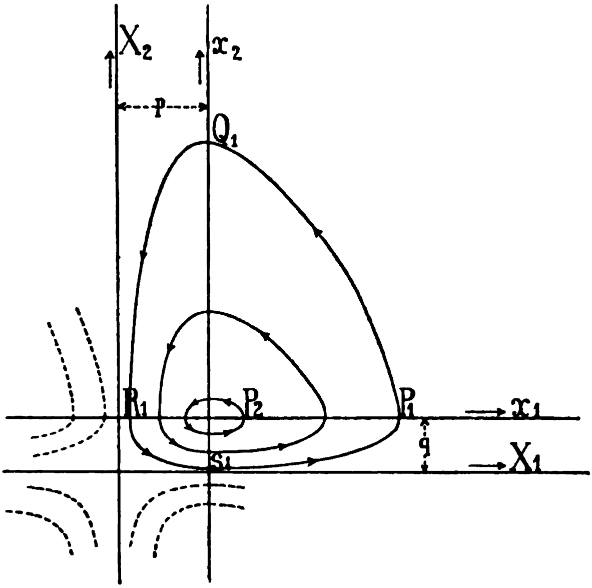

Fig. 1.—Diagram showing general character of the integral curves of Equation 8. In the positive quadrant of X_1X_2 these are closed curves, contained entirely within that quadrant, and intersecting the aces of x_1x_2 orthogonally. Near the origin of x_1x_2 the curves are very nearly elliptical.

The solution (10) enables us to plot X_2 as a function of X_1. We can then plot point for point

$$\varphi(X_1) = \frac{1}{a_1X_1 - b_1X_1X_2} \tag{18}$$

and Equation (6) then takes the form

$$\frac{dX_1}{\varphi(X_1)} = dt \tag{19}$$

$$t = \int \frac{dX_1}{\varphi(X_1)} \tag{20}$$

from which we obtain by simple quadrature (*e. g.*, with the planimeter), an expression for t as a function of X_1, or, say

$$X_1 = \Phi_1(t). \tag{21}$$

In exactly similar manner we obtain

$$X_2 = \Phi_2(t) \tag{22}$$

thus completing our solution of the system of differential Equations 6, 7.

The Character of the Functions Φ.—It has already been observed that within the positive quadrant of X_1X_2 (which alone interests us, since masses cannot be negative) the integral curves (10) are closed curves.

Furthermore, it can be seen by inspection of (6) that

$$\frac{dX_1}{dt} \gtreqless 0 \tag{23}$$

according as

$$X_2 \lesseqgtr \frac{a_1}{b_1} \tag{24}$$

that is to say, by (12), according as

$$x_2 \lesseqgtr 0. \tag{25}$$

A glance at Fig. 1 shows that this means the point X_1X_2 travels in counter clockwise direction around the integral curves as the process represented by (6), (7) takes its course.

From this, again, it is plain that $\Phi_1(t)$, $\Phi_2(t)$ are periodic functions of t. We may, therefore, expand them into Fourier's series.

$$\left.\begin{aligned} X_1 = \Phi_1(t) = A_0 &+ A_1 \cos nt + B_1 \sin nt \\ &+ A_2 \cos 2nt + B_2 \sin 2nt \\ &+ \ldots . \end{aligned}\right\} \tag{26}$$

$$\left.\begin{aligned} X_2 = \Phi_2(t) = A'_0 &+ A'_1 \cos nt + B'_1 \sin nt \\ &+ A'_2 \cos 2nt + B'_2 \sin 2nt \\ &+ \ldots . \end{aligned}\right\} \tag{27}$$

The constants n, A, B may be evaluated by substituting (26), (27) in (6), (7) and equating coefficients of homologous terms.

We thus find, in particular, for n

$$n = \pm \sqrt{a_1 b_2} \tag{28}$$

that is to say, the reaction is oscillating, with a period

$$T = \frac{2\pi}{\sqrt{a_1 b_2}}. \tag{29}$$

It is interesting to observe that the amplitude of the oscillation, as defined by the constants A, B, A', B', depends on the initial masses X_1, X_2, but the period of oscillation T is independent of these. Hence if two systems of the kind here considered be started off simultaneously, but from different initial concentrations, they will forever after keep time with each other, although one may be making much greater excursions than the other. In terms of Fig. 1 this means, for example, that if one system starts from point P_1 at a given instant, the other from point P_2, they will periodically pass through P_1 and P_2 simultaneously, though one travels in one cycle around the large circuit $P_1Q_1R_1S_1P_1$ the other one around the small (nearly) elliptical circuit P_2.

Two Types of Equilibrium.—It is interesting to note the topography of the integral curves about the two equilibrium points. These curves have been drawn in dotted lines also in the negative and mixed quadrants where they have only a geometrical meaning.

Around the point

$$X_1 = \frac{b_2}{a_2} \quad \text{or} \quad x_1 = 0$$

$$X_2 = \frac{a_1}{b_1} \quad \text{or} \quad x_2 = 0$$

the curves form closed contour lines, like those which on a map represent a mountain crest or a trough-shaped valley.

On the other hand near the point

$$X_1 = 0 \quad \text{or} \quad x_1 = -p$$

$$X_2 = 0 \quad \text{or} \quad x_2 = -q$$

the curves follow a course such as the contour lines near a saddle or col in a landscape.

These features are typical of the two kinds of equilibrium. The crest corresponds to a center of oscillation. The saddle point corresponds to a position of unstable equilibrium. For details regarding this feature the reader is referred to a previous publication by the writer.[1]

Rhythmic phenomena are of particular interest in connection with biological systems (*e. g.*, heart-beat). An extension of the method here set forth, in its application to certain biological systems, will appear in a forthcoming issue of the Proceedings of the National Academy of Sciences.

BROOKLYN, N. Y.

[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY, HARVARD UNIVERSITY.]

THE HEATS OF COMBUSTION OF BENZENE, TOLUENE, ALIPHATIC ALCOHOLS, CYCLOHEXANOL, AND OTHER CARBON COMPOUNDS.

BY THEODORE W. RICHARDS AND HAROLD S. DAVIS.

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This paper is a continuation of extended researches concerning the physico-chemical properties of typical compounds of carbon. It enumerates the careful quantitative combustion in an adiabatic calorimeter of the following substances, cane sugar, naphthalene, benzoic acid (these 3 taken as standard substances); benzene, toluene, tertiary butyl benzene, cyclohexanol; together with methyl, ethyl, propyl, butyl and isobutyl alcohols. The main features of the present investigation, which lead to the hope that it may be an improvement over earlier

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[1] Lotka, *Science Progress*, 14, 406 (1920).

work (whether here or elsewhere) are as follows, great care was taken in purifying some of the organic substances; the method of closing the bomb was improved; special study was made of the best method of igniting and burning volatile liquids; particular care was taken to test the completeness of ignition, by analysis of the resulting gases for carbon monoxide or other unoxidized substances; and the thermometer readings were corrected by reference to a very adequately installed platinum thermometer. The calorimetric results were obtained over 6 years ago, but their publication has been postponed by the war, which delayed work needful for the complete removal of a slight uncertainty concerning the thermometric scale.

Apparatus and Method.

The details of the method, together with the necessary apparatus and precautions, have been described already at such length[1] that a very brief recapitulation will suffice. The apparatus consisted of a modification of the Atwater form of the Berthelot bomb,[2] whicn has been described in the papers just noted; the chief modifications being the doubled ridged closure of the bomb, the continuous gold foil to protect the lead; the firm steel adjustment for the firing connection, and the large phosphor-bronze ring or washer to prevent friction during the screwing into place of the steel cap of the bomb.[3] The Hotchkiss steel[4] cup of the bomb weighed 1609.5 g.; the tool steel[4] collar, cover, and screw valves weighed 1377.4 g.; the platinum parts 190.0 g.; the pure silver calorimeter-can 881.5 g.; the German silver stirrer 61.4 g.; the phosphor-bronze washer 38.8 g. Taking the specific heats of the several substances as 0.1114, 0.1087, 0.032, 0.056, 0.095, 0.087, respectively, these 6 portions would have the heat capacities 179.4, 149.7, 6.1, 49.3, 5.9 and 3.5. Other small items including a brass nut, mica insulation, the lead gasket, the gold lining on the cover, oxygen ($^1/_8$ mol.), thermometer, amounted together to 6.7 cal./°C. 2257.0 g. of water was also present. Hence the heat capacity of the whole adds up to 2657.6—a result not far from that (2660.0) found from the average of the standard materials furnished by the Bureau of Standards, as will be seen. The latter must be taken as the more accurate, since the specific heats of the different kinds of steel in the bomb are perhaps hardly well enough known for the purpose in hand.

The rise of temperature of this calorimetric system (containing the bomb

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[1] T. W. Richards and F. Barry, THIS JOURNAL, 37, 993 (1915); T. W. Richards and H. S. Davis, *ibid.*, 39, 341 (1917). Earlier work describing the evolution of the method is referred to in the former of these articles.

[2] W. O. Atwater and J. F. Snell, *ibid.*, 25, 659 (1903).

[3] These improvements are described on pp. 1004 and 342, respectively of the papers quoted above.

[4] Atwater and Snell, *loc. cit.*, p. 694.

completely immersed under water) was paralleled in an environing bath so that no correction for cooling was needed. The temperature of this bath was automatically controlled to follow as closely as possible that of the calorimeter proper, by a device explained in our earlier paper.[1] Since this device demanded in the case of each new substance a few preliminary experiments in order to discover the precise nature of the curve of temperature change, one or two early trials in each case were usually made merely for the purpose of orientation and are not included in the tables given below. The numbers attached to the several experiments on sugar are the original numbers as recorded in the notebook, the others are serial for convenience. Each series as given below is consecutive, except in the case of sugar, as noted below.

The mercury-in-glass thermometer (No. 11258) used in the calorimeter proper was carefully made for this purpose. It was standardized in 1910 by the Bureau of Standards and also by comparison with the Harvard Baudin instruments so often referred to in communications from this laboratory. Since these standardizations left something to be desired, the instrument has been recently re-standardized by Mr. O. C. Bridgeman with very great care through comparison with a standard calorimetric platinum thermometer. The thermometric resistance box was installed in a thermostat, with every precaution to avoid parasitic effects. It was for this final standardization that the publication of the results had been temporarily withheld. The final estimates agreed usually within 0.001° with the older ones, but gave a somewhat more divergent correction at the 20° point. All the readings were corrected to this final platinum standard and are recorded below in its terms.

Various methods of introducing volatile liquids into the bomb were tried. The old Berthelot method of soaking the volatile liquid into pellets of cellulose, as well as Stohman's later method of enclosing the liquid in glass bulbs, which were broken just before ignition, undoubtedly allowed some of the vapor to evaporate and escape unburned.[2] Later Stohman,[3] suspecting this, used a small flask of platinum having about one cc. capacity to contain the liquid and over it laid a weighed leaf of collodion, or some other material, fastened to the neck by a thick platinum ring. In 1898 Zubow[4] modified this method by placing the liquid in a small platinum cup with a protruding platinum tube covered with a platinum stopper. The top of the cup was sealed with a film of collodion, the substances to be experimented upon being poured in by means of a funnel. This method seems to have given good results, but there is dan-

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[1] *Loc. cit.*

[2] T. W. Richards and R. H. Jesse, Jr., THIS JOURNAL, 32, 282 (1910).

[3] *J. prakt. Chem.*, 44, 336 (1891).

[4] *J. Russ. Phys.-Chem. Soc.*, 28, 687 (1896); 30, 926 (1898); 33, 708; 35, 815 (1903).

ger of throwing some of the liquid out of the side tube without complete combustion. Later Roth and his collaborators[1] developed a method which has much in common with Stohman's and Zubow's latest procedure. A thin glass test-tube was filled nearly to the edge with the liquid to be burned, closed by a tightly fitting gelatine cap, and held in a vertical position in a platinum dish by means of a small glass support. Cotton thread (fastened between the gelatine and the glass in such a way as not to be moistened by the liquid) served for the ignition. It was admitted, however, that with liquids having a high vapor pressure there is danger of blowing off the gelatine cap, incompletely burned. Precisely the same objection applies to the final methods of Stohman and Zubow. According to our experience with methyl alcohol and benzene, if the gelatine cap is fitted over the little test-tube tightly enough to prevent evaporation, it is usually broken inwards when oxygen pressure is applied. Moreover, it prohibits exhausting the air from the bomb before admitting oxygen—an important precaution as regards completeness of combustion, and necessary to diminish the amount of nitric acid formed. Again, the glass tube sometimes seals itself at the high temperature of combustion, and then the sudden explosion drives the vapor out quickly enough to cause incomplete combustion. Nevertheless, with high boiling liquids the method, when carefully executed, will doubtless give good results, as Roth has shown. We have used it with success, *e. g.*, combustion No. 62 below; but the amounts of nitric acid, carbon monoxide and residual carbon were often large, and on the whole we have found it to be less satisfactory than the method of sealing the liquid in perfectly full, very thin, flattened glass bulbs,[2] the method used in almost all the following work. The ignition was effected by the flame from a weighed ring of paraffin encircling the inner rim of the small platinum crucible containing the glass bulbs. The paraffin itself was ignited by a wisp of cotton wool wrapped by a short spiral of exceedingly fine platinum wire (0.02 mm. in diameter) which needed less than an ampere for $^1/_5$ second for the purpose.[3] Fired in this fashion little, if any, of the volatile substance was found to escape combustion. Among the most important features are the size and shape of the small platinum crucible, which should be about 21 mm. diameter and 26 mm. high. The full details

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[1] *Ann.*, 385, 104 (1911).

[2] This method is an improvement over the somewhat similar one independently devised by Berthelot and Delépine, *Ann. chim. phys.*, [7] 21, 289 (1900), which we had overlooked until after the present work was completed.

[3] The amount of extra heat thus communicated to the system was computed in various ways to be less than 2 calories. Since it was essentially constant (except perhaps where the rise of temperature was only 2°) even this small correction is eliminated in calculation, occurring both with the standard substance and with the substance to be determined.

may be gathered from the papers already cited, and need not be reiterated.[1]

Attention in these previous papers was called to the fact that different results obtained by different experimenters might well be due to lack of completeness of combustion. This is especially true in the case of volatile substances, such as benzene.[2] Accordingly in many of the present combustions very careful tests for carbon monoxide were made in the residual gases, by passing them slowly through the following train of apparatus: two U-tubes filled with concentrated potassium hydroxide solution and glass pearls; a Liebig absorption tube with saturated barium hydroxide solution in order to make sure that all the carbon dioxide had been absorbed in the preceding potash; a drying tube filled with phosphorus pentoxide; a tube of copper oxide at dull red heat; and finally another tube of phosphorus pentoxide. The carbon dioxide in the gas emerging from this apparatus was estimated at first gravimetrically in a Liebig's potash bulb, but later by absorption in a spiral filled with a known quantity of 0.1 N barium hydroxide solution which was titrated at the conclusion of the experiment. When the combustion had been conducted in the older ways, considerable quantities of carbon monoxide were found, but usually very little remained in combustions made by the most approved method.

When carbon monoxide was found, the corresponding correction (2.4 cal. per mg. of the gas, or 0.0009° rise in temperature of our calorimetric system) was added to the observed thermal output of the reaction. Unconsumed carbon in the crucible, if any, was likewise weighed, and its appropriate correction (8.1 cal. per mg.) added. The thermal equivalents of these substances are larger in this relation than is usually appreciated, and the corrections are occasionally important. In the case of sugar, Combustions Nos. 10 and 16 were tested for carbon monoxide, in the case of benzoic acid, No. 21, in the case of naphthalene, No. 23; none was found in any one of these 4 trials. With the other substances (except methyl alcohol) every combustion was tested. Usually the combustion was complete, but in Nos. 21, 32 and 33 (benzene ignited with sugar), 44, 45, 56 and 62[3] the amounts were important; in the last case (conducted by Roth's method) as much as 6 mg. of carbon monoxide were present.

Nos. 9 and 16, showed traces of unburned carbon; all those with benzoic acid (Nos. 20, 21 and 22) left nearly a milligram of carbon a piece. Naphthalene left no carbon in any case, neither did butyl benzene, cyclo-

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[1] T. W. Richards and F. Barry, *loc. cit.*, pp. 1003–1012, also especially the present authors, *loc. cit.*, p. 349.

[2] See Richards and Barry, *loc. cit.*, p. 1017; also Roth and Auwers, *loc. cit.*, p. 162.

[3] Unfortunately the other combustions of methyl alcohol were not tested for this gas.

hexanol, or isobutyl alcohol. On the other hand, slight traces of residual carbon or soot were found in Nos. 31, 32, 33, 34, 35, 37, 39 (the other experiments with benzene gave complete combustion), 41, 42, 43, 46, 53, 54, 57, 59, 52, 63, 70 and 71. The necessary corrections in these latter cases could never have amounted to more than 0.001°.

In addition to the additive corrections corresponding to these usually small quantities of unburned material, further corrections had to be applied to the results to take account of the considerable quantity of auxiliary substance used in ignition, the correction for stirring (usually 0.008°), the trace of nitric acid (usually about 0.0003°) and a further correction for the temperature of the protruding thermometer stem. Of these, the quantity corresponding to the heat of combustion of the auxiliary substance was by far the greatest. All are added algebraically together in the figures given under the caption "Total Correction" in the tables which follow. The "Observed Rise in Temperature" in the column preceding gives the difference in thermometric readings corrected for the calibration corrections of the thermometer. The difference between this observed rise and the total correction in each case gives the corrected rise in temperature (given in the next to the last column) corresponding to the weight of substance burned; and in the last column of the table is given the corresponding rise in the temperature of the calorimeter (heat capacity 2,660.0) per gram of substance. For the sake of saving space, the names of the auxiliary substances, cotton, paraffin, beeswax and gelatine are usually abbreviated as "cot.," "par.," "bsw.," and "gel.," respectively.

The possibility of the residual presence of other unburned vapors of compounds of carbon was also considered. Benzene being the most likely substance to have been incompletely burned, the gases remaining from a benzene combustion were tested for reducing vapors by bubbling through a weak solution of potassium permanganate made alkaline with sodium carbonate. Moreover, they were tested for ozone by letting them impinge on filter paper soaked in potassium iodide solution and starch. Both tests gave negative results. In this connection, the question as to the purity of the original oxygen may be raised. It was tested for halogens, and found to contain none. Since it had been prepared by the evaporation of liquid air, its chief impurity was argon. The presence of any combustible substance in it was unlikely; if any were present its effect must have been felt nearly equally with each substance, and, therefore, eliminated in the calculation.

The Source and Preparation of Materials.

The value of an investigation of this sort depends largely on the intelligent purification of the materials burned. Although admixture of some impurities (*e. g.*, toluene in benzene) makes very little difference in the result, the admixture of others (especially, of course, water) makes a very serious difference. Therefore, space must be given to a description of the sources or methods of preparation of the 13 pure substances.

Sucrose.—The first specimen was prepared from a very pure sample of sugar (designated "Diamond A" by the American Sugar Refining Company[1]) through one precipitation from a solution in 50% alcohol by concentrated alcohol. The second preparation was the same material recrystallized twice, and the third, the latter recrystallized yet once more, or 3 times in all. Another sample (our No. 4) was obtained from the United States Bureau of Standards (their No. 17). The first 3 samples were placed over solid potassium hydroxide and calcium chloride in order to remove the water and alcohol and occasionally stirred and pulverized. They lost no important further weight when placed over quicklime or phosphorus pentoxide in a vacuum desiccator. For example, about 5 g. of sugar once recrystallized and dried over calcium chloride and potassium hydroxide was placed in a weighing tube, and after several days over phosphorus pentoxide in a sealed vessel under a pressure of 0.005 mm. mercury (measured on a McLeod gage), the weight was found to be the same to within less than 0.1 mg. Sugar thus carefully dried could be weighed in the dry air of the steam-heated laboratory without important error. Even in half an hour samples weighing 2 g. gained only 0.2 or 0.3 mg. This would doubtless not be the case in an atmosphere of greater humidity.

Thus it is seen that sugar may be dried in a satisfactory way without very elaborate precautions—a conclusion which is confirmed through some very careful work by Bates and R. F. Jackson at the United States Bureau of Standards, kindly furnished us, at the time, in manuscript. They state that in their experience the air-dried and pulverized sample lost in weight only about 0.01 to 0.02% at the first drying operation and practically nothing thereafter. Nevertheless, we are inclined to agree with Swientoslawski[2] as to the undesirability of sugar for this purpose, for his reasons numbered (1) and (4).

Benzoic Acid and Naphthalene.—These substances had been prepared with care by the Bureau of Standards to serve as standards (B. of S. Nos. 39 and 38, respectively). Their appearance was entirely satisfactory, and neither left a weighable trace of residue on evaporation.

Benzene.—Three samples of benzene were used in this work. The first and least pure was numbered 4 and was prepared in the following way. A very pure commercial benzene (warranted free from thiophene and once crystallized) after standing several months over sulfuric acid,

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[1] This material was obtained through the kindness of F. O. Murphy, a chemist of the company.

[2] W. Swientoslawski, This Journal, 39, 2597 (1917).

was thoroughly washed, allowed to remain over sodium for a long time, and then recrystallized twice. The freezing point was constant to within about 0.01° during the complete solidification of the substance. After further standing over sodium, this Sample 4 was crystallized once more and thus yielded Sample 3, which showed no difference as to heat of combustion. Sample 6 had been prepared synthetically from benzoic acid and later recrystallized by J. W. Shipley 5 times.[1] The fourth and fifth recrystallizations gave the same freezing point to within 0.001° and this point was as high as that of any sample which Shipley was able to prepare, thus showing great purity.

Toluene.—One of the specimens of toluene was that very carefully prepared by F. Barry. Another similar specimen was prepared from commercial toluene, shaken with sulfuric acid until it gave no color to the acid, agitated with mercury until it ceased polluting a clean mercury surface, washed and repeatedly distilled. Both these samples boiled at essentially the same point, between 100.3° to 100.4° under normal pressure.

Tertiary Butyl Benzene.—This substance was prepared with great care by an assistant (J. C. Howard) under the direction of G. L. Kelley, to whom we are indebted for his oversight of the work. We redistilled and fractionated a product boiling between 168.6° and 168.7° (barometer, 759 mm.). The substance had a density at 20° of 0.8671.[2]

Decane (Di-iso-amyl).—This substance had been prepared in 1912 by a prominent German firm. It was redistilled several times under normal pressure and collected in the following fractions: Sample 1, 159.2° to 159.5°; Sample 2, 159.5° to 159.7°; Sample 3, 159.7° to 160.1°. No difference could be detected in their heats of combustion.

Methyl Alcohol.—Very pure methyl alcohol made by Shipley[3] for an earlier investigation was used. It had been prepared by the following processes; (1) the preparation of pure methyl oxalate; (2) the saponification of the ester; (3) the fractionation of the liquid product until a product boiling between 68° and 70° was obtained; (4) treatment of this product with a little iodine and sodium hydroxide to eliminate foreign organic matter; (5) drying the alcohol, with potassium carbonate, calcium oxide and pure sodium; (5) fractionation of the alcohol. Density at 20°/4°, 0.7923. Boiling point, 64.51°, bar. 761.5 mm. The combustions with this substance were the least satisfactory, perhaps because of its volatility. Unfortunately only one could be analyzed for carbon monoxide, because of lack of time.

Ethyl Alcohol.—Both the samples of ethyl alcohol described below

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[1] THIS JOURNAL, 36, 1830 (1914).

[2] For details see *ibid.*, 37, 1001 (1915).

[3] Richards and Shipley, *ibid.*, 38, 996 (1916).

were obtained through the kindness of L. B. Coombs,[1] who prepared them. Sample 1 was prepared from Squibb's 99.8% alcohol. It was refluxed over metallic calcium for a day, then fractionated. B. p. 78.55°–78.60°, bar., 763.9 mm. During distillation, the receiver was carefully protected from aqueous vapor by freshly ignited lime. The alcohol was preserved in a stoppered bottle over sulfuric acid in a desiccator. Sample 2 was prepared in the same way as (1). B. p. 78.50°, bar. 767 mm. This material was doubtless less trustworthy than the methyl alcohol.

Propyl Alcohol already very pure was redistilled with the following outcome: Sample 1, b. p. 96.6°–96.7°; Sample 2, b. p. 96.7°–96.9°; Sample 3, b. p. 96.9°–97.1° (bar. 757 mm. in each case); Sample 4, all the previous fractions were mixed and refluxed with calcium for 2 hours, b. p. 96.8°–97.0°, bar. 766.0 mm.

Butyl Alcohol (Normal).—The butyl alcohol used was that which had been prepared long ago by one of us in collaboration with J. H. Mathews[2] during work on the latent heats of evaporation. It was redistilled, the greater part coming over between 116.0°–116.8°, bar. 766 mm. (Sample 1). This distillate was then refluxed with calcium for 2 hours, the greater part now coming over at 116.3°–117.3°, bar. 765.5 mm. (Sample 2). In spite of the change in the boiling point, the 2 samples differed in their heats of combustion by an amount no greater than possible experimental error.

Isobutyl Alcohol was prepared from the purest obtainable German materials by distillation after refluxing with calcium. B. p. 107.2°–107.3°, bar. 763.4 mm. This appeared to be very pure, all distilling over within the tenth of a degree.

Cyclohexanol.—Cyclohexanol was prepared from a mixture of this substance with cyclohexanone, which had been prepared, with his unfailing courtesy, by G. L. Kelley from phenol by reduction according to the method of Sabatier and Senderens. J. W. Shipley kindly carried out for us the separation of the ketone by means of freshly made sodium hydrogen sulfite, and the cyclohexanol thus obtained was further purified by drying over sodium carbonate, direct distillation and fractional crystallization in a drop-funnel. The samples in the combustion were (A) cyclohexanol recrystallized 8 times, (original m. p. 21.9°), which had, however, remained standing for several months in an ordinary stoppered bottle. This sample had undoubtedly absorbed moisture with its characteristic eagerness, and its results were a full per cent. lower than the others. They are not recorded below, but showed how careful one must be in dealing with

[1] Richards and Coombs, This Journal, 37, 1669 (1915).

[2] Richards and Mathews, *ibid.*, 33, 863 (1911).

a substance so hygroscopic. (B) Cyclohexanol freshly distilled from sodium, b. p. 160.8° (bar. 759 mm.). (C) Cyclohexanol obtained from Sample B by crystallization 4 times in a drop-funnel protected by drying tubes from the moisture of the air. (D) Material prepared by Shipley from Sample B by recrystallization. The freezing point of this last sample indicated that the amount of moisture in it must have been less than 0.1%.[1] Zubow's material, purified by fractional distillation, had almost the same boiling point (160.4° under 751 mm.) as ours.

Cotton Wool.—The cotton used was a good, clean-looking sample of absorbent cotton, of the kind used for surgical dressings. Its heat of combustion was found to be 4020 cal. per g.

Gelatine Capsules.—The gelatine capsules (from a prominent American firm) were the kind ordinarily used to enclose disagreeable medicines. The nitric acid formed in the bomb per gram of capsule was about 0.00033 g. The heat of combustion was 4160 cal. per g.

Paraffin.—The samples of hard paraffin used for the combustions were cut from different parts of a uniform-looking cake, so as to obtain a fair average. Its heat of combustion was found to be 11210 cal. per g.

The Beeswax was the hard white commercial material, and yielded on burning 12660 cal. per g.[2]

TABLE I.

Rise of Temperature in Calorimetric System (Heat Capacity 2660.0) Caused by Combustion of 1,0000 g. (Weighed in Air) of Sundry Substances.

Sucrose, Series I, Samples 1 and 2.

Expt. No.	Sample.	Weight of sub. in air. G.	Ignition material in mg.		Final temperature. ° C.	Obs. Rise in temp. ° C.	Total correction. ° C.	Corrected rise in temp. ° C.	Rise per gram. ° C.
3	1	2.2006	Cotton[a]		19.9	3.2727	0.0113	3.2614	1.4820
7	1	2.2038	Cotton		20.0	3.2809	0.0105	3.2704	1.4840
8	1	2.9737	Cotton		20.3	4.4225	0.0145	4.4080	1.4823
14	1	1.3714	Cotton	11.5	18.4	2.0598	0.0242	2.0356	1.4843
15	1	2.1357	Cotton	18.1	19.6	3.2027	0.0341	3.1686	1.4837
16	1	2.2620	Cotton	13.5	19.1	3.3836	0.0283	3.3553	1.4833
17	1	2.0326	Cotton	11.7	19.2	3.0401	0.0266	3.0135	1.4826
6	2	2.2002	Cotton		19.8	3.2761	0.0143	3.2618	1.4825

Average, 1.4831

[a] In the earlier determinations of sugar, the wisp of cotton was weighed with the sugar, and counted as sugar since their heats of combustion per gram are very nearly the same. In such cases the weight of cotton is not recorded above.

Two combustions, Nos. 1 and 13, were rejected; the first because it was merely preliminary, the other because far too much cotton was used. All the remaining work with sugar is given in full.

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[1] Richards and Shipley, THIS JOURNAL, 41, 2008 (1919).

[2] These last 4 heats of combustion are given in our earlier paper, *loc. cit.*, p. 352.

TABLE I (*continued*).

Sucrose, Series II, Sample 3.

Expt. No.	Sample.	Weight of sub. in air. G.	Ignition material in mg.	Final temp. ° C.	Obs. rise in temp. ° C.	Total correction. ° C.	Corr. rise in temp. ° C.	Rise per gram. sub. ° C.
2	3	2.1992	Cotton	20.3	3.2770	0.0092	3.2678	1.4842
4	3	2.1987	Cotton	19.8	3.2705	0.0091	3.2614	1.4833
5	3	2.1985	Cotton	20.3	3.2685	0.0094	3.2591	1.4825
9	3	2.7335	Cotton	20.2	4.0675	0.0144	4.0531	1.4828
10	3	2.2316	Cotton	19.4	3.3192	0.0094	3.3098	1.4830
11	3	2.2298	Cotton	18.9	3.3220	0.0116	3.3104	1.4846
12	3	2.1146	Cotton	19.6	3.1466	0.0104	3.1362	1.4831

Average, 1.4832

Sucrose, Series III, B. of S. Sample.

Expt. No.	Sample.	Weight of sub. in air. G.	Ignition material in mg.	Final temp. ° C.	Obs. rise in temp. ° C.	Total correction. ° C.	Corr. rise in temp. ° C.	Rise per gram. sub. ° C.
18	4	1.8561	Cotton 6.7	18.5	2.7760	0.0242	2.7518	1.4825
19	4	2.1896	Cotton 3.5	19.3	3.2641	0.0175	3.2466	1.4827

Average, 1.4826

Average of 18 Combustions, 1.4831

Benzoic Acid.

Expt. No.	Sample.	Weight of sub. in air. G.	Ignition material in mg.	Final temp. ° C.	Obs. rise in temp. ° C.	Total correction. ° C.	Corr. rise in temp. ° C.	Rise per gram. sub. ° C.
20	B. of S.	1.3273	Cotton 5.2	19.1	3.1686	0.0133	3.1553	2.3773
21	B. of S.	1.1830	Cotton 4.5	19.4	2.8268	0.0131	2.8137	2.3784
22	B. of S.	0.9810	Cotton 5.4	17.9	2.3483	0.0150	2.3333	2.3784

Average, 2.3780

Average corrected for firing heat,* 2.3778

* Whenever the rise of temperature in the calorimeter was about 4°, the heat generated electrically in the platinum wire used for firing was eliminated from the result in latter calculation; but with a rise of temperature of only 2°, half of this firing heat (2 cal.) is not thus eliminated, and must be allowed for as above to secure consistency in the results.

Naphthalene.

(Two Series, with Diverse Quantities and Different Final Temperatures.)

Expt. No.	Sample.	Weight of sub. in air. G.	Ignition material in mg.	Final temp. ° C.	Obs. rise in temp. ° C.	Total correction. ° C.	Corr. rise in temp. ° C.	Rise per gram. sub. ° C.
23	B. of S.	1.1226	Cotton 3.5	19.8	4.0779	0.0149	4.0630	3.6193
24	B. of S.	1.1537	Cotton 7.8	20.2	4.1949	0.0220	4.1729	3.6170
25	B. of S.	1.1002	Cotton 9.5	20.0	4.0062	0.0260	3.9802	3.6177
26	B. of S.	1.1023	Cotton 7.3	20.1	4.0100	0.0220	3.9880	3.6180

Average Series I, 3.6180

Expt. No.	Sample.	Weight of sub. in air. G.	Ignition material in mg.	Final temp. ° C.	Obs. rise in temp. ° C.	Total correction. ° C.	Corr. rise in temp. ° C.	Rise per gram. sub. ° C.
27	B. of S.	0.8286	Cotton 8.2	19.4	3.0200	0.0230	2.9970	3.6170
28	B. of S.	0.5415	Cotton 9.2	18.1	1.9843	0.0250	1.9593	3.6182
29	B. of S.	0.5183	Cotton 11.5	17.9	1.9052	0.0291	1.8761	3.6182
30	B. of S.	0.5511	Cotton 10.1	18.0	2.0214	0.0265	1.9949	3.6198

Average Series II, 3.6186

Average of Series II corrected for firing heat, 3.6182

Total average of Series I and II corrected, 3.6181

TABLE I (*continued*).

Expt. No.	Sample.	Weight. G.	Ignition material in mg.		Final temp. ° C.	Obs. rise in temp. ° C.	Total correction. ° C.	Corr. rise in temp. ° C.	Rise per gram. ° C.
				Benzene.					
31	3	0.6743	Sug.	143.0	19.1	2.7627	0.2165	2.546	3.775
32	3	0.7166	Sug.	185.0	19.5	2.9835	0.2805	2.703	3.772
33	4	0.7435	Sug.	212.1	19.3	3.1340	0.3300	2.804	3.771
34	3	0.6284	Par. Cot.	27.2 13.2	19.0	2.5090	0.1423	2.367	3.767
35	4	0.7738	Bsw. Cot.	25.6 23.0	19.7	3.0538	0.1400	2.914	3.766
36	4	0.7988	Bsw. Cot.	27.0 20.3	19.6	3.1532	0.1412	3.012	3.771
37	4	0.6752	Bsw. Cot.	34.8 24.9	19.2	2.7283	0.1830	2.545	3.769
38	6	0.8438	Par. Cot.	139.3 10.3	20.3	3.7842	0.6128	3.172	3.759
39	6	0.8106	Par. Cot.	103.4 5.0	20.1	3.5083	0.4545	3.054	3.768
								Average,	3.769
				Toluene.[a]					
40	2	0.7982	Bsw. Cot.	27.3 4.8	19.8	3.1781	0.1236	3.0545	3.827
41	2	0.8374	Bsw. Cot.	35.2 2.6	19.5	3.3488	0.1488	3.2000	3.821
42	2	1.1059	Par. Cot.	48.0 3.1	20.0	4.0960	0.2170	3.8790	3.818
43	1	0.9154	Par. Cot.	98.2 3.6	19.9	3.9230	0.4258	3.4972	3.820
44	2	0.9986	Par. Cot.	95.3 3.0	19.8	4.2326	0.4144	3.8172	3.823
45	3	1.0566	Par. Cot.	79.7 7.9	20.4	4.3725	0.3348	4.0377	3.821
								Average,	3.822
				Tertiary Butyl Benzene.					
46	1	1.0024	Par. Cot.	119.8 5.1	20.46	4.4589	0.5220	3.937	3.927
47	1	0.8420	Par. Cot.	106.8 6.5	19.9	3.7806	0.4720	3.929	3.929
48	1	0.9070	Par. Cot.	122.3 4.3	20.1	4.0884	0.5276	3.926	3.926
								Average,	3.927

[a] Determinations 43, 44 and 45 are those given in THIS JOURNAL, 39, 353 (1917). The slightly different figures now recorded are due to the recalibration of the thermometer. The average of the 3 remained unchanged. Nos. 44 and 45 were among the worst of those which left unburned CO, as detailed in the place just cited.

TABLE I (*continued*).

Expt. No.	Sample.	Weight. G.	Ignition material in mg.		Final Temp. ° C.	Obs. Rise in Temp. ° C.	Total Correction. ° C.	Corr. Rise in Temp. ° C.	Rise per gram. ° C.
			Cyclohexanol.						
49	B	1.0610	Sug.	153.3	20.2	3.7849	0.2380	3.5469	3.343
50	B	0.7824	Sug.	124.4	18.7	2.8026	0.1924	2.6102	3.336
51	C	1.0233	Bsw.	24.6	20.3	3.5846	0.1650	3.4196	3.342
			Cot.	20.9					
52	D	0.8545	Bsw.	47.7	18.9	3.0814	0.2242	2.8572	3.344
			Cot.	6.0					
								Average of last two,	3.343
			Decane (Di-iso-amyl).						
53	1	0.7436	Par.	88.1	19.8	3.5607	0.3856	3.1751	4.270
			Cot.	3.6					
54	1	0.8176	Par.	112.3	20.0	3.9931	0.5001	3.4930	4.272
			Cot.	9.7					
55	2	0.7839	Par.	111.4	19.7	3.8341	0.4930	3.3411	4.262
			Cot.	7.4					
56	3	0.8210	Par.	120.0	20.2	4.0252	0.5179	3.5073	4.272
			Cot.	8.3					
57	3	0.8040	Par.	122.0	19.9	3.9667	0.5351	3.4316	4.268
			Cot.	6.2					
								Average,	4.269
			Methyl Alcohol.[a]						
58	1	1.4337	Sug.	95.1	19.7	3.0344	0.1513	2.883	2.011
59	1	1.4462	Sug.	103.3	19.6	3.0510	0.1587	2.892	2.000
60	1	1.6788	Sug.	94.3	20.2	3.4975	0.1464	3.351	1.996
61	1	1.8720	Sug.	112.8	20.3	3.9382	0.1771	3.761	2.009
62	1	0.7207	Gel.	43.0	17.7	1.5490	0.1020	1.447	2.008
			Cot.	18.0					
								Average,	2.005
			Ethyl Alcohol						
63	1	0.9749	Par.	102.0	20.1	3.0581	0.4511	2.6070	2.674
			Cot.	7.9					
64	1	1.1711	Par.	111.0	20.3	3.6156	0.4862	3.1294	2.672
			Cot.	6.4					
65	1	0.8960	Par.	104.5	19.9	2.8576	0.4606	2.3970	2.675
			Cot.	7.0					
66	2	1.0400	Par.	115.5	19.6	3.2887	0.5117	2.7770	2.670
			Cot.	8.7					
								Average,	2.673

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[a] These combustions were on the whole the least satisfactory of all, but they are probably at least as good as other published work concerning this substance. The result is only about 0.1 % less than the usually accepted value, which depends chiefly on Thomsen's results.

TABLE I (*continued*).

Expt. No.	Sample.	Weight. G.	Ignition material in mg.		Final temp. ° C.	Obs. rise in temp. ° C.	Total correction. ° C.	Corr. rise in temp. ° C.	Rise per gram. ° C.
			Propyl Alcohol.						
67	3	1.1434	Par.	128.1	19.9	4.0190	0.5649	3.4541	3.021
			Cot.	9.0					
68	3	0.7576	Par.	124.4	19.2	2.8455	0.5522	2.2933	3.027
			Cot.	10.9					
69	4	0.8417	Par.	120.7	19.3	3.0916	0.5424	2.5492	3.022
			Cot.	12.7					
70	4	0.6696	Par.	114.7	19.8	2.5317	0.5048	2.0269	3.027
			Cot.	6.5					
								Average,	3.024
			Butyl Alcohol—Normal.						
71	1	0.7000	Par.	139.0	19.1	2.8823	0.6126	2.2697	3.242
			Cot.	10.0					
72	2	0.7781	Par.	114.1	19.4	3.0251	0.5010	2.5241	3.244
			Cot.	6.0					
								Average,	3.243
			Isobutyl Alcohol.						
73	1	0.8628	Par.	113.2	19.9	3.2942	0.4999	2.7943	3.239
			Cot.	6.5					
74	1	1.0774	Par.	103.7	19.9	3.9423	0.4571	3.4852	3.235
			Cot.	7.5					
								Average,	3.237

Heats of Combustion of the Several Substances.

As already stated, the above results with sucrose, benzoic acid and naphthalene were used as standards in calculating the heats of combustion of the other substances. The samples of sugar were evidently nearly but not exactly alike. The two samples, 1 and 3, prepared here, gave results almost precisely identical. The average of all the results with each standard substance was taken as the value corresponding to that substance. According to the values furnished by the Bureau of Standards, the heat capacity of our calorimetric system in 20° calories is calculated from the results with these 3 substances as follows.

	Rise of temperature per gram (in air). Degrees.	Combustion heat (B. of S.).[*]	Heat capacity of system in 20° calories.
Sucrose	1.4831	3949	2662.9
Benzoic acid	2.3778	6329	2661.7
Naphthalene	3.6181	9622	2659.4
		Average,	2661.3

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[*] Bureau of Standards, *Circ.* 11, 2nd Ed., 16 (1915).

In 18° calories (actually used by us) this becomes 2660.0,[1] which is taken as the heat capacity of our calorimetric system in calculating the results for the other substances. The individual averages upon which it depends are more divergent than is desirable, the extreme divergences from the mean amounting to about 0.07%. Evidently naphthalene in our hands yielded a larger heat of combustion in relation to sugar than it did at the Bureau of Standards, although even our value is distinctly less than that found by some Europeans. Benzoic acid falls between the two others. Whether or not the reason of the difference is to be found in incomplete combustion in some cases, we do not attempt to decide. If at any time the discrepancy is explained and one or the other of these substances is proved to be the best standard of reference, the results can easily be calculated into that standard by reference to the figures just given. We are inclined to think that naphthalene may be found the best substance, when its purification has been perfected and its heat of combustion certainly established.[2] The whole question of the true standard of reference is discussed at such length in the interesting recent papers by Swietoslawski[3] and by Roth,[4] as well as in one of the Harvard papers,[5] that further treatment at present is unnecessary. The establishment of a thoroughly trustworthy and generally recognized standard of reference is one of the desiderata of this kind of work. The Bureau of Standards and Swietoslawski have made important advance in this direc-

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[1] See Richards and Barry, *loc. cit.*, p. 1016, Cal. (18°) = (Cal. 20°) × 1.0005. As already stated, when there was a 4° rise of temperature, no correction is applied to these figures for the small amount of heat evolved electrically by the fine platinum wire in firing, because this small quantity appears in practically equal measure in each combustion, and is eliminated in the later calculation. Swietoslawski, in recalculating Zubow's results, used the 15° calorie, which is perhaps 0.07% greater than the 18° calorie.

[2] Naphthalene has a vapor pressure of 0.064 mm. at 20° according to Barker (*Z. physik. Chem.*, 71, 235 (1910)). Care must, therefore, be taken that none evaporates after weighing, either outside or within the bomb. The loss of one liter of its vapor at 20° means a loss of about 2 cal. on burning.

[3] Three years ago, after our experimental work was finished, Swietoslawski published his interesting paper on the use of benzoic acid as the standard unit in the thermochemistry of organic compounds (THIS JOURNAL, 39, 2595 (1917)). With the general conclusions in this article we heartily agree. Unfortunately our own determinations with benzoic acid were too few in number to use them alone as the basis of our heat capacity determinations. Moreover in each of them a correction had to be made for nearly a milligram of carbon remaining unburned. Therefore, for the present the average value given above seems to us the safest. Swietoslawski's very valuable recent paper, giving a recalculation of Zubow's work upon a satisfactory basis, shows that in general Zubow's results are reasonably close to ours. This paper appeared after the present contribution was submitted for publication, and hence cannot be considered in detail here. (THIS JOURNAL, 42, 1312 (1920).

[4] Roth, v. Auwers (and Wallasch), *loc. cit.*, pp. 113–127, 162.

[5] Richards and Barry, *loc. cit.*, p. 1016.

tion, but evidently more remains to be done, as they themselves would doubtless agree.

The heat capacity of the calorimetric system having been thus determined, it may be used to calculate the heats of combustion of the several substances. The resulting values are given below, not only on the basis of the weighings in air (corresponding to the results given above as well as to the values given by the Bureau of Standards), but also upon the vacuum basis. Moreover the molal heats of combustion are recorded likewise in the following table, both in large calories and in kilojoules, the atomic weights used being the present international values, C = 12.005, H = 1.0076 and O = 16.000.

TABLE II.

Heats of Combustion in Constant Volume of the Several Substances, Including Reduction to Vacuum Standard.[a]

(The Heat Capacity of the Calorimetric System between 16° and 20° is taken as 2660.0, Cal. (18°)/° C., its materials having been weighed in air. 4.182 joules are taken as equivalent to the 18° Calorie.)

	Rise of temp. in cal. system. ° C.	Comb. heat per 1.0000 g. (weighings in air).	Density.	Comb. heat per 1.0000 g. (weighing substance in vacuum).	Mol. wt.	Heat of combustion per mol. (weigh. in vac.).	
						Large Cal.	Kilojoules.
Sucrose.................	1.4831	3945	1.61	3943	342.23	1349.4	5643
Benzoic acid.............	2.3778	6325	1.32	6320	122.08	771.55	3227
Naphthalene.............	3.6181	9624	0.97	9614	128.11	1231.6	5151
Benzene.................	3.769	10026	0.88	10014	78.076	781.85	3269.7
Toluene.................	3.822	10167	0.87	10155	92.095	935.23	3911.1
Tertiary butyl benzene....	3.927	10446	0.87	10434	134.16	1399.8	5854
Cyclohexanol, $C_6H_{11}(OH)$..	3.343	8892	0.96	8882	100.12	889.3	3719.0
Di-isoamyl..............	4.269	11356	0.73	11339	142.22	1612.6	6744.0
Methyl alcohol...........	2.005	5333	0.79	5326	32.035	170.61	713.4
Ethyl alcohol............	2.673	7110	0.79	7101	46.056	327.04	1367.7
Propyl alcohol...........	3.024	8044	0.80	8033	60.075	485.80	2031.6
Butyl alcohol............	3.243	8626	0.81	8615	74.095	638.33	2669.5
Isobutyl alcohol..........	3.237	8610	0.80	8599	74.095	637.14	2664.5

[a] Attention may be called to another very small correction, namely, the correction for the heat rendered latent in evaporating water in the bomb between 16° and 20°. In our bomb (containing 375 cc.) about 1.4 mg. of water must have been evaporated for 4° rise in temperature, or for the output of 10700 cal. Hence, each value should be raised $100 \times 0.0014 \times 540/10700 = 0.007\%$. This is so small as to be less than the experimental error, and is, therefore, not applied above.

The comparison of these results with those of others is interesting and leads to the conclusion that the heats of combustion of some of these substances are now known, at least relatively, with considerable accuracy. The best method perhaps of tracing the comparative values is to state the heat of combustion of volatile substances, such as benzene and toluene (which offer the greatest difficulties) in relation to some one standard substance, such as sugar, which has been the most often used. Benzene was found by Berthelot[1] to give out 2.52 times as much heat as sugar, gram for gram, on burning. Stohmann's[2] value, obtained in one way, was 2.5325, and in another 2.5275. Richards, Henderson and Frevert[3] concluded that 2.534 was the minimum value, but found that nitrogen in their bomb interfered with complete combustion and believed the true value to be higher. One of us, in collaboration with R. H. Jesse, Jr.,[4] verifying this prediction, found the value corrected to the vacuum standard 2.5382 (almost identical with our present value 2.5397, which we believe to be very near the true one). The later finding (in collaboration with F. Barry) of a lower value 2.533,[5] again raised suspicions of incomplete burning. At that time no determinations of the carbon monoxide in the residual gases were made; but there can be little question that the deficiency in the last named value is due to this cause, because our present repetitions of the methods which yielded it (involving the auxiliary use of sucrose, combustions 31, 32 and 33) yielded results more than 0.1% too low until corrected for the carbon monoxide found in the residual gases (on the average 2.5 cc. per combustion). Seemingly trivial details in manipulation may determine whether or not the flame of the burning liquid reaches the cool walls of the bomb in such a way as to have its combustion partially inhibited. The method employing a ring of naphthalene, used almost exclusively in the present work, is doubtless much superior to that in which a small heap of sugar is the auxiliary substance. That the trouble was due to incomplete burning of the volatile liquid and not to other faulty procedure is shown by the fact that the results of Richards and Barry on toluene (2.5769 times sugar) were almost identical with the figures which we have just detailed (2.5754 times sugar). The most recent values of Roth and von Auwers[6] for benzene, 10,012 (±2) per g. and for toluene 10,146 (±6) based upon their electrical calibration of the calorimeter as well as upon the burning of benzoic acid (assuming Fischer and Wrede's[7] value as correct) are apparently very near ours (which are, respectively, 10,014 and 10,155). Unfortunately, the agreement is not quite as close as it seems, since their calculation assumes the heat of combustion of a gram of the standard benzoic acid (weighed in vac.) to be

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[1] M. Berthelot, *loc. cit.*

[2] Stohmann, *ibid.*

[3] Richards, Henderson and Frevert, *Proc. Am. Acad.*, 42, 573 (1907).

[4] T. W. Richards and R. H. Jesse, Jr., THIS JOURNAL, 31, 288 (1910).

[5] T. W. Richards and F. Barry, *loc. cit.*

[6] W. A. Roth and K. von Auwers, *Ann. chim.*, 407, 109 (1914).

[7] Fischer and Wrede, *Z. physik. Chem.*, 75, 81 (1910). The very elaborate work of W. Swietoslawski (*J. Russ. Phys.-Chem. Soc.*, 46, 935–75 (1914)) found a value as low as 6310 for the heat of combustion of benzoic acid. His recommendations concerning the use of the adiabatic calorimeter (*ibid.*, p. 1284) are excellent; but more of them had been anticipated at Harvard than he seems to have realized.

6325.5 cal., whereas ours takes this figure as 6320. Reduced to our standard, the results of Roth and Auwers become 10003 and 10137—results less than ours by 0.11 and 0.18%, respectively. Whether this difference is due to differences in the substances or to incomplete combustion in the German work it is impossible to say. The details of the work of Roth are carefully elaborated and it is clear at least that he got better results with his method than we were able to obtain until we analyzed the residual gases, a step which he did not take.

Further comparison of the new results with those of others, especially in view of the detailed discussion given by Roth in the paper so often quoted, may be omitted.

The new figures give another accurate basis for computing the effect on the heat of combustion of the familiar increment CH_2 of homologous series.

TABLE III.

Increase in Combustion Heat Due to CH_2.

(Substitution of CH_3 for H in alcohols and side chains.)

Difference between.		Kilojoules.
Ethyl alcohol-Methyl alcohol	= 1368.7 — 713.4	= 654
Propyl alcohol-Ethyl alcohol	= 2031.6 — 1367.7	= 654
Butyl alcohol-Propyl alcohol	= 2669.5 — 2031.6	= 638
	Average of 3 differences in alcohols	= 649
Ethyl benzene-Toluene	= 4555.0 — 3911.1	= 644
Propyl benzene-Ethyl benzene	= 5202 — 455	= 647
Isopropyl benzene-Ethyl benzene	= 5206 — 4555	= 651
Tert. butyl benzene-Propyl benzene	= 5854 — 5205	= 652
Tert. butyl benzene-Isopropyl benzene	= 5854 — 5206	= 648
	Average of 5 differences in aromatic substances	= 648

Evidently the addition of CH_2 produces on the average an increase in the heat of combustion of 648 kilojoules or 153.5 Cal.—a quantity almost identical with the provisional figures, 644 kilojoules reported by Richards and Jesse[1] and 646 reported by Richards and Barry.[2] This new value is different from that of Thomsen, 660 kilojoules or 158 Cal., doubtless because Thomsen's "universal burner" gave increasingly too high results with decrease in volatility.

The thermochemical effect disclosed in the above table refers to the substitution of the methyl group for hydrogen attached to a carbon singly bound to another: for in the aromatic compounds given, the additions are to the side chain. The effect seems to be slightly different when the methyl group replaces a hydrogen attached directly to the ring, as is shown by the following table—a table not full enough, indeed, to give a certain

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[1] Richards and Jesse, *loc. cit.*, p. 296.

[2] Richards and Barry, *ibid.*, p. 1019.

value to the average, but nevertheless serving as some indication of the differing effect.

TABLE IV.

Increase in Combustion Heat Due to CH_2 Added to the Benzene Ring.

Difference between			
Toluene-Benzene	= 3911.1	— 3269.7	= 641
Xylene (*o*- or *m*-)-Toluene	= 4557	— 3911	= 646
Xylene (*p*)-Toluene	= 4541	— 3911	= 630
Mesitylene-Xylene (*m*)	= 5191	— 4557	= 634
		Average,	638

Further conclusions concerning the essential relations of these to one another and to other trustworthy data of the same kind are reserved for a later communication.

We take pleasure in expressing our indebtedness to the Rumford Fund of the American Academy of Arts and Sciences for the calorimetric bomb employed and to the Carnegie Institution of Washington for much of the rest of the apparatus.

Summary.

This paper gives detailed figures for the heats of combustion of the following substances in 18°-calories per gram (weighed in a vacuum): sucrose 3943, benzoic acid 6320, naphthalene 9614, benzene 10014, toluene 10155, tertiary butyl benzene 10434, cyclohexanol 8882, di-iso-amyl 11339, methyl alcohol 5326, ethyl alcohol 7101, propyl alcohol 8033, butyl alcohol 8615, isobutyl alcohol 8599.

It is hoped that in several respects most of these figures are more trustworthy than previous values, especially because more precaution was taken than usual to make sure that the combustion was in each case complete, and because the substances were in most cases very carefully purified and always carefully dried.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE DIVISION OF DRUGS, BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE.]

THE USE OF ORGANIC SOLVENTS IN THE QUANTITATIVE SEPARATION OF METALS. III. THE SEPARATION OF MAGNESIUM FROM SODIUM AND POTASSIUM CHLORIDES.

BY S. PALKIN.

Received June 14, 1920.

In a previous communication,[1] the author has shown that sodium and potassium chlorides can be quantitatively precipitated from an acidified water solution by the use of alcohol and ether. Advantage was taken of this fact to effect a separation of these alkali metals from their third member, lithium, as the chloride of the latter is readily soluble in a mixture of alcohol and ether. Experiments with magnesium chloride have shown that this salt too is soluble in an alcohol-ether mixture and can be separated easily from the chlorides of sodium and potassium, using essentially the same procedure as that outlined for the separation of lithium from the other alkali metals.

The only method on record, involving the use of an organic solvent for the separation of magnesium from the alkali metals, is that of Gooch and Eddy.[2] In this method a solution of ammonia and ammonium carbonate in *alcohol* is used to precipitate the magnesium, while the alkali chlorides (except lithium) are determined in the filtrate.

Like the Gooch-Eddy separation, the alcohol-ether method herein proposed, makes it possible to determine magnesium and the alkalies in the same sample, with the additional advantage that the reagents used are readily volatile on the steam bath and the precipitate is that of the alkali chlorides instead of magnesium (as is the case in other methods), thus making it possible to secure a more rapid and direct determination of the alkali metals, where that is particularly desired. The magnesium may then be determined in the filtrate.

Very pure magnesium chloride was prepared by further purification of C. P. magnesium chloride obtained in the market. This was done in order to free it from traces of alkali chlorides and other substances insoluble in alcohol-ether mixture. In like manner samples of C. P. sodium chloride and potassium chloride, respectively, were treated to remove traces of magnesium chloride and other substances soluble in alcohol-ether mixture. The method of purification used was essentially the method of separation here described. Alcoholic solutions of the pure magnesium chloride were prepared and an aliquot portion pipetted off for

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[1] THIS JOURNAL, 38, 2326 (1916).

[2] *Am. J. Science*, 25, 444 (1908).

each experiment. Errors of volume change due to temperature were eliminated by making all pipetting at the same temperature.

A mixture of equal weights of the pure dried sodium and potassium chlorides was used and the required amount weighed out for each experiment.

The following is a table of results obtained by the proposed method, using various proportions of magnesium and alkali chlorides. In some experiments values obtained in the first precipitation are recorded in addition to the value of the total alkali chlorides by the two precipitations.

Results Obtained by Proposed Method.

	Weight NaCl, KCl.		Weight $Mg_2P_2O_7$. due to $MgCl_2$ solution.		Wt. NaCl, KCl found by first precipitation G.
Expt.	Used. G.	Found. G.	Used.[a] G.	Found. G.	
1	0.5000	0.4996	0.0070	0.0078	...
2	0.3800	0.3795	0.1743	0.1748	....
3	0.2500	0.2499	0.3486	0.3483	....
4	0.5000	0.4995	0.0060	0.0067	....
5	0.3800	0.3801	0.1501	0.1500	....
6	0.2500	0.2505	0.3002	0.3017	....
7	0.0500	0.0503	0.3004	0.3006	....
8	0.5000	0.5005	0.0300	0.0307	0.4960
9	0.5000	0.5005	0.0300	0.0302	0.4965
10	0.5000	0.5000	0.0300	0.0304	0.4990
11	0.4000	0.4006	0.1147	0.1157	0.3989
12	0.3000	0.3004	0.2294	Spattered,	0.2978
13	0.1000	0.1002	0.4587	0.4577	0.0970
14	0.2500	0.2500	0.2293	0.2286	0.2477
15	0.5000	0.5000	0.0229	0.0227	0.4947
16	0.0500	0.0506	0.2748	0.2746	....
17	0.5000	0.5003	0.0055	0.0058	....
18	0.2000	0.2001	0.0054	0.0056	....
19	0.5000	0.5002	0.0599	0.0610	0.4983
20	0.5000	0.5008	0.0599	0.0605	0.4950
21	0.5000	0.5005	0.1498	0.1491	0.4945
22	0.4500	0.4499	0.0990	0.0977	0.4474
23	0.3800	0.3805	0.2476	0.2480	0.3791
24	0.2500	0.2509	0.4952	0.4955	0.2476
25	0.0050	0.0051	0.4952	0.4960	....

[a] Calculated from blank determinations.

Method.

The total chlorides of magnesium, sodium and potassium are dissolved in a minimum amount of cold water in a 100–150 cc. beaker-flask. About 1.5 cc. is sufficient for 0.5 g. of salt.[1] When all is in solution, one drop of conc. hydrochloric acid is added and, gradually, 25 cc. of absolute alcohol, the alcohol being dropped into the center of the beaker (not on the

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[1] The magnesium chloride content should not exceed 0.3 g. and the total chlorides 0.5 g.

sides) while rotating. The sodium and potassium chlorides should precipitate in a perfectly uniform granular condition. In a similar manner, while rotating the flask, 25 cc. of U. S. P. ether is added and the mixture is allowed to stand about 5 minutes or until the precipitate is agglomerated and the supernatant liquid almost clear. If there is any tendency for the precipitate to become gelatinous, a few cc. of absolute alcohol is added and the flask rotated. This tendency to gel occurs only when a relatively large amount of magnesium chloride is present and an excessive amount of moisture has been introduced.

The mixture is then filtered through a weighed Gooch crucible into a 150 cc. Erlenmeyer flask, using a bell-jar arrangement and permitting only mild suction, in order to avoid sucking the precipitate dry too soon.[1] The beaker-flask is thoroughly washed with a mixture of one part alcohol and 4 parts ether, and adhering particles of salt are removed with the aid of a rubber-tipped rod. The precipitate in the Gooch crucible is also well washed and the crucible set aside.

The filtrate is evaporated to dryness on the steam bath (using air-blast if available). The residue is taken up with 10 cc. of absolute alcohol, warming if necessary, so that nearly everything passes into solution, and *one* drop of conc. hydrochloric acid is added. If a slight film remains on the bottom of the flask and sides, it is loosened by rubbing with a rubber-tipped rod. A fine powder of sodium and potassium chloride (a few mg.) will probably separate. While rotating the flask 50 cc. of U. S. P. ether is added *gradually* and the mixture allowed to stand for about 20 minutes. This is then filtered through the original Gooch crucible containing the bulk of sodium and potassium chlorides, into a tall beaker (about 250 cc.). The same *careful precautions* are taken as outlined in the first filtration. The crucible containing the sodium and potassium chlorides is dried, gently ignited, cooled and weighed.

Determination of the Magnesium.

The filtrate containing the magnesium chloride is evaporated on the steam bath to dryness, or nearly so, using air-blast if available. It is then taken up with 5 to 10 cc. of conc. hydrochloric acid, the requisite amount of water and sodium hydrogen phosphate added and the magnesium determination made in the usual way. The crystalline form of the magnesium ammonium phosphate is obtained much more readily if the precipitate first formed with the ammonia is redissolved with hydrochloric acid, and then neutralized a second time by the very gradual addition of the ammonia with constant stirring until most of the precipitate has formed, after which excess of ammonia is added.

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[1] This filtration can best be accomplished by using a 2-hole rubber stopper for the funnel, and covering up the second hole with the finger while filtering, then releasing the suction by removal of the finger as soon as desired.

Summary.

The author's method for the separation of lithium from the other alkali metals has been studied with the view to its adaptability to the separation of magnesium from these metals. With some modifications, the procedure has been found to be well adapted to magnesium. The method depends on the *progressive* precipitation of the sodium and potassium chlorides from a concentrated aqueous solution by the use of alcohol and ether and is divided into 2 stages, (1) in which all but a few mg. is precipitated, and (2) in which the last few mg. is removed from solution.

The method has several advantages, *viz.*, (1) it affords a direct determination of the sodium and potassium chlorides in that they are precipitated *first* (rather than after magnesium as in other methods), (2) the reagents used are readily volatile organic solvents, and (3) no foreign base or salts is introduced as a precipitating agent.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY, HARVARD UNIVERSITY.]

AN INDIRECT METHOD OF DETERMINING THE SPECIFIC HEAT OF DILUTE SOLUTIONS, WITH PRELIMINARY DATA CONCERNING HYDROCHLORIC ACID.

BY THEODORE W. RICHARDS AND ALLAN W. ROWE.

Received June 16, 1920.

Method and Apparatus.

The specific heat of a dilute solution can be determined indirectly from the difference in the heat evolved on diluting a known concentrated solution to a solution of the desired strength at 2 different temperature.[1] This method rests upon the familiar consequence of the first law of thermodynamics known as Kirchhoff's Law, *viz.*,

$$K_M - K'_M = (U' - U)/\Delta\theta \qquad (1)$$

In this equation K_M and K'_M represent, respective, the molal heat capacities of the reacting substances and of the products, and U and U' the re-

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[1] Berthelot pointed this out long ago, but did not test it experimentally (*Mecanique chimique*, 1, 278 (1879)). Perhaps the first experimental application of the principle has been made by one of us and A, B. Lamb, *Proc. Am. Acad.* 40. 675 (1905). As these authors pointed out, the process is a very accurate one, the errors being divided instead of multiplied by it. Tucker's interesting work deals primarily with concentrated solutions (*Phil. Trans.* [A] 215, 319 (1915)). This was published some time after the present work (the publication of which was much delayed by the war) was completed. The "continuous flow" method used for heats, of neutralization by J. B. Dickson at the suggestion of A. A. Noyes and under the direction of F. G. Keyes might be used for work of this kind, but has not yet been so employed (*Thesis* submitted to Faculty of Mass. Inst. Tech., 1917).

spective total energy changes—in the case in hand, the heats of dilution—at the temperatures θ and $(\theta + \Delta\theta)$.

According to this principle, when once the heat capacity of a concentrated solution has been determined, that of any less concentrated solution can be obtained merely by the measurement of 2 heats of dilution. Hence the method is highly convenient, because heats of dilution are easier to determine than specific heats. The present paper exemplifies the experimental use of the method, and confirms the specific heats of a number of solutions needed in other work.

The appparatus was planned in such a way that the 2 liquids to be mixed should be at precisely the same temperature before mixing. In principle similar to those employed in 1905 by one of us, first with the help of A. B. Lamb[1] and later in improved form with the help of L. J. Henderson,[2] it embodied the further improvements which we have already described and pictured.[3] In this apparatus the concentrated solution was enclosed in an inner platinum receptacle partly immersed beneath the water in the calorimeter; when both liquids had attained exactly the same temperature, the inner receptacle was put into communication with the outer, and by suitable stirring the fluids were mixed. The thermochemical measurement was accomplished adiabatically.

Several combinations of calorimeter apparatus were necessary in order to accommodate the varying proportions of liquids. For the main receptacle, either one of two cylindrical platinum cans was used; the first, *A*, having a capacity of 1.4 liters and the second, *B*, having a capacity about half of this amount. These cans contained in each case the water to serve as diluent.

According to the amount of concentrated solution to be diluted, one of 4 inner receptacles was employed. Each of these inner receptacles answered in general to the description already given, but they varied in volume from 0.7 liter to 0.025 liter. A detailed description of each follows.

a. This inner receptacle (used only with Can *A*) had a capacity of about 0.7 liter, making it possible to mix equal volumes. The great difficulty in this case is to conduct the mixing in such a way as to cause the temperature to rise regularly in all parts of the calorimeter. If this is not accomplished, irregular losses of heat are bound to occur, no matter what calorimetric method is used. Since the combination *A a* was used not only in this work, but also in many determinations of the heat of neutral-

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[1] *Loc. cit.*

[2] T. W. Richards and L. J. Henderson, *Proc. Am. Acad.*, 41, 11 (1905); *Z. physik. Chem.*, 52, 560 (1905).

[3] T. W. Richards, A. W. Rowe and L. L. Burgess, THIS JOURNAL, 32, 1180 (1910). Tucker's apparatus (*loc. cit.*) was a modified form of this arrangement, embodying the same idea.

ization, its manner of use may be described in full. It is indicated in the sectional diagram, Fig. 1. The large platinum calorimeter can, *A*, was placed within a "submarine" jacketing vessel (*S*) protected by an annular air space which was maintained by the use of thin cork wedges at the bottom and sides. A 2-stage narrow platinum ring-stirrer, *O*, alternating 45 times per minute, thoroughly agitated the liquid without causing appreciable heating effect. The stirrer was suspended upon hard rubber rods of the smallest possible diameter in order to minimize the pumping of air through the copper tubes and consequent extraneous heat changes. Circulation of air through the tube was prevented by loose plugs of cotton wool (not shown in the diagram). The inner edges of the stirrer carried several fine platinum wires (*f*) which effectually prevented its catching on the edge of the inside receptacle.

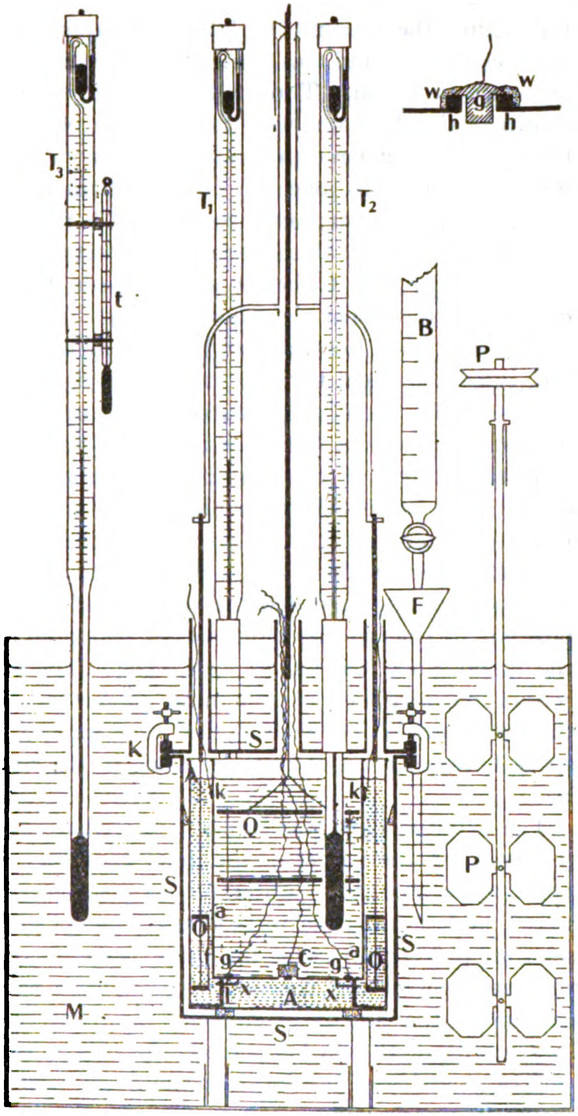

Fig. 1.—Adiabatic thermochemical apparatus for mixing equal volumes of liquids. It consists of a calorimeter *A* to contain one of the liquids and an inner vessel *a* to contain the other, with valves *C*, *g*, *g*, *k*, *k* for communication. Its working is fully explained in the letter press. The small valves *g*, *g*, are shown in the greatly enlarged detail in the upper right-hand corner.

This vessel, which contained the solution to be diluted, was mounted upon stout platinum legs of L shape, the outer circumference of which was that of the inner circumference of the calorimeter. As is evident from the figure, the amount of lateral clearance of the calorimeter stirrer was very slight, and this centering device was necessary to avoid cramping when in action. Three lugs at the upper edge of the inner can (not shown in the diagram) were found to be of assistance in preventing any tilting of the inner receptacle (*a*). The floor of this latter was perforated with 3 short tubes, one (*C*) of large diameter—1.5 cm.—closed by the small rubber stopper; and two of small bore—0.15 cm.—closed by small platinum valves (*g*), all made fast with beeswax. The detail of the smaller valves can be seen to better advantage in the greatly enlarged detailed drawing in the upper right-hand corner. The platinum plug *g* rested in the opening *hh*. Beeswax (*ww*), easily melted into place with a hot glass rod, cemented them together, making a tight joint impervious to water. All the valves were manipulated by means of attached platinum wires. The small platinum baffles (*x,x*) served to deflect the outflowing liquid from the bottom of the calorimeter. In addition to the valves already described, 2 more (*kk*) were placed in the upper part of the inner container and were of the same size and general description as the large valve in the container floor. A 2-stage platinum stirrer *Q*, alternating 45 times per minute, agitated the contents of the inner can, working in opposition to that in the outer vessel and producing a pumping effect in the liquid when the valves were open. The suspension was through a rod of hard rubber of minimum diameter. Two carefully calibrated thermometers (T_1T_2) were at first used, one in the water in the annular space between the two cans, and one in the solution in the inner receptacle.

The external bath was brought to within 0.1° of the proposed initial temperature, the valves of the inner container were then made fast, the appropriate amount of water (about 0.55 liter) was placed in the outer vessel, and the solution to be diluted was placed in the closed inner vessel after making sure that the valves were all tight. The liquids in both the inner vessel and the outer vessel were weighed and the apparatus containing the liquids assembled. The stirrers were put in place, the lugs arranged, the gasket added, the case cover put on, the set screws (*K*) tightened and the level of the outer bath restored to the position shown in the drawing. The rest of the apparatus was then rapidly assembled. The alternating stirrers were actuated by metal rods working in guides which insured that uniformity of position of the moving parts, essential to their perfect functioning.

In a few minutes after the stirrers were set in motion, the calorimetric system was thermally homogeneous—the temperature of the outside bath being carefully regulated to accord with that of the calorimeter. Under these conditions the calorimetric temperature would remain constant for an indefinite period. After a 10- to 15-minute interval of constant readings, the inner thermometer, T_2, was carefully read. On an up-stroke of the inner stirrer, the small platinum valves were withdrawn and a portion of the acid was automatically sucked up into the inner chamber.[1] The pumping effect of the 2 stirrers now effected a gradual mixing of the 2 solutions, which caused a steady rise of temperature in both the inner and outer chambers. So perfect was the interchange and so efficient the mixing that at no time during an experiment was there an important difference in temperature (0.020–0.030°) between the inner and outer liquids,[2] even when a reaction involving a 4° total rise was concerned. This observation was further confirmed by raising and lowering the thermometers, these differences producing no essential change in their readings.[3] When the mixing had approached completion and the speed of change had greatly diminished, the large rubber valve in the floor and, one minute later, those in the walls were opened. Complete equalization was speedily realized, as was indicated by constant readings of the thermometers. During the change of temperature in the calorimeter, the temperature of the jacket was correspondingly altered, the difference between the two at no time exceeding a few hundredths of a degree. After a 10- or 15-minute interval of constant readings, the inner thermometer was again carefully read, the rise from the initial constant point constituting the value Δt_1 or Δt_2 of the subsequent computations. It remained only to break down, wash, dry and reassemble the apparatus for a new experiment.

b. The second dilution receptacle has been already described and pictured in a previous article.[4] This contained about 0.25 liter, was wide open at the top, and had a single small opening in the bottom. It was suspended on 3 stout, platinum wires, connected with thin hard-rubber tubes and rods above. The single lower small opening was stopped by means of a small rubber stopper; from which a wire for withdrawal projected through the cover of the calorimeter, just as with the central orifice in receptacle *a*. The weighed quantity of concentrated liquid in the inner receptacle was stirred by a 2-stage platinum reciprocating stirrer, which moved always in the direction opposite to that of the annular reciprocating stirrer in the outer concentric vessel. The calculated amount of water was placed in the platinum calorimeter, that of the solution in the

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[1] The apparatus was so designed that with the originally computed amounts of liquid, the outer level was slightly the higher.

[2] When this fact had been thoroughly established by experiment, the use of the second (outer) thermometer (T_1) was discontinued.

[3] The difference in hydrostatic pressure thus produced were not enough to effect the thermometer readings by 0.001°.

[4] Richards, Rowe and Burgess, *loc. cit.*, p. 1179.

receptacle *b*, and the apparatus was assembled in the "submarine" vessel exactly as in the case of *a*. The conduct of the determination did not differ essentially from that described under the preceding head, except that, before the conclusion, the top of the receptacle *b* was lowered beneath the liquid level to insure complete mixing.

c. The third receptacle, *c*, was a gold vessel similar in all details except size and material to the preceding, and contained about 100 cc.

d. The fourth receptacle, *d*, was a small platinum container holding about 25 cc., similar to *b* and *c*.

The heat capacities of these several outfits, with the appropriate stirrers, thermometers, etc., in the combinations employed, were as follows.

A a, 19.0; *A b*, 15.4; *A c*, 16.1; *A d*, 12.4.
B b, 11.0; *B c*, 11.7; *B d*, 7.9. (cal./°C.).

When the large calorimeter, *A*, was used, either with *a*, *b*, or *c* as accessory, the amounts of solution and water taken were such that the total heat capacity was usually in the neighborhood of 1100 cal./°C.; whenever the small calorimeter, *B*, was used, the corresponding figure was about 550 cal./°C. With the former outfit, the solid parts of the calorimeter averaged about 1.5% of the total heat capacity; with the latter outfit, about 2.0%. That is to say, the factor *f* (referred to later) is 1.015 in one case and 1.02 in the other. These approximate values are usually exact enough to correct the actual values of $(\Delta t_2 - \Delta t_1)$ to the ideal values which would have been observed if the calorimeter had possessed zero heat capacity, as will be seen more clearly soon.

The mercury-in-glass thermometer used for measuring the temperature changes had been especially constructed for the purpose by an expert. The bulb had a capacity of nearly 4 milliliters, and the scale (which showed a range of temperature from 15.5° to 20.8°) was 40 cm. in length. Each degree was divided into hundredths by fine, clear lines, making the reading of 0.0005° a matter of ease and certainty. The thermometer was originally filled under an atmosphere of hydrogen to obviate the possible formation of a film of oxide. This precaution insured a freely moving thread, which was gently tapped before a reading. The scale was carefully calibrated in the usual manner by comparison with 2 normal thermometers (Baudin, Nos. 15200 and 15276). For work of this nature, where small temperature intervals are to be measured at different parts of the scale, it is evident that a large number of adjacent points must be determined if reasonable accuracy is to be secured, especially in those parts of the column which show irregularity. Clearly the usual method of calibrating thermometers by comparison with a standard at a few points only in the scale may tend to give misleading data for some of the intervening points. Of course, when (as in this case) the temperature intervals are small, a small error in reading is a large per cent. of the whole. Although we did our best with the means at our disposal to effect an adequate standardization at frequent intervals over the whole scale, we believe this to have been the least satisfactory part of the work. The electrical methods, when properly outfitted and handled with elaborate precaution, are better in such cases; but at the date of making these determinations (1912) we had no electrical apparatus which would yield a degree of precision equal to that of the mercury-in-glass instrument. The description of the general method will, however, serve our main purpose, even if the final figures may ultimately need slight revision.

The Data of a Typical Determination in Full.

A specimen series of experiments may be given together with the calculations in order to show the magnitude of the quantities concerned, the method of experiment, and the details of the calculation. The case of hydrochloric acid is chosen. The original solution contained 9.174% of pure hydrogen chloride (the mean of 2 gravimetric analyses giving 9.173 and 9.175, respectively) and, therefore, has the concentration HCl, 20.03 H_2O. This was diluted in 2 series (of 3 experiments each) to the concentration $HCl.100H_2O$, at 2 different temperatures.

TABLE I.

Heat of Dilution of $HCl.20H_2O$ to $HCl.100H_2O$.

(Heat Capacity of Solid Parts of Calorimeter = 15.4 Cal./*t*.)

			At the lower temperature.		At the higher temperature.	
Expt.	HCl sol. G.	H_2O. G.	t_1.	Δt_1.	t_2.	Δt_2.
1	225.0	817.3	15.80°	+0.249°	20.41	+0.266°
2	225.0	817.3	15.84°	0.249°	20.49	0.267°
3	225.0	817.3	15.86°	0.249°	20.47	0.267°
		Average	15.83°	0.2490°	20.46	0.2667

In order to calculate from these figures the specific heat of the dilute solution, that of the original more concentrated acid $HCl.20H_2O$ must be known. This was found by the method described in a preceding paper[1]—a definite weight of the acid being raised in temperature by the heat given out by neutralization of a known weight of pure dil. sulfuric acid in an enclosed, sunken receptacle, and the result being compared with a similar procedure with a definite weight of pure water calculated to the same temperature. The calorimetric outfit had a total heat capacity of 139.09 cal./°C. in addition to that of the liquid to be determined.

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[1] T. W. Richards and A. W. Rowe, *Proc. Am. Acad.*, 49, 173 (1913); *Z. physik. Chem.* 84, 585 (1913). See especially pp. 190 and 601 respectively.

TABLE II.

Specific Heat of $HCl.20H_2O$.

(*a*) Averages of Experiments with Pure Water.[a]

Average.	Water G.	H_2SO_4 G.	t_2	t_2-t_1.
1	450.18	114.85	20.72	4.225
2	450.17	114.86	19.77	4.234
Interp	450.18	114.85	20.33	4.228

(*b*) Individual Experiments with the Acid Solution.

Expt.	$HCl.20H_2O$. G.	H_2SO_4. G.	t_2.	t_2-t_1.	Sp. Ht. $HCl.20.03H_2O$.
1	503.24	114.86	20.36°	4.400°	0.8489
2	503.26	114.87	20.13°	4.402°	0.8491
3	503.25	114.85	20.05°	4.402°	0.8492
4	503.24	114.86	20.62°	4.398°	0.8485
5	503.26	114.86	20.27°	4.401°	0.8488
6	503.25	114.87	20.54°	4.397°	0.8490
Average	503.25	114.86	20.33	4.400	0.8489[b]

[a] T. W. Richards and A. W. Rowe, *Proc. Am. Acad.*, 49, 191 (1913).

[b] An earlier determination of this quantity by a somewhat less satisfactory method (*ibid.*, 43, 475 (1908)), gave the nearly identical value, 0.8488.

These 6 individual experiments evidently agree closely. The method of calculating the values given in the last column is exemplified as follows. From the interpolated value for water at $t_2 = 20.33°$ and the average data of Series (*b*), the following equation gives the specific heat x of the more concentrated solution:

$$(503.25\,x + 139.09)\,4.400 = (450.18 + 139.09)\,4.228 \times 1.0001$$

in which the last factor takes account of the fact that slightly less sulfuric acid was neutralized in Series (*a*) than in Series (*b*). Hence, $x = 0.8489$, the specific heat of $HCl.20.03\,H_2O$. Corrected to exactly $HCl.20.00\,H_2O$ this value becomes 0.8487.

The Calculation of the Result for the Dilute Solution.

The data are now all at hand for the calculation of the specific heat of the more dilute acid, and we may turn again to the data of Table I. To assist in the correct substitution of the several quantities in the Kirchhoff equation, it is well to define each quantity and use a definite notation throughout, as follows.

U and U' = heats of dilution of amounts employed, at lower and higher temperatures, respectively.

U_M and U'_M = heats of dilution with molal amounts, at lower and higher temperatures, respectively.

M = molal weight of total solution (*e. g.*, $HCl.100\,H_2O$ = 1838.07).

t_1 = $\theta - 273.1$ = centigrade temperature after dilution at lower temperature.

t_2 = $\theta + \Delta\theta - 273.1$ = centrigrade temperature after dilution at higher temperature.[1]

$\Delta\theta$ = $t_2 - t_1$ = range of temperature covered by Kirchhoff equation.

Δt_1 = rise of temperature on dilution at lower temperature.

Δt_2 = rise of temperature on dilution at upper temperature.

f = factor necessary to correct K_1 and K_2 for heat capacity of calorimeter vessels.

f' = $1.0005 - 0.00025\ (t - 16)$ = another factor taking account of changing specific heat of water.

n = number of mols of *reacting substance* in experiment.

K_1 and K_2 = initial capacities of whole system over the ranges $\Delta t°_1$ and $\Delta t°_2$, respectively.

K = average initial heat capacity of reacting material (excluding calorimeter) between $t_1°$ and $t_2°$.

K' = average final heat capacity of reacted material (excluding calorimeter) between $t_1°$ and $t_2°$.

K_M and K'_M = K/n and K'/n = corresponding heat capacities of molal quantities.

S_c = specific heat of initial concentrated solution.

S_d = specific heat of final dilute solution.

(Both referred to water as unity over the same range of temperature.)

(The atomic weights are those of the current International Table. H_2O = 18.016; HCl = 36.47.)

The quantity of heat (U) actually evolved in the calorimeter on dilution at t_1 is $K_1\Delta t_1$, and that (U') at t_2 is $K_2\Delta t_2$. Hence the Kirchhoff calculation takes the following exact form:

$$K - K' = \frac{K_2\Delta t_2 - K_1\Delta t_1}{\Delta\theta} \qquad (2)$$

now

$$S_d = \frac{K'}{Mn} = \frac{K - (K_2\Delta t_2 - K_1\Delta t_1)/\Delta\theta}{Mn} \qquad (3)$$

or

$$S_d = \frac{K}{Mn} - \frac{K_2\Delta t_2 - K_1\Delta t_1}{Mn\Delta\theta} \qquad (4)$$

Another less exact but often adequate and more convenient mode of computing the results may also be given. As an approximation, Equation 2 may be simplified by taking account of the fact that K_1 and K_2 differ

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[1] Since the heat capacities of the *factors* of the reaction were used in making the calculation, the *final* temperature of each dilution is that which must be called the temperature of the experiment (Richards, THIS JOURNAL, 25, 209 (1903)).

(when $\Delta\theta = 4°$) by only about 0.1%[1] and that each is essentially equal to Kf. When the deviation of 0.1% is too small to be of any account, the Kirchhoff Equation (2) may be taken as

$$K - K' = \frac{Kf(\Delta t_2 - \Delta t_1)}{\Delta\theta} \qquad (5)$$

which affords the most convenient means of calculating the heat capacity change from the small rises of temperature observed on dilution at 2 temperatures. The equation is not sufficiently accurate in this form if Δt_1, Δt_2 or $\Delta\theta$ are large.

The factor f was computed by, comparison of heat capacities, but it may be just as well considered in relation to the temperature changes. Evidently, by multiplying the two Δt values by this factor we shall obtain the amounts which the temperature would have risen if the calorimeter had been an ideal one, without heat capacity. The result ($f\Delta t$) will be entirely independent of the size or nature of the apparatus, and will hold for any amounts of the two liquids, provided only that they are in the definite proportion corresponding to the given degree of dilution.

Hence the approximate calculation with Equation 5 may be carried out at once on a gram molecular basis. Substituting the appropriate quantities of the present case in Equation 5, we find

$$K_M - K'_M = \frac{1778.2 \times 1.015\ (0.2667° - 0.249°)}{4.63°} = 6.9 \text{ cal./°C.}$$

The molal heat capacity of K_M of the factors ($HCl.20\,H_2O + 80\,H_2O$) was $396.8 \times 0.849 + 1441.3 = 1778.2$. Hence that of the product $K'_M = 1778.2 - 6.9 = 1771.1$. This number is the molal heat capacity of $HCl.100\,H_2O$. The weight being 1838.1, the specific heat of $HCl.100\,H_2O$ referred to water over the same range of temperature must be $1771.1/1838.1 = 0.9636 = S_d$. The error in this result (caused by the fact that the changing specific heat of water is not considered in it), is less than one in the last place of decimals. This error may be corrected by subtracting from the quantity $K_M - K'_M$, a small correction numerically equal to 1/4000 of $K_M\Delta t$, which takes account of the change in the specific heat of water between t_1 and t_2.

The result 0.9636 just given agrees well with an earlier direct determination (0.9634) of the specific heat of this solution. The closeness of agreement is indeed partly accidental since the possible experimental error might have led to a somewhat wider divergence.

Similarly, an approximate but usually adequate method may be used for calculating U_M and U'_M (which are, respectively, equal to $K_1\Delta t_1/n$ and $K_2\Delta t_2/n$). The details of K_1, K_2 and n are bulky, and accordingly in

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[1] The heat capacity of water at 16° may be taken as 0.05% greater and that at 20° as 0.05° less, than the average value over the range 16–20°.

the table for the sake of economizing space K_M alone is recorded. The quantity K_M may be reduced to its value at any temperature (t) between 16° and 20° through multiplication by a factor (almost unity) $f' = 1.0005 - 0.00025\ (t - 16)$.[1] This factor in most cases produces so little effect that it is applied below only for the sake of completeness.

Data for Various Dilutions of Hydrochloric Acid.

The details concerning the manipulation and essential data of a single case having been given, the outcome of a number of experiments involving the dilution of hydrochloric acid may be very briefly detailed.

Two fairly concentrated solutions were used in the dilution experiment with hydrochloric acid.[2] The first ($HCl.10\,H_2O$) was taken as 0.752, a result which depends chiefly upon Thomsen's[3] observed value 0.749 and Marignac's 0.760[4] giving the former about twice the weight of the latter. Sundry theoretical considerations which need not be detailed here support this value. The second hydrochloric acid solution ($HCl.20H_2O$) was found to have a specific heat 0.849 in the experiments detailed in Table II. These values for the specific heats were used in calculating the heat capacities of the factors in the reaction; they need not be known very accurately, since the concentrated solutions, as a rule, formed but a small part of the total heat capacity.

The values Δt_1 and Δt_2 (the actual observed rises of temperature of the calorimeter) were each the result of an average of at least 2 determinations, and sometimes of 3 or 4, when there seemed to be any doubt about the value. The experiments already given are typical. Apart from the possible errors in the standardization of the thermometer, these figures can hardly be in error more than 0.0005°.

TABLE III.

Observations Giving Rise of Temperature on Dilution at Two Different Temperatures.

Factors in Reaction.	Calorimeter.	t_2. °C.	$\Delta\theta = t_2 - t_1$. °C.	Δt_1. °C.	Δt_2. °C.	$\Delta t_2 - \Delta t_1$. °C.
$HCl.10H_2O + 15H_2O$........	B *b*	19.65	1.84	1.5835	1.6075	0.0240
$HCl.10H_2O + 40H_2O$..........	A *b*	19.75	2.75	1.0245	1.0550	0.0305
$HCl.10H_2O + 90H_2O$..........	A *c*	19.85	3.36	0.5720	0.5975	0.0255
$HCl.20H_2O + 80H_2O$..........	A *b*	19.92	4.11	0.2490	0.2655	0.0165
$HCl.20H_2O + 80H_2O$..........	A *b*	20.69	4.63	0.2490	0.2667	0.0177
$HCl.10H_2O + 190H_2O$.........	A *c*	19.83	3.74	0.3053	0.3190	0.0137
$HCl.20H_2O + 180H_2O$.........	A *b*	20.31	4.51	0.1417	0.1520	0.0103
$HCl.10H_2O + 390H_2O$.........	A *c*	19.88	3.58	0.1595	0.1670	0.0075
$HCl.10H_2O + 790H_2O$.........	A *d*	18.19	..	0.084	..	..

The results given in this table may be used for calculating 2 different but allied quantities, namely the heat of dilution on the one hand and the

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[1] Of course this is merely approximate, the true relation being curved, not linear.

[2] *Loc. cit.*, p. 198.

[3] J. Thomsen, "Thermochemische Untersuchungen," 1, p. 38.

[4] Oeuvres Compl. 2, 238.

specific heat of the dilute solution on the other hand. Considering the exposition already given it will be sufficient to give tables detailing these results without further explanation. Immediately following is the table giving the molal heat of dilution. Attention is called to the fact that the values of U_M and U'_M may be calculated not only from the fashion indicated below, but also from the data given according to the equation $U_M = K_M ff' \Delta t_1$, with the sufficient accuracy for the present purpose. On this account the detailed data for K_1, K_2, and *n* need not be given herewith, although they were used in the actual calculation of the *U* values.

Table IV.

Molal Heat of Dilution of Hydrochloric Acid.

Factors in Reaction.	$\Delta\theta$.	K_M. (at 18°.)	$U_M = K_1\Delta t_1/n_1$.	$U_M = K_2\Delta t_2/n_1$.	$\Delta U/\Delta\theta = (K_M - K'_M.)$	$U_{20°}$.
$HCl.10H_2O + 15H_2O$...	1.84	433.1	701	712	5.9	714
$HCl.10H_2O + 40H_2O$...	2.75	883.5	918.5	946	10.0	949
$HCl.10H_2O + 90H_2O$...	3.36	1784.3	1036	1081	13.3	1082
$HCl.20H_2O + 80H_2O$...	4.11	1778.2	449.8	479.0	7.1	480
$HCl.20H_2O + 80H_2O$...	4.63	1778.2	449.8	481.4	6.8	477
$HCl.10H_2O + 190H_2O$..	3.74	3585.9	1110	1159	13.1	1161
$HCl.20H_2O + 180H_2O$..	4.51	3579.4	515	552	8.2	549
$HCl.10H_2O + 390H_2O$..	3.58	7189.1	1163	1217	15.1	1219
$HCl.10H_2O + 790H_2O$..	..	..	1220	..	15.3[a]	1247[a]

[a] These values are extrapolated.

Yet another table records the steps in the calculation of the specific heat of the dilute solutions as follows.

Table V.

Specific Heat of Dilute Hydrochloric Acid of Several Concentrations.

Factors in Reaction.	K_M = Heat Cap. of Factors.	$K_M - K'_M$.	K'_M = Heat Cap. of Product.	Molal Wt. Product. M.	Product.	Sp. Heat Product. $S_d = K'_M/M$.
$HCl.10H_2O + 15H_2O$	433.1	5.9	427.3	486.87	$HCl.25H_2O$	0.8776
$HCl.10H_2O + 40H_2O$	883.5	10.0	873.5	937.27	$HCl.50H_2O$	0.9320
$HCl.10H_2O + 90H_2O$	1784.3	13.3	1770.9	1838.07	$HCl.100H_2O$	0.9634
$HCl.20H_2O + 80H_2O$	1778.2	7.1	1770.6	1838.07	$HCl.100H_2O$	0.9633
$HCl.20H_2O + 80H_2O$	1778.2	6.8	1771.2	1838.07	$HCl.100H_2O$	0.9636
$HCl.10H_2O + 190H_2O$	3585.9	13.1	3571.4	3639.67	$HCl.200H_2O$	0.9812
$HCl.20H_2O + 180H_2O$	3579.4	8.2	3571.4	3639.67	$HCl.200H_2O$	0.9812
$HCl.10H_2O + 390H_2O$	7189.1	15.1	7174.1	7242.87	$HCl.400H_2O$	0.9905

These values are in remarkably close agreement with those found from Marignac's[1] formula for the molecular heat (K'_M) of hydrochloric acid solutions, his calculated values for the 50, 100 and 200 H_2O solutions being, respectively, 874, 1773 and 3572, whereas the values which we find

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[1] C. Marignac, "Oeuvres Completes," 2, 479, reprinted from *Bibl. Univ. Archives,* 39, 238 (1870).

are 873.0, 1771.2, and 3571.4 (See Col. 4, Table V). Thomsen's[1] figures are in good agreement for the more concentrated solutions, but his value 3557 for HCl.200 H_2O seems to be seriously in error.

An interesting check upon the accuracy of the values $K_M - K'_M$ is afforded by the several results for HCl.100 H_2O and HCl.200 H_2O obtained in different ways. For the more concentrated of these 2 solutions 3 values of the specific heat are obtained, 0.9634, 0.9633, 0.9636. A direct determination of the specific heat of this same solution gave 0.9634.[2] The more dilute solution, namely, HCl.200 H_2O, gave 0.9812, whereas a direct determination of this solution gave 0.9814.[3]

This agreement is as satisfactory as could be expected and leads one to infer that the last figure given in the last column of Table V is not likely to be much in error. Taking account of the possible causes of uncertainty, one may guess that the specific heats are probably determined within 0.05%.

Although the specific heats depending upon $K_M - K'_M$ derived from $\Delta t_2 - \Delta t_1$ are thus apparently trustworthy within one cal./° C. or thereabouts, the values of the heats of dilution are apparently not so accurate. A comparison of two cases in the last column of Table IV points to a larger error. Subtracting the mean (480) of the fourth and fifth figures in that column from the third figure (1081) we get the value 601 for the heat of dilution of HCl.10 H_2O to HCl.20 H_2O. On the other hand, subtracting the seventh figure (552) in that column from the sixth (1159) we get the value 607 for the same dilution. This is a discrepancy of nearly a per cent. One possible explanation for the consistency of the differential values and the less satisfactory consistency of the single values is to be found in the fact that the experiments with the 10H_2O and 20H_2O solutions were done at different times and under somewhat different conditions whereas the Δt_2 and Δt_1 values in any one case were determined immediately after one another in any one instance, and all the conditions were as nearly as possible identical. The chief cause of the large error of the single values is, however, the widely different effect of error in thermometric reading or calibration on the 2 results. An error of 0.001° in Δt_1 with HCl.200 H_2O would cause an error of nearly 4 calories in U, whereas it would cause an error of only one cal./° C. in the case of $K_M - K'_M$ and but 0.0003 difference in the specific heat of the dilute solution HCl.200 H_2O. Evidently the agreement of the results is, therefore, as good as could be expected.

As regards the relationship of the figures one to another, attention may

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[1] J. Thomsen, "Thermochemische Untersuchungen," 1, 39 (1882), reprinted from *Aus. Pogg. Ann.*, 142, 337–379 (1871).

[2] Richards and Rowe, *Proc. Am. Acad.*, 49, 173 (1913).

[3] *Loc. cit.*

be called to the fact that in every case the heat of dilution increases with rise of temperature. This signifies that in every case the total heat capacity of the reacting substances decreases during the act of dilution, a fact which was pointed out by Thomsen[1] and Marignac[2] long ago, but is worthy of reiteration. Modern theory, of course, refers this decrease of heat capacity to increase of ionization. The phenomenon is exactly opposite to that which occurs during neutralization, when the total sum of the heat capacities of acid and alkali (each containing 100 H_2O per mol) *increases* by about 49 cal./*t*. when the 2 ions H′ and OH′ disappear. The actual loss of heat capacity when $HCl.10\,H_2O$ (perhaps 40% ionized) is diluted to $HCl.100\,H_2O$ (perhaps 77% ionized) is of the same order as would be predicted from the gain of heat capacity on neutralization, although not exactly concordant.

Another interesting circumstance is the fact that the change of heat capacity on dilution of such a case as $HCl.10\,H_2O$ bears an almost linear relation to the mol-fraction of hydrochloric acid in the diluted solution, when the solution is dilute. The most convenient means of exhibiting this relationship is to plot $K_M - K'_M$ (taken from Table V) in relation to the fraction of a mol. of hydrochloric acid corresponding to a mol. of water. This is shown in the accompanying diagram, Fig. 2. With more concentrated solutions the relation is by no means linear, because of decreasing dissociation;[3] but the relation indicated by the almost straight line for concentrations between $HCl.25\,H_2O$ and very dilute solutions falls within the limit of experimental error of every one of the values for $K_M - K'_M$. This diagram has the further convenience of making possible the computation of the specific heats of any solution of hydrochloric

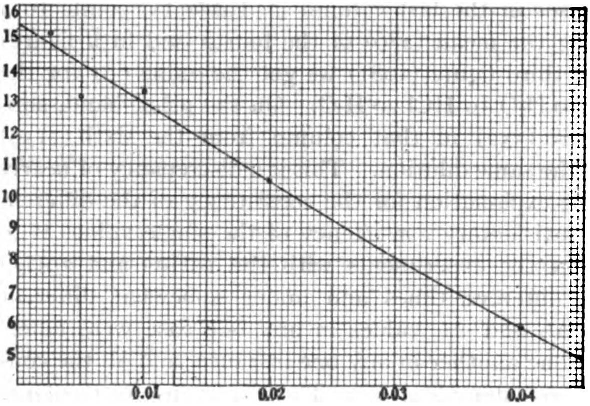

Fig. 2.—Change of heat capacity on dilution of HCl. $10H_2O$. Fractions of mol HCl per 1 mol H_2O plotted as abscissas (the amount of water being that in the final dilute solution). $K_M - K'_M$ plotted as ordinates.

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[1] J. Thomsen, "Thermochemische Untersuchungen," 1, 39 (1882); reprinted from *Aus. Pogg. Ann.*, 142, 337–379 (1871).

[2] C. Marignac, "Oeuvres Completes," 2, p. 479, reprinted from *Bibl. Univ. Archives*, 39, 238 (1870).

[3] Tucker (*loc. cit.*) has found a simple expression for calculating the specific heats of solutions more concentrated than $HCl.15H_2O$.

acid between $HCl.25H_2O$ and infinite dilution. All that one has to do is to read off on the curve the value of $K' - K$, which corresponds to the particular solution. This value is subtracted from the heat capacity 162.9 (the heat capacity of $HCl.10\,H_2O$) and the result added to that of the additional water. The result is then the heat capacity of the dilute solution, and when divided by the total molal weight of this solution gives its specific heat. For example, required the specific heat of the solution $HCl.40\,H_2O$. $K_M - K'_M$ is found from the curve to be 9.2. Hence, $(162.9 + 540.0 - 9.2)/757.0 = 0.9164 =$ the calculated specific heat of $HCl.40\,H_2O$.

Further theoretical considerations bearing upon these figures will be reserved for a later communication.

Many other similar dilution experiments have been carried out by this method upon the following substances: nitric acid, lithium, sodium and potassium hydroxides; lithium, sodium, potassium and cesium chlorides; lithium, sodium, potassium and cesium nitrates.

These results enable one to calculate the specific heats of a great variety of solutions as well as to calculate the change of the heat of neutralization with the change of temperature. Heats of neutralization themselves have likewise been determined in an extended investigation, using the calorimeter combination *A a* described above, which proved itself especially suitable for this work. These results will be collated and published as soon as time can be found for the considerable task.

We take pleasure in acknowledging our indebtedness to the Carnegie Institution of Washington for important financial assistance in this extended and expensive investigation.

Summary.

In this paper the indirect method of determining specific heats of dilute solutions by measuring their heat of dilution at 2 different temperatures has been carried into effect. By its means the specific heats of a great number of acids, alkalies and salts have been determined with a degree of accuracy as regards the more dilute solutions of perhaps 0.05%. The results for hydrochloric acid, which alone are given in this preliminary paper, are as follows: $HCl.10H_2O$, 0.752; $HCl.20H_2O$, 0.849 (these two the basis of computation); $HCl.25H_2O$, 0.8776; $HCl.50H_2O$, 0.9320; $HCl.100H_2O$, 0.9634; $HCl.200H_2O$, 0.9812; $HCl.400H_2O$, 0.9905. The paper is nevertheless rather an indication of an advantageous method than a final contribution. With the experience gained, yet more accurate results may be obtained in the future.

CAMBRIDGE, MASS.

[Contribution from the Chemical Warfare Service.]

THE PREPARATION OF IODIC ACID AND ITS ANHYDRIDE.[1]

By Arthur B. Lamb, William C. Bray and Walter J. Geldard.

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In the work at the American University Experiment Station on the absorption of carbon monoxide,[2] pure, almost anhydrous iodine pentoxide was needed both in the analysis for carbon monoxide and in the preparation of one of its absorbents.[3] Since an adequate supply of iodine pentoxide could not be secured, it was necessary to make in the laboratory most of our supply of this material. Moreover, since at one time the absorbent containing it appeared to be the best available one for carbon monoxide, it was necessary to have in readiness a satisfactory method for the preparation of iodine pentoxide on a large scale.

Considerable quantities of iodic acid were prepared by the usual method of oxidation of iodine with nitric acid. We soon discovered, both from our own experiments and from those carried on for us elsewhere, that while this material is perhaps suitable for the occasional preparation of small quantities in the laboratory, it is too difficult, wasteful and expensive for any larger operations. Two new methods based on well-known reactions were, therefore, worked out. Both of them start with iodine, the cheapest available source of the element, and barium chlorate, which is available in large quantities and is relatively inexpensive. In the first method the iodine is directly oxidized by an acidified solution of barium chlorate, and the resulting insoluble barium iodate is transformed into iodic acid by means of sulfuric acid. In the second method the reverse procedure is followed; a solution of pure chloric acid is prepared from barium chlorate and sulfuric acid, and the iodine is oxidized to iodic acid by means of it. The latter method proved to be particularly satisfactory, both on account of its simplicity, ease and adaptability to large scale operations, and also on account of the purity of its product. We shall first give a brief description of the barium chlorate method, and then a fuller description of the chloric acid method.

Barium Chlorate Method.—The two stages of preparation of iodic acid by the barium iodate process correspond to the following equations:

$$\left.\begin{aligned} I_2 + Ba(ClO_3)_2 &= Ba(IO_3)_2(\text{solid}) + Cl_2 \\ Ba(IO_3)_2(\text{solid}) + H_2SO_4 &= BaSO_4(\text{solid}) + 2HIO_3 \end{aligned}\right\} \quad (1)$$

This method is evidently a simplification of the method of Millon[4] who first oxidized iodine with an acidified solution of potassium chlorate, pre-

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[1] Published by permission of the Director of Chemical Warfare Service and of the Director of the Bureau of Mines.

[2] Lamb, Bray and Frazer, *J. Ind. Eng. Chem.*, 12, 213 (1920).

[3] Lamb, Bray and Frazer, *loc. cit.*, p. 216.

[4] *Ann. chim. phys.*, [3] 9, 400 (1840).

cipitated barium iodate with barium chloride, and following Gay Lussac, set free iodic acid by means of sulfuric acid.

While the first step in this process does take place substantially in accordance with the above equation, it appears certain that, as in the similar case of potassium chlorate, this equation does not represent the real mechanism of the reaction.[1] A neutral solution of barium chlorate does not react with iodine even when the mixture is heated, but the reaction can be made to take place quite rapidly at 85° if a small amount of nitric acid or hydrochloric acid is added. Moreover, after the reaction between equivalent amounts of iodine and barium chlorate (with nitric acid as inductor) the filtrate is found to contain a considerable quantity of hydrochloric acid. It is evident that in addition to Reaction 1 the following reaction takes place to some extent

$$3I_2 + 3Ba(ClO_3)_2 + 3H_2O = 3Ba(IO_3)_2 + HClO_3 + 5HCl. \quad (2a)$$

In experiments in which slightly less than an equivalent amount of barium chlorate was used, the filtrate contained iodic acid in addition to hydrochloric, the corresponding reaction then being

$$6I_2 + 5Ba(ClO_3)_2 + 6H_2O = 5Ba(IO_3)_2 + 2HIO_3 + 10HCl. \quad (2b)$$

These observations made only incidentally lead us to conclude that the real chemical reaction involved is the same as in the chloric acid process (see below); that is, namely, an *oxidation* of iodine by chloric acid or the chlorate ion in acid solution and not simply a replacement of the chlorine by the iodine. This is in agreement with the conclusions of Michael and Conn[2] who showed that the observations of Kaemmerer[3] on which the idea of a direct replacement of one halogen by another had been based were wholly erroneous, and that all the other evidence indicated that the process was merely one of oxidation.

In each of our experiments a 250 g. portion of finely divided iodine was taken and this was usually treated with a nearly equivalent amount (320 g.) of the chlorate $Ba(ClO_3)_2H_2O$, in one liter. When a little acid was added to start the reaction, and the temperature was maintained at about 85° and the mixture shaken at intervals, the reaction proceeded steadily and all the iodine disappeared in about 90 minutes. In the second and later experiments of a series the barium chlorate was dissolved in the filtrate from the barium iodate precipitate; this procedure was adopted in order to prevent any loss of iodine by Reaction 2*b*, and because presence of acid in the filtrate rendered unnecessary the further addition of acid to start the reaction. In the last series of experiments the time of reaction was materially lessened by the use of a 50% excess of chlorate, 480 g. in

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[1] See Bassett, *J. Chem. Soc.*, 57, 761 (1890); also Schloetter, *Z. anorg. Chem.*, 45, 270 (1905).

[2] *Am. Chem. J.*, 25, 89 (1901).

[3] *J. prakt. Chem.*, 4, 169 (1870).

one liter, in the first experiment. As this excess remained in the filtrate, the usual amount, 320 g., was dissolved in the filtrate in the second and subsequent experiments of the series. An important advantage of the use of excess chlorate is that no iodine distilled into the neck of the flask during the run, as had been the case in the earlier experiments. A practically quantitative yield of barium iodate was secured in this way.

The second step in the process is not so satisfactory. The reaction between solid barium iodate and dil. sulfuric acid is slow and could not be made to take place in a reasonable time even when the solid was digested with an excess of the dil. sulfuric acid. This difficulty is perhaps in part due to the solubility of barium sulfate in iodic acid solution.[1] If an excess, or indeed if only an equivalent amount of sulfuric acid is used it is very difficult to remove the sulfuric acid with which the filtrate will be contaminated,[2] and the presence of even a small amount of sulfuric acid in the iodic acid promotes decomposition during dehydration.

The best method which we have found for purifying the iodic acid from this impurity is recrystallization from diluted nitric acid. A convenient quantity of iodic acid, *e. g.*, 300 g., is dissolved in an equal weight of hot water; an equal volume of conc. nitric acid, sp. gr. 1.42, is added, and the mixture is evaporated in a large evaporating dish without boiling for about 30 minutes, until crystallization is fairly complete, and then allowed to cool. The supernatant liquid is drained off and either evaporated further or added to a second solution of the iodic acid in water. The crystals of iodic acid are washed 3 times with ice-cold nitric acid, sp. gr. 1.42, then dissolved in a small volume of hot water and the solution evaporated to dryness. This yields a product practically free from sulfate and containing but a trace of nitric acid which can be removed if necessary by repeated solution and evaporation.

As a result of the incompleteness of this second step in the process and the losses incident to recrystallization, no more than 85 or 90% of the theoretical yield of iodic acid is usually obtained from a definite weight of iodine.

The Chloric Acid Method.—While it is known that iodine can be transformed into iodic acid by means of chloric acid,[3] quantitative data seem to be lacking, and it was necessary for us to determine experimentally whether a simple, rapid and economical manufacturing process could be developed.

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[1] Guichard, *Compt. rend.*, 147, 1306 (1909).

[2] This agrees with the observation of Stas, who concludes that pure iodic acid cannot be secured in this way, and with the statements of Baxter (THIS JOURNAL, 32, 1591 (1910)), who found that 11 crystallizations were necessary for the complete elimination of sulfate.

[3] *E. g.*, Friend, "Text-book of Inorganic Chemistry," 8, 238 (1915).

We first assured ourselves that the preparation of pure chloric acid solution would present no difficulties. When to a hot barium chlorate solution (2 molal or less) an equivalent amount of hot sulfuric acid solution is added slowly, the barium sulfate settles quickly and is easily filtered, and a solution of chloric acid of any desired concentration up to 33% can be obtained. In practice a very slight excess of barium chlorate was used in order to ensure the absence of sulfate in the chloric acid solution, since as has already been mentioned, a sulfuric acid impurity in the resulting iodic acid is harmful. Small quantities of more concentrated solution were obtained by evaporation at low temperature (40°) and reduced pressure, and one sample of 40% chloric acid was prepared. The concentrations were determined by the Bunsen distillation method with conc. hydrochloric acid, the chlorine being passed into potassium iodide solution and the iodine formed titrated with thiosulfate.

Small scale experiments were performed with chloric acid solutions of various concentrations to determine the most satisfactory conditions for the oxidation of iodine. 10% chloric acid does not react at room temperature, and after the reaction is started by heating it proceeds rather slowly, even when the mixture is heated nearly to boiling; with equivalent amounts of iodine and chloric acid considerable iodine vaporizes from the heated mixture. When very concentrated chloric acid (33 to 40%) is used the reaction starts practically immediately at room temperature, and proceeds with almost explosive violence; it is necessary to cool the container with ice-cold water during the reaction. 24 to 26% acid finally was chosen as the most suitable (though a somewhat more dilute acid, 20%, was also satisfactory). The reaction usually did not begin at once, but when once started (after standing 10 or 15 minutes, or by gentle heating) the iodine disappeared in 15 or 20 minutes; the reaction was very rapid but cooling was unnecessary. Iodine fumes were not given off during the reaction, nor when the resulting solution was boiled.

This behavior indicates an autocatalytic reaction. The beginning of the reaction appears to depend on the formation of a little chlorine, one of the products of the reaction. Suddenly the evolution of chlorine becomes rapid, the solution turns yellow and any iodine vapor in the flask is replaced by the heavy yellow fumes of iodine trichloride and chlorine. These indications that the mechanism of the reaction is not a simple replacement of the chlorine in the chloric acid by iodine according to the equation

$$I_2 + 2HClO_3 = Cl_2 + 2HIO_3 \qquad (3)$$

were corroborated by analyses of the final solution after it had been heated to boiling: large amounts of hydrochloric acid and some chloric acid were found, which were smaller as the concentration of the chloric acid used was increased. Since when the mixture was boiled some hydrochloric acid must have reacted with chloric or iodic acid, it is certain that much larger amounts of hydrochloric acid would have been found if the solution had been analyzed after the iodine had disappeared but before the mixture had been boiled. Evidently much of the chloric acid is reduced to chloride during the reaction (*cf.* Reaction 2b).

$$3I_2 + 5HClO_3 + 3H_2O = 6HIO_3 + 5HCl. \qquad (4)$$

The presence of hydrochloric acid in the iodic acid solution seemed likely to prevent the development of a quantitative method, since it was known that iodic acid is reduced by hydrochloric when a solution containing the two substances is evaporated.[1]

$$2HIO_3 + 10HCl = I_2 + 5Cl_2 + 6H_2O. \qquad (5)$$

In fact the existing method for recovering iodic acid from such solutions involves the removal of the chloride by precipitation as silver chloride.[2] However, Reaction 5 is reversible and rapid; the reverse reaction is known to take place rapidly when sufficient water is present, and the direct reaction between iodic acid and hot conc. hydrochloric acid, although at first rapid, is by no means complete. This last point was demonstrated by experiments with the Bunsen distilling flask: about $^1/_3$ of the iodic acid remained unreduced after half of the conc. hydrochloric acid had been distilled out of the flask. We concluded that an equilibrium is established fairly rapidly between the substances listed in Equation 5 (and iodine trichloride), and that in the solution to be evaporated the iodic and hydrochloric acids are so dilute that the concentration of iodine is negligibly small. Furthermore, it seemed possible that the presence of chloric acid in the solution would maintain the iodine as iodic acid even while the solution was evaporated, and also remove the chloride as chlorine. This idea proved to be correct, and a *3% excess of chloric acid* (based on Reaction 3) was found to be sufficient to prevent any loss of iodine. In fact, during evaporation the net reaction is simply

$$5HCl + HClO_3 = 3Cl_2 + 3H_2O, \qquad (6)$$

though it is possible that this reaction is catalyzed by the iodic acid present. In contrast to Reaction 5 which is rapid and reversible, Reaction 6. is slow and under the present conditions irreversible.

The experimental evidence was obtained by carefully investigating Reactions 3 and 4. Preliminary experiments with equivalent amounts of iodine and chloric acid (based on Reaction 3) had indicated a loss of from 2 to 10% iodine in the preparation of the iodic acid solution, but in these experiments the yield of iodic acid was determined by the possibly inaccurate method of precipitating and weighing barium iodate. Accordingly methods were developed for analyzing the iodic acid solution for

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[1] Sodini, *Ber.*, 9, 1126 (1876).

[2] Friend, *loc. cit.*, 8, 237 (1915).

acid, iodate, chlorate and chloride; for determining the amount of iodine in the small precipitate of barium iodate formed (the chloric acid solution contained a trace of barium chlorate); and for determining iodine and chlorine in the gas evolved during the reaction. In the last case the gas was absorbed in excess alkaline sulfite solution, and the iodine and chlorine could be present only as iodide and chloride, respectively.

Analytical Methods.—The iodic acid solution and the alkaline sulfite solution were diluted to known volumes and portions of each taken for the various determinations. If any barium iodate precipitate formed during the run, or on cooling the resulting solution, it was collected on a filter before the solution was diluted.

Acid was determined with 0.1 *N* potassium hydroxide solution and phenolphthalein.

Iodate was determined iodimetrically. That the presence of chloric acid did not interfere when the concentrations of sulfuric acid and iodide were low was proved by test analyses with iodic acid alone and in the presence of an amount of chloric acid comparable to that in the solutions to be analyzed. The amount of barium iodate was determined by the same method; all of the precipitate was washed into an iodide solution acidified with hydrochloric acid, and an aliquot part of the resulting solution was titrated with thiosulfate.

Chlorate, in the absence of iodate, was determined by the Bunsen distillation method already referred to. The iodate in the portion of the solution to be analyzed for chlorate, was precipitated as barium iodate; the precipitation was found to be practically complete only when the solution was neutral and nearly ice-cold. Barium chloride was used as the precipitating agent, since nitrate would interfere with the chlorate analysis.

Chloride, in the absence of iodate, was determined by the Volhard method. The method of removing iodate was the same as that described in the preceding paragraph, except that barium nitrate was used instead of barium chloride. Chloride in the alkaline sulfite solution was also determined by the Volhard method after the removal of sulfite and iodide (see below) by means of potassium permanganate; any excess of permanganate added was removed by the addition of a small amount of a dilute solution of sulfurous acid.

Iodide in the sulfite solution was tested for by the permanganate-carbon tetrachloride method recommended by Bray and MacKay.[1] Test analyses showed that the method was applicable in the presence of sulfite.

Experiments with 24-Gram Portions of Iodine.—Several experiments were performed with 24 g. of iodine and 28.5 to 34% chloric acid in small excess, which was 5 to 10% excess referred to Reaction 3. After the iodine had disappeared the solution was heated to boiling for several

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[1] Bray and MacKay, This Journal, 32, 1193 (1910).

minutes and a slow current of air passed through it to carry the chlorine over into the alkaline sulfite solution contained in 2 wash bottles arranged in series. Complete absorption of the chlorine was demonstrated by the fact that a potassium iodide solution beyond the sulfite solution remained colorless. The results in the various experiments were concordant, and details will be given for only one run.

Reacting substances:	Iodine 24.24 g. 99%	= 0.1891 gram atoms	
	Chloric acid 61.7 cc. (28.5%)		
	By analysis	= 0.2080 mol chlorate	
		and 0.2011 equivalent acid	
		Gram atoms	
Total Iodine recovered:	As HIO_3 in solution	0.1830	
	In barium iodate	0.0064	
	In sulfite solution	0.0000	
		0.1894	
			= 100.2%
Total Chlorine recovered:	As $HClO_3$ in solution	0.0225	
	As HCl in solution	0.0437 (?)	
	In sulfite solution	0.1491	
		0.2153	
			= 102.2%
Total acid in Iodic acid solution:		0.2371 equivalent	

Increase in acid during the run = 0.2371 — 0.2011 = 0.0360 equivalent.

Since, by Equation 4, 5 mols HCl are formed when the increase in acid is 6 equivalents, the calculated amount of HCl is 0.0300 equivalent.

The striking result of this and other runs is that all the iodine used was converted into iodic acid in solution, and none was carried over with the chlorine into the alkaline sulfite solution.

In the above experiment there was evidently an error in the determination of the amount of hydrochloric acid in the iodic acid solution, since in another run the amount of hydrochloric acid calculated by means of Equation 4 agreed fairly well with that found by direct analysis.[1] This point was not more carefully investigated because the real purpose of the experiments had been attained, *viz.*, the demonstration of the quantitative yield of iodic acid in solution.

The next question investigated was the recovery of iodic acid by evaporation in the presence of the small excess of chloric acid. In each of the following experiments 0.2 of the iodic acid solution obtained in the above run was evaporated to dryness; in the first case the residue was heated for a short time at 100°, in the second case for one hour in a flask in a Crisco bath at 210°. In each case no iodine fumes were evolved, and the residue was pure white in color.

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[1] This was also shown by the fact that the sum of the separately determined acids exceeded the observed value by 0.0121 equivalent.

	HIO_3.	$HClO_3$.	HCl.	
Original solution (one-fifth) contained	0.0366	0.0045	0.0060 (?)	mols
Residue from the 1st evaporation expt. contained	0.0371	0.0008	0.0026	mols
Residue from the 2nd evaporation expt. contained	0.0368	0.00014	0.0000	mols

These results and others which are not quoted demonstrated conclusively that there is no loss of iodic acid on evaporation, that much of the hydrochloric and chloric acids are removed by evaporation and heating at 100°, and that all the former is destroyed by heating at 210°. Subsequent experiments showed that the removal of the chloric acid is complete during the dehydration process at 240°, which will be described below.

Experiments with 500-Gram Portions of Iodine.—Having thus demonstrated that the process was most satisfactory, we proceeded to manufacture iodic acid in the laboratory. 500 g. portions were found to be convenient and several runs were made simultaneously. In connection with the first runs the minimum excess of chloric acid necessary was found to be about 3% (based on Equation 3). It was not necessary, although more convenient, to add this excess at the beginning of the experiment, since the danger of loss of iodine was greater during the evaporation than during the oxidation of the iodine. When less than the 3% excess chloric acid was added the dark color of free iodine appeared during the evaporation or heating; but loss of iodine could then be prevented by adding at once a small amount of chloric acid. The concentration of chloric acid finally chosen was 24 to 26%.

39 runs of this sort were made, and the total yield of powdered iodic anhydride obtained, based on its weight and the weight of iodine used, was 99.6%.

The procedures used are outlined below.

Preparation of Chloric Acid.—The preparation was carried out in large earthenware crocks, and the quantities of materials used depended on the size of the crocks. The proportions were as follows. 625 g. of barium chlorate (90% $Ba(ClO_3)_2$) was dissolved in one liter of nearly boiling water and poured into the crock; the barium sulfate was precipitated by slowly adding, with stirring, the required quantity of hot sulfuric acid solution. The latter solution was prepared by adding 200 g. of H_2SO_4, sp. gr. 1.84, to 109 g. water, these quantities corresponding to equal parts by volume. It is necessary to have a very small excess of barium chlorate rather than of sulfuric acid, and the chloric acid solution should be tested for sulfate and for barium until the procedure is standardized. The mixture was allowed to stand until the barium sulfate settled out, which required at least one hour. About $^2/_3$ of the chloric acid solution could then be removed by decantation or by a siphon, but filtration of this solution was sometimes necessary. Nearly all of the remaining acid was separated from the precipitate by filtration through a Büchner funnel with suction. The barium sulfate can be washed and saved if desired.

The acid solution was stored in glass-stoppered bottles. It was practically colorless and did not change appreciably in concentration in several weeks, even when exposed to the diffused light of the laboratory. Acid kept in an unstoppered bottle in the hot laboratory increased in concentration due to the loss of water by evaporation. Each sample of acid was analyzed for chlorate.

Oxidation of the Iodine.—500 g. of commercial "resublimed" iodine was weighed into a 3-liter glass flask, and to this was added an amount of chloric acid 3% in excess of the theoretical amount (one mol of chlorate per gram atom of iodine). The flask was connected with an absorption train of 3 wash bottles partly filled with a cold 20% solution of sodium hydroxide (or with milk of lime if bleaching powder was desired instead of sodium hypochlorite solution; the latter was used in another process in our laboratory). A slow current of air was passed through the apparatus after the reaction started. If the mixture was heated to start the reaction and again when only a small amount of iodine remained, a run could be completed in 20 minutes. When the initial heating was omitted the reaction started within 10 or 15 minutes.

The solution was then cooled, filtered to remove barium iodate or any foreign matter, transferred to a large evaporating dish, and evaporated just to dryness with frequent stirring. If during the evaporation a yellow-brown color appeared, a small amount of chloric acid was at once added. The material was heated in a hot-air oven at a temperature of 150–160° for 3 hours, and then removed from the evaporating dish for more complete dehydration.

Dehydration of Iodic Acid.—In the dehydration process finally adopted the coarsely powdered dry material was loosely packed in glass tubes 30 mm. in diameter and closed at one end. The column of iodic acid was held in position by glass wool at each end. A thermometer was imbedded in the iodic acid to show the actual temperature of the material. Near the bottom of each tube a small tube was inserted, through which a slow current of dry air could be drawn; the air was thus preheated by passing through the length of the oven before reaching the iodic acid. The air was dried by passing through a train which consisted of a sulfuric acid bead-tower and a U-tube containing phosphorus pentoxide and soda lime. The rate of flow was regulated by observation of the bubbling through the acid tower.

One or more tubes were placed in a horizontal position in a well insulated horizontal oven which was uniformly heated by a number of gas flames. A constant temperature of 235–240° was maintained for at least 3 hours, during which time the slow current of dry air was drawn through the material.

When material prepared by the chloric-acid process was dehydrated in this way the product was of a uniform white or faintly pink color, and contained not more than 0.2 or 0.3% water (see below). The intensity of the color as it varies from pink to violet is an indication of the amount of decomposition during dehydration, due to local overheating or to the presence of impurities. It was found that pure iodic anhydride may be heated to 250° without the slightest liberation of iodine.

The dehydrated material was ground in a ball mill to pass an 80-mesh screen. During this process it absorbed a small amount of water vapor from the air, and the final product contained 0.5 to 0.6% of water vapor. As this material is hygroscopic it was stored in sealed containers.

Iodic acid prepared by the nitric acid method was not easily dehydrated without decomposition. A temperature of 200° could not be exceeded, at least in the first hour or two, and the dehydration was correspondingly less complete in a 3-hour treatment. Iodic acid contaminated with sulfuric acid decomposed even more readily during dehydration. The chloric acid process thus has a marked advantage over the other processes in this respect.

In agreement with the greater stability of iodic acid and iodic anhydride prepared in this way is our observation that it does not decompose when in the course of the analysis for carbon monoxide it is heated with pure air. Iodic anhydride, as usually prepared, when heated hot enough to react satisfactorily with carbon monoxide, invariably gives a positive blank, for which a correction must be applied even with the purest air. This difficulty, which is the limiting factor in the precise analysis of small concentrations of carbon monoxide, can be eliminated by using iodic anhydride prepared in the above way.

Analysis of Iodine Pentoxide, Water Content.—The water content of the iodine pentoxide samples was determined by a method devised by Baxter[1] depending on its decomposition by heat into iodine, oxygen and water vapor, the removal of the iodine by means of metallic silver and the absorption and weighing of the water.

The silver used was prepared by placing copper wire spirals in silver nitrate solution. The precipitated silver was washed thoroughly and finally heated to constant weight at a temperature of 350–400°. As this heating had a tendency to clump the silver, it was broken up and made to pass through a 16-mesh screen before use.

One half of an 80 cm. hard, glass combustion tube, 2 cm. in diameter, was packed with alternate layers of the silver and glass wool. This method of packing was adopted to prevent the formation of lumps of silver iodide

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[1] This Journal, 31, 210 (1909).

during the analysis. By means of a suction pump, air, dried in a train consisting of sulfuric acid, soda lime and phosphorus pentoxide, was drawn through the apparatus and then through an absorption tube which could be conveniently weighed. Between this tube and the pump a phosphorus pentoxide tube was inserted to prevent access of water vapor through the pump. A convenient form of absorption tube was a U-tube half filled with pumice or glass beads moistened with sulfuric acid, and containing enough acid just to seal the bend.

The combustion tube containing the silver was strongly heated and the current of dry air was passed until the absorption tube was constant in weight. A weighed amount of the iodine pentoxide to be analyzed, in a porcelain boat, was introduced into the combustion tube in front of the silver packing, and this portion of the tube was carefully heated until the pentoxide was completely decomposed. The current of air brought the iodine into contact with the heated silver and swept the water vapor into the absorption tube.

The accuracy of the method is demonstrated by the duplicate analyses of the samples in the following list, marked (*a*) and (*b*).

1. Nitric acid process, one 3-hour dehydration at 200°.
    (*a*) 1.10% H_2O, corresponding to 21.6% hydration.[1]
    (*b*) 1.13% H_2O, corresponding to 22.1% hydration.
2. General Chemical Company, as received.
    (*a*) 1.84% H_2O, corresponding to 35.9% hydration.
    (*b*) 1.83% H_2O, corresponding to 36.0% hydration.
3. Chloric acid process, one dehydration at 240°.
    0.31% H_2O, corresponding to 6.0% hydration.
4. Ditto, after grinding.
    0.55% H_2O, corresponding to 10.7% hydration.

Many other samples were analyzed, but the above results are representative. It is to be noted that iodine pentoxide as ordinarily prepared is far from being completely dehydrated.

Other Analyses and Tests were made in examining the various samples of iodine pentoxide. The iodine pentoxide content was determined iodimetrically: one mol of iodine pentoxide liberates 12 gram atoms of iodine. The free iodine content could have been determined by adding a weighed amount of the sample to water, extracting the iodine with carbon tetrachloride, and adding the latter to a potassium iodide solution for titration with thiosulfate; but this analysis was not necessary since the amount of iodine obtainable from a pink sample was negligible. The non-volatile matter was determined after ignition; it did not exceed 0.1%, which proved the absence of appreciable amounts of barium iodate. The test for sulfate was made after precipitation of silver iodate by the addition of silver nitrate solution in excess. Nitrate was tested for by

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[1] The water is assumed to be present as HIO_3.

the method recommended by A. A. Noyes,[1] which depends on the removal of the iodate by means of silver sulfate, and distillation of the filtrate with sulfuric acid and ferrous sulfate.

Summary.

1. A simple and rapid method has been developed for the preparation of iodine pentoxide, which depends on the oxidation of iodine to iodic acid by means of 24–26% chloric acid solution, the evaporation of the solution, and the dehydration of the iodic acid. The product is pure white, analyzes practically 100% oxidizing value, and contains no detectable impurities except traces of water and barium iodate. It is decidedly more stable towards heat than is iodic anhydride as ordinarily prepared, and, therefore, possesses decided advantages for use in the analysis for small quantities of carbon monoxide in air. The yield of pentoxide from iodine is almost theoretical.

2. In the preparation a small excess (3%) of chloric acid is intentionally used; this ensures the complete removal of the hydrochloric acid formed during the oxidation process, which otherwise would reduce the iodic acid during the evaporation.

3. When this small excess of chloric acid is used the net result of the oxidation reaction is expressed by the equation

$$I_2 + 2HClO_3 = 2HIO_3 + Cl_2.$$

The mechanism of this reaction undoubtedly does not correspond to a direct replacement of the chlorine by the iodine. The second product of the reaction, chlorine gas, can be conveniently recovered as sodium hypochlorite solution or bleaching powder.

4. The chloric acid solution is made by the direct action of sulfuric acid on barium chlorate solution. There is no decomposition of the chloric acid, and the only loss is the small amount of solution absorbed by the barium sulfate. The by-product, barium sulfate, can be recovered if desired.

5. The various analytical methods needed in this investigation were carefully tested. Several of them, though not absolutely new, have previously received little attention.

6. The chloric acid method, when tried on a semi-manufacturing scale presented no difficulties.

7. Two other methods for the preparation of iodine pentoxide were used in the laboratory but gave less satisfactory results. One of these was the conventional nitric acid method, and the other involved the preparation of barium iodate and the treatment of this difficulty soluble substance with sulfuric acid.

In conclusion we wish to acknowledge our indebtedness to the following

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[1] A. A. Noyes, "Qualitative Analysis," 1914, p. 113.

members of the Chemical Warfare Service for their assistance in the experimental work: A. W. Kenney, C. L. Dougherty, W. M. Craig and D. O. E. Peterson.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

CONDUCTIVITY AND FREQUENCY.

BY E. D. EASTMAN.

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There is reason to suppose that the general form of the conductivity-frequency curve for solutions of electrolytes may correspond in type to that shown in Fig. 1. The features of this general curve are the rise, from *A* to *B*, to a maximum of conductivity as the frequency is increased from zero, and the subsequent decrease, from *B* to *C*, and asymptotic approach to zero conductivity at infinite frequency. The necessity of the approach to zero as the frequency is indefinitely increased is obvious, and the portion of the curve from *B* to *C* requires little comment other than to point out the possibility that certain resonance effects may make the curve less simple in this region than the one here shown, and that the decrease in conductivity undoubtedly begins only at frequencies far higher than those ordinarily used in conductivity measurements. It is in the portion *AB* of the curve that the interest of the present paper centers, and the basis of the assumption of increase in conductivity in this portion of the curve may be briefly discussed.

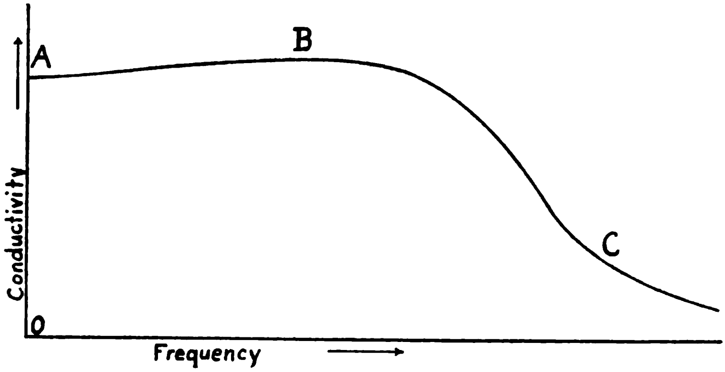

Fig. 1.—Theoretical form of conductivity-frequency curve.

If current theories are correct there are present in solutions of electrolytes numerous electric dipoles, or multipoles, consisting of molecules or ions of solute in various stages of dissociation and solvation. Under the influence of an alternating electric field these polar molecules should all be more or less free to take part in oscillatory rotation about their centers, and this rotation should contribute to the current carried by the solution and ordinarily attributed exclusively to the linear motion of free ions. Other effects due to the alternating field may be readily imagined, but these probably do not affect conductivities as ordinarily measured. For example, oscillations, in the direction of the electric field, of the charged parts of undissociated molecules may occur, or electrons may vibrate between atoms of the same molecule or of different molecules. But the forces opposing the external field in such vibrations are no doubt elastic in character, affecting the capacity rather than the conductance of the solution, and the effects may, therefore, be compensated by the use of capacities in the external circuit. These considerations do not apply, however, to the rotation of the molecules, the resistance to which is probably largely frictional and of the same nature as the resistance to the motion of the ions. The magnitude of this rotational effect, owing to the present imperfect state of knowledge of the structure of solutions, cannot be calculated. Approximations which may be made on the basis of various simple assumptions as to the possible number and electrical moments of the complexes involved, give 1% of the total current as the order of the effect for *N* potassium chloride solution at 1000 cycles per second.

On the experimental side there is in the literature no work which definitely precludes a difference of this magnitude. The best of the older researches comparing direct and alternating current conductivities is that of Sheldon.[1] The average of his final results for various salts at different concentrations shows good agreement between the two methods. But the possible constant errors in his methods are such that the agreement found might well be purely fortuitous. Again, the results which have been thus far obtained, in various laboratories, while far from complete or conclusive, seem to indicate that at frequencies of the order of one or two thousand cycles, changes of conductivity with frequency are in general quite small, *i. e.*, a portion of the curve in Fig. 1 is horizontal or slopes but slightly. It does not follow, however, from the approximate constancy of the values obtained by measurements at these frequencies, or by extrapolation from lower frequencies,[2] that the values corresponding to zero frequency are identical with them. At intermediate frequencies polarization appears as a disturbing factor, largely destroying the value of the results.

As it appears then that a variation in conductivity with frequency may theoretically be expected even at low frequencies, and as the magnitude

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[1] Sheldon, *Ann. Physik*, 34, 122 (1888).

[2] Taylor and Acree (This Journal, 38, 2396 (1916)) suggest this method. If only an electrode effect is involved, and no real change of conductance with frequency, the method is perhaps justified, though "extrapolation to infinite frequency" is misleading.

of this variation cannot be judged from existing data nor readily studied by the usual methods, the experiments below were undertaken. Their primary object was not the study of the effect in itself, though this is of some interest, but rather to find whether the expected differences are large enough at ordinary frequencies to affect calculations seriously, such as degree of dissociation, based on conductivity measurements, or to afford a method of study of the "structure" of solutions of electrolytes. The scheme first adopted was the measurement by a direct current method and comparison with alternating current values of some of the conductivities most accurately determined by Kohlrausch. This was done with *N* potassium chloride and with maximum conducting sulfuric acid. Later a method by which alternating and direct current measurements could be directly compared in the same cell was tried with *N* potassium chloride solution and with 10 *N* lithium chloride solution.

The Direct Current Conductivity of Normal Potassium Chloride Solution and of Maximum Conducting Sulfuric Acid by a Potentiometric Method.

Potassium chloride was selected for study because of the reproducibility of its solutions, and because of the accurate determination by Kohlrausch of its conductivity, and its consequent use as a standard in conductivity work. It is not, however, of the type which would be expected to show the largest effect of the kind considered. Of the other substances recommended by Kohlrausch as standards, sulfuric acid seemed most likely to exhibit a large effect, and was chosen for this reason.

The method of measurement follows. The solution to be studied is placed in a cell of the type shown in Fig. 2. This is connected, in series, with a standard resistance and with a source of steady current, by means of non-polarizable electrodes dipping into the reservoirs *A*, *A*. The potential at similar electrodes in *B*, *B*, and at the terminals of the standard resistance, is then measured by a potentiometer. The "cell constant" is determined in the same way, the electrolyte being replaced by mercury.

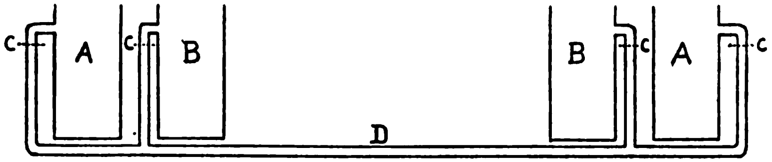

Fig. 2.—Direct current conductivity cell.

The electrodes were of very large reacting surface. Calomel and mercurous sulfate electrodes were used for the potassium chloride and sulfuric acid solutions, respectively, the electrolyte in the cell differing from that in the electrodes only in that it contained no dissolved calomel or mercurous sulfate. Both sets of electrodes were very constant. The correction to the potentiometer reading, which had to be made because the electrodes were not quite equivalent to each other, was of the order of a few hundredths of one per cent. of the reading.

All details affecting the accuracy of the results were carefully studied. The resistance used were compared with coils recently certified by the Bureau of Standards. The currents employed were systematically varied, giving readings in widely different ranges of the accurate potentiometers which were used. Heating effects, and the effects of impurities in all materials were shown experimentally to have been eliminated. Temperatures were constant to 0.01° and correct to 0.02°. The weights used in preparing the solutions were compared with a standard gram.

The mean of 8 series of observations upon 3 independently prepared solutions gave 5038.3 ohms as the resistance of the cell containing *N* potassium chloride solution (71.422 g. of potassium chloride per 1000 g. solution) at 25°, the average of the deviations of individual values from the mean being 0.014%. For the sulfuric acid solutions the corresponding values are 682.63 ohms and 0.±018%, and for mercury 0.054138 ohm and ±0.032%. From the definition of the international ohm, the specific conductance of mercury at 0° is 1.0630×10^4 reciprocal ohms. The temperature coefficient of resistance of mercury between 0° and 100° has been accurately determined by Jaeger and Steinwehr.[1] From their work the specific conductance at 25° is 1.03930×10^4 reciprocal ohms. The specific conductance of *N* potassium chloride solution is then calculated to be 0.11168 and of the sulfuric acid 0.8242 reciprocal ohm. The corresponding Kohlrausch values are 0.11180 and 0.8257 reciprocal ohm, which are 0.11% and 0.18%, respectively, higher than the results above. These differences are in the direction expected, and their magnitude exceeds the experimental error, ±0.05%, which can be assigned to the present work.

Newbery,[2] in a paper which was unknown to the writer until after the completion of this portion of the work gives a direct current measurement for potassium chloride which is 0.7% higher than the one here obtained, and is apparently in error by nearly this amount. Because the accuracy of Kohlrausch's work (though it is believed to be excellent) is not definitely known, a more direct comparison seemed desirable and was made in the experiments described below.

Direct and Alternating Current Conductivities by a Modified Bridge Method.

The principle of a method by which alternating current may be used in a cell of the type described in the preceding was suggested to the

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[1] Jaeger and Steinwehr, *Ann. Physik*, 45, 1089 (1914).

[2] Newbery, *J. Chem. Soc.*, 113, 701 (1918). Newberry's method is similar in principle to that described above, except that the cell constant is obtained from its dimensions, instead of from its conductance when filled with mercury. The accuracy of his results is estimated by him as 0.1%.

writer by Dr. R. F. Newton. It may best be made clear by reference to Fig. 3. Here E and F are the points of connection to the source of current, a and b are resistances of known ratio, and R_1, R_2, R_3 are variable known resistances. The points A and D correspond to the reservoirs A, A, in Fig. 2, and the points B and C are the points of connection to the reservoirs B, B of Fig. 2. The resistance of the part BC is referred to as the resistance of the cell, as before, and called R. The procedure in measurement is to adjust the sum $R_1 + R_2 + R_3$ so that balance is obtained in the telephone T_1. Still maintaining $R_1 + R_2 + R_3$ constant, R_1 and R_2 are adjusted for silence in T_2, and lastly, maintaining $R_2 + R_3$ constant, adjustment of them is made for balance in T_3. When this has been done the value of R is known from the relation

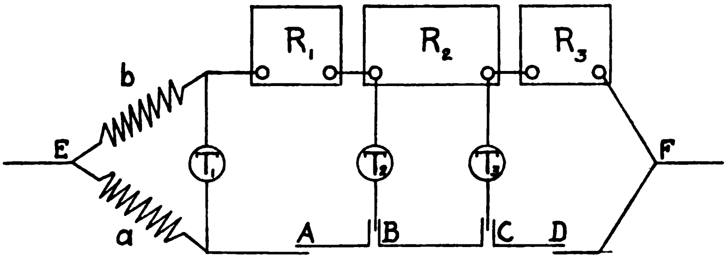

Fig. 3.—Modified bridge.

$$R = a/b\, R_2.$$

The same method is applicable with direct current, using suitable non-polarizable electrodes, and replacing the telephones by galvanometers. In practical operation a single telephone or galvanometer with appropriate switches may be used, and it may also be arranged to change, by the throw of a switch, from one type of current to the other, giving nearly simultaneous comparisons.

In the actual set-up, a and b were various combinations of a set of standardized Curtis coils. At times a calibrated rotary slide wire, with end coils, was substituted for these fixed ratio coils, the sliding contact in this case being at E in Fig. 3. The ratio a/b was widely varied in the different measurements. R_1 and R_3 were dial resistances and R_2 a dial box of Curtis coils. It was first arranged so that condensers could be thrown in parallel with either arm of the particular portion of the bridge being balanced, but it was later found that the adjustment of a condenser in any part of the system, *e. g.*, in parallel with R_3 or CD, sufficed to sharpen the minima in balancing the other portions. Alternating current of approximately 1000 cycles was obtained from a Siemens-Schuchert alternator, the external circuit being tuned with suitable capacities. The necessary shielding and grounding was provided. A hot wire milliammeter and a direct current milliammeter served to indicate the currents employed, though the alternating currents were too small to be accurately measured by the instrument used.

The alternating current in the cell was reduced to the lowest value consistent with sharp minima. It was on continously during the measurements, the heating effect being estimated by doubling the current in the cell. The correction, to be added to the resistance found for the lower current is then $^1/_3$ of the difference between the resistances at the higher and at the lower currents. This correction was negligible in several instances, was about 0.01% in many, and did not exceed 0.03% in any of the measurements.

The direct currents varied between 0.02 and 0.5 milliampere, and being on momentarily only were without appreciable heating effect. As the galvanometer circuit was always closed, deflections being noted when the main current was passed through the bridge, "parasitic" effects were eliminated. In balancing, the first deflection of the galvanometer was used, since the polarizing effect of the main current, in spite of the calomel electrodes, caused a change in the apparent resistance of the whole cell (through of course not in R). Though this reversal of direction of throw of the galvanometer appeared quickly, there was no difficulty experienced in making settings with the required accuracy.

The thermostat was an oil bath constant to 0.005°, the temperature of which was read on a Beckmann thermometer which had been compared with 3 standard Baudin thermometers.

The mean of the 15 alternating current observations which were made using N potassium chloride solution gives 5033.7 ohms as the cell resistance, the average deviation of individual results from the mean being 0.02%. Between each pair of alternating current measurements, a direct current measurement on the same solution was taken, the resulting value of the resistance being 5037.1 ohms, ±0.015%. The latter it is seen is in agreement with the result previously obtained.

Direct Comparison of Alternating and Direct Current Conductivities of Potassium Chloride and Lithium Chloride Solutions.

The individual measurement above were in general more or less independent, involving numerous settings of different resistances, etc. To eliminate as many variable factors as possible a few measurements were made, in which all preliminary adjustments were determined before the final readings were taken. For example, with nearly correct settings of the resistances, the slide wire would be adjusted for balance, the settings of R_1, R_2 and R_3 accurately made as desribed above, and the slide wire setting again made, all with alternating current. Changing immediately to direct current, the new setting of the wire and minor adjustments, all in the unit dials, of the resistances could be quickly made.

The difference, direct minus alternating current resistance, found by this method in a series of 4 measurements with *N* potassium chloride solution varied between 0.004 and 0.058%, the average being 0.028%. In a set of 6 experiments with 10 *N* lithium chloride, in which the bath temperature was constant to 0.002° and heating effects were negligible, one negative deviation of 0.012% was obtained, the remainder falling between +0.014 and +0.039%, the average of all being +0.018%. Tests of the same method of comparison using metallic resistances of the same magnitude and approximately equivalent capacity in place of the electrolytic cell showed agreement by the two methods to 0.004%, the direct current resistance being apparently larger by this amount than the alternating.

Discussion.

The numerical results of the preceding absolute measurements are collected and compared with those of Kohlrausch in Table I.

TABLE I.
Conductivities at 25°.

Solution	Method	Conductivity
N KCl	D. C. Potentiometric	0.11168
N KCl	D. C. Modified Bridge	0.11170
N KCl	A. C. Modified Bridge	0.11177
N KCl	Value of Kohlrausch	0.11180
Max. Cond. H_2SO_4	D. C. Potentiometric	0.8242
Max. Cond. H_2SO_4	Value of Kohlrausch	0.8257

The agreement of the Kohlrausch values with all the others in the table is probably within the combined experimental error of the 2 sets of results. The divergence of 0.068% between the alternating and direct current values obtained in this work cannot, however, all be ascribed to the accidental error, ±0.02% in each measurement. After allowing for these chance errors the difference of about 0.03% which remains between the 2 values is of the same order as that found in the most direct comparisons which could be made, and is in the direction anticipated. The differences found in the direct comparisons are, therefore, believed to show the order of magnitude of a real effect, which is however too small to be of consequence in any ordinary measurements or calculations, and too small to be accurately determined with the facilities available in this work.

The failure of the difference experimentally found to equal in magnitude that given by the rough calculation referred to in the introduction cannot be definitely "localized" in the failure of any one of the assumptions involved regarding the number and moments of the polar aggregates pictured. The results, therefore, do not offer any evidence as to the state of electrolytes in solution. Considered in conjunction with the results of Sheldon, whose conclusion from a large number of less accurate experiments may be regarded as verified by the few more precise measurements described here, they indicate that the effect is too small at all concentrations to permit a study of this question, at least at low frequencies. The frequency at which the assumed maximum (*B* in Fig. 1) occurs is not known. If it can be located and if the effect there is appreciably larger than at 1000 cycles, a study of the change of the effect with concentration might contribute definite evidence concerning dissociation.

The accuracy of the absolute conductivities given above is of the order of 0.05%, which is probably about that of the measurements of Kohlrausch. That true conductivities of great accuracy are not often required is probably responsible for the fact that the experiments of Kohlrausch with potassium chloride, and other standard solutions, have not been repeated, introducing the more recent refinements of technique. The desirability of such a repetition has nevertheless been suggested by several authors. It seems in order to point out in this connection that if such a work is undertaken it should, for the sake of added definiteness, be paralleled with direct current measurements made with the high precision of which they are capable.

Summary.

In this paper it is suggested that the conductivity of solutions of electrolytes should be smaller at zero frequency than at any frequency in a certain range (of unknown limit) immediately above zero. Various measurements made to test this idea are described. It is concluded that the difference between direct current conductivities and those at 1000 cycles does not exceed 0.02–0.03% in the cases studied, but is in the expected direction. Incidentally, the conductivity of *N* potassium chloride at 25° given by Kohlrausch is confirmed, within 0.1%, by the measurements made here.

BERKELEY, CAL.

NOTE.

The Use of Potassium Hydrogen Phthalate as a Standard in Alkalimetry.—In 2 recent papers Professor Hendrixson has shown the advantage of potassium hydrogen phthalate as a standard in alkalimetry.[1] Since this substance has been in use in my laboratory for 15 years (I advocated its use as a standard first in a paper read before the New York Section of the American Chemical Society, on January 8, 1904, and later in a published article in 1915,[2] it is gratifying even at this late date to have its merits recognized.

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[1] THIS JOURNAL, 37, 2352 (1915) and 42, 724 (1920). In the former my original paper is referred to, but in the latter, undoubtedly by an oversight, this has not been done. Patten, Johnson and Mains (*ibid.*, 40, 1156 (1918)) quote almost verbatim from my article without acknowledgment.

[2] *J. Ind. Eng. Chem.*, 7, 29 (1915.)

However, for the benefit of any who are using, or may consider using this substance, I would call attention to an advisable precaution in its preparation. A saturated solution of the acid phthalate on chilling will deposit crystals of a more acid salt, having the formula, $2KHC_8H_4O_4.C_8H_6O_4$. These crystals are in the form of prismatic needles, easily distinguished under the microscope from the 6-sided orthorhombic plates of the salt, $KHC_8H_4O_4$. A contamination of the acid phthalate with this "triphthalate" would be fatal for its use as a standard, but the formation of the latter can be entirely avoided by crystallization at temperatures above 20°.

The writer hopes soon to present the results of a detailed chemical and crystallographic study of the acid phthalates, which has proved interesting in various ways. F. D. DODGE.

BROOKLYN, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY.]

THE ACTION OF ACETIC ANHYDRIDE ON ALPHA NAPHTHYL PROPIOLIC ACID.[1]

BY BYRON L. WEST.

Received February 7, 1920.

Introduction.

Over twenty years ago, Michael and Bucher[2] found that phenyl propiolic acid, when treated with acetic anhydride, yields α-phenylnaphthalene-2,3-dicarboxylic anhydride. This compound was unexpected, and its identity was unknown for almost 2 years. In a previous research[3] they found that acetic anhydride reacts with acetylene dicarboxylic acid to form the anhydride of acetoxyl-maleic acid; and on treating this anhydride with water, they obtained oxalacetic acid. If acetic anhydride would act on phenyl propiolic acid in an analogous manner, the anhydride of β-acetoxyl-cinnamic acid would be formed, and this compound, on treatment with water, would yield β-hydroxycinnamic acid.

Their explanation of the unexpected formation of the α-phenylnaphthalene derivative may be best explained by the following formulas.

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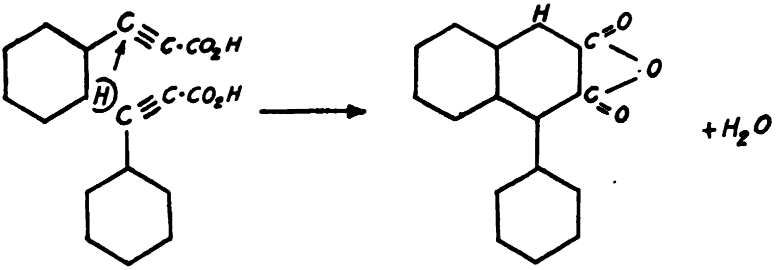
[1] This is an abstract of a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Brown University by the holder of the Morgan Edwards Fellowship founded by the Philadelphia Alumni of Brown University. The investigation was conducted in the Chemical Laboratory of Brown University at the suggestion and under the personal direction of Professor John E. Bucher. The author wishes to express his gratitude to Doctor William Williams Keen, President of the Philadelphia Alumni, for his constant and helpful interest and encouragement.

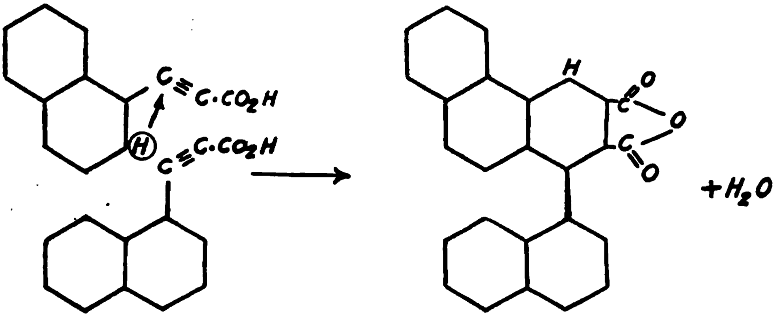
[2] Michael and Bucher, *Am. Chem. J.*, **20**, 89 (1898).

[3] *Ber.*, **28**, 2511 (1895).



It will be seen that their explanation is based on the fact that the *ortho* hydrogen atom of the first molecule of the phenyl propiolic acid wanders to the β-carbon atom of the same molecule. The β-carbon atom of the second molecule unites with the *ortho* carbon atom of the first molecule from which the hydrogen wandered, and the 2 α-carbon atoms of the side chains unite to complete the naphthalene ring.

This reaction has been found to hold for phenyl propiolic acids in general, and the following substituted phenyl propiolic acids polymerize with the above treatment to their corresponding α-phenyl-naphthalene-2,3-dicarboxylic anhydrides: *o*-chloro-, *o*-bromo-, *m*-nitro-, *p*-chloro-, *p*-bromo-, *p*-iodo-, *p*-methoxy-, *p*-methyl-, and a number of other phenyl propiolic acids. It has been further shown by Holt[1] that symmetrical tribromophenyl propiolic acid is not condensed to a naphthalene derivative by the action of acetic anhydride, the anhydride of the bromo acid only being formed. The reason for this is apparently that the 2 *ortho* bromine atoms are held too firmly for either to wander from the nucleus, as would be necessary if a similar condensation took place. However, Foote[1] was unable to obtain any condensation product from β-anthraquinoyl propiolic acid where there were 2 hydrogen atoms on the nucleus. He explained the result by showing that his acid decomposed at 135°.



The purpose of this investigation has been to determine whether this interesting condensation, which seems general for propiolic acids of the phenyl series, could be extended to the naphthalene series as well. If

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[1] Unpublished researches.

an analogous condensation should take place, the product would be an α-naphthyl-phenanthrene di-carboxylic anhydride, as shown by the preceding formulas.

Previous Methods of Preparing α-Naphthyl Propiolic Acid.

A new and satisfactory method for obtaining α-naphthyl propiolic acid from the present limited supplies of chemicals was first worked out. The action of acetic anhydride on this acid was then investigated. In a manner analogous to that of Glaser[1] who prepared phenyl propiolic acid by treating potassium phenyl acetylene with carbon dioxide under pressure, Leroy[2] prepared α-naphthyl propiolic acid with poor and uncertain yields from potassium naphthyl acetylene and carbon dioxide. However, just as in the phenyl series, this method did not seem to us feasible for obtaining the acid in large quantities. Moreover, there is room for doubt as to whether Leroy ever obtained an absolutely pure acid uncontaminated by its β-isomer. He prepared his α-naphthyl ketone (from which he obtained his acetylene derivative) by the method of Claus and Feist,[3] and Pampel and Schmidt.[4] In this method acetyl chloride and naphthalene are condensed with aluminum chloride. In 1889, Müller and Pechman[5] performed this same Freidel and Crafts reaction and obtained a ketone that differed widely in properties from that described in either of the 2 articles published; they called their product the β-ketone. Claus and Terstegen[6] attempted to explain the differences and said that the experiment at higher temperatures gave an α- and at lower temperatures a β-ketone. In 1896, however, 5 years after Leroy's article on the propiolic acid preparation, was published Rousset[7] stated that none of these authors had succeeded in isolating the ketones and obtaining them pure. He found it necessary to form their picrates in order to separate the 2 isomers.

Bucher[8] prepared many of the propiolic acids mentioned previously from the corresponding cinnamic acids. They made the cinnamic ester dibromide and heated the latter with alcoholic potash. The value of this method depends on the ease with which the corresponding aldehydes can be obtained from which the cinnamic acids are prepared by means of the Perkins synthesis. However, a satisfactory method of preparation for α-naphthaldehyde was not available. Methyl naphthalene cannot be obtained without great expense. Furthermore,

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[1] *Ann.*, 154, 140 (1870).

[2] Leroy, *Bull. soc. chim.*, [3] 7, 644 (1891).

[3] Claus and Feist, *Ber.*, 19, 3180 (1886).

[4] Pampel and Schmidt, *ibid.*, 19, 2898 (1886).

[5] Müller and Pechman, *ibid.*, 22, 2561 (1889).

[6] Claus and Terstegen, *J. prakt. Chem.*, 50, 517 (1894).

[7] Rousset, *Bull. soc. chim.*, [3] 17, 58 (1896).

[8] Bucher, *Am. Chem. J.*, 32, 212 (1910).

Scherler[1] in attempting to halogenate the side chain, found that the chlorine or bromine atoms are just as liable to replace the hydrogens on the ring as those on the side chain.

The usual method for obtaining aldehydes which involves heating the calcium salt of α-naphthoic acid with calcium formate, yields mostly naphthalene and only faint traces of the aldehyde.[2] Gatterman and Maffezzoli[3] have prepared α-naphthaldehyde by use of the Grignard reaction from magnesium bromo-naphthalene and an excess of formic ester. Owing to the difficulties involved and because of a desire to use only comparatively inexpensive and easily obtainable materials, this method has not been used. Rousset[4] obtained α-naphthaldehyde from the corresponding naphthyl-glyoxylic acid. In obtaining this acid he had to separate the α- and β-isomers, and this proved difficult.

The best known method for obtaining α-naphthaldehyde has been described by Brandis[5] as a long, tedious "time-consuming process" with poor yields. It is that of Bamberger and Lodter[6] and consists of the reduction of the thioamide to the methyl amine and the subsequent changing of this product to the naphthyl-methyl alcohol which in turn is oxidized to the aldehyde.

It appeared, therefore, the problem was to be solved either by (1) devising a method for obtaining α-naphthyl propiolic acid without the use of the aldehyde as a starting point, or by (2) discovering more efficient means for the preparation of α-naphthaldehyde.

Considerable time and effort was spent on the first of these 2 possibilities in an attempt to prepare the propiolic acid from α-naphthyl acetic ester. This work was discontinued because of the success of the following method.

New Method for Obtaining α-Naphthaldehyde.—Guereschi[7] prepared benzyl alcohol by reducing benzamid in a hydrochloric acid and water containing ether solution. Later Hutchinson[8] prepared *o*-toluyl alcohol in an analogous manner from *o*-toluic amide, using 15% alcohol instead of ether. His yield was 40–45%. In this laboratory, Barnard in investigating Guereschi's work, increased the latter's yield from 31.5% to 56% by the use of 95% alcohol.

α-Naphthoic amide is very readily prepared, as is well known, and its

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[1] Scherler, *Ber.*, 24, 3927 (1891).

[2] Bamberger and Lodter, *ibid.*, 21, 259 (1888).

[3] Gatterman and Maffezzoli, *ibid.*, 36, 4152 (1903).

[4] Rousset, *Bull. soc. chim.*, [3] 17, 313 (1896).

[5] Brandis, *Ber.*, 22, 2153 (1889).

[6] Bamberger and Lodter, *ibid.*, 21, 259 (1888).

[7] Guereschi, *ibid.*, 7, 1462 (1874).

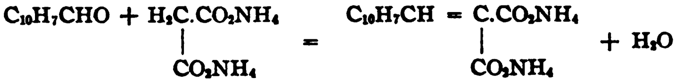
[8] Hutchinson, *ibid.*, 24, 175 (1891).

several methods will be discussed later. The most feasible was that of Hoffman[1] who obtained it directly from the nitrile.

By use of a mechanical stirrer, α-naphthamide was successfully reduced in 95% alcohol solution with 4% sodium amalgam and commercial hydrochloric acid to α-naphthyl-methyl alcohol and yields of 70% obtained with several 100 g. lots.

The alcohol was readily oxidized to the aldehyde by the use of sodium dichromate and dil. sulfuric acid following a method similar to that of Bamberger and Lodter.[2]

Perkin's well known synthesis was used by Brandis[3] and Lugli[4] and Rousset[5] to obtain the acrylic acid. The yields at best were only 45 to 50% of the theory after 50 to 60 hours heating and the product was exceedingly difficult to purify. The malonic acid synthesis used by Knoevenagel[6] on benzaldehyde to obtain benzal malonic acid and from it the cinnamic acid gave much better results. The reaction completed itself in a few hours and gave a comparatively very pure product. The method consists of heating one molecule of α-naphthaldehyde and one molecule of malonic acid with 2 molecules of an 8% alcoholic ammonia solution



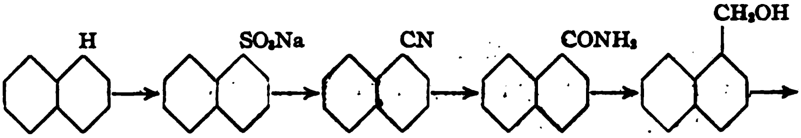
$$C_{10}H_7CHO + \begin{array}{l}H_2C.CO_2NH_4\\ \quad| \\ CO_2NH_4\end{array} = \begin{array}{l}C_{10}H_7CH = C.CO_2NH_4\\ \qquad\qquad\quad | \\ \qquad\qquad CO_2NH_4\end{array} + H_2O$$

On acidification the naphthal malonic acid was readily changed to the acrylic acid on heating.

$$\begin{array}{l}C_{10}H_7CH = C.CO_2H\\ \qquad\qquad\quad | \\ \qquad\qquad CO_2H\end{array} = C_{10}H_7CH = CHCO_2H + CO_2$$

From this compound the method of Michael and Bucher was successfully used to obtain the α-naphthyl propiolic acid. The acrylic ester dibromide was readily made and the subsequent treatment with alcoholic potash (3 molecules) yielded the α-naphthyl propiolic acid.

The whole synthesis follows



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[1] Hoffman, *Compt. rend.*, 66, 486 (1868).

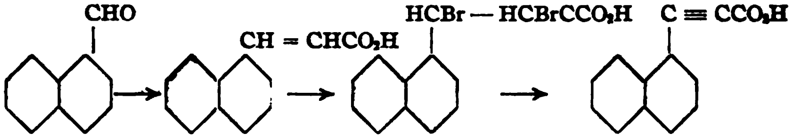
[2] *Loc. cit.*

[3] Brandis, *Ber.*, 22, 2153 (1889).

[4] Lugli, *Gazz. chim. ital.*, 11, 393 (1881).

[5] Rousset, *Bull. soc. chim.*, [3] 17, 813 (1896).

[6] Knoevenagel, *Ber.*, 31, 2604 (1898).



This synthesis proved very interesting, for the pure halogen-free propiolic acid was obtained by forming of the more soluble ammonium salt by means of ammonium carbonate. A final recrystallization from carbon tetrachloride yielded the product pure in well-formed needles.

The next step, after the acid had been obtained and identified, was to boil it with acetic anhydride in a manner similar to that of Michael and Bucher. The possible outcome has been briefly reviewed and the results of the experiments are reserved until the explanation of the experimental part and the final conclusion.

Experimental Part.

Sodium Salt of α-Naphthalene Sulfonic Acid.—Commercial naphthalene was used in forming the α-sulfonic acid. The standard method of preparation need not here be described. The sulfonation was carried out below 60° and any β-isomer was removed when the calcium salt was made. Treating this with sodium carbonate readily yielded the sodium salt of α-naphthalene sulfonic acid.

Alpha Naphtho Nitrile.[1]—Fifty g. of potassium cyanide was first finely ground and then mixed and intimately ground with 100 g. of pulverized sodium α-naphthalene sulfonate which had been dried at 200°. The whole charge was placed in an iron retort and slowly distilled by heating gradually and increasing the heat toward the end to a dull red. Yields averaged 55–57 g. of crude nitrile. Several hundred g. was obtained by repeating this experiment.

Purification of the Nitrile.—Attempts to obtain pure naphthoic amide directly from the crude nitrile yielded an impure product discolored by a tarry substance, the solubility of which in alcohol was about the same as the amide itself. This impurity is fluorescent in alcohol. As is well known, one of the chief impurities in this crude nitrile is naphthalene which is readily volatile in steam at 100°, while the nitrile is practically non-volatile at this temperature. Consequently, 200 g. of the impure nitrile was distilled with steam until the odor of naphthalene was no longer discernible in the distillate. The temperature of the steam was raised by means of a superheater and the nitrile was readily distilled at 195° to 200°, coming over with an equal volume of water, as a slightly yellow oil which when cooled with ice water soon solidified to a white cake. At the end of the distillation a more difficultly volatile substance solidified in the condenser. This was discarded with the residue in the

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[1] Merz and Mühlhauser, *Ber.*, 3, 709 (1870).

flask. The pure nitrile thus obtained melted at 37–38°. Yield, 154 g.

α-Naphthamide. (*1*) *Hydrogen Peroxide Method.*—Analogous to the method of Radnozewski[1] who prepared benzamide from benzo-nitrile in quantitative yields by the use of alkaline hydrogen peroxide, 2.5 g. of the nitrile was added to a 3% solution of hydrogen peroxide made alkaline with caustic soda. The temperature was maintained at 40° and on vigorous shaking the oily drops soon solidified. The amide, recrystallized from alcohol, showed the yield to be practically quantitative. However, for preparation on a large scale, because of the expense of the process and the difficulty of keeping the amide formed from occluding unchanged nitrile, this method was not used. The yield was quantitative. M. p. 202°.

(*2*) *Sodium Hydroxide Method*, $C_{10}H_7CN + H_2O = C_{10}H_7CONH_2$.—Forty g. of sodium hydroxide was dissolved in 400 cc. of 95% alcohol and filtered into a flask containing 150 g. of pure α-naphtho-nitrile. The flask was provided with a return condenser, heated for $^1/_2$ hour and cooled. The large crop of crystals of amide which resulted was filtered off and washed with alcohol. The filtrate was again boiled for $^1/_2$ hour as before, and a second crop of crystals was obtained. The process was repeated a third time. After a thorough washing with water to remove all sodium naphthoate, the amide existed as pure white glassy needles. Yield, 100 g.; m. p. 203° (uncorr.).

The filtrates and washings were combined and from them the theoretical quantity of α-naphthoic acid not obtained as amide was recovered.

(*3*) *Amide from Acid*,

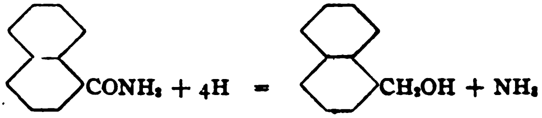
$$C_{10}H_7COOH + PCl_5 = C_{10}H_7COCl + POCl_3 + HCl$$

$$C_{10}H_7COCl + 2NH_3 = C_{10}H_7CONH_2 + NH_4Cl.$$

Seventy-five g. of naphthoic acid was dissolved in 375 g. of carbon tetrachloride in a flask provided with a return condenser. To this was added, in small quantities, 91 g. of phosphorus pentachloride. After the last addition, the flask was heated on a water-bath until no more hydrogen chloride was evolved. The product was then cooled with ice and saturated with dry ammonia. Finally an excess of ammonium hydroxide (sp. gr. 0.9) was added and the carbon tetrachloride was recovered by distillation. The amide was filtered off and washed with water and a little alcohol. Yield of pure white amide, 50 g.

From the filtrate, the unchanged acid was recovered.

α-Naphthyl-methyl Alcohol,



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[1] Radnozewski, *Ber.*, 18, 355 (1885).

Eighty-three g. of α-naphthamide was dissolved in 1500 g. of 95% alcohol in a large battery jar. To this 57.6 cc. of 28% hydrochloric acid was added, theoretically the amount necessary to form the hydrochloride of the amide. The apparatus was provided with a mechanical stirrer. It was found to be very important to have this stirrer project almost to the bottom of the jar in order that the mercury and the liquid amalgam subsequently present might be thoroughly stirred up and the most efficient contact with the solution obtained.

4500 g. of a 4% sodium amalgam was added gradually at the rate of 100 g. every 15 minutes. Each hundred g. of amalgam was accompanied by the addition of 20.5 cc. of 28% hydrochloric acid. This was a molecular equivalent of the amount of amalgam and kept the acidity of the solution almost constant. 980 cc. of 28% hydrochloric acid was required.

After the last addition had been made, the stirring was allowed to continue for 30 to 45 minutes. The solution was next made alkaline with caustic soda, filtered from sodium chloride and mercury and the ethyl alcohol was distilled off on a water bath. On the surface of the liquid in the flask the crude α-naphthyl-methyl alcohol appeared as a light brown oil which soon solidified on cooling. The readily soluble naphthylmethyl alcohol was easily separated from unchanged amide and other impurities by grinding up this cake in a mortar with a little ether and filtering. The ether was distilled off and the crude α-naphthyl-methyl alcohol was obtained. Yield, 46 g., 63%. M. p. 58–60°.

Thirty-two g. of amide was recovered, m. p. 188°. When recrystallized the m. p. was 202°.

Distillation.—Distilled at 10 mm. pressure, the boiling point was 193° and the distillate was a clear, almost colorless oil which solidified to pure white needles on cooling. M. p. 57–60°. Bamberger and Lodter[1] gave m. p. 59.5° and b. p. 301° at 715 mm.

α-Naphthaldehyde.[2]—After the last traces of ether, alcohol and water had been removed by distillation *in vacuo* on a water bath, 44 g. of the crude α-naphthyl-methyl alcohol was suspended in 330 cc. of 20% sulfuric acid. 10% of impurities was allowed for in calculating for the amount of sodium dichromate to be used which thus was found to be 25 g. This was dissolved in 330 cc. of water. The flask was vigorously shaken to form an emulsion of the aromatic alcohol in the acid, and the dichromate solution was added a few cc. at a time. Bamberger and Lodter added the solid dichromate, but this method did not work as well and gave lower yields. As the oxidation progresses, a very characteristic, penetrating aldehyde-like odor is emitted. After the last addition of the dichromate solution, the contents of the flask is quickly cooled and washed

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[1] *Loc. cit.*

[2] Bamberger and Lodter, *loc. cit.*

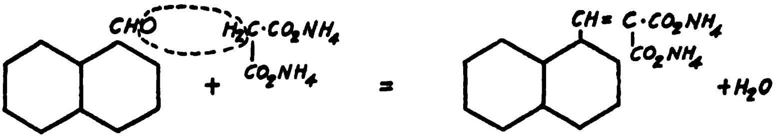
out and extracted with ether. After washing the extract with sodium carbonate solution and finally with water, the ether was distilled off and the product cooled. It was immediately stirred up with a freshly prepared saturated solution of sodium hydrogen sulfite and suddenly solidified to a yellowish cake. An excess of bisulfite solution was next added and the cake was stirred up to the form of a paste which was kept in the refrigerator overnight.

This aldehyde addition product was filtered and washed with alcohol and ether, and finally was ground up with ether in a mortar and washed and filtered again. It was then dried *in vacuo*. Yield, 36 g. of addition product plus some sodium hydrogen sulfite, or 17 g. of aldehyde, equivalent to 42%.

Oxidation to Naphthoic Acid.—A small quantity of the addition product was dissolved in water and treated with sodium carbonate solution. The product was then extracted with ether, which on evaporation yielded an oil that had a characteristic, penetrating, aldehyde-like odor. After standing exposed to the air, it soon lost its odor and crystallized. These crystals readily dissolved in sodium carbonate solution, and on acidifying the solution, were thrown out as a white precipitate. M. p. 158°. Pure α-naphthoic acid melts at 160°.

α-Naphthyl-acrylic Acid. (*1*) *Perkin's Synthesis.*[1]—The usual Perkin's synthesis as described in the literature was tried and various amounts of potassium acetate and acetic anhydride were used, with no improvement in the yield. Long heating (50–60 hours) was necessary and the product obtained was difficultly purified from tarry impurities. Yield, 45%.

(*2*) *α-Naphthyl-malonic Acid Method,*



The aldehyde itself was prepared from the addition product by dissolving 12.5 g. of the bisulfite compound in water (and filtering if any remained undissolved). The solution was then treated with an excess of sodium carbonate solution and finally was extracted with ether. After being washed with water, the ether extract was placed in a tared flask from which the ether was distilled off on a boiling-water bath and last traces removed *in vacuo*, which would leave the aldehyde free from any dissolved water or alcohol. After cooling, the flask was weighed and to the aldehyde (69) was added 6 g. of malonic acid. 24.4 cc. of 8% alcoholic ammonia was then added to the mixture slowly. The flask

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[1] Brandis, *Ber.*, **22**, 2153 (1889); Lugli, *Gazz. chim. ital.*, **11**, 393 (1881); Rousset, *Bull. soc. chim.*, [3] **17**, 813 (1896).

was cooled and vigorously shaken and soon the mixture became a crystalline paste. The flask was now provided with a return condenser and was heated on a water bath for 30 minutes, when all the crystals went into solution. Then the alcohol was distilled off and the last traces removed *in vacuo*. The product now existed as a slightly yellow cake.

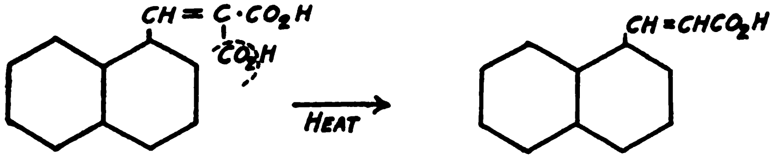
Save for a slight amount of tar, this solid was almost entirely soluble in water containing strong ammonia. A benzene extraction readily left the water solution clear after a filtration through a water-moistened filter paper.

The acid, precipitated with an excess of dil. sulfuric acid, filtered and washed free from mineral acid, was a white solid. The filtrate was evaporated to recover the slight amount of the acid which had shown itself to be slightly soluble in water.

Yield, 4.9 g., m. p. 185–187° with the evolution of carbon dioxide.

0.2762 g. of acid was titrated and required 0.0797 g. of sodium hydroxide. This value would indicate a molecular weight of 278 for a dibasic acid or 139 for a mono-basic acid. Naphthyl-malonic acid has a molecular weight of 242, while that of naphthyl-acrylic acid is 198. The obtained value would be correct for 65% malonic and 35% acrylic acids.

α-Naphthyl-acrylic Acid.—4.1 g. of the α-naphthyl-acrylic malonic acid mixture was heated on an oil bath at 210° to 215° for one hour. The product entirely melted at 190° with the evolution of a gas which gave a test for carbon dioxide. The residue soon crystallized on cooling and was a slightly colored mass of well formed needles that melted at 209–212°. Beautiful needles sublimed and clung to the neck of the flask. These melted at 207.5°. Yield, 3.54 g. From the aldehyde this is a 55.6% yield, a great improvement over Perkin's synthesis when the purity of the product is considered.

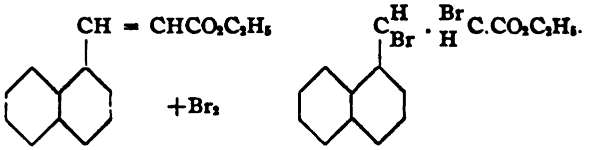


Oxidation of the Acrylic Acid.—To a cold sodium carbonate solution of a small amount of the acrylic acid, dil. potassium permanganate solution was added and was immediately decolorized. An excess was added and the test-tube was heated. The distinct odor of α-naphthaldehyde was very noticeable. When extracted with ether, an oily residue was left on evaporation of the ether. Saturated sodium hydrogen sulfite solution formed an addition product with this oil. After standing in the air the oil soon lost its aldehyde-like odor, and crystals were formed which dissolved in dil. sodium carbonate solution and were reprecipitated on acidifying the solution. This oxidation reaction of acrylic acids to lower aldehydes seems to be general for aromatic acrylic acids.

α-Naphthyl-acrylic Ester.—3.54 g. of α-naphthyl-acrylic acid was added to a flask containing a mixture of 36 g. of absolute alcohol and 4 cc. of conc. sulfuric acid (sp. gr. 1.84). The flask was provided with a return condenser and was heated for 8 hours on a water bath. One-half of the alcohol was then distilled off and the product was poured over finely ground ice to which had been added a solution of sodium carbonate just sufficient to neutralize both acids at the start of the esterification. The ester was quickly extracted with ether, washed with a little water and placed in a tared flask from which the ether was distilled and the last traces of alcohol and water removed *in vacuo* by heating on a water bath. The ester was a slightly brown viscous oil. Yield, 3.54 g., or 89%.

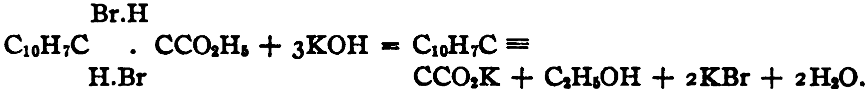
The unchanged acrylic acid was recovered.

α-Naphthyl-α,β-dibromo-acrylic Ester,



To a flask containing 3.54 g. of the acrylic ester 10 cc. of carbon disulfide was added. 25.05 g. of a 10% bromine solution in carbon disulfide was added from a dropping funnel while the flask was being vigorously shaken. The bromination was conducted in the sunlight and was hastened by the acid of a concave mirror. As each drop of the bromine solution struck the surface, it was almost immediately decolorized. The flask was allowed to stand in the sunlight after all of the bromine had been added. Then the carbon disulfide was distilled off and was only slightly pink colored from the trace of unchanged bromine. The ester dibromide soon solidified on standing.

α-Naphthyl-propiolic Acid,



$$C_{10}H_7\overset{\text{Br.H}}{\underset{\text{H.Br}}{C}}\;.\;CCO_2H_5 + 3KOH = C_{10}H_7C\equiv CCO_2K + C_2H_5OH + 2KBr + 2H_2O.$$

5.7 g. of the ester dibromide was dissolved in 45 cc. of 95% alcohol and 15.6 cc. of a 15.9% alcoholic potash was added. This made the alkali concentration about 4%. The flask was provided with a return condenser and was heated 6 hours on a steam bath. The alcohol was then distilled off and the product was evaporated to dryness. It was next taken up in a little water, which dissolved almost all of it but a small amount of tar. A benzene or carbon disulfide extraction left the solution entirely clear. To get rid of any dissolved solvent, the solution was warmed. Before acidifying, it was cooled with ice and then was made strongly acid with 20% sulfuric acid. The propiolic acid came down as a brownish oil, which on standing solidified to a porous, brittle solid. This when filtered and dried, did not show itself to be halogen free.

The filtrate was tested with silver nitrate and nitric acid and gave an abundant precipitate of silver bromide, which showed that bromine had been removed in the reaction.

Purification.—The solid was ground up with solid ammonium carbonate and the mixture was treated with a little water. The greater part went into solution and was filtered from a small amount of sticky substance through 3 thicknesses of filter paper. On precipitation, the acid came down as flakes, quite solid. Yield 2.4 g., or 85%. Still, it was not totally halogen-free as indicated by the Beilstein copper-gauze test. One crystallization from carbon tetrachloride, however, gave an acid absolutely halogen-free. M. p., 133–134°. A second recrystallization gave a m. p. of 134–135°. After having been recrystallized from carbon tetrachloride and twice from carbon disulfide the m. p. was 138–139°. However, a portion of the same lot, exposed to air and light, melted at 134–135° with decomposition. 0.062 g. neutralized 2.85 cc. of sodium hydroxide solution (1 cc. = 0.004444 g.) corresponding to a molecular weight of 196.

Properties.—Slightly yellowish white, well-formed microscopic needles from carbon tetrachloride in which it is very soluble hot and only sparingly soluble cold. It is very soluble in carbon disulfide.

Oxidation with Potassium Permanganate.—The following test was performed to distinguish this acid from the acrylic acid. Dil. potassium permanganate solution was immediately decolorized when added to a cold sodium carbonate solution of the pure propiolic acid. This shows it to be unsaturated. An excess of permanganate was added and the tube was heated. No odor of aldehyde could be detected whatsoever, nor did an ether extraction remove anything from the solution. The propiolic acid showed itself to differ in this respect as well as in its melting point from the acrylic acid.

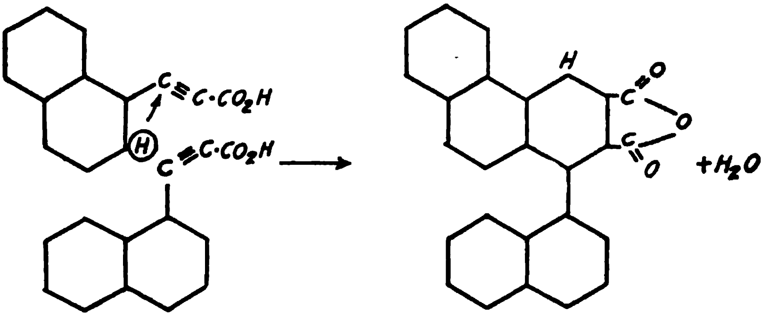
Action of Acetic Anhydride on the Propiolic Acid.

One-half g. of the propiolic acid was heated with 2 cc. of acetic anhydride and immediately went into solution. It was boiled on a return condenser for 5 hours. The solution was then evaporated to $^1/_2$ its volume by distilling off the acetic anhydride under diminished pressure. On cooling, the whole solidified to burr-shaped clusters of needles which, when pressed out on a porous plate and washed with glacial acetic acid, were pure white and melted at 207–209°. This compound showed itself to be saturated in that it would not reduce potassium permanganate in cold solution.

Sodium Salt of the Condensation Product.—Attempts to dissolve this product in sodium hydroxide were attended with great difficulties. Even long boiling failed to have any appreciably noticeable effect on it. The adding of a few drops of 95% alcohol served 2 purposes: it first dissolved a small amount of the compound so that it could come into more intimate contact with the alkali; then too, it helped completely to salt out the sodium salt which appeared as a white solid.

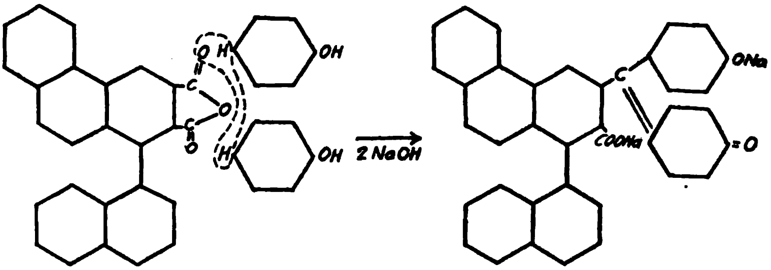
This sodium salt differed widely from any that had been met with in the whole series. First, it was exceedingly insoluble; and then after being dissolved after long boiling in water, it would not reduce potassium permanganate in cold solution.

From the theory already advanced, it is to be supposed that a condensation had taken place analogous to that of the phenyl-propiolic acid series, and that 2 molecules of α-naphthyl-propiolic acid had condensed to form an 8-α-naphthyl-phenanthrene-6,7-dicarboxylic anhydride as follows.



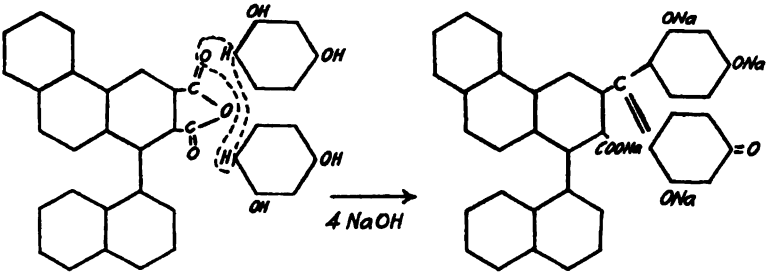
Proof of the Di-ortho Anhydride Condition.

1. **Baeyer's Phthalein Reaction.**—When a few crystals of the condensation product were heated with phenol and a few drops of conc. sulfuric acid, the resulting product was an indicator—red in alkaline solution and colorless in acid solution.



2. **Baeyer's Fluorescein Test.**—A small amount of the condensation product was heated with resorcinol and sulfuric acid for a few minutes. The product, on being poured on water made alkaline with sodium hy-

droxide, showed a very deep, reddish-green fluorescence. The reaction was in all probability as follows.



From all these tests and the extensive work of Michael and Bucher, it seems reasonable to suppose that the new product is 8-α-naphthyl-6,7-phenanthrene-dicarboxylic anhydride.

Summary.

I. It has been shown that α-naphthyl-propiolic acid can be prepared efficiently, satisfactorily, without great expense and in good yields, from commercial naphthalene as a starting point.

II. Incidentally, a satisfactory method has been found for obtaining α-naphthaldehyde, which has long been a most difficult compound to prepare.

III. It is of further interest that the treatment of saturated α,β-dibromo-naphthyl propionic ester with alcoholic potash readily removes both molecules of hydrogen bromide to form the propiolic acid, which is obtained halogen-free with very good yields by the use of ammonium carbonate. In the case of the analogous preparation of phenyl-propiolic acid, it is exceedingly difficult to remove the second molecule of hydrogen bromide.

IV. Finally, it has been shown that the action of acetic anhydride on α-naphthyl-propiolic acid produces a new compound that is saturated and has properties entirely different from the propiolic acid, and that the polymerization has probably produced an 8-α-naphthyl-6,7-phenanthrene-dicarboxylic anhydride.

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[CONTRIBUTION FROM THE FEDERAL POLYTECHNIC INSTITUTE, ZURICH, SWITZERLAND.]

PSEUDO-MUSCARINE ("SYNTHETIC MUSCARINE.")

BY ALBERT B. WEINHAGEN.

Received March 26, 1920.

Muscarine is a very powerful base occurring in the fly-agaric, (*Amanita muscaria*). A very small amount stops a frog's heart in diastole, an action which can be blocked or promptly relieved by atropine. In the fungus, the base is associated with choline, and since muscarine differs from choline merely by one additional atom of oxygen, Harnack[1] gave it the formula of the choline derivative, $OHN(CH_3)_3CH_2CH(OH)_2$. As a matter of fact, by evaporating choline with nitric acid, Schmiedeberg and Harnack[2] soon after obtained a base (synthetic or pseudo-muscarine) which stopped the heart in a similar manner to muscarine. This seemed to prove the supposition that natural muscarine and the oxidation product of choline are identical.

However, Boehm[3] and Honda[4] and H. Meyer[5] showed that there are differences between the pharmacological actions of the natural and the synthetic base, the most marked difference being that the latter has a distinct curare action upon the motor nerve terminations which the natural base lacks entirely. With a view towards a solution of this discrepancy, numerous investigations have concerned themselves with the compound obtained by evaporating choline with nitric acid. The compound was generally examined and described in the shape of the chloroplatinate itself.

Schmiedeberg and Harnack[6] thus obtained the chloroplatinate of "synthetic muscarine" to which they gave the formula $(ClN(CH_3)_3CH_2\text{-}CH(OH)_2)_2PtCl_4$, and when using more dilute acid, a by-product which they looked upon as nitro-oxyethyl-dimethylamine.

Nothnagel[6] isolated the same "synthetic muscarine" as Schmiedeberg and Harnack, and as a by-product obtained the nitrous acid ester of choline, $(ClN(CH_3)_3CH_2CH_2ONO)_2PtCl_4$. When using more dilute acid he obtained a by-product agreeing in many respects with that of Schmiedeberg and Harnack.

Schmidt and Wagner[7] found only the nitrous acid ester of choline.

Boehm[3] formulated his chloroplatinate of "synthetic muscarine" as Schmiedeberg and Harnack did theirs. This formula was furthermore corroborated or accepted by numerous other investigators.[8]

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[1] Harnack, *Arch. exp. Path. Pharm.*, 4, 168 (1876).

[2] Schmiedeberg and Harnack, *ibid.*, 6, 101 (1877).

[3] Boehm, *ibid.*, 19, 87 (1885).

[4] Honda, *ibid.*, 65, 454 (1911); 64, 72 (1910).

[5] Nothnagel and H. Meyer, *Arch. Pharm.*, 231, 261 (1893); *Ber.*, 26, 804 (1893).

[6] *Loc. cit.*

[7] Schmidt and Wagner, *Ann. Chem.*, 337, 37 (1904).

[8] Boehm, Honda, Nothnagel and Meyer, *loc. cit.* See also later references to Fuehner, Harmsen, Straub, Walter and Schott.

The problem was reinvestigated in 1914 by A. J. Ewins[1] and H. H. Dale[2] Ewins found but one chloroplatinate, *i. e.*, that of the nitrous acid ester of choline, $(ClN(CH_3)_3CH_2CH_2ONO)_2PtCl_4$. By a critical examination of the analytical data, Ewins showed that the "synthetic muscarine" of former investigators had all consisted of the nitrous acid ester of choline. Dale showed that the nitrous acid ester of choline exhibits precisely those pharmacological properties which previous investigators had ascribed to "synthetic muscarine." Ewins concludes that the action of conc. nitric acid upon choline in all cases leads to the formation of but one compound, the nitrous acid ester of choline.

My own investigation was originally based upon the supposition that "synthetic muscarine" might indeed be identical with the natural base, and that the additional curare-action and other divergences of the synthetic product might be due to the presence of active by-products. Some support had been lent to this supposition by the fact that I had previously isolated even trimethylamine from the products when preparing "synthetic muscarine," and, therefore, suspected the presence of intermediate decomposition products as well. In this paper are submitted the data of the most typical of a series of attempts with the above-mentioned action of nitric acid upon choline.

Experimental.

Pure choline chloroplatinate was prepared from the choline of egg lecithine, and from choline obtained by the method of Renshaw.[3] The characteristic 6-sided crystals contained by analysis 31.57 and 31.62% of platinum, respectively, as compared with the calculated 31.65%.

Sample I.

Here, as well as with the following samples, choline chloroplatinate was treated with nitric acid according to the original directions of Schmiedeberg and Harnack. The chloroplatinate (5.5 g.) was dissolved in nitric acid (sp. gr. 1.4) on the water bath and then evaporated to dryness on the sand bath. The resultant product was extracted successively with alcohol and several times with small amounts of cold water (these extracts being preserved for subsequent examination). The undissolved portion was fractionally recrystallized from hot water.

First Fraction (2.4 g.).—This, the least soluble fraction of chloroplatinate, crystallized in the shape of very minute octahedra and the combination of octahedron and cube. These small crystals could in no way be obtained larger. At times the octahedra intergrew end-to-end forming chains or large aggregates, generally in the shape of 4 papal crosses joined concentrically at right angles. By altering the concen-

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[1] A. J. Ewins, *Biochem. J.*, 8, 209 (1914).

[2] H. H. Dale, *J. Pharm. expt. Therap.*, 6, 147 (1914).

[3] Renshaw, THIS JOURNAL, 32, 128 (1910).

tration, etc., the aggregates could be converted into the small separate octahedra and *vice versa*. The salt was anhydrous. It melted with decomposition at 234° (bath 200°). One part dissolves in 103 parts of water at 20°. The chloroplatinate gave a distinct nitroso reaction (dark blue) with diphenylamine and sulfuric acid, and the chloride gave the Liebermann reaction.

Subs. (vacuum dried), 0.1853, 0.2199, 0.2125: Pt, 0.0534, 0.0637, 0.0613. Subs. 0.1628, 0.1688: AgCl, 0.2060, 0.2130.

Calc. for $(ClN(CH_3)_3CH_2CH_2ONO)_2PtCl_4$: Pt, 28.92; Cl, 31.57. Found: Pt, 28.81, 28.98, 28.83; Cl, 31.30, 31.28.

This was evidently the chloroplatinate of the nitrous acid ester of choline as described by Ewins.[1]

The salt is anhydrous and loses weight neither in vacuum over sulfuric acid nor when heated to 100°. The loss of weight occurring above 100° is evidently due to decomposition. A sample of 0.1450 g. kept at 130–140° lost 2.75% in 2 hours, 3.51% in 5 hours, 8.41% in 8 hours, and 12.62% when heated to 150°.

The Hydrochloride.—Several grams of chloroplatinate was decomposed with potassium chloride, and the hydrochloride extracted with alcohol. It is best recrystallized by adding ether to a hot concentrated alcoholic solution until the solution just begins to cloud. Upon cooling, the hydrochloride crystallized in clear, transparent, small prismatic needles and prisms which melted at 165°, and contained $2H_2O$. It gave the nitroso reaction.

Subs., 0.1153, 0.1380: AgCl, 0.0808, 0.0964. Found: Cl, 17.39, 17.28.
Calc. for $ClN(CH_3)_3CH_2CH_2ONO{:}2H_2O$: Cl, 17.34; H_2O, 17.60.

The water of crystallization cannot be determined directly, seeing that it is given off slowly and only at temperatures approaching the melting point, whereas at such temperatures the hydrochloride also splits off chlorine, *viz.*,

0.1206 g. vac. dry, dried 1 hr. at 130° lost 0.0000 g.
0.1206 g. vac. dry, dried 1 hr. at 160° lost 0.0106 g. = 8.79%.
0.1206 g. vac. dry, dried 3 hr. at 160° lost 0.0247 g. = 20.53%.
0.1206 g. vac. dry, dried 6 hr. at 160° lost 0.0302 g. = 25.04%.

The residue then gave 0.0447 g. AgCl, *i. e.*, 9.18% Cl. It will be noted that the loss of weight at 160° plus the chlorine left in the residue practically amount to the sum of chlorine plus water of crystallization required by the formula of the hydrochloride.

The Aurichloride.—This crystallized from very dil. hydrochloric acid in small, pointed flakes.

Subs., 0.1756, 0.1867: Au. 0.0732, 0.0784.
Calc. for $ClN(CH_3)_3CH_2CH_2ONO.AuCl_3$: Au, 41.71. Found: 41.68, 41.98, 41.71.

The Free Base.—The base was prepared by decomposing its phos-

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[1] *Loc. cit.*

photungstate. It represented a clear, faintly yellowish oil with a distinctly basic odor; it was hygroscopic; it rapidly absorbed carbon dioxide from the air; it is soluble in water and in alcohol, but insoluble in ether. When kept in vacuum over sulfuric acid, it crystallized in short, broad needles and in spear-shaped crystals which tended to join 4 concentrically at right angles. The base gave a distinct nitroso reaction with diphenylamine and sulfuric acid.

The Sulfate and the Perchlorate.—The former crystallized from water in hair-like crystals, the latter in thin, transparent flakes.

The Second, Third and Fourth Fractions (1 g.).—These 3 fractions of chloroplatinate proved to be identical with the first fraction.

Subs., 0.2092, 0.2659, 0.2726: Pt, 0.0602, 0.0770, 0.0785.
Found: Pt, 28.77, 28.97, 28.80.

The Fifth Fraction (0.4 g.).—This chloroplatinate crystallized in small, well-defined, clear-cut, 4-, 5- and 6-sided plates and in 3-cornered prisms. The crystals were orange-red, transparent and glistening, and did not effloresce in a vacuum over sulfuric acid. M. p. 204–205° without charring but with voluminous orange foam. The salt gave an intense nitroso reaction with diphenylamine and sulfuric acid.

Subs., 0.1332, 0.1121: Pt, 0.0385, 0.0324. Found: Pt, 28.83, 28.90.

Although the platinum content practically agrees with that of the nitrous acid ester of choline (see first 4 fractions), the distinct differences in crystal forms, pharmacological properties (see Summary), and other properties disprove such identity. This compound was probably identical with the nitro-oxyethyl-dimethylamine isolated by Schmiedeberg and Harnack.[1] $((CH_3)_2NCH_2CH_2ONO_2)_2H_2PtCl_6$ requires 28.79% Pt.

The Sixth Fraction (0.7 g.).—This, the last fraction, consisted entirely of trimethylamine chloroplatinate. It crystallized in what at first seemed to be medium-sized octahedron-cube combinations, but after some time could be recognized as thick 5- and 6-sided plates and combinations resembling the octahedron-cube type. It melted with decomposition at 235°, and was thus in all respects identical with trimethylamine chloroplatinate prepared for the sake of direct comparison. This chloroplatinate did not give a reaction with diphenylamine and sulfuric acid, and split off trimethylamine when treated with alkali.

Subs., 0.1777, 0.2682: Pt, 0.0657, 0.0988.
Calc. for $((CH_3)_3N)_2H_2PtCl_6$: Pt, 36.97. Found: 36.97, 36.84.

The Alcoholic Extraction.—The extracts resulting at the outset when the product of the reaction was washed with alcohol and with cold water were examined. The aqueous extract contained only unchanged choline chloroplatinate (0.2 g.). The alcoholic extract furnished 0.5 g. of chloroplatinate which crystallized from water in small plates, some pointed,

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[1] *Loc. cit.*

some oblong with indentations on the 2 shorter sides, some almond-shaped, and some like miniature arrow-heads. When recrystallized, it at times represented short prisms and prismatic needles and at times wedge-shaped flakes. It melted without charring at 186°. The chloroplatinate thus differs distinctly from that of the nitrous acid ester of choline and from that isolated in the fifth fraction.

Subs., 0.2283, 0.1347: Pt, 0.0656, 0.0385. Found: Pt, 28.73, 28.60.

It gave a distinct nitroso reaction with diphenylamine and sulfuric acid. As noted, only a very small amount of this compound was isolated.

Sample II.

Choline chloroplatinate was here treated with nitric acid as described in the case of Sample I, the sole difference being that it was evaporated with the acid 5 times instead of only once.

The First and Second Fractions.—The chloroplatinate of these fractions crystallized from water in cubes and short prisms, which could at times be converted into small plates, large striated flakes, and spear-shaped forms. It was anhydrous and melted with decompositions at 208°.

Subs., 0.1368, 0.1312, 0.1724: Pt, 0.0411, 0.0393, 0.0515.
Found: Pt, 29.97, 29.93, 29.88.

It will be noted that this chloroplatinate differs distinctly from that of the nitrous acid ester of choline as well as from that obtained in the remaining fractions of Sample I. The platinum contents, as a matter of fact, agrees very well with Schmiedeberg and Harnack's muscarine formulation, *viz.*, $(ClN(CH_3)_3CH_2CH(OH)_2)_2PtCl_4$, which requires 30.15%.

The Third and Fourth Fractions.—This chloroplatinate crystallized from water in very clear-cut, transparent, 4-, and 6-sided plates which effloresced in a vacuum over sulfuric acid. It will be noted that the chloroplatinate obtained in the fifth fraction of Sample I crystallized in plates which although very similar did not effloresce. The chloroplatinate gave a distinct nitroso reaction with diphenylamine and sulfuric acid. It melted without charring at 204°. The exact nature of this compound could not be determined.

Subs., (3) 0.1463, (4) 0.1130: Pt, (3) 0.0414, (4) 0.0320. Found: Pt, (3) 28.30, (4) 28.33.

The Fifth, Sixth, and Seventh Fractions.—These fractions, representing by far the greatest portion of compound here obtained, consisted of trimethylamine chloroplatinate.

Subs., (5) 0.1598, (6) 0.1454, (7) 0.1216: Pt, (5) 0.0588, (6) 0.0534, (7) 0.0448. Found: Pt, (5) 36.81, (6) 36.71, (7) 36.92.

Sample III.

Here 5 g. of choline chloroplatinate was treated with nitric acid precisely as described in the case of Sample I.

The First, Second, and Third Fractions.—These yielded 3.4 g. choline nitrous acid ester chloroplatinate (see Sample I, first fraction).

The Fourth and Fifth Fractions.—These yielded 1.3 g. of a chloroplatinate crystallizing from water in oddly-shaped aggregates formed exactly like miniature bird feathers, no matter how often recrystallized. The compound gave the nitroso reaction with diphenylamine and sulfuric acid. It melted with decomposition at 207°.

Subs., (4) 0.1711, (4) 0.1881, (5) 0.1566: Pt, (4) 0.0568, (4) 0.0625, (5) 0.0556.
Found: Pt, (4) 33.20, (4) 33.24, (5) 33.14.

The amount of this compound did not suffice for a definite chemical characterization, but it will be noted that the value found agrees for the nitrous acid ester of amino-ethyl alcohol (see Summary), *viz.*, $(NH_2\text{-}CH_2CH_2ONO)_2H_2PtCl_6$, which requires 33.10% of platinum.

The alcoholic extraction yielded a very small amount of the same compound as the alcoholic extraction in the case of Sample I.

Subs., 0.1088: Pt, 0.0313. Found: 28.77.

Sample IV.

Choline chloroplatinate was here treated with nitric acid precisely as in the case of Sample I.

The first 4 fractions yielded choline nitrous acid ester chloroplatinate (see Sample I, first fraction).

Subs., 0.1789: Pt, 0.0417. Found: Pt, 28.87.

The fifth and last fraction consisted exclusively of trimethylamine chloroplatinate.

Subs., 0.1866: Pt, 0.0687. Found: Pt, 36.81.

No further compound could be isolated in this attempt.

Sample V.

Here the nitrous acid ester of choline was obtained by the direct action of nitrous anhydride gas upon the free base choline suspended in dry chloroform. Upon evaporation at low temperature there was obtained a clear oily residue, which was dissolved in dil. hydrochloric acid and freed from traces of insoluble wax-like by-products by filtration. The chloroplatinate obtained from the filtrate was fractionally recrystallized.

The first 2 fractions (about 10% yield) consisted of the chloroplatinate of the nitrous acid ester of choline (see Sample I, first fraction).

Subs., 0.1614: Pt, 0.0568. Found: 28.99.

All subsequent fractions yielded unchanged choline chloroplatinate.

Subs., 0.2800, 0.1207: Pt, 0.0885, 0.0381.
Calc. for $(ClN(CH_3)_3CH_2CH_2OH)_2PtCl_4$: Pt, 31.65. Found: 31.62, 31.57.

It appears that the yield of choline nitrous acid ester by this method is at all times comparatively very small.

Summary.

These results show that the action of nitric acid upon choline chloroplatinate according to the original directions of Schmiedeberg and Harnack does not produce a single new compound, but that the product generally contains several new compounds as by-products. Furthermore, even small unintentional variations in the reaction cause a variation in the product resulting; and finally a deviation even merely to the extent illustrated by Sample II of this investigation can cause the formation of quite a different main product. Considering these facts, it would seem that many of the numerous exact qualitative and quantitative pharmacological examinations of "synthetic muscarine" thus prepared from choline (among these Honda,[1] Harmsen,[2] Boehm,[1] Fuehner,[3] Straub,[4] Meyer[1] Walter,[5] Schott,[6] etc.), should be considered with these facts in mind.

In the majority of cases, to be sure, when the original directions for the reaction are observed (Samples I, III and IV), the greater portion of the resultant product consists of the nitrous acid ester of choline. One cc. containing chloroplatinate equivalent to 0.8 mg. of the hydrochloride of this compound stopped the heart of a frog (subcutaneously; frog 38 g.) in diastole within 13 minutes. The arrest was momentarily relieved by atropine. This was found to be the minimum dose for complete arrest Boehm[1] and Honda[1] quote 0.5 to 1.5 mg. as the dose for "synthetic muscarine."

In addition to trimethylamine, there was isolated a secondary decomposition product (fifth fraction of Sample I), which was probably nitrooxyethyl-dimethylamine. This compound was without influence upon the rate of the frog heart. One cc. containing chloroplatinate equivalent to one mg. of hydrochloride of this compound (subcutaneously; frog 40 g.) did not affect the heart of a frog except that it showed a very slight and merely very temporary decrease of its rate. The successive injection of 6 additional mg. showed absolutely no influence upon the rate which had again become normal, whereas, as has been noted, as little as 0.8 mg. of choline nitrous acid ester suffice to stop the heart.

Another secondary decomposition product (fourth and fifth fractions of Sample III) seemed to be the nitrous acid ester of amino-ethyl alcohol, $NH_2CH_2CH_2ONO$. Seeing that choline is readily formed by methylating amino-ethyl alcohol,[7] it seems but natural that the reverse process

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[1] *Loc. cit.*

[2] Harmsen, *Arch. expt. Path, Pharm.*, 50, 361.

[3] Fuehner, *ibid.*, 59, 179 (1906); 61, p. 283.

[4] Straub, *Pflueger's Arch.*, 119, 127 (1907); 110, 492 (1905).

[5] Walter, *ibid.*, 78, 597 (1899).

[6] Schott, *Arch. expt. Path. Pharm.*, 65, 239 (1911).

[7] Trier, *Z. physiol. Chem.*, 80, 409 (1912).

might readily be induced by nitric acid in this instance. One cc. containing chloroplatinate equivalent to one mg. of the hydrochloride of this compound merely succeeded in decreasing the rate of a frog's heart (subcutaneously; frog 41 g.) from 40 to 32 per minute at the end of half an hour. The successive injection of 8 additional mg. merely decreased the rate to 24 per minute. Finally an attempt was made to stop this heart by injecting choline nitrous acid ester, of which 0.8 mg. normally suffice to stop a frog's heart. With this heart the injection of 0.8 mg. merely decreased the rate from 24 to 16; additional 1.6 mg. furthermore decreased it to 12, and this rate could not be further decreased even by 2 additional injections of 1.6 mg. each. The heart thus continued at the rate of 12 beats per minute even after 5.6 mg. of choline nitrous acid ester had been injected. The compound evidently had an action antagonistic to the muscarine action of choline nitrous acid ester. The test was repeated with similar results.

A further by-product was isolated from the alcoholic extracts (Samples I and II). The platinum contents were very similar to those of choline, nitrous acid, ester, chloroplatinate, but the crystal forms, melting points, etc., disprove such identity. The nature of this compound could not be established.

By deviating from the original directions as illustrated by Sample II, the formation of the nitrous acid ester of choline was circumvented entirely. The main product here (first and second fractions) agreed in platinum contents with the requirements of Harnack's muscarine formula, $(OH)N(CH_3)_3CH_2CH(OH)_2$. Seeing that the greater portion of choline was decomposed to trimethylamine, the yield of base was very small.

As an additional product there was in this case (third and fourth fractions, Sample II) obtained a chloroplatinate which differed from all the by-products so far obtained. In spite of great similarity, it differs (efflorescence and platinum contents) also from the chloroplatinate of the fifth fraction of Sample I. One cc. containing chloroplatinate equivalent to one mg. of the hydrochloride of this compound (subcutaneously; frog 36 g.) had no influence upon the rate of a frog's heart. Similarly, the successive injection of 4 additional mg. had practically no effect, whereas the final injection of one mg. of choline nitrous acid ester quickly brought diastolic arrest, thus showing that there was here no antagonism, as opposed to the compound of the fourth fraction of Sample III.

In Sample V it was shown that choline nitrous acid ester can be obtained by the interaction of nitrous acid anhydride and the base choline, but that the yield by this method is very small.

It may be noted that the chloroplatinate of the first and second fractions of Sample II, although agreeing therewith tolerably well as regards platinum contents, differ distinctly from the chloroplatinate of natural muscarine in crystal forms, the latter crystallizing in octahedra which have no definite melting point.[1]

[Contribution from the Division of Agricultural Biochemistry, Minnesota Agricultural Experiment Station.]

THE COLORIMETRIC ESTIMATION OF TYROSINE BY THE METHOD OF FOLIN AND DENIS.[2]

By Ross Aiken Gortner and George E. Holm.

Received April 12, 1920.

Folin and Macallum,[3] in 1912, noted that uric acid and phenols produced a deep blue color in solutions of phosphotungstic acid when alkali was subsequently added. This observation was rapidly followed by a paper by Folin and Denis[4] in which they give detailed directions for the preparation of 2 reagents, one of which contains phosphotungstic acid and the other both phosphotungstic and phosphomolybdic acids. The former reacts with uric acid but not with monohydric phenols including tyrosine, while the latter reagent produces a beautiful blue color with phenol solutions, the reaction, according to Folin and Denis, being unmistakably positive with 1 part of tyrosine in 1,000,000 parts of water.

In a third paper Folin and Denis[5] apply the phenol reagent to the colorimetric estimation of tyrosine in proteins, without, however, reporting any careful quantitative study of the reagent when pure tyrosine was used. In all some 27 proteins were tested for tyrosine content by the new reagent and in every instance more tyrosine was found than was recorded in the literature from gravimetric determinations. The average percentage of tyrosine found was 5.065% by the colorimetric method and 2.647% by the gravimetric method for the 20 proteins where both figures are available. Folin and Denis express their belief that tyrosine is the only component of the proteins which reacts with the phenol reagent and that the colorimetric method gives an accurate measure of the amount of tyrosine present.

Shortly after Folin's paper appeared Abderhalden and Fuchs[6] and Abderhalden[7] stated that tryptophane, oxytryptophane and oxyproline

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[1] A. J. Ewins, *Biochem. J.*, 8, 209 (1914).

[2] Published with the approval of the Director as Paper No. 203, Journal Series of the Minnesota Agricultural Experiment Station. Presented before the Division of Biological Chemistry at the Spring Meeting of the American Chemical Society, St. Louis, April 12–16, 1920.

[3] *J. Biol. Chem.*, 11, 265–6 (1912).

[4] *Ibid.*, 12, 239–243 (1912).

[5] *Ibid.*, 12, 245–251 (1912).

[6] *Z. physiol. Chem.*, 83, 468 (1913).

[7] *Ibid.*, 85, 91 (1913).

likewise gave the blue color with Folin's phenol reagent and that, if these amino acids were present, reliable tyrosine values could not be obtained.

Only recently Johns and Jones[1] have reviewed the previous work. They point out that Abderhalden's criticism is based on qualitative tests. Consequently they proceed to make a quantitative study of the behavior of tryptophane. They state:

> "It is true that tryptophane gives a blue color with the reagent of Folin and Denis, but the intensity of the color is much less than that given by an equivalent weight of tyrosine. It is well known that tryptophane is decomposed by acid hydrolysis. To ascertain whether this decomposition is complete and that the decomposition products do not give a color with the reagent of Folin and Denis, the following experiment was made: 5% of tryptophane was added to 0.5 g. of kafirin, and the mixture was boiled with 20% hydrochloric acid for 12 hours. The tyrosine in the hydrolysate was estimated by the method of Folin and Denis and was found to be 4.36%. A hydrolysis of kafirin, performed under similar conditions without the addition of tryptophane, gave 4.84% of tyrosine. Hence the tryptophane was completely decomposed and its decomposition products gave no blue color with the reagent of Folin and Denis. It is also to be expected that oxytryptophane, if present, would be decomposed by acid hydrolysis, since the presence of the hydroxyl group would probably render it less stable than tryptophane. A sample of gelatin to which tryptophane had been added was also hydrolyzed. The blue color obtained with the reagent of Folin and Denis was of the same intensity as that obtained by a control hydrolysis where no tryptophane was added. The faint blue color obtained from the hydrolysate of the gelatin was probably due to tyrosine since the gelatin gave a distinct test for tyrosine with Millon's reagent.
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> Abderhalden states that *l*-oxyproline gives a blue color with the reagent of Folin and Denis. On the other hand, Folin and Denis obtained only a faint blue color from the hydrolysate of gelatin which contains 3 to 6 % of oxyproline. This color was probably due to tyrosine. We tested a number of high-grade samples of gelatin and did not find one that did not respond to the test for tyrosine with Millon's reagent. Even gelatin prepared from carefully cleaned cartilaginous rings of ox trachea gave a decided test for tyrosine."

Johns and Jones, therefore, conclude that reliable values for the tyrosine content of a protein can be obtained by the use of Folin's phenol reagent.

We recently desired to estimate the amount of tyrosine remaining in a series of mixtures of pure amino acids which had been boiled for some time in the presence of hydrochloric acid, and in some instances in the presence of formaldehyde. Tyrosine was present in 3 of the mixtures, tryptophane was present in 2, while in one neither tyrosine nor tryptophane was present.[2] The samples in which the "tyrosine" content was measured were the solutions of the "bases" and the "filtrate from the bases" as separated by Van Slyke's method.[3]

In certain of the experiments our method of work was such that all

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[1] *J. Biol. Chem.*, 36, 319–322 (1918).

[2] For a composition of the mixture see Gortner and Holm, "The Origin of the Humin Formed by the Acid Hydrolysis of Proteins. V," THIS JOURNAL, 42, 821–27 (1920).

[3] *J. Biol. Chem.*, 10, 15–55 (1911).

tyrosine had been removed from the soutions *before* testing with the phenol reagent.[1] What was our surprise, therefore, to find that both the "bases" and the "filtrate from the bases" gave, in every instance, a blue color with Folin's phenol reagent, this being the case even in the mixture where no tyrosine was present. We accordingly felt justified in regarding the color developed in this last instance as a "blank" and by subtracting the value of the color developed in the "blank" from the remaining experiments of the series we found that practically 100% of the tyrosine added was present in those solutions to which tyrosine but no aldehyde had been added, while in corresponding solutions to which aldehyde had been added no tyrosine remained. The added aldehyde, therefore, had quantitatively removed 100 mg. of tyrosine, or at least changed it so that it no longer gave a color with the phenol reagent, but besides the tyrosine there was still some compound present in each solution which reacted with the phenol reagent but which was not tyrosine. We therefore decided to make a careful quantitative study of the effect of various amino acids, and of various other factors upon the development of the blue color in solutions containing the phenol reagent.

Experimental.

The Reagent.—A large quantity of Folin's phenol reagent was prepared exactly as outlined by Folin and Denis.[2] 100 g. of sodium tungstate, 20 g. of phosphomolybdic acid, and 50 cc. of 85% phosphoric acid were added to 750 cc. of distilled water and the mixture was refluxed for 2 hours and then diluted to one liter. Folin and Denis'[3] directions for the use of this reagent in the quantitative estimation of tyrosine in proteins are as follows.

> "One gram of the dry protein is accurately weighed out and transferred to a 500-cc. Kjeldahl flask, 25 cc. of 20% hydrochloric acid is then added, the flask closed by means of a Hopkins condenser made from a large test-tube, and the contents of the flask boiled for twelve hours over a microburner. At the end of this time the flame is removed, the contents of the flask transferred on cooling to a 100 cc. volumetric flask and made up to volume. One or two cubic centimeters of this solution are then transferred to a 100-cc. volumetric flask, 5 cc. of the tyrosine reagent added, and after five minutes, 25 cc. of a saturated solution of sodium carbonate, and the mixture then made up to volume with cold tap water. The maximum color develops in about ten minutes. Therefore, the reading should not be made before this time has elapsed. Fading is very slow in the presence of the large excess of reagent used. As nearly at the same time as possible a standard is prepared by treating 1 mgm. of pure tyrosine with 5 cc. of the phosphotungstic-phosphomolybdic reagent, then adding 25 cc. of saturated sodium carbonate solution and making up to volume. The color comparison is made by means of a Duboscq colorimeter, the standard solution being placed at 20 mm.

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[1] The tyrosine had been combined with formaldehyde to form "soluble humin." See Gortner and Holm, *loc. cit.*

[2] *J. Biol. Chem.*, 12, 239–43 (1912)

[3] *Ibid.*, 12, 245–251 (1912).

As a standard solution, we use a solution of pure tyrosine in decinormal hydrochloric acid which is made of such a concentration that 5 cc. contain 1 mgm. of tyrosine."

We have followed these directions with the following exceptions. (1) Distilled water was used in ever instance instead of tap water. (2) 10 cc. of the reagent was used instead of the 5 cc. recommended by Folin and Denis. The reasons for this variation will be given later. (3) All readings were made with a Kober colorimeter, carefully adjusted and standardized.

Qualitative Tests on Amino Acids.—Our first tests were purely qualitative and we obtained, using 50 mg. of the amino acid, deep blue solutions from tyrosine, tryptophane, arginine, lysine hydrochloride and proline; light blue solutions from phenyl alanine, cystine, histidine and alanine; and pale blue solutions from serine (synth.) and valine, while leucine, glycine, aspartic acid and glutamic acid gave no color. We were aware that our arginine and proline were not absolutely pure and to date we have failed to obtain these amino acids in such a degree of purity that we fell justified in accepting the color values as final. We may say, however, that as purification has proceeded the color-producing power has, in some measure, decreased, indicating that at least a part of the color-producing power may have been due to an impurity. Likewise, our lysine dihydrochloride, while apparently pure, had been prepared from the picrate so that even though it gave no Millon's test, we have omitted this amino acid from our final studies. By careful manipulation we obtained a Millon's reaction with the phenylalanine and alanine so that their reaction was probably due, in part at least, to traces of tyrosine.

Preliminary Quantitative Experiments.—The qualitative experiments were repeated using 100 mg. of each amino acid. In these experiments only 5 cc. of Folin and Denis' reagent was used. The color values were read against a standard of one mg. of tyrosine + 5 cc. of the reagent. The results are shown in Table I. *This table is of value only in indicating that amino acids analyzing 100% pure by our accepted methods of analysis may actually contain as much as 1% (as in the case of phenylalanine isolated from protein) of some other amino acid.*[1]

The table also indicated that any interference of the other amino acids with a tyrosine determination would be practically negligible. However, we could detect no tyrosine in our tryptophane preparation. Inasmuch as we had available 7 samples of typtophane which had been prepared by various workers at different times, we decided to see whether the color was due to tryptophane itself or to a tyrosine contamination, since it appeared improbable that all samples would be contaminated to an equal

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[1] The high values for arginine and proline are ignored because, as stated above, we knew that these amino acids were somewhat impure. The color values for tryptophane, as will be shown later, are not due to an impurity but to the tryptophane itself.

TABLE I.

The Color Equivalent of the Various Amino Acids Tested. (100 mg. of amino acid + 5 cc. of Folin and Denis' Reagent to 100 cc. Volume.)

Amino acid.	Color intensity equivalent to mg. tyrosine.[1]
Tryptophane	2.5
Arginine	1.48
Proline	1.40
Phenyl alanine	1.17
Phenyl alanine (synth.)	0.075
Alanine	0.60
Alanine (synth.)	None
Cystine	0.21
Histidine dihydrochloride	0.16
Serine (synth.)	0.15
Valine	0.085
Glycine	Trace
Leucine	None
Glutamic acid	None
Aspartic acid	None

[1] See statement in text regarding these color values.

degree. In this new experiment we used quantities of tryptophane varying from 20 to 50 mg. with amounts of phenol reagent varying from 2.5 to 5 cc. The resulting solutions were made to a volume corresponding to a concentration of one mg. of the tryptophane in each cc. of final volume. The results are shown in Table II.

TABLE II.

Color Value of Different Samples of Tryptophane Under Various Experimental Conditions.

Sample.	Tryptophane. Mg.	Vol. reagent. Cc.	Final vol. Cc.	Color value. 100 mg. tryptophane = mg. tyrosine.
1	50	2.5	50	2.5
2	25	2.5	25	4.71
3	20	2.5	20	6.09
4	50	5.0	50	4.83
5	50	5.0	50	4.80
6	50	5.0	50	5.09
7	50	5.0	50	4.97

It will be noted that *Samples 2, 4, 5, 6 and 7 gave almost identical color values, that Sample 1, which gave only half of the color value, contained only $^1/_2$ as much phenol reagent, and that Sample 3, which had 25% excess of reagent, gave 24.8% more color.* In other words, all samples were apparently identical and the color developed was dependent on a ratio of amino acid to the phenol reagent. By doubling the amount of reagent the color increased approximately 100%. This suggested a quantitative study of the effect of concentration of the amino acid on the color produced when all other factors, such as volume of reagent, final volume, etc., were kept constant.

The effect of concentration of reactive substance upon color depth. Insofar as we are aware, no study of the relation of color intensity to concentration of reactive substance has been made, although the phenol reagent has been used by various workers. Folin and Denis[1] state, "two cubic centimeters will give the maximum color with 1 mg. of tyrosine or uric acid," but give no data to show exact relations between color and concentration of reagents.

We have, therefore, measured the depth of color produced in solutions of tyrosine, tryptophane, uric acid, ferrous iron, and α-methyl indole in the presence of the phenol reagent. In every instance 10 cc. of the phenol reagent, 25 cc. of sodium carbonate and a final volume of 100 cc. were used, the only variable being the reactive organic compound which was used in concentrations ranging from 0.5 mg. to 100 mg. The colors in every instance were read against a tyrosine standard of one mg. of tyrosine + 10 cc. of reagent in a final volume of 100 cc. Table III shows the colori-

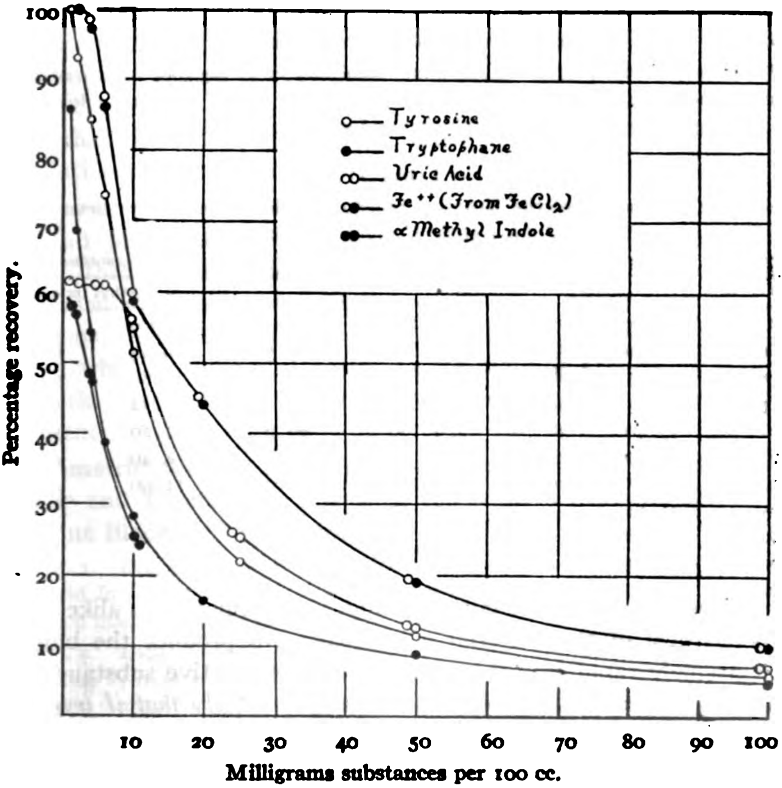

Fig. 1.—Showing the relation of color developed by the Folin-Denis phenol reagent to the concentration of reactive material.

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[1] *J. Biol. Chem.*, 12, 240 (1912).

metric ratios which were obtained. These data were recalculated so as to show the percentage of material which would have been indicated on the basis of the colorimetric data, using a tyrosine standard. These figures are given in Table IV and in the form of curves in Fig. 1.

TABLE III.

Showing the Relation of Final Color Depth to Concentration of Reactive Materials.

Concentration of substance in 100 cc. of final volume.	Ratio of color developed in solutions of the following substances at different concentrations to the color of the standard tyrosine solution.					
					α-Methyl indole.[1]	
Mg.	Tyrosine.	Tryptophane.	Uric acid.	Fe''.	Mg. indole.	Color ratio.
1	1.00	0.858	0.614	0.995	0.44	0.272
2	1.859	1.370	1.157	2.072	0.88	0.515
4	3.365	2.162	2.427	3.885	1.32	0.760
6	4.404	2.326	3.649	5.162	2.20	1.250
10	5.150	2.798	5.492	5.883	4.40	2.075
20	...	3.278	...	8.800	11.00	2.631
25	5.460	...	6.290	....	...	...
50	5.741	4.520	6.410	9.526	...	...
100	5.741	4.900	7.092	10.000	...	...

[1] The α-methyl indole has a maximum solubility of 22 mg. per 100 cc. of solution. Therefore, no more than 11 mg. could be used in our work (50 cc. of indole solution, 10 cc. of reagent, 25 cc. of Na_2CO_3 solution and water to 100 cc.).

TABLE IV.

Showing the Percentage of the Reactive Substance which would have been Indicated by the Color Depth, Using a Tyrosine Standard.

Concentration of substance in 100 cc. of final volume.	Percentage of reactive substance "recovered" by colorimetric measurement.					
					α-Methyl indole.	
Mg.	Tyrosine.	Tryptophane.	Uric acid.	Fe''.	Mg. indole.	%.
1	100.00	85.84	61.40	99.5	0.44	61.83
2	92.95	68.50	57.90	103.6	0.88	58.57
4	84.13	54.05	60.70	97.1	1.32	57.57
6	73.40	38.76	60.80	86.0	2.20	56.83
10	51.50	27.98	54.92	58.8	4.40	47.15
20	....	16.39	...	44.0	11.00	23.92
25	21.84	...	25.16	...	...	...
50	11.48	9.00	12.82	19.0	...	...
100	5.74	4.90	7.09	10.0	...	...

It will be noted that the curves in Fig. 1 are remarkably alike and that the percentage of the material which reacts to produce the blue color falls extremely rapidly as the concentration of reactive substance in the solution is increased. *These curves show conclusively that if tryptophane or any other easily oxidizable substance is present, color values will be obtained almost, if not quite, as great as those given by tyrosine itself, and that, therefore, tyrosine can be estimated colorimetrically only if all other easily oxidizable substances, such as tryptophane, ferrous iron, etc., are known to be absent.* In addition, it is unsafe to assume that the color given by an aliquot is an accurate measure of the reactive material which is present, for if an aliquot actually contained 25 mg. of tyrosine a colorimetric reading, under the conditions of our experiments, would record the presence of only 5.46 mg. In our experiments we used 10 cc. of the reagents which, according to Folin and Denis, should be sufficient to give the maximum color with 5 mg. of tyrosine, but according to our curves, if 5 mg. had been present the color developed would have indicated the presence of only 3.90 mg.

Our study of the reaction of α-methyl indole was undertaken to ascertain whether or not the color was due to the presence of the indole nucleus. Folin and Denis[1] state that indole and its derivatives do not react with the reagent. This is certainly an error. We did not have sufficient pure indole to justify our taking our entire supply to make a quantitative study of the color values at the various concentrations, but a single quantitative test of a one mg. sample of pure white crystalline material gave a color value equal to 0.71 mg. of tyrosine, or approximately equal to the color value of tryptophane. We did have a considerable amount of pure α-methyl indole and, therefore, ran our quantitative color curve with that material, with the result that we have conclusively demonstrated that the indole nucleus will react with the phenol reagent and give relatively high color values.

In view of the results which we obtained, it seemed remarkable that Johns and Jones should have arrived at a conclusion diametrically opposed to that indicated by our data. In looking over their paper for some reason why they obtained the results upon which they base their conclusions, we observed that *they decolorized their hydrolysate with carbon (Norite)*, whereas Folin and Denis do not mention the use of carbon or bone black. We therefore decided to repeat and amplify Johns and Jones' experiment.

Colorimetric Studies of Gelatin with and without the Addition of Tyrosine and Tryptophane and with and without Previous Decolorizing with Bone Black.—The following solutions were prepared for this work.

Expt. 1. One g. of gelatin was hydrolyzed by boiling with 25 cc. of 20% hydrochloric acid for 12 hours. The acid was then removed by evaporation *in vacuo* and the solution made to 100 cc. volume.

Expt. 2. Expt. 1 was repeated with the exception that 20 mg. of tryptophane was added before hydrolysis.

Expt. 3. Expt. 2 was repeated with the exception that the hydrolysate was decolorized with one g. of acid-washed bone black after the excess of hydrochloric acid had been removed and before making to the final volume.

Expt. 4. Expt. 2 was repeated, using 20 mg. of tyrosine instead of 20 mg. of tryptophane.

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[1] *J. Biol. Chem.*, 12, 241 (1912).

Expt. 5. This experiment was a duplication of Expt. 3 with the exception that tyrosine was used instead of tryptophane.

Expt. 6. This experiment was a duplication of Expt. 5 with the exception that untreated bone black was used, *i. e.*, the calcium phosphate was not previously removed by washing the bone black with hydrochloric acid.

The results of the colorimetric study are given in Table V, the concentration of reagents being the same as we have used above. The data of Table V are shown graphically in the form of curves in Fig. 2. In Fig. 3 are shown the curves for percentage recovery of the added tyrosine and tryptophane. These figures were arrived at by subtracting the values of the color present in the hydrolysate where only gelatin was present from the corresponding values obtained in the hydrolysates when tyrosine or tryptophane had been added.

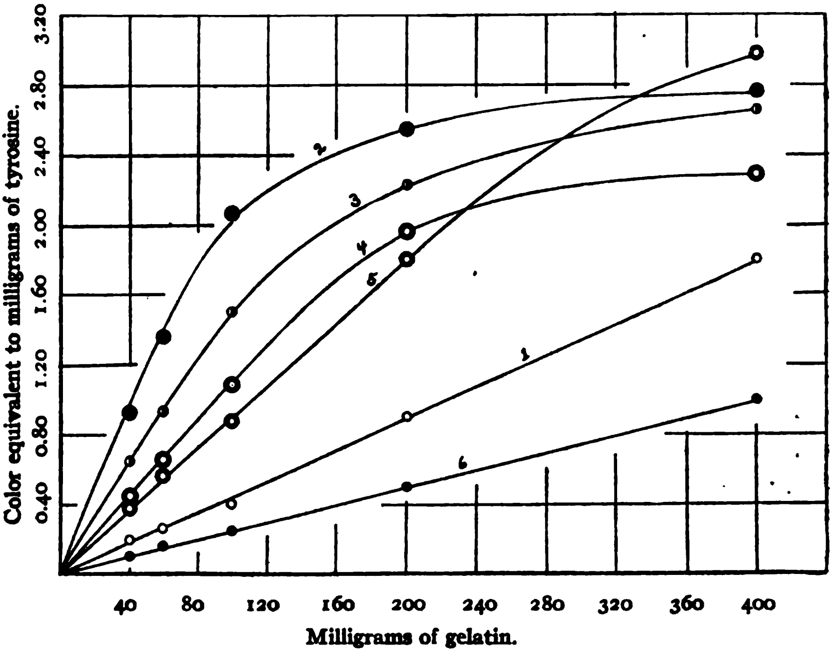

Fig. 2.—Showing quantitative changes in color produced by Folin's phenol reagent in hydrolyzates of gelatin and of gelatin + tyrosine and tryptophane, respectively. The curves also show the diminution of color values when the hydrolyzates have been treated with bone black.

1. Gelatin only.
2. Gelatin + 20 mg. of tyrosine per g. of gelatin.
3. Gelatin + tyrosine, hydrolyzate cleared with untreated bone black.
4. Gelatin + tyrosine, hydrolyzate cleared with acid-washed bone black.
5. Gelatin + 20 mg. of tryptophane per g. of gelatin.
6. Gelatin + tryptophane, hydrolyzate cleared with acid-washed bone black.

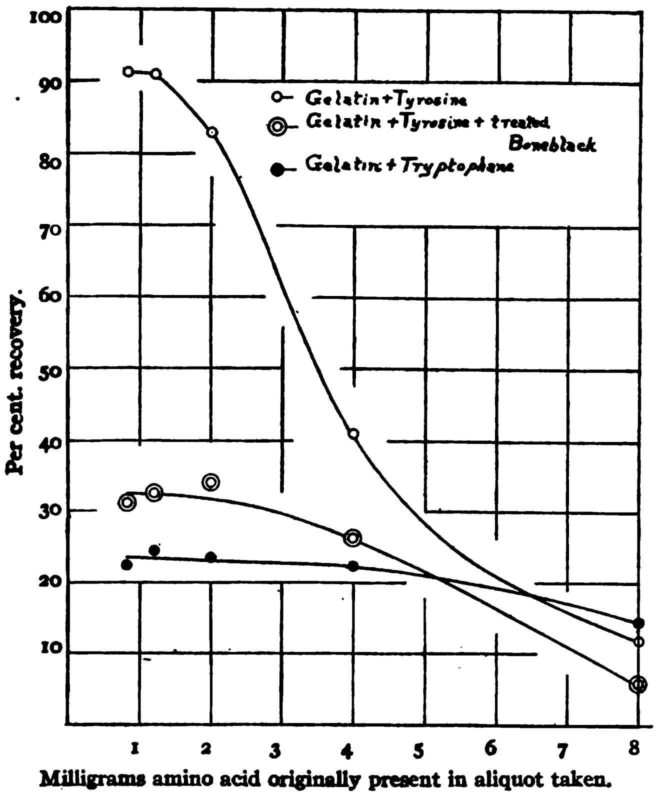

Fig. 3.—The percentage recovery, measured colorimetrically, of tyrosine and tryptophane when added to gelatin. Correction has been made for the color produced by gelatin alone.

TABLE V.

The Color Intensities of Various Dilutions of the Solutions in Expts. 1 to 6 Inclusive, as Compared with a Standard Tyrosine Solution Containing 1 mg. of Tyrosine (1 mg. Tyrosine = 1).

Aliquot taken contained gelatin. Mg.	Expt. 1. Gelatin only. Color intensity.	Expt. 2. 1 g. of gelatin + 20 mg. of tryptophane. Color intensity.	Expt. 3. 1 g. of gelatin + 20 mg. of tyrosine + acid-washed bone black. Color intensity.	Expt. 4. 1 g. of gelatin + 20 mg. of tyrosine. Color intensity.	Expt. 5. 1 g. of gelatin + 20 mg. of tyrosine + acid-washed bone black. Color intensity.	Expt. 6. 1 g. of gelatin 20 mg. of tyrosine + untreated bone black. Color intensity.
40	0.20	0.38	0.13	0.93	0.45	0.65
60	0.268	0.562	0.164	1.36	0.66	0.94
100	0.408	0.879	0.250	2.07	1.09	1.50
200	0.907	1.801	0.508	2.55	1.96	2.23
400	1.810	2.980	1.040	2.77	2.29	2.66

This study makes it apparent why Johns and Jones arrived at the conclusions which they published. It will be noted that the color values for gelatin alone when plotted form a straight line, indicating that with 400 mg. of gelatin present there is still a direct proportionality of color produced. This is a strong indication that the compounds which react with the reagent to produce color are present in gelatin in minimal amounts. We have recently shown[1] that in all probability our sample of gelatin contains approximately 0.035% of tryptophane and 0.47% of tyrosine, figures which are in excellent agreement with the present color values where a content of 0.45% of tyrosine + tryptophane is indicated. These values are also a strong indication that proline or oxyproline does not produce appreciable color values with the phenol reagent, contrary to the belief of Abderhalden and Fuchs.[2] When, however, tryptophane is added, *and the solution is not treated with carbon or bone black*, there is a sharp rise in the color values up to approximately 25% of the color value of the added tryptophane. The reason why 100% of the added tryptophane was not recovered is perfectly obvious if our previous publications on humin formation are kept in mind. We have shown[3] that the black acid insoluble humin of a protein hydrolysate is due to the presence of tryptophane in the protein. We have also shown that proteins apparently contain some unknown factor, perhaps an aldehyde, which induces humin formation. This unknown factor is present in small quantities in our sample of gelatin.[4] Therefore, in the present experiment, although we added 20 mg. of tryptophane, a part of the tryptophane was converted into insoluble humin and only the remaining portion reacted with the phenol reagent. However, in our calculations we used the 20 mg. as 100 %, whereas probably 15 mg. had been converted into insoluble humin and only 4.5 mg. (basing our calculation on the color values at 200 mg. of gelatin) or 22.5% of the added tryptophane remained to react with the phenol reagent. If this reasoning be true, our color values actually record quantitatively the amount of tryptophane which was not converted into insoluble humin. At any rate, the data show that tryptophane which we added does increase the color values practically 100%.

When, however, we investigate the color values for the corresponding hydrolysate which has been treated with bone black, we find that not only is there no added color value, due to the added tryptophane, but that *the color depth is less in the decolorized solution of the hydrolysate of gelatin + tryptophane than it is in the hydrolysate of gelatin alone.* In other words, the carbon which Johns and Jones used removed not only all of the tryptophane which they added but also some of the tyrosine and tryptophane

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[1] Holm and Gortner, THIS JOURNAL, 42, 637 (1920).

[2] *Loc. cit.*

[3] Gortner and Blish, THIS JOURNAL, 37, 1630–1636 (1915); Gortner, *J. Biol. Chem.*, 26, 177–204 (1916); Gortner and Holm, THIS JOURNAL, 38, 2477–2501 (1917); 42, 632–640, 821–827 (1920).

[4] Holm and Gortner, *ibid.*, 42, 639 (1920).

originally present in their proteins, so that the color values which they obtained were less in the decolorized hydrolysate to which tryptophane was added than in the original protein hydrolysate to which no tryptophane was added. They conclude from their findings that "tryptophane is completely decomposed during the hydrolysis of proteins and the decomposition products do not interfere with the determination of tyrosine by the method of Folin and Denis." As a matter of fact, (1) tryptophane is not[1] completely decomposed during the hydrolysis of proteins; (2) certain of the decomposition products do give colors with the reagent of Folin and Denis, but the explanation of Johns and Jones' findings lies in the fact that the carbon which they used adsorbed both tyrosine and tryptophane, together with decomposition products, so that their color values were not the true color values for the hydrolysates under investigation.

This adsorption of amino acids by bone black is shown very markedly by Curves 2, 3 and 4 of Fig. 2. It is interesting to note that untreated bone black apparently adsorbs less tyrosine than does bone black which has been washed with hydrochloric acid to remove calcium phosphate. Such, however, is not necessarily the case and only illustrates the ease with which a false conclusion may be reached. The reason why the untreated bone black gives more intense color values lies in the fact that the *untreated bone black contains some substance capable of giving an intense blue color with the phenol reagent.* The acid washnigs of bone black react with the phenol reagent to form blue solutions. This is probably due to ferrous iron inasmuch as the acid washings decolorize permanganate and also give a blue color with Folin and Denis' uric acid reagent just as does ferrous iron. Probably the iron originally present in the bones was reduced to metallic iron by ignition in the presence of the carbon and this reduced iron dissolves in acid solutions to give ferrous ions. Because of the presence of this ferrous iron the unwashed bone black, Curve 3, Fig. 2, represents the balance between the adsorption of amino acids which reduces the color intensity, and the addition of ferrous salts which intensifies the color. We have not thought it worth while to investigate the quantitative relationships of these 2 opposing factors. The fact, however, that when one adds bone black to an acid solution he adds at the same time ferrous iron should be taken into account in future work. Perhaps some of the properties of "active" bone black are in reality due to the presence of reduced iron.

Discussion.

From the foregoing data it becomes perfectly obvious that the phenol reagent of Folin and Denis cannot be used to estimate colorimetrically the tyrosine content of a protein unless it is absolutely certain that no

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[1] A study detailing additional evidence on these points will be published as a subsequent paper.

other substances are present which will react with the phenol reagent. Inasmuch as tryptophane and certain tryptophane decomposition products will react to produce almost as much color depth as an equal weight of tyrosine, and inasmuch as we know that tryptophane is a normal constituent of most proteins, it is not surprising that Folin and Denis found values for the tyrosine content of proteins, measured colorimetrically, far in excess of the values obtained by gravimetric determinations.

Whether or not there are other constituents of the protein molecule which react analogously to tyrosine and tryptophane, we are unable to state with certainty. We believe, however, that such is the case, for we have on hand at the present time fractions of protein hydrolysates which certainly contain no tyrosine and which as certainly contain no unaltered tryptophane, but which, nevertheless, give intensive colorations with the phenol reagent. However, we know that these fractions do not consists of a single pure amino acid, and until we have investigated them further we are unwilling to commit ourselves as to the nature of the substance which causes the reaction.

A study of the curves in Fig. 1 indicates another unfortunate characteristic of the phenol reagent, *i. e.*, that the color intensity is not directly proportional to the concentration of the reacting substance, but that the color value is constantly changing with the concentration of the tyrosine, tryptophane, etc. If this be the case, we fail to see how the colorimetric data can be correctly interpreted in the case of an unknown solution unless the investigator runs a color curve similar to our curves in Figs. 1 and 2 and ascertains whether or not the color which is developed is the maximum possible, *i. e.*, whether the concentration of the reactive material is low enough so that 100% of the reactive substance reacts with the phenol reagent. At extremely low concentrations of tyrosine, tryptophane, uric acid, etc., where the concentration lies between approximately 0.4 and 1.8 mg. of reactive material, the color intensities when plotted form approximately a straight line and are directly proportional to the concentration of the reactive substance and it is only in this region of the curve that accurate quantitative measurements of the reactive material in an unknown solution are possible.

However, the most serious objection to the use of the phenol reagent lies in the fact that apparently any substance which is easily oxidized will react with the reagent and cause the production of the blue color. Folin and Wu[1] have recently applied the phenol reagent to blood analysis, using it to estimate the sugar content of the blood. In this method the sugar is oxidized by a weakly alkaline copper tartrate solution and the cuprous copper formed is estimated colorimetrically by the phenol re-

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[1] *J. Biol. Chem.*, 38, 106 (1919).

agent.[1] Although we have not investigated the form of the cuprous copper curve, it appears extremely improbable that it is different in general form from our curve for ferrous iron (Fig. 1), and if that should prove to be the case our criticism as to color intensity and concentration would hold for the sugar work.

During our study of the ferrous iron curve we made quantitative studies on both ferrous sulfate solutions and ferrous chloride solutions, checking the content of ferrous salt in each instance by a permanganate titration. We were much surprised to find that the 2 curves did not coincide at identical concentrations of ferrous iron, but that the ferrous sulfate curve was consistently lower than the ferrous chloride curve which is given in Fig. 1. Obviously more factors were involved than simply the concentration of the ferrous iron, but whether the discrepancies were due to hydrogen ion concentration, or to the nature of the anion, or to other unknown factors, we are unable to state, inasmuch as we did not pursue our observations further. We further noted that ferrous iron produced the same blue coloration in solutions where Folin and Denis' uric acid reagent replaced the phenol reagent.

That accurate colorimetric data cannot be obtained if 2 reacting substances are present because of different reactivity of different amino acids at the same concentration is illustrated by reference to the tyrosine and tryptophane curves of Fig. 2. Here at a low concentration of amino acids the color intensity of the tyrosine-containing solution is far greater per milligram of tyrosine than is that of the tryptophane solution; nevertheless, at a higher concentration of amino acid the tyrosine color intensity falls off rapidly while the tryptophane color intensity decreases only slightly so that at 8 mg. of added amino acid the tryptophane color curve has crossed the tyrosine color curve.

As a result of our study we are firmly convinced that a quantitative measurement of the blue color produced by the phenol reagent in a solution is only an indication that easily oxidizable substances are present in that solution, and that accurate quantitative data can only be had when one knows that only one such substance is present in the solution, and even then the approximate concentration of the reacting material must be known or else a series of colorimetric determinations must be made so as to ascertain whether or not the maximum color in proportion to concentration is being developed.

Summary.

As the results of a study of the various factors influencing the color intensity of protein hydrolysates to which have been added the phenol

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[1] Folin and Wu, *J. Biol. Chem.*, 41, 367–374 (1920), have recently published the formula of a similar phosphotungstic-phosphomolybdic acid reagent which they state is preferable to the phenol reagent for this purpose.

reagent of Folin and Denis, according to their directions for the quantitative estimation of tyrosine, we are forced to conclude that:

1. Tyrosine cannot be quantitatively estimated in a protein hydrolysate by the use of the phenol reagent because

2. Tryptophane, if present, will also produce intense colors with the reagent, the color produced by one mg. being approximately 85% of that produced by tyrosine at an equivalent concentration.

3. Indole and indole derivatives, contrary to the statement of Folin and Denis, react strongly with the phenol reagent to produce the blue color.

4. Ferrous iron, and apparently any other easily oxidizable material, also reacts with the reagent.

5. There is considerable evidence that tyrosine and tryptophane are not the only protein constituents which produce blue colors with the phenol reagent.

6. The amount of color which is developed in a solution is not a linear function of the concentration of the reactive material, but the color values fall off sharply as concentration increases until only an insignificant fraction of the reactive material is indicated by a measurement of the color values of the solutions containing any considerable amount of the reactive substance.

7. Because of the peculiar form of the color curves in relation to concentration, it becomes necessary for one to know the approximate concentration of reactive material in advance of the colorimetric determination so that the colors may be developed and read at such a concentration that the maximum color values will be developed.

8. Because of the fact that solutions of tyrosine and tryptophane do not give the same color values at equivalent concentrations, it is impossible to measure accurately the sum of these amino acids in a mixture which contains no other reactive substances.

9. Protein hydrolysates must not be decolorized with carbon or bone black if they are to be used subsequently for a quantitative determination of amino acid content, for the bone black adsorbs at least tyrosine, tryptophane and tryptophane decompositions products in appreciable amounts, Whether or not other amino acids were adsorbed was not determined.

10. Bone black contains some easily oxidizable material, probably reduced iron, which dissolves in acid solutions. These acid solutions give the blue color with the phenol reagent.

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ON INULIN IN THE GLOBE ARTICHOKE.

BY RUTH OKEY AND ANNA W. WILLIAMS.

Received April 27, 1920.

The artichoke, *Cyanara scolymus*, sometimes called the bur or globe artichoke, is a common article of food, especially in California. Comparatively little has, however, been published as to its composition. In 1883, an Italian investigator, de Regibus,[1] found in the flowering head of this plant, a carbohydrate which he considered to be inulin. He also found that this carbohydrate disappeared as the seed matured, and that the reserve foodstuff finally stored was a fatty oil.

The composition of canned artichoke hearts, as determined by routine analysis, was reported by Wiley.[2] His investigation, however, dealt primarily with the adulterants present, and with the economic value of the canned goods. The percentage of carbohydrate present was evidently estimated by difference, and no attempt made to determine its nature. Careful study of the abstract journals has failed to reveal any further reports on the composition of this plant.

The possibility that the artichoke might be a source of inulin suggested itself to the writers as a result of inquiries as to the nature of the white deposit, soluble in hot water, which separated in canned artichokes. This suggestion, combined with the local interest in the use of the artichoke as a food in California, and the meagerness of the available information, as to its composition led to the investigation which is reported here.

Material.—The artichokes used were purchased from a local market at various times between December, 1919, and April, 1920. The part of the plant usually sold as food, *i. e.*, the immature flowering head, with about an inch and a half of the flower stalk, was used.

Preparation of Inulin.—In general, the technique used was that of Dean,[3] modified as was found necessary. The artichokes were chopped with a sharp knife or put through a food chopper and, within 2 or 3 minutes after the beginning of the operation, thrown into an excess of boiling distilled water containing calcium carbonate. Boiling was continued for 40 minutes, or until the mass was soft and the separate pieces of material more or less thoroughly disintegrated. The extract was then poured off through a filter, replaced by a second portion of distilled water, and the extraction at boiling temperature repeated 3 or 4 times. The extracts obtained were treated exactly according to Dean's directions.[3]

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[1] P. e. de Regibus, *Giorn. d. R. Acad. medic.*, 45, 560 (1883); cf. H. Fischer, *Cohn's* "Biol. der Pflanzen," 8, 103 (1902).

[2] H. W. Wiley, *Bur. Chem. Bull.*, 13, pt. 8, 1128 (1893).

[3] A. L. Dean, *Am. Chem. J.*, 32, 69 (1904).

It was found desirable to subject the cut artichokes to the temperature of boiling water as quickly as possible, in order to prevent the blackening of the artichokes and the probable hydrolysis of the inulin by enzymes liberated in the bruising of the plant tissue.

Properties and Identification.—The substance obtained was easily precipitated as a white solid by 60% alcohol. It did not reduce Benedict's solution until after it had been hydrolyzed; after this process, however, an abundant précipitate was obtained, and Seliwanoff's reaction for levulose was positive. The hydrolyzed product was, moreover, levorotatory, and gave on treatment with phenylhydrazine hydrochloride and sodium acetate, in the usual manner, an osazone which had the crystalline form, and, after recrystallization from 50% alcohol, the melting point (205–6°) of dextrosazone. A sample was carefully purified, washed with absolute alcohol and absolute ether, and finally dried for several hours in a water oven at 100°. The rotation was then measured in aqueous solution, using a Schmidt and Häntsch saccharimeter. The value obtained was

$$[\alpha] = -\frac{2.5 \times 100 \times 0.3468}{5.0 \times 0.5} = -34.68°.$$

These properties agreed with those of Dean's inulin. Moreover, it was shown that the specific rotation was very nearly identical with that of a similar solution of inulin which the writers had prepared in the same way from the tubers of the Jerusalem artichoke, *Helianthus tuberosus*.[1] The substance was, therefore, considered to be inulin.

General Analysis.

Since Wiley's analyses[2] had dealt with canned artichoke hearts only, a routine analysis of the material used seemed worth while, as did also an attempt to find the approximate percentages of the different types of carbohydrate present.

One large artichoke was put through a food chopper and portions for the various analyses weighed as rapidly as possible. Moisture, protein, ether extract, ash, and crude fiber were determined according to the official methods outlined in Bureau of Chemistry *Bulletin* No. 107 and the *Journal of Official Agricultural Chemists*. The figure for total carbohydrate was obtained by difference. Results are tabulated on p. 1695. The figures given represent the results of at least 2 check determinations in each case.

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[1] In general it was found that the inulin from the Jerusalem artichoke was precipitated more slowly by 60% alcohol than that from the globe artichoke. It seems probable, moreover, that there is a greater percentage of levulans of lower molecular weight in the Jerusalem artichoke than in the globe artichoke.

[2] *Loc. cit.*

	%.
Moisture	85.5
Ash	1.1
Crude fiber	2.4
Protein	2.8
Ether extract	1.4
Total Carbohydrate	6.8
	100.0

In order to get some idea of the percentage of this carbohydrate which consisted of inulin, fresh artichokes were taken, the blackened ends of the stems cut off, the flowering head and the stem quartered longitudinally. The samples so obtained were weighed rapidly and plunged, without loss of time, into boiling distilled water, and the boiling continued until the samples were soft. The water extract was poured off through a filter, replaced by a fresh portion of boiling distilled water, and the extraction repeated. After some 16 to 20 extractions had been made in this manner, the extracts were united, cooled, made up to definite volume (1000 cc. for a sample weighing about 40 g.) and the reducing sugar determined by the modified Benedict[1] colorimetric method, which has been shown by one of the writers[2] to be applicable to the determination of levulose in the presence of small amounts of inulin. Hydrolyses of aliquot parts of the extract were then carried out, using 1% hydrochloric acid at 100°, for lengths of time which had been shown[2] to be sufficient for the complete hydrolysis of inulin. The resulting solutions were neutralized, made up to twice their original volumes and the levulose determined as before, the final time of heating the tubes being, in every case, 15 minutes, and the standard being pure glucose. Samples from different artichokes hydrolyzed separately gave results which checked in every case to 0.1%.

The residues from the water extracts were then heated on a water bath with 1% hydrochloric acid for several hours, the resulting acid solutions poured through a filter, the residues washed thoroughly, and the washings added to the acid extracts. These were neutralized, made up to definite volume, and the reducing sugar in aliquot parts of the resulting solutions determined as before. The results obtained are listed below:

	%.
Reducing sugar (Corrected for color produced by inulin)	0.6
Reducing sugar after hydrolysis of water extract	3.4
Reducing sugar in residue from water soluble extract after hydrolysis	0.6
Probable reducing sugar derived from inulin	2.8
Probable inulin (2.8 × 0.9)	2.5
Total carbohydrate extracted by water and 1% HCl	4.2
Difference from value, routine analysis (6.8)	2.6

[1] S. R. Benedict and E. Osterberg, *J. Biol. Chem.*, 34, 195 (1918).

[2] R. Okey, *ibid.*, 38, 33 (1919).

There may be some question of the accuracy of results obtained by this method, because of the possible presence of other reducing substances, and the fact that the error is multiplied by such a large factor; but it seems fair, at least to consider that they represent proximate maximum values. The difference between the values for "Total carbohydrates extracted by water and 1% HCl" and for "total carbohydrates by difference" would indicate the presence of hemicellulose-like substances. Moreover, the structure of the artichoke makes this seems the more probable.

It has been shown[1] that the human digestive tract secretes no enzymes capable of digesting either hemicellulose or inulin, and there is some evidence[2] that inulin is not utilized by the animal body.

There is some reason to doubt, therefore, whether the larger part of the carbohydrate of the globe artichoke is in a form that can be utilized by the human organism.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, No. 336.]

THE SPECIFIC ROTATION OF FRUCTOSE.

BY WARREN C. VOSBURGH.[3]

Received May 21, 1920.

In the course of an investigation of the determination of the amount of sucrose and invert sugar in their mixtures it was found that considerable disagreement exists in the literature as to the specific rotation of fructose. For example the specific rotation for a concentration of 5 g. per 100 cc. (4.93% by weight) according to several observers is as follows.

$[\alpha]^{20}_{D}$	$[\alpha]^{25}_{D}$	
89.64	86.84	Jungfleisch and Grimbert[a]
89.40	86.04	Honig and Jesser[b]
92.45	89.65[c]	Ost[d]
91.0[e]	88.0	Nelson and Beegle[f]

[a] Jungfleisch and Grimbert, $[\alpha]^{t}_{D} = -(101.38 - 0.56\,t + 0.108\,(c - 10))$, *Compt. rend.*, 107, 390 (1888).

[b] Honig and Jesser, $[\alpha]^{t}_{D} = -(88.13 - 0.2385\,p + 0.6714\,(t - 20))$, *J. Deut. Zucker-ind.*, 38, 1028 (1888).

[c] Using the temperature coefficient of Jungfleisch and Grimbert.

[d] Ost, $[\alpha]^{20}_{D} = -(91.90 + 0.111\,p)$, *Ber.*, 24, 1636 (1891).

[e] Interpolated between 15° and 25°.

[f] Nelson and Beegle, THIS JOURNAL, 41, 559 (1919).

[1] Cf. M. D. Swartz, *Trans. Conn. Acad. Sci.*, 16, 297 (1911), for a review of this literature.

[2] R. Okey, *J. Biol. Chem.*, 39, 149 (1919).

[3] National Research Fellow.

There is disagreement also as to the temperature coefficient of the specific rotation. In order, therefore, to obtain accurate values of the specific rotation for different concentrations at 25° which were needed in the above mentioned investigation, it was necessary to make several measurements for various concentrations.

In this investigation it has been found that:

(1) The specific rotation of fructose at 25° can be expressed, in terms of the per cent. by weight, p, and the concentration in grams per 100 cc., c, respectively, by means of the equations,

$$[\alpha]_D^{25} = -(88.50 + 0.145\,p) \qquad \text{(I)}$$

$$[\alpha]_D^{25} = -(88.50 + 0.150\,c - 0.00086\,c^2). \qquad \text{(II)}$$

These equations are based on experimental results for the range $p = 2.6$ to $p = 18.6$ and $c = 2.6$ to $c = 20$.

(2) The temperature coefficient of the specific rotation is a function of the concentration.

(3) The relation between specific rotation and temperature for temperatures between 15° and 37° can be expressed as

$$[\alpha]_D^t = [\alpha]_D^{25} + (0.566 + 0.0028\,c)\,(t - 25). \qquad \text{(III)}$$

(4) The values for the specific rotation found in this investigation are from 2° to 3° higher than those calculated from the formulas of Jungfleisch and Grimbert, and Honig and Jesser.

(5) The formula of Ost gives values higher at concentrations below 10% and lower above 10% than the specific rotations found in this investigation.

(6) The equation $[\alpha]_D^{20} = -(91.50 + 0.133\,p)$ expresses Ost's results better than the equation given by him.

(7) Ost's experimental values for the specific rotation for concentrations up to 10% are in good agreement with the values calculated from Equations I and III of this investigation.

Purification of the Fructose.—Five different lots of fructose were purified by recrystallization from strong acetic acid solution as recommended by Hudson and Dale[1] for the purification of glucose. The purified fructose was dried for several hours at 40° *in vacuo* over conc. sulfuric acid and preserved in glass-stoppered bottles in a desiccator over conc. sulfuric acid.

Preparations 1 and 2 resulted from recrystallization of some fructose previously purified in this laboratory by Nelson and Beegle.[2]

Preparation 3 was obtained by 2 recrystallizations of some commercial fructose.

Preparation 4 was the result of a third recrystallization of a portion of

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[1] Hudson and Dale, This Journal, 39, 320 (1917).

[2] *Loc. cit.*

Preparation 3. The good agreement of the specific rotation of this preparation with that of the other preparations is good evidence of the purity of the material used in this investigation.

Preparation 5 was the result of 3 recrystallizations of fructose similar to that used in Preparation 3.

Procedure.—The required amount of fructose was weighed, dissolved in distilled water and made up to 100 cc. at the temperature of measurement in a calibrated volumetric flask. The solution was then weighed in order that the per cent. by weight could be calculated in addition to the volume concentration. In some of the experiments of Tables III and IV the solution was made up at one temperature and the rotation measured at another. In that case the density was determined at the temperature in question as well as at the temperature at which the solution was made up to volume and the required concentration calculated. All weights were reduced to a vacuum in the calculations.

All solutions were allowed to stand until mutarotation was complete.[1] The angular rotation of at least 2 samples of each solution was then measured and the mean value taken as the angular rotation of the solution.

For the measurement of the angular rotation a Schmidt and Haensch polarimeter sensitive to 0.01° was used. The solution being measured was maintained accurately at the desired temperature by the use of the thermostat described by Nelson and Beegle.[2] The polariscope tubes were measured and found to be 199.94 mm. and 200.39 mm. in length respectively and all observed angular rotations given were corrected to apply to a 200 mm. tube. At least 4 polariscope settings were made for each sample in the manner recommended by Browne.[3]

Two different light sources were used in the polariscopic measurements. Most of the measurements were made with the use of a sodium lamp, the light from which was not purified. The other source of light, which was used in the experiments of Table V, was a mercury-vapor lamp the light from which was purified by passing through a Wratten No. 74 filter, giving light of wave length $\lambda = 546\mu\mu$.

The Specific Rotation at 25°.—Determinations were made as given in Table I using sodium light. The first column gives the weight of fructose in 100 cc. of solution. The second gives the density as determined by weighing the 100 cc. of solution. The third column gives the composition in per cent. by weight calculated by dividing the weight per 100 cc. by

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[1] A calculation from the results of Nelson and Beegle, *loc. cit.*, shows that the mutarotation of pure β-fructose would be 99.9% complete after 84 minutes at 15° or after 35 minutes at 25° at the hydrogen ion concentration giving minimum velocity.

[2] *Loc. cit.*

[3] Browne, "A Handbook of Sugar Analysis," 1912, p. 106.

the density of the solution. The figures in the fourth column refer to the particular preparation of fructose used. The fifth column gives the angular rotation, and the sixth the specific rotations calculated from the observed rotations and the volume concentrations.

Table I.

Specific Rotation of Fructose at 25°.

Conc. in g. /100cc.	Density.	% by wt.	Fructose.	Observed rotation.	Specific rotation.
2.632	1.0073	2.61	1	— 4.68	—88.91
2.632	1.0071	2.61	2	— 4.67	—88.72
2.632	1.0062	2.62	3	— 4.69	—89.09
5.003	1.0164	4.92	1	— 8.94	—89.35
5.003	1.0160	4.92	2	— 8.91	—89.05
5.003	1.0160	4.92	3	— 8.91	—89.05
5.265	1.0170	5.18	1	— 9.42	—89.46
5.265	1.0173	5.18	2	— 9.39	—89.17
7.900	..	...	1	—14.16	—89.62
7.900	1.0268	7.69	3	—14.16	—89.62
10.006	1.0348	9.67	1	—17.99	—89.90
10.006	1.0349	9.67	2	—17.98	—89.85
10.006	1.0350	9.67	4	—17.99	—89.90
15.009	1.0539	14.24	3	—27.18	—90.55
15.009	..	...	3	—27.21	—90.65
20.012	1.0729	18.65	4	—36.48	—91.14

Ost[1] and Honig and Jesser[1] have expressed the specific rotation of fructose as a linear function of the per cent. fructose by weight, while Jungfleisch and Grimbert[1] express it as a linear function of the volume concentration. However if the per cent. by weight is plotted against the volume concentration a curve is obtained which is not quite a straight line showing that there is not a direct proportionality between the two. specific rotation therefore cannot be a linear function of both. When the specific rotation was plotted against both per cent. and concentration it was found that in the former case the observed points lay more nearly on a straight line than in the latter. The relation between specific rotation and per cent. fructose, p, is shown graphically in Fig. 1, the values for the specific rotation being the mean values given in Table II. The equation of the straight line in Fig. 1 is

$$[\alpha]_D^{25} = -(88.50 + 0.145\,p). \qquad \text{(I)}$$

As it is often more convenient to deal with concentrations by volume an equation expressing the specific rotation as a function of the concentration, c, in g. per 100 cc. was derived by the method of least squares, from the values in Table II.

$$[\alpha]_D^{25} = -(88.50 + 0.150\,c - 0.00086\,c^2). \qquad \text{(II)}$$

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[1] *Loc. cit.*

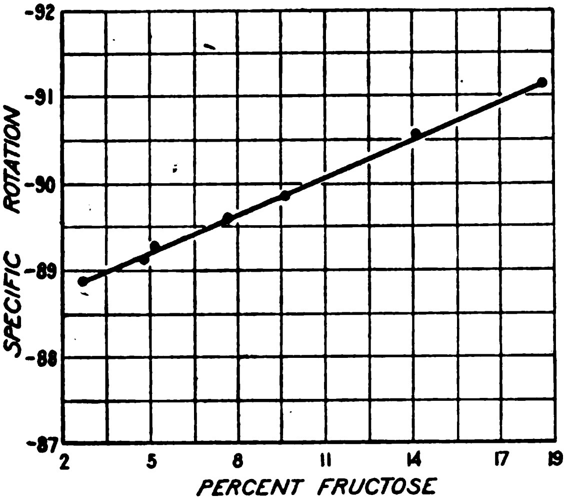

Fig. 1.—Variation of the specific rotation of fructose with concentration.

These equations obviously have not been experimentally verified outside the limits p = 2.6 to p = 18.6 in I, and c = 2.6 to c = 20 in II.

Table II gives a summary of the mean values of the observed specific rotations as given in Table I, together with values calculated by means of Equations I and II for the same concentrations. The equations are shown to give values which agree very closely with the experimental values.

Table II.

Comparison of the Observed Specific Rotation with that Calculated from Equations I and II.

Conc. in g. /100 cc.	% by wt.	Specific rotation at 25° Observed.	Calc. I.	Calc. II.
2.632	2.61	—88.91	—88.88	—88.89
5.003	4.92	—89.15	—89.21	—89.23
5.265	5.18	—89.32	—89.25	—89.27
7.900	7.69	—89.62	—89.62	—89.63
10.006	9.67	—89.89	—89.90	—89.91
15.009	14.24	—90.60	—90.56	—90.56
20.012	18.65	—91.14	—91.20	—91.16

Temperature Coefficient.—There is considerable disagreement also as to the temperature coefficient of the specific rotation of fructose. Jungfleisch and Grimbert[1] give 0.56° as the temperature coefficient while Honig and Jesser[1] found 0.671° for a 9% solution and 0.692° for a 23.5% solution. Nelson and Beegle[1] found a difference of 6.0° in the specific rotations at 15° and 25° and a difference of 7.0° between 25° and 37°. Assuming a constant coefficient over this range their temperature coefficient is 0.59° per degree centigrade, determined for a concentration of 5 g. per 100 cc.

The temperature coefficient was therefore determined by means of the experiments given in Table III. The temperature was maintained at the figures given within ±0.05°. The solutions were made up at the

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[1] *Loc. cit.*

temperatures at which the measurement was to be made except in case of the measurements at 0°, 15° and 20° in which case the densities at the 2 temperatures were determined and the concentration at the temperature of measurement calculated. In all cases care was taken to allow the solution to stand at the temperature of measurement long enough for mutarotation to be completed before measurements were made.

TABLE III.

Specific Rotation of Fructose at Various Temperatures.

Temperature. °C	g. per. 100 cc.	Observed rotation.	Specific rotation. Observed.	Calculated.[a]	Difference.
0.2	5.038	—10.34	—102.63	—103.65	—1.02
15.3	5.039	— 9.55	— 94.76	— 94.78	—0.02
25.0	5.003	— 8.92	— 89.15	..	..
30.0	5.003	— 8.62	— 86.15	— 86.25	—0.10
37.1	5.003	— 8.24	— 82.35	— 82.13	+0.20
0.2	10.080	—20.89	—103.63	—104.75	—1.12
15.0	10.080	—19.32	— 95.83	— 95.84	+0.01
20.0	10.028	—18.64	— 92.94	— 92.87	+0.07
25.0	10.006	—17.99	— 89.90	..	..
30.0	10.006	—17.39	— 86.90	— 86.93	—0.03
37.1	10.006	—16.57	— 82.80	— 82.73	+0.07

[a] $[\alpha]^t_D = [\alpha]^{25}_D + (0.566 + 0.0028\,c)(t - 25)$.

When the observed specific rotations are plotted against temperature between 15° and 37° for both concentrations, as in Fig. 2, two straight lines are obtained which are not parallel, showing that the temperature coefficient does not vary with temperature over this range but that it does vary with concentration. The slope of the specific rotation-temperature line for a concentration of 5 g. per 100 cc., Curve II, is $d[\alpha_5]^t_D/dt = 0.580$ and for a concentration of 10 g. per 100 cc., Curve I, $d[\alpha_{10}]^t_D/dt = 0.594$. Assuming the difference in slopes to be proportional to the difference in concentrations[1] the difference for one g. difference in concentration is $^1/_5$ (0.594–0.580) or 0.0028 and the slope for zero concentration is

$$d[\alpha_0]^t_D/dt = 0.580 - (5 \times 0.0028) = 0.566.$$

Therefore for any concentration

$$d[\alpha]^t_D/dt = (0.566 + 0.0028\,c).$$

Integrating,

$$[\alpha]^t_D = (0.566 + 0.0028\,c)\,t + C.$$

When $t = 25°$, $[\alpha]^t_D = [\alpha]^{25}_D$, and $C = [\alpha]^{25}_D - 25\,(0.566 + 0.0028\,c)$.

Therefore $$[\alpha]^t_D = [\alpha]^{25}_D + (0.566 + 0.0028\,c)\,(t - 25). \qquad \text{(III)}$$

The values for the specific rotation under the conditions of the experi-

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[1] This assumption is sufficient for the purpose if only roughly true since the correction to the temperature coefficient is small and a large error in the correction would make little difference in the result.

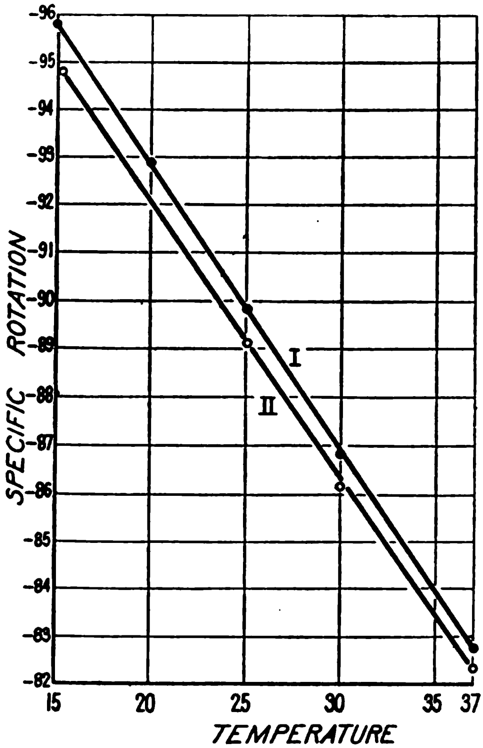

FIG. 2.—Variation of the specific rotation of fructose with temperature. Curve I, concentration of fructose, 10 g. per 100 cc. Curve II, concentration of fructose, 5 g. per 100 cc.

ments of Table III were calculated by means of this equation and are given in Table III. The maximum difference between observed and calculated, except at 0.2°, is 0.2° or 2.4 parts per thousand, corresponding to an error in the observed rotation of 0.02°.

The equation evidently does not hold at 0.2° and consequently cannot be depended upon much below 15°.

Results of Other Observers.—Comparison of the specific rotation for a concentration of 5 g. per 100 cc. as given in Table II with the values given by the formulas of Jungfleisch and Grimbert, and Honig and Jesser, as given above, shows that the latter values are 2° to 3° too low, as Ost has pointed out.[1]

The specific rotation as given by the formula of Ost is too high for concentrations up to about 10% and too low above this point as compared with the results of this investigation, as the following figures show.

% Fructose.	5.	10.	15.	20.
$[\alpha]_D^{20}$ Ost..................	92.45	93.01	93.57	94.12
$[\alpha]_D^{20}$ I and III............	92.13	92.93	93.73	94.53

The specific rotation increases too slowly with concentration in the equation proposed by Ost and the value for zero concentration is too high if the results of this investigation are correct. An examination of Ost's experimental results shows that they can be expressed as well or better by the equation $[\alpha]_D^{20} = -(91.50 + 0.133\ p)$. Moreover values calculated from above Equations I and III agree with Ost's experimental values up to the 10% solution, and the values for 5 and 10% given by Equations I and III are closer to the experimental values than those calculated from either of the other equations. Table IV demonstrates these facts. The first 3 columns are taken from Ost's paper and the last 3 were calculated by the author.

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[1] *Loc. cit.*

TABLE IV.

Ost's Observed Values for the Specific Rotation of Fructose Compared with Values Calculated by Various Empirical Formulas.

% Fructose.	Observed rotation.	Specific rotation			
		Observed.	Calc. A (1).	Calc. B (2).	Calc. C (3).
1.0100	— 3.67	—90.64	—92.01	—91.63	—91.50
1.0324	— 3.74	—90.36	—92.01	—91.64	—91.50
1.9949	— 7.37	—91.79	—92.12	—91.77	—91.65
2.0263	— 7.49	—91.84	—92.13	—91.77	—91.65
4.9395	— 18.56	—92.30	—92.45	—92.16	—92.12
4.9575	— 18.59	—92.11	—92.45	—92.16	—92.12
4.9710	— 18.64	—92.10	—92.45	—92.16	—92.12
7.8051	— 29.86	—92.90	—92.77	—92.54	—92.57
8.9724	— 34.50	—92.96	—92.90	—92.69	—92.76
9.8195	— 37.88	—92.92	—92.99	—92.81	—92.89
10.5198	— 40.72	—93.00	—93.07	—92.90	—93.00
18.5161	— 74.61	—93.73	—93.96	—93.96	—94.28
20.2638	— 82.47	—94.03	—94.15	—94.20	—94.56
29.7995	—128.23	—95.51	—95.20	—95.46	...
30.1157	—129.60	—95.39	—95.24	—95.50	...

(1) $[\alpha]^{20}_{D} = -(91.90 + 0.111\,p)$

(2) $[\alpha]^{20}_{D} = -(91.50 + 0.133\,p)$

(3) $[\alpha]^{20}_{D} = -(88.50 + 0.145\,p) + (0.566 + 0.0028\,c)(20-25)$

Ling, Eynon and Lane[1] find $[\alpha]^{18.5}_{D} = -93.83$ when $c = 10$ for some fructose which they describe as of high purity. Calculation by means of the above Equations II and III gives $[\alpha]^{18.5}_{D} \doteq -93.77$, agreeing with this experimental value within one part in a thousand.

Specific Rotation Measured with the Yellow-Green Line of Incandescent Mercury Vapor.—After most of the above determinations were completed a mercury vapor lamp was installed in this laboratory for use in polariscopic measurements, and a determination was made of the ratio of the specific rotations for the unpurified sodium light as used in the measurements above and the line $\lambda = 546\mu\mu$ obtained by passing the light from the mercury vapor lamp through a Wratten No. 74 filter. For this purpose the rotation of the solutions used for the determination of the temperature coefficient was determined by the use of mercury light as well as sodium light, the light source being changed during the measurements without changing the solutions in the polariscope tubes. The ratio of the rotation using mercury light to that using sodium light was calculated and is the same as the ratio of the corresponding specific rotations. The specific rotation of fructose with the line $\lambda = 546\mu\mu$ as the light source can therefore be calculated from the above results by multiplying by the proper factor. The experimental results and factors to be so used are given in Table V.

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[1] Ling, Eynon and Lane, *J. Soc. Chem. Ind.*, 28, 730 (1909).

TABLE V.

Determination of the Ratio $\frac{[\alpha]^t_{\lambda = 546\mu\mu}}{[\alpha]^t_D}$ for Fructosee.

Temperature ° C.	Conc. in g. /100 cc.	Observed rotation. D line.	Observed rotation. λ = 546 μμ.	$\frac{[\alpha]^t_D}{[\alpha]^\lambda_{t = 546\mu\mu}}$.	$\frac{[\alpha]^t_{\lambda = 546\mu\mu}}{[\alpha]^t_D}$.	Variation from mean.
0.2	5.038	—10.34	—12.21	0.8468	1.1809	±0.0000
15.3	5.039	— 9.55	—11.27	0.8474	1.1801	—0.0008
25.0	5.003	— 8.92	—10.55	0.8455	1.1828	+0.0019
30.0	5.003	— 8.62	—10.20	0.8451	1.1833	+0.0022
37.1	5.003	— 8.24	— 9.76	0.8443	1.1845	+0.0036
0.2	10.080	—20.89	—24.63	0.8482	1.1790	—0.0019
15.0	10.080	—19.32	—22.75	0.8492	1.1775	—0.0025
25.0	10.006	—17.99	—21.27	0.8458	1.1823	+0.0014
30.0	10.006	—17.39	—20.51	0.8479	1.1794	—0.0015
37.1	10.006	—16.57	—19.55	0.8476	1.1799	—0.0010
25.0	15.0	—27.09	—32.00	0.8466	1.1812	+0.0003
25.0	20.0	—36.34	—42.87	0.8477	1.1797	—0.0012

The ratios of the specific rotations using mercury and sodium lights respectively seem to vary with temperature at a concentration of 5 g. per 100 cc. becoming slightly larger as the temperature increases, but in the case of 10 g. per 100 cc. the ratio seems to be constant over the temperature range considered. If the values at 25° for the different concentrations are considered a regular variation with concentration amounting to less than 3 parts per thousand is noticed. However these variations are hardly larger than the experimental errors and for most purposes the mean value of the ratio, namely 1.1809, or its reciprocal, 0.8467, can be used. The average variation from the mean in the above figures is about one part in a thousand while the extreme variation is 3 parts per thousand.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY.]

RESEARCHES ON AMINES. VIII.[1] THE PREPARATION OF AMINO-ACETANILIDE.

BY ARTHUR J. HILL AND ERWIN B. KELSEY.

Received May 24, 1920.

In order to develop certain phases of an extended research on thiocyanates and isothiocyanates, now in progress in the Sheffield Laboratory, it became necessary to obtain representatives of a series of amines of the general formula $RNHCOCH_2NH_2$, of which amino-acetanilide, $C_6H_5NHCOCH_2NH_2$, is the prototype. Our attention was first turned to this latter compound, since it was evident that the principles underlying a successful method for its preparation would apply directly to the

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[1] Paper VII, *J. Ind. Eng. Chem.*, 12, 636 (1920).

synthesis of its homologs or derivatives. A search revealed that, with one exception,[1] the directions for its preparation were given in the patent literature. Majert, in 1891, patented[2] several processes for the preparation of amino-acetanilide and derivatives of the same. These compounds were stated by him to possess valuable therapeutic properties, since they were both antipyretic and analgesic in their action. Of these, amino-phenacetin, or "phenocoll," $C_2H_5O.C_6H_4NHCOCH_2NH_2$, it appears, has found application.

Upon attempting to utilize these patents, the writers found it impossible to obtain amino-acetanilide without considerable modification of the directions. This observation also finds corroboration in the recent investigations of Dubksky and Granacher,[3] who experienced the same difficulty, and were also compelled to utilize a modified procedure in order to obtain this base by the action of alcoholic ammonia upon chloroacetanilide.

The methods of preparation, which are covered by Majert's patents, are indicated by the following equations.

1.[4] $C_6H_5NHCOCH_2Cl + 2NH_3 = C_6H_5NHCOCH_2NH_2 + NH_4Cl$

In this process, alcoholic or aqueous ammonia is used and the operation carried on at ordinary temperature, or in an autoclave, either at 50–60° or at 110°.

2.[5] $2C_6H_5NH_2 + HCl.NH_2CH_2COOC_2H_5 =$
$C_6H_5NH_2HCl + C_6H_5NHCOCH_2NH_2 + C_2H_5OH$

3.[5] $C_6H_5NH_2 + NH_2CH_2CONH_2 = C_6H_5NHCOCH_2NH_2 + NH_3$

Our investigations have been confined, first, to a study of the action of alcoholic or aqueous ammonia upon chloro-acetanilide, and second, to the interaction of ethyl amino-acetate with aniline. The action of ammonia upon chloro-acetanilide was investigated as early as 1875 by Tommasi,[6] who states that in dil. alcohol ammonia functions as a metallic hydroxide and reacts with chloro-acetanilide as follows,

$$C_6H_5NHCOCH_2Cl + NH_4OH = C_6H_5NHCOCH_2OH + NH_4Cl$$

forming the phenylamide of glycollic acid. He assigned to this substance a melting point of 65°. The anilide of glycollic acid has since been prepared by Bischoff and Walden,[7] and others, and neither the melting point

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[1] Dubksky and Granacher, *Ber.*, 50, 1701 (1917).

[2] *D. R. P.*, 59,121; *Chem. Zentr.*, 1892, (1) 550; *Wagner Tech.*, 37, 606 (1891); *D. R. P.*, 59,874; *Wagner Tech.*, 37, 608 (1891).

[3] *Loc. cit.*

[4] *D. R. P.*, 59.121.

[5] *Ibid.*, 59,874.

[6] *Bull. soc. chim.*, 22, 3 (1874).

[7] Bischoff and Walden, *Ann.*, 279, 49 (1894); Norton and Tcherniak, *Bull. soc. chim.*, 30, 104 (1878).

of their product (96–97°), nor its physical properties, agree with that of the compound prepared by Tommasi. Meyer[1] heated chloro-acetanilide, as well as chloro-acetoluide, under pressure with an excess of alcoholic ammonia at 100°. The product in each case was the *secondary* and not the *primary* base, *i. e.*,

$$2C_6H_5NHCOCH_2Cl + 3NH_3 = (C_6H_5NHCOCH_2)_2NH + 2NH_4Cl$$

$$2C_6H_4(CH_3)NHCOCH_2Cl + 3NH_3 = (C_6H_4(CH_3)NHCOCH_2)_2NH + 2NH_4Cl.$$

Theoretically, 3 products should be formed by the action of alcoholic or aqueous ammonia upon chloro-acetanilide, namely, (1) amino-acetanilide, $C_6H_5NHCOCH_2NH_2$; (2) di-(phenylamide) of diglycol-amidic acid, $(C_6H_5NHCOCH_2)_2NH$; and (3) tri-(phenylamide) of triglycol-amidic acid, $(C_6H_5NHCOCH_2)_3N$. Majert states in the German patent No. 59121 that either 1 or 2 may be formed in this reaction, the former by the action of a large excess of alcoholic ammonia upon chloro-acetanilide, and the latter, when the theoretical amount of ammonia is employed.

The writers have investigated this reaction and have been able to obtain excellent yields of amino-acetanilide through changes of conditions and manipulative procedures. We have found moreover, that even under the conditions productive of the maximum yields of amino-acetanilide, a comparatively large amount of the secondary base is formed, together with a small amount of the tertiary base, a compound not hitherto described.

Our method differs essentially from that of Dubksky and Granacher's in that the use of an autoclave is obviated, since the reaction is carried out entirely at room temperatures. The procedure for the isolation of the pure base also differs quite materially in detail, and is much simpler. Our yield, however, is but slightly better, namely 74%, as compared to 68%. The various details of our process are described below in the experimental part of the paper.

Experimental Part.

The Preparation of Amino-acetanilide from Chloro-acetanilide and Ammonia.—A large 5-gallon stoppered bottle was used for this experiment. Five hundred and fifty g. of chloro-acetanilide was added to 11 kg. of 95% alcohol, previously saturated with ammonia gas at 10°. This solution was allowed to stand at a temperature of 20° for 5 days. It was then evaporated under diminished pressure to $^1/_4$ of its original volume. At this concentration a small amount of material separated from the alcohol. This concentrated solution was poured into 3500 cc. of water, when an oil separated, which soon solidified. This product, the secondary amine, was filtered, washed with water and then purified as

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[1] Meyer, *Ber.*, 8, 1152 1875).

described below. The aqueous filtrate was evaporated nearly to dryness in order to decompose the ammonium chloride. The non-volatile amino-acetanilide is sufficiently basic to liberate ammonia from its salts. The residual material was then dissolved in 2 parts of hot water,[1] and the resulting solution decolorized with the vegetable carbon, "Norite." After the solution had been cooled in an ice bath it was saturated with ammonia gas. In a short time amino-acetanilide crystallized either in long silky needles or in stout colorless transparent needles, depending on the rate of crystallization. This product was the hydrated base containing 2 molecules of water of crystallization. Majert states in his patent that the hydrated base contains 1.5 molecules of water of crystallization. Our observation is confirmed by Dubksky and Granacher.[2]

Water determination by drying at 100°.

Calc. for $C_6H_5NHCOCH_2CH_2.2H_2O$: H_2O, 19.35. Found: (I) 19.34, (II) 19.12.

Nitrogen determination (Kjeldahl method).

Calc. for $C_6H_5NHCOCH_2NH_2.2H_2O$: N, 15.05. Found: (I) 14.80; (II) 14.95.

The hydrate was crystallized from 95% alcohol. A yield of 424 g. was obtained, corresponding to 70%. This hydrate may be crystallized from water. It is a colorless compound, soluble in water and alcohol, and insoluble in benzene or in ether. It melts at 62°.

The anhydrous base may be prepared by allowing the hydrated base to stand over sulfuric acid in a vacuum desiccator for several days. It is a strongly basic compound which colors litmus and will absorb carbon dioxide from the air. Hot aqueous solutions displace ammonia from its salts. It is colorless when freshly prepared, but becomes yellow on long standing. It has no well defined melting point.

The hydrochloride of the base is a colorless compound, soluble in water and in alcohol, but insoluble in ether and in benzene. It crystallizes from water or alcohol in thick transparent plates, which melt between 190–195°. The melting point is not well defined.

Nitrogen determination (Kjeldahl method).

Calc. for $C_8H_{10}ON_2.HCl$: N, 15.02. Found: 14.99, 15.21.

Secondary Base. The Di-(phenylamide) of Diglycol-amidic Acid, $(C_6H_5NHCOCH_2)_2NH$.—The solid which was obtained when the partially evaporated alcoholic liquor was poured into water, was easily purified by crystallization from 95% alcohol. Seventy-eight g. of the di-phenylamide of diglycol-amidic acid was obtained. This secondary base is insoluble in water, but crystallizes from alcohol in colorless needles melting

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[1] A slight modification of this procedure was also used successfully. The residue was dissolved in warm alcohol instead of water. The hydrochloride of the base crystallized from the former upon cooling. The free base was obtained by dissolving the hydrochloride in 2 volumes of water and then saturating the solution with gaseous ammonia.

[2] *Loc. cit.*

at 141°. If a concentrated alcoholic solution is saturated with hydrogen chloride the hydrochloride is precipitated in white plates. It may be purified by crystallization from warm water or alcohol. It crystallizes from the latter solvent in thin colorless plates melting at 235–237°, with effervescence.

Nitrogen determination (Kjeldahl method).

Calc. for $C_{16}H_{17}O_2N_3.HCl$: N, 13.14. Found: 13.10, 13.28.

Tertiary Base. The Tri-(phenylamide) of Triglycol-amidic Acid, $(C_6H_5NHCOCH_2)_3N$.—This base is formed in small quantities only. In fact, oftentimes it is not possible to identify it in a run. It appears as an insoluble body when the crude secondary base is dissolved in alcohol. It is insoluble in the common solvents, alcohol, ether, benzene and water, but crystallizes readily from glacial acetic acid in small plates melting at 238–239°, with slight decomposition. A molecular weight determination by the ebullioscopic method, with glacial acetic acid as the solvent, gave a value of 395. The calculated value is 416.

Nitrogen determination (Kjeldahl method).

Calc. for $C_{24}H_{24}O_3N_4$: N, 13.46. Found: 13.48, 13.40.

The results of 2 of our larger scale experiments are summarized in Table I. An innovation was introduced in Expt. 2 in that the reaction mixture was saturated every other day with ammonia, in order to maintain the concentration of the base. Moreover, the initial amount of the alcoholic solution was reduced to 13 parts by weight instead of 20. In this experiment the yield was slightly better than the first, but, on the other hand, the ratio of primary to secondary amine was not as good. Subsequent observations have lead us to believe that this occasional saturation with ammonia is of doubtful advantage and that, in general, the conditions set forth in the first experiment are to be preferred. So far we have been unable to obtain a yield better than 74% of the theoretical.

TABLE I.—LARGE SCALE EXPERIMENTS.

Expt.	Chloro-acetanilide. G.	Alcoholic ammonia. Kg.	Time. Days.	Anhyd. primary amine. G.	Secondary amine. G.	Ratio primary to secondary amine.
1............	550	11	5	340	78	4.4:1
2............	700	9.1	10	463	115	4.0:1

The procedure described above for the preparation of amino-acetanilide and the isolation of the secondary and tertiary bases, was the result of a series of experiments carried out with 25 g. units of chloro-acetanilide. It is hardly necessary to describe all of these in detail. Suffice it to say that the major difficulty was in evolving an efficient procedure for the isolation of the products of this reaction in a state of purity. When this had been accomplished, the factors of time, concentration, etc., were easily established. Some of the more important experiments will be discussed.

Table II records the experiments which were made in order to fix a suitable time period of reaction, as well as the optimum concentration of ammonia.

TABLE II.—TIME PERIODS.

25 g. of Chloro-acetanilide Used in Each Experiment.

Expt.	Alcoholic ammonia G.	Time days.	Prim. amine HCl salt. G.	Sec. amine. G.	Yield of primary amine salt. %.
1	325	8	16	5.0	59
2	325	6	15	5.0	54
3	325	4	15	5.0	54
4	325	2	16	5.0	59
5	325	1	17	5.0	63
6	500	1	20	4.5	74
7	625	1	19.7	4.5	73

With regard to the time period it may be seen that with small quantities of chloro-acetanilide the reaction is quite rapid, and even a time period of one day is productive of results quite comparable with those obtained when longer time periods were used. Moreover, it should be noted that the yield of secondary amine is a constant value. Upon increasing the alcoholic ammonia to 500 g. (Expt. 6) an 11% increase in yield was obtained. Beyond this amount (Expt. 7), 625 g., the effect was negligible. It should be emphasized at this point that in none of the above experiments was chloro-acetanilide recovered unchanged.

The utilization of the best time period evolved from the above experiments did not prove successful when larger amounts of chloro-acetanilide were employed. In one run of 125 g., unchanged material was recovered, and the yield was 30% instead of the usual 74%. As a result, it was found that a time period of 5 days was required to effect the transformation of larger quantities of chloro-acetanilide.

With regard to the temperature factor, it is obvious that the use of an autoclave is essential in order to conduct experiments above room temperatures. A characteristic result is shown below when the temperature of 60° was utilized. Our most favorable results were always obtained at room temperatures. On the other hand, in one experiment, the temperature was reduced to 5°. In this instance a large amount of chloro-acetanilide was recovered unchanged, and the yield of amino-acetanilide fell to 14%.

In his patent Majert recommended the use of an autoclave, and a temperature of 60°, although he also stated that the reaction could be carried out "by standing for some time in the cold, or by heating at higher temperatures, preferably 110°."

In order to ascertain the efficiency of Majert's autoclave method, the following experiments were carried out.

1. Fifteen g. of especially purified chloro-acetanilide was heated in an autoclave at 60° with 450 g. of strong alcoholic ammonia. The autoclave was heated for 24 hours. The reaction product was worked up in accordance with our own procedure and not that of Majert's. The yield of amino-acetanilide was 9 g., or 54%.

2. An experiment carried out with 28% of aqueous ammonia under the above conditions produced a yield of 20%. An endeavor was made to catalyze the reaction by the use of copper powder, but no improvement in yield was produced. Moreover, it was found that the removal of traces of copper from the reaction product was attended with considerable difficulty.

The Action of Aniline on the Hydrochloride of Ethyl Amino-acetate.— In the German patent, No. 59,874, Majert described the preparation of amino-acetanilide from aniline and the hydrochloride of ethyl amino-acetate. As in the case of the chloro-acetanilide method, no statement of yields was made. One hundred and thirty-three g. (2 moles) of aniline and 100 g. of the hydrochloride of ethyl amino-acetate were heated for 6 hours in an oil bath. The patent recommends a temperature of 130–150°. In this run the initial temperature was 140°, but this could not be maintained as the reaction progressed, inasmuch as the boiling point of the mixture fell below 140° and, after 6 hours heating, to a constant temperature of 125°. The mixture was a clear amber liquid which solidified upon cooling. Unchanged aniline was then removed by steam distillation. The residue was treated with weakly acidulated water (hydrochloric acid), filtered and cooled. It was then made slightly alkaline with ammonia, and after a small amount of resinous material had been removed by filtration, the filtrate was treated with a large excess of strong ammonia. According to Majert, this latter operation should have precipitated the amino-acetanilide. We were unable to confirm this. Moreover, concentration of the solution yielded no better results. Upon complete evaporation a gummy material was obtained.

Considerable difficulty was experienced in devising a suitable procedure for the isolation of amino-acetanilide from this material. Extraction with absolute alcohol yielded a small amount of crystalline solid which proved to be the hydrochloride of amino-acetanilide.

The above run was repeated under similar conditions except that, after the neutralization with ammonia, the solution was evaporated as near to dryness as possible and allowed to cool and solidify. This residue, upon extraction with alcohol, gave 21 g. of the primary amine hydrochloride, corresponding to a yield of 15%. As in the first case, a considerable amount of gummy material interfered with the isolation of pure amino-acetanilide.

A third modification was tried. The same proportions of the reacting materials were employed, but a distinct difference in procedure was instituted. After the removal of the aniline, the solution was strongly acidified with hydrochloric acid, and then evaporated to dryness This manipulation apparently prevented the formation of resinous materials, or at least accomplished their solution, for upon extraction with absolute alcohol, 47 g. of amino-acetanilide hydrochloride was obtained. We have been unable to better this yield, which is approximately 35%.

NEW HAVEN, CONN.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY.]

RESEARCHES ON THIOCYANATES AND ISOTHIOCYANATES. XIV. A NEW METHOD OF SYNTHESIZING 2-THIOHYDANTOINS.

BY TREAT B. JOHNSON, ARTHUR J. HILL AND ERWIN B. KELSEY.

Received May 24, 1920.

At the present time there exists a difference of opinion with respect to the chemical behavior of potassium and sodium thiocyanates towards the anilide derivatives of chloro-acetic acid, II. It is well known that these salts of thiocyanic acid interact with halides of this

$$\underset{\text{I}}{ClCH_2.COOH} \qquad \underset{\text{II}}{Cl.CH_2CONHC_6H_5}$$

type II, to give rhodanide or thiocyanate combinations which easily undergo isomerization to cyclic pseudo-thiohydantoins. One interpretation of the mechanism of this characteristic change is based on the assumption that the primary reaction involves the formation of a normal thiocyanate, III, which then undergoes rearrangement to give labile and stable pseudo-thiohydantoins (V and VI). The other conception is a mechanism of reaction involving the formation of an isothiocyanate IV as the primary product of reaction. This change is then followed by a triple rearrangement giving first the normal thiocyanate III and, finally, the 2 modifications of the pseudo-thiohydantoin. In other words, one group[1] of workers conceives the normal thiocyanate III as the only acyclic product of reaction to be considered, while the other group[2] views this primary change as a tautomeric one giving either a thiocyanate, an isothiocyanate or a mixture of these 2 isomers in unstable equilibrium. In some cases the thiocyanate structure predominates, and in others the mustard oil or iso-thiocyanate, depending on the constitution of the anilide. The two interpretations of the mechanism of reaction may be expressed as follows.

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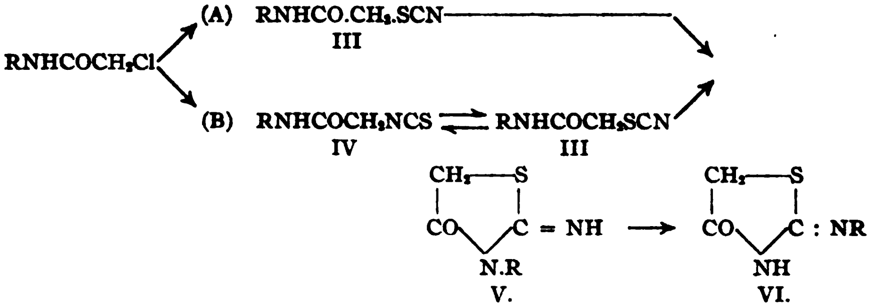
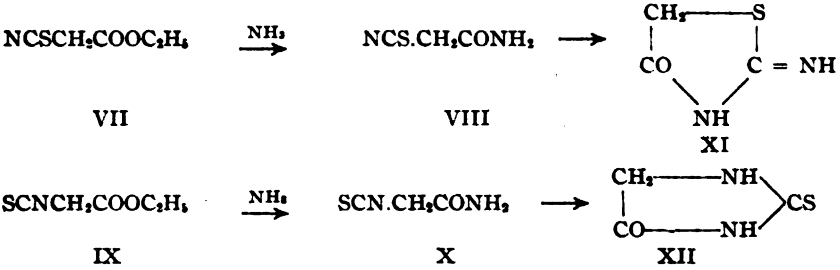
[1] Wheeler and Merriam, THIS JOURNAL, 23, 283 (1900); Wheeler and Johnson, *Am. Chem. J.*, 28, 121 (1902); Johnson, THIS JOURNAL, 25, 483 (1903); Johnson and Ticknor, *Proc. Nat. Acad. Sci.*, 3, 303 (1917); THIS JOURNAL, 40, 636 (1918).

[2] Beckurts and Frerichs, *Arch. Pharm.*, 237, 286, 304 (1899); 238, 9, 329, 615 (1900); Grothe, *ibid.*, 258, 160 (1900); Beckurts and Frerichs, *ibid.*, 253, 233 (1915); Frerichs and Foster, *C. A.*, 4, 2294 (1910).



It was for the purpose of throwing new light on this interesting question that we undertook the work now discussed in this paper. We now present new and very conclusive evidence that these reactions proceed according to Scheme A, or that an isothiocyanate IV is not a product of reaction in these transformations. We have obtained no evidence supporting the assumption that a thiocyanate corresponding to Formula III can undergo rearrangement to its iomeric isothiocyanate IV as expressed in Scheme B.

In a previous paper from the Sheffield Laboratory by Johnson and Hemingway,[1] it was shown that the ethyl ester of iso-thiocyano-acetic acid, IX, interacts with ammonia in benzene solution in a unique manner. Instead of combining as expected to form the corresponding thio-urea derivative. $NH_2SCNH.CH_2COOC_2H_5$, they interact smoothly to give the normal 2-thiohydantoin XII. In other words, the ester grouping is the point of attack by ammonia, giving apparently an amide of iso-thiocyano-acetic acid X as an intermediate product, which immediately condenses at low temperature, giving the 2-thiohydantoin XII. Thus, while the 2 isomeric esters VII and IX react with ammonia in an analogous manner, the products of reaction isomerize in an entirely different manner, giving *pseudo*- and *normal*-thiohydantoin, respectively.[2]



This unique behavior of ethyl iso-thiocyano-acetate in the presence of ammonia suggested to the writer that a substituted amide of iso-thio-

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[1] This Journal, 38, 1550 (1916).

[2] Claesson, *Ber.*, 10, 1349 (1877); Miolati, *Gazz. chim. ital.*, [1] 23, 94 (1893); Johnson and Hemingway, *loc. cit.*

cyano-acetic acid (Formula IV), if once formed, would behave in a manner similar to its prototype X, and would undergo immediate isomerization to a substituted 2-thiohydantoin. In order to decide this point and, furthermore, to obtain experimental evidence in favor of Equations A or B represented above, it only remained, therefore, to synthesize an anilide of this type IV by a method which excludes from consideration the possible formation of an isomeric thiocyanate III and study its chemical behavior. A method of synthesis which permits us to obtain isothiocyanate combinations of this type has now been worked out and applied successfully for the preparation of the anilide of iso-thiocyano-acetic acid XVII. The further application of this synthesis is now in progress and the results obtained will be published in a later paper.

The starting point of our synthesis is the anilide of amino-acetic acid XIV, which can be obtained easily and in quantity for synthetical work by the method of preparation recently described by Hill and Kelsey.[1] Interaction of this anilide XIV with carbon disulfide in alcohol solution at ordinary temperature leads to the formation of an almost quantitative yield of the corresponding dithio-carbamate XIII. This change is expressed by the following equation:

$$\underset{\text{XIV}}{2C_6H_5NH.COCH_2NH_2} + CS_2 = \underset{\text{XIII}}{C_6H_5NH.COCH_2NH.CSSH.NH_2CH_2CONHC_6H_5}.$$

The next stage of our synthesis is the treatment of this salt XIII with ethyl chloroformate in ether solution when 2 compounds are formed as products of the reaction, namely, the urethane and the dithio-carbamate corresponding to Formulas XVI and XV, respectively. The dithio-carbamate is the chief product of reaction.

$$\underset{\text{XIII.}}{C_6H_5NH.COCH_2NHCSSH.NH_2CH_2CONHC_6H_5} + ClCOOC_2H_5 =$$

$$\underset{\text{XV.}}{C_6H_5NHCOCH_2NHCSS.COOC_2H_5} + HCl.NH_2CH_2CONHC_6H_5$$

$$\downarrow$$

$$\underset{\text{XVI}}{C_6H_5NHCOCH_2NHCOOC_2H_5} + CS_2.$$

Andreasch[2] has shown that dithio-carbamates corresponding to Formula XV decompose on distillation with formation of iso-thiocyanates. Johnson and Ticknor[3] prepared the dithio-carbamate of ethyl amino-acetate and showed that this compound undergoes an analogous change on heating, giving the corresponding iso-thiocyanate IX. We now find that the ester XV breaks down in a similar manner on distillation, giving the desired anilide of iso-thiocyano-acetic acid XVII. This compound, however, was not isolated on account of its great instability. Just as we an-

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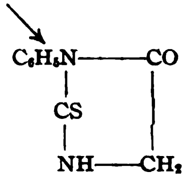
[1] THIS JOURNAL, 42, 1704 (1920)

[2] Andreasch, *Monatsh.*, 27, 1906 (1211).

[3] *Loc. cit.*

ticipated, it exhibited a unique behavior and underwent an immediate isomerization at the temperature of formation giving quantitatively 1-phenyl-2-thiohydantoin.[1] We obtained no evidence of the formation of the labile or stabile forms of phenyl pseudo-thiohydantoins V and VI (R = phenyl), proving that the normal thiocyano-acetanilide III is not formed here in this change by molecular rearrangement of the iso-thio-cyanate XVII. This result again confirms our previous conclusions that the change $R.SCN \longrightarrow R.NCS$ is not a reversible reaction, and that a normal thiocyanate is the primary product of reaction when potassium thiocyanate interacts with an anilide derivative of chloro-acetic acid. These fundamental changes are expressed by the following equations:

$$\underset{XVI}{C_6H_5NH.COCH_2NHCSS.COOC_2H_5} \xrightarrow{\text{heat}} \underset{XVII.}{C_6H_5NHCOCH_2.NCS} + COS + C_2H_5OH.$$



XVIII.

The 1-phenyl-2-thiohydantoin is also formed by distillation of the dithiocarbamic acid salt XIII with mercuric chloride. This change involves the primary formation of the iso-thiocyanate XVII and then a molecular rearrangement to the thiohydantoin XVIII.

This new method of synthesizing 2-thiohydantoins will be thoroughly investigated in this laboratory and the results obtained described in a future publication. We shall investigate particularly those cases where it has been interpretated that iso-thiocyanates are the products of reaction when an alkali thiocyanate interacts with an anilide derivative of chloro-acetic acid. For further information regarding the details of our work the reader is referred to the experimental part of this paper.

Experimental Part.

Amino-acetanilide, $NH_2.CH_2.CONHC_6.H_5$.—All of this reagent used in the following research was prepared according to the method recently described by Hill and Kelsey.[2]

Interaction of Amino-acetanilide with Carbon Disulfide. The Formation of Amino-acetanilide Dithio-carbamate, $C._6H._5NH.CO.CH._2NH.-CSSH.NH_2CH_2CONHC_6H_5$.—The method of operation which led to the production of a good yield of this new salt was as follows.

Fifty-five g. (1.33 moles) of carbon disulfide was slowly added, with

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[1] Aschan, *Ber.*, 17, 420 (1884); Marckwald, Neumark and Stelzner, *ibid.*, 24, 3278 (1891); Wheeler and Brautlecht, *Am. Chem. J.*, 45, 446 (1911).

[2] *Loc. cit.*

frequent agitation, to a well cooled solution of 175 g. of dry amino-acetanilide (2 moles) in 300 cc. of absolute alcohol. A slightly endothermic reaction took place. When approximately $^2/_3$ of the carbon disulfide had been added a white solid began to separate from the reaction mixture, and when all had been added, the solution became quite solid from a mass of small colorless needles.

After standing for about one hour, the insoluble dithio-carbamate was filtered off and then triturated very thoroughly with 500 cc. of cold water in order to remove unchanged amino-acetanilide. Following this treatment, it was washed successively with small amounts of alcohol and ether, and then dried at a temperature of 50°. The yield was 200 g. or 91%. When the reaction is applied in 95% instead of absolute alcohol the yield of carbamate is reduced considerably.

The salt is rather unstable. When moderately heated, or even when allowed to stand exposed to the air for a few hours, it turns a delicate pink color and the odor of hydrogen sulfide is plainly perceptible. On this account, the salt was always freshly prepared for reactions in which it was to be used.

It is fairly soluble in alcohol, but decomposes rather readily in this solvent with evolution of hydrogen sulfide. It is less soluble in warm water and apparently more stable in this solvent than in alcohol. From water, it crystallizes in thin plates of a light salmon color, which melt at 145° with decomposition.

For analysis the salt was crystallized from water, washed with alcohol and ether, and then dried at room temperature.

Calc. for $C_{17}H_{20}O_2N_4S_2$: N, 14.89; S, 17.03. Found: N, (I) 14.88; (II) 14.96; S, 16.84.

Carbethoxyl Amino-acetanilide Dithio-carbamate, $C_6H_5NHCOCH_2NHCSS.COOC_2H_5$.—This interesting anhydride is formed by the action of ethyl chloroformate on amino-acetanilide dithio-carbamate suspended in anhydrous ether.

Two hundred g. of the finely pulverized dithio-carbamate was suspended in one liter of anhydrous ether and 57 g. (one molecule) of ethyl chloroformate added rather rapidly, with thorough agitation. No visible reaction occurred. The mixture was then heated gently on the water bath for 3 hours. During the period of heating it was found desirable to agitate the solution frequently in order to prevent caking. After standing in the cold for 12 hours, the ether solution had assumed a yellow color and the insoluble residue was more granular in appearance than the original material.

The suspension was then filtered, the precipitate was washed repeatedly with fresh ether, and the washings were added to the original filtrate. If the reaction had proceeded quantitatively, the residue should have weighed 99 g. We obtained 165 g. of a mixture consisting of amino-acetanilide hydrochloride and unchanged dithio-carbamate. The ether solution was found to contain unchanged ethyl chloroformate corresponding to the unaltered dithio-carbamate.

When the ether solution was evaporated, we obtained as a residue a yellow oil which soon solidified partially to a mass of light yellow crystals. The crystalline material weighed 60 g., after it was dried at room temperature, and was identified as a mixture of the dithio-anhydride and the normal urethane of amino-acetanilide. The air-dried product decomposes at 100° with considerable effervescence. It has a pleasant aromatic odor. Owing to its instability in almost all solvents except ether, it is practically impossible to obtain it in a state of purity. Its principle impurity, the urethane described below, can be removed only in part by trituration with ether.

Several attempts were made to improve the yields in this reaction. The best results were obtained by using smaller amounts of the reacting substances and increasing the proportion of ethyl chloroformate to 1.33 moles. Under these conditions a yield of 47% was obtained. A vigorous mechanical agitation of the reaction mixture would undoubtedly increase this yield.

The analyses of the reaction product showed results low for sulfur and high for nitrogen. It was contaminated with small quantities of the urethane, $C_6H_5NHCOCH_2NHCOOC_2H_5$, which could not be removed completely owing to the fact that the instability of the dithio-carbamic ester rendered it impossible to utilize a choice of solvents in order to effect the separation.

Calc. for $C_{12}H_{14}O_3N_2S_2$: N, 9.4. Calc. for $C_{11}H_{14}O_3N_2$: N, 12.6. Found: 10.2, 10.4.

The urethane formed in this process is not a product of reaction between ethyl chloroformate and the hydrochloride of amino-acetanilide. For example, 10 g. of the hydrochloride and ethyl chloroformate, respectively, were suspended in 50 cc. of ether and the solution was boiled for 4 hours. The resulting precipitate remaining after this treatment was then filtered off and was identified as unchanged hydrochloride. Evaporation of the ether left behind a clear oil which was identified as unaltered ethyl chloroformate. The weight of the latter was practically the same as that originally taken (10 g.).

Behavior of Carbethoxyl Amino-acetanilide Dithio-carbamate on Distillation. Its Conversion into 1 - Phenyl - 2 - thiohydantoin, $C_6H_5\underline{NCSNHCH_2CO}$.—Sixty g. of the air-dried ester were placed in a distilling flask which was connected with a small ice-cooled receiver, and this in turn with a bulb containing a strong solution of sodium hydroxide in 50% alcohol. The system was evacuated to a pressure of 55 mm. and the ester heated in an oil bath to a temperature of 120° when decomposition ensued, and soon became so brisk that the vacuum was practically lost. A few cc. of a colorless distillate collected in the receiver. The contents of the flask were liquid at first but soon set to a light brown mass. After the decomposition was over the vacuum was restored and the heating was continued for 15 minutes. The products of the reaction were investigated as follows:

The caustic alkali solution, through which the gases of decomposition were passed during destructive distillation was evaporated nearly to dryness on the steam-bath in order to remove the alcohol. The residual aqueous solution gave a strong positive test for sulfur, indicating that carbon oxysulfide or carbon disulfide had been evolved during distillation.

The distillate collected in the receiver boiled at 80° under atmospheric pressure. It gave iodoform with caustic potash and iodine, and acetaldehyde by oxidation with potassium dichromate and sulfuric acid. The distillate was, therefore, ethyl alcohol and the total amount collected was 6 g. or 66%.

The residue in the flask was of a light brown color and crystal faces could be detected throughout the mass. The customary tests for a mustard oil gave negative results. A small portion, however, when digested with alkaline lead acetate, gave a black precipitate of lead sulfide. The entire residue was warmed with 100 cc. of alcohol in order to disintegrate the cake. The highly colored alcoholic liquors were filtered and the residual solid washed with fresh alcohol. As a result of this treatment a yellow, finely crystalline material was obtained. The total weight of the latter was 30 g. It was sparingly soluble in glacial acetic acid and in alcohol. After crystallization from the latter solvent it melted at 240–242° with slight decomposition. The melting point was identical with that of 1-phenyl-2-thiohydantoin. A mixture of the 2 substances melted also at 240°. That we were dealing with this hydantoin was also established by its behavior towards benzaldehyde and chloro-acetic acid.

Condensation with Benzaldehyde. 1-Phenyl-2-thio-4-benzalhydantoin, $C_6H_5\underline{N.CS.NHC : (CHC_6H_5).CO}$.—Five g. of 1-phenyl-2-thiohydantoin was digested in an oil bath with 3 g. of benzaldehyde and 10 g. of sodium acetate in 60 g. of glacial acetic acid. After being heated for 2 hours the mixture was poured into water. A yellow solid immediately separated. This product was filtered and then purified by crystallization from alcohol. The melting point of the compound corresponded to that of 1-phenyl-2-thio-4-benzalhydantoin and a mixture of the two melted unchanged at 204°.[1]

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[1] Wheeler and Brautlecht, *loc. cit.*

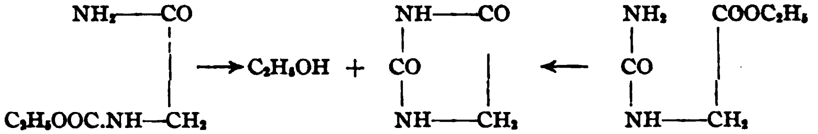
Desulfurization of the Thiohydantoin by Digestion with Chloro-acetic Acid. 1-Phenylhydantoin, $C_6H_5N.CO.NH.CH_2.CO$.—Five g. of the thiohydantoin was digested on the water bath for 2.5 hours with a solution of 15 g. of chloro-acetic acid in 75 cc. of water. After filtration, the solution was evaporated to a small volume on the water bath. After trituration with ether to remove oily products, a white solid crystallized from the liquor. This was filtered and then crystallized from a small volume of water. It crystallized from this solvent in glistening needles melting at 159° (corr.).[1] A mixture of this substance with 1-phenylhydantoin melted at the same temperature.

Carbethoxy Amino-acetanilide, $C_6H_5NHCOCH_2NHCOOC_2H_5$.—The alcoholic liquors resulting from the trituration of the crude 1-phenyl-2-thiohydantoin (above) were evaporated to dryness. The residue was then redissolved in a small volume of alcohol and decolorized with a little of the vegetable carbon "Norite." When this solution was diluted with 5 volumes of water and then cooled a colorless compound finally crystallized from the solution in characteristic plates melting at 137.5°. Seven g. of this solid was obtained; it was identified as the urethane derivative.

Calc. for $C_{11}H_{14}O_3N_2$: N, 12.61. Found: (Kjeldahl) (I), 12.78, (II), 12.52.

Four g. of ethyl chloroformate was slowly added to a suspension of 10 g. of amino-acetanilide in 75 cc. of dry ether. A fairly vigorous reaction ensued. After the addition of the ester, the solution was warmed for 2 hours on the steam bath. The precipitate was then filtered and triturated with 100 cc. of water in order to remove the hydrochloride of amino-acetanilide and the insoluble material crystallized from dil. alcohol. It melted at 137.5° and proved to be identical with that produced by destructive distillation during the formation of 1-phenyl-2-thiohydantoin. The urethane is quite soluble in alcohol and sparingly soluble in ether and hot water.

The Conversion of Carbethoxy Amino-acetanilide into 1-Phenylhydantoin, $C_6H_5N.CO.NH.CH_2.CO$.—Fischer and Otto[2] were unable to convert carbethoxy-glycinamide into hydantoin either by application of heat or by treatment with acid or alkali. In fact they were led to suggest this reaction as a means of differentiation between this type of urethane and the isomeric hydantoic esters.



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[1] Mouneyrat, *Ber.*, 33, 2394 (1900).

[2] *Ibid.*, 36, 2109 (1903).

Later, however, Koenig and Mylo[1] were successful in accomplishing this transformation by means of a dil. solution of sodium hydroxide, followed by treatment with dil. hydrochloric acid. Their yield, however, was very poor.

In the light of the above work it seemed of interest to determine whether the introduction of the phenyl group, as in the case of carbethoxy-amino-acetanilide would affect the reactivity of the adjacent hydrogen atom. Five g. of the urethane was added to a warm solution of 2 g. of potassium hydroxide in 50 cc. of alcohol, and the mixture was allowed to stand for 18 hours. The solution was then made strongly acid with alcoholic hydrochloric acid. After filtration of the precipitated potassium chloride, the filtrate was evaporated to a small volume on the steam-bath. A colorless solid was precipitated by the addition of 2 volumes of ether. This material was filtered off and purified by crystallization from hot water, when it was obtained in the form of colorless needles melting at 159°. It proved to be identical with 1-phenylhydantoin and melted at an unchanged temperature when mixed with a known sample of this compound. The yield was 50%. Koenig and Milo obtained a 10% yield in the transformation of carbethoxy-glycinamide into hydantoin. We were unable to accomplish this change either by heat or through the agency of either aqueous or alcoholic hydrochloric acid. In the first case no reaction occurred until the product had been heated to a temperature of 260°. At this temperature decomposition took place and a resin was formed. Two hours heating with alcoholic hydrochloric acid resulted in the decomposition of our urethane into amino-acetanilide. On the other hand, evaporation with aqueous hydrochloric acid had no effect and the hydrochloric acid salt of the urethane was recovered. The latter was transformed into the urethane by treatment with sodium hydrogen carbonate.

The Action of Mercuric Chloride on Amino-acetanilide Dithio-carbamate, $C_6H_5NHCOCH_2NH.CSSH.NH_2CH_2CONHC_6H_5$.—This salt undergoes a normal transformation when digested with mercuric chloride and is converted into the mustard oil $C_6H_5NH.COCH_2.NCS$. Since the latter is unstable, it condenses to give the corresponding thiohydantoin.

Thirty g. of the dithio-carbamate was added to a solution of 10 g. of mercuric chloride in 150 cc. of water. A little less than one molecular proportion of mercuric chloride was employed in order to avoid desulfurization of the hydantoin. A white precipitate of the mercury salt soon separated, but this became black when it was gently warmed; at the same time hydrogen sulfide was evolved. Gentle heat was applied until the evolution of hydrogen sulfide had ceased. When the reaction was over, the precipitate was filtered and extracted repeatedly with hot alcohol. When the alcoholic solution was cooled, 1-phenyl-2-thiohydan-

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[1] Ber., 41, 4431 (1908).

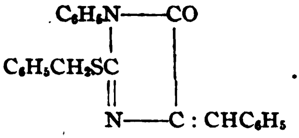
toin crystallized in characteristic prisms which melted at 240°. This melted unchanged with a known sample of 1-phenyl-2-thiohydantoin. The yield was 7 g., corresponding to 46%. It is a very significant fact that hydrogen sulfide was evolved freely in this decomposition. According to Anschutz[1] the hydrogen sulfide evolved in such reactions is destroyed at once by interaction with the mustard oil to give a thio-urea combination. This change is expressed as follows,

$$2R.NCS + H_2S = CS_2 + CS(NHR)_2.$$

In our experiment we obtained no evidence of the formation of the thiourea derivative of amino-acetanilide. Apparently the mustard oil derivative immediately after formation is converted into the thiohydantoin. XVIII

$$2C_6H_5NHCOCH_2NCS + H_2S = CS_2 + CS(NHCH_2CONHC_6H_5)_2.$$

1-Phenyl-2-benzylmercapto-4-benzalhydantoin,



. — Five g. of 2-thio-4-benzalhydantoin was dissolved in a solution of sodium ethylate, prepared by dissolving 0.6 g. of sodium in 30 cc. of absolute alcohol. Then 5 g. of benzyl chloride was added slowly to the alkaline solution of the thiohydantoin. There was an immediate reaction and the solution became solid. After standing for 2 hours, the precipitate was filtered and then triturated with hot alcohol in order to separate the benzyl derivative from sodium chloride. This was then purified by crystallization from boiling alcohol and separated in the form of yellow needles melting at 178°.

Calc. for $C_{23}H_{18}ON_2S$: N, 7.57. Found: (Kjeldahl), 7.46, 7.74.

NEW HAVEN, CONN.

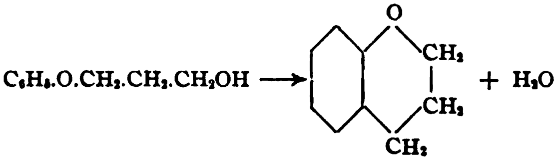
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

HETEROCYCLIC COMPOUNDS OF *N*-ARYLAMINO ALCOHOLS.

BY R. E. RINDFUSZ AND V. L. HARNACK.

Received May 28, 1920.

A simple method has recently been published[2] for the preparation of chromanes and coumaranes according to the following reaction



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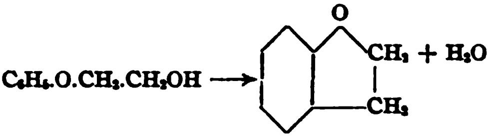
[1] Anschutz, *Ann.*, 371, 211 (1909).

[2] THIS JOURNAL, 41, 665 (1919); 42, 157 (1920).



The hydroxy ethers are easily prepared by treating phenol or its homologues either with trimethylene chlorohydrine or with ethylene chlorohydrine. They are dehydrated by treatment either with zinc chloride or with phosphorus pentoxide; the latter gives the better results. The present investigation was undertaken to see whether similar reactions could be applied to the preparation of analogous ring compounds of nitrogen.

The starting point in each case is aniline; but there is no reason for assuming that substituted anilines, phenylene diamines, naphthyl amines and similar compounds could not be used, although the products would be somewhat more complex.

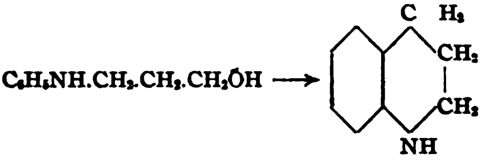
When aniline is treated either with trimethylene chlorohydrine or with ethylene chlorohydrine in the presence of sodium carbonate, 2 products are formed; one in which a single hydrogen of the amine group is substituted and the other in which both are replaced.

$$C_6H_5NH_2. \xrightarrow{Cl.CH_2.CH_2CH_2OH} C_6H_5NH.CH_2.CH_2.CH_2OH + C_6H_5N : (CH_2.CH_2.CH_2OH)_2$$

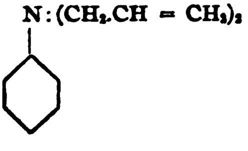
$$C_6H_5NH_2 \xrightarrow{Cl.CH_2.CH_2OH} C_6H_5NH.CH_2CH_2OH + C_6H_5N : (CH_2.CH_2OH)_2$$

These compounds in each case have widely differing boiling points and are easily separated and purified.

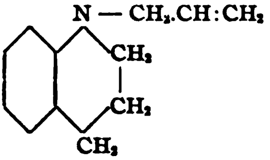
The products of dehydration of the first 2 compounds above are the simple rings one would expect from the analogous work in the chromane syntheses. Hydroxypropyl aniline gives the well known compound, tetrahydroquinoline



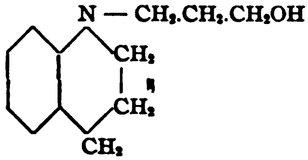
Dehydration of di-γ-hydroxy-propyl-aniline, however, offers a number of possible products as follows



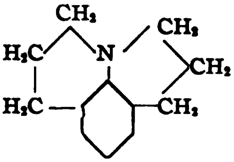
(I).



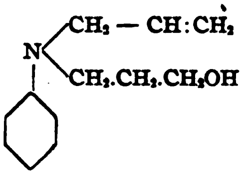
(II).



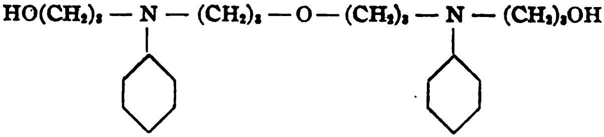
(III).



(IV).



(V).



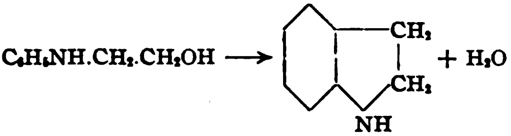
(VI).

Of these, III, V, and VI are eliminated by analysis since each of these formulas shows the loss of but one molecule of water. Formula I represents a known compound, but its constants do not agree with the product formed. A substance corresponding to Formula II was prepared by treating tetrahydroquiniline with allyl bromide and found to be a different substance. By elimination, IV alone is left. This represents julolidine, previously prepared by G. Pinkus[1] and J. von Braun[2] and the physical constants agree with those given.

In the case of the oxygen compounds referred to above, the dehydration of β-hydroxy-ethylphenyl ether, $C_6H_5—O—CH_2—CH_2OH$, forms coumarane, $C_6H_5\text{-}O—CH_2—CH_2$ in a manner exactly analogous to the preparation of the 6-membered ring compound chromane,

$$C_6H_5\text{-}O\text{-}CH_2—CH_2—CH_2.$$

However, with the nitrogen compounds, this is not the case. β-Hydroxy-ethyl-aniline would be expected to yield dihydro-indol, a liquid boiling at 220°.



In the laboratory a very small amount of liquid did distill over, beginning at this temperature, but it was not enough to purify. The chief product of the reaction is a white crystalline solid melting at 160–162°. This is undoubtedly diphenyl piperazine for which melting points ranging from 157° to 164.5° have been reported.[3] It is formed by dehydration between 2 molecules. Thus

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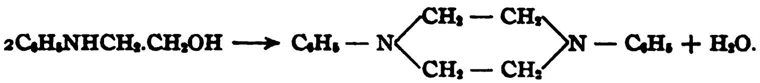
[1] *Ber.*, 25, 2801 (1892).

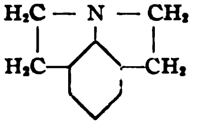
[2] *Ibid.*, 51, 1215 (1918).

[3] *Jahresb. Chem.*, 1858, 352; 1859, 388.



Again, the treatment of di-β-hydroxy-ethyl-aniline results in the formation of a 6-membered ring, this time by dehydration within the molecule.

This represents phenyl morpholin and is identified; first, by analysis, since the formation of the 5-membered ring compound by dehydration into the benzene ring would yield



with the elimination of 2 molecules of water; second, phenyl morpholine has been prepared by Knorr,[1] who observed a boiling point "around 270°" and a melting point of 53°. The product here found boiled at 165° to 170° under 45 mm. pressure and melted at 52°.

Thus, it is evident that these nitrogen compounds, unlike the analogous oxygen rings, show a marked preference for the formation of 6-membered rings rather than those of 5 atoms.

Experimental Part.

Preparation of γ-hydroxy-propyl-aniline, $C_6H_5.NH.CH_2.CH_2.CH_2OH$.—A mixture of 120 g. of aniline, 125 g. of trimethylene chlorohydrine and 125 g. of anhydrous sodium carbonate was refluxed for 3 or 4 hours. After filtering and washing the residue with ether, the liquid was distilled. The first reaction consisted of unchanged aniline; the desired product boiled at 192° under 30 mm. pressure. It is a viscous, lemon-colored liquid which turned red on standing. Yield, 92 g. or 67.5%. $[n]^{20}$ 1.502; d_{26}, 1.063.

Subs., 0.1660: CO_2, 263.4 cc. (25°, 744 mm.). Blank 0.0034 g. C.
Calc. for $C_9H_{13}ON$: C, 71.5. Found: 71.8.

Preparation of Di-γ-hydroxy-propyl aniline, $C_6H_5N = (CH_2CH_2CH_2OH)_2$.—A third fraction from the above distillation boiled at 241–2° under 25 mm. pressure. When first distilled, it was colorless but it turned red on standing. Yield, 45 g. or 25.3%. $[n]^{24}$, 1.565; d_{26}, 1.097.

Subs., 0.2308: CO_2, 345.3 cc. (24.1°, 745.1 mm.). Blank 0.0034 g. C.
Calc. for $C_{12}H_{19}O_2N$: C, 68.9. Found: 68.6.

Tetrahydro Quinoline.—A solution of 90 g. of γ-hydroxy-propyl-aniline in 125 cc. xylene was refluxed with 40 g. of phosphorus pentoxide

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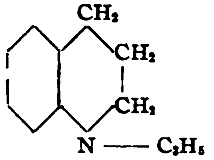
[1] *Ber.*, **22**, 2094 (1889).

for about an hour. This caused the entire mixture to become liquid. At this stage it was washed with sodium hydroxide and with water, dried and distilled. A yield of 17 to 18 g., about 22%, was obtained as a pale yellow liquid which boiled between 205° and 210° at 75 mm. pressure. $[n]^{24}$, 1.569; d_{24}, 1.051. The constants in the literature are, b. p., 251°, d_{25} 1.057.

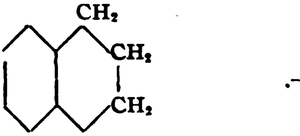
Julolidine.—To 22 g. of di-γ-hydroxy-propylaniline dissolved in hot xylene, 30 g. of phosphorus pentoxide was added. After this mixture had been warmed for a short time, vigorous action commenced and continued for several minutes without further application of heat. The mixture was heated under a reflux condenser for about 3 hours, which caused the pentoxide to become a viscous layer so that the xylene could be decanted easily. The residue was washed with ether and added to the xylene solution which was distilled. Yield, 2 g. or 11%. B. p. 170–173° at 31 mm. $[n]_{25}$, 1.568; d_{20}, 1.003. The boiling point given by von Braun[1] is 155–6° at 17 mm.

Subs., 0.2673: CO_2, 496.4 cc. (30.3°, 740.3 mm.).
Calc. for $C_{12}H_{15}N$: C, 83.2. Found: 83.3.

***N*-Allyl-tetrahydro-quinoline,** 

.—Six g. of tetrahydro-quinoline and the theoretical amount of allyl bromide were refluxed for 3 hours in the presence of anhydrous sodium carbonate.

The sodium bromide and excess sodium carbonate were separated and washed with ether. The filtrate and wash ether were then distilled. Yield, 4 g. B. p. 135° at 25 mm. $[n]^{24}$, 1.556; d_{24}, 1.024.

***N*-γ-Hydroxy-propyl-tetrahydro-quinoline,** 

.—

Twenty-four g. of tetrahydro-quinoline was refluxed for about 3 hours with 17 g. of trimethylene chlorohydrine and an excess of anhydrous sodium carbonate. The mixture was then taken up in ether and distilled. This yielded 27 g. of a thick, viscous, yellow liquid, which turned red on standing. B. p. 227–9° at 18 mm. $[n]^{31}$, 1.561; d_{27}, 1.091.

Subs., 0.1571: CO_2, 263.8 cc. (26.6°, 743.3 mm.). Blank 0.0034 g. C.
Calc. for $C_{12}H_{17}ON$: C, 75.4. Found: 75.2.

Julolidine from *N*-γ-Hydroxy-propyl-tetrahydro-quinoline.—Julolidine may be prepared by the dehydration of the γ-hydroxy-propyl-tetrahydroquinoline just described, but in the one run made, the yield was very

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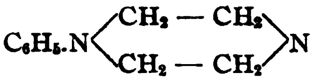
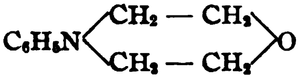
[1] *Ber.*, 51, 1215 (1918).

small. The dehydration was carried out in xylene as described above and evidently proceeds with difficulty since 3 hours' action on 27 g. of the hydroxy compound gave less than a gram of julolidine with a boiling point and refractive index the same as that given above.

β-Hydroxy-ethylaniline, $C_6H_5NH.CH_2.CH_2.OH$, **and Di-β-hydroxy-ethylaniline,** $C_6H_5N:(CH_2.CH_2.OH)_2$.—These compounds were prepared from aniline and ethylene chlorohydrine in a manner exactly analogous to that used for the γ-hydroxy-propyl derivatives described above. The constants observed for the first compound were b. p. 188°, at 30 mm.; $[n]^{24}$, 1.576; d_{24}, 1.101; and for the second, b. p. 228° at 15 mm.; m. p. 53.5–54°.

Diphenyl-piperazine,  —To 65 g. of β-hydroxy-ethylaniline dissolved in xylene, a total of 25 g. of phosphorus pentoxide was added in 3 portions. After refluxing this mixture for an hour, the xylene layer was decanted and distilled. A small amount of a liquid, presumably dihydro-indol, came over between 220 and 270°. The remainder distilled around 245° at 30 mm. and crystallized as a white solid. After purification by solution in alcohol and precipitation with water several times, it melted at 160–162°. Yield, 5 g.

Phenyl-morpholin,  —When di-β-hydroxy-ethylaniline was dehydrated with an amount of phosphorus pentoxide calculated to remove 2 molecules of water, most of the mixture carbonizes. However, when less pentoxide was used—30 g. in 2 portions to 50 g. of the aniline derivative in xylene—no carbonization took place. A water-clear liquid distilled between 165 and 170° at 45 mm.; this liquid turned red on standing and crystallized slowly. After recrystallization from alcohol, it melted at 52°.

Subs., 0.1500: CO_2, 247.2 cc. (26.9°, 743.3 mm.). Blank 0.0034 g. C.
Calc. for $C_{10}H_{13}ON$: C, 73.6. Found: 73.5.

Summary.

1. Cyclic nitrogen compounds may be formed by the dehydration of N-arylamino alcohols.
2. Where 6-membered rings may be so formed, the dehydration takes place in such a way as to close a side ring adjacent to the benzene nucleus.
3. Where a 5-membered ring would be formed as a side ring annealed to the benzene nucleus, a 6-membered ring outside is usually formed. This is unlike the behavior of analogous oxygen compounds.
4. The reaction on nitrogen compounds has not been carried out in enough cases to show that these inferences are general.

URBANA, ILL.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, No. 335.]

FAT ASSOCIATED WITH STARCH.

BY T. C. TAYLOR AND J. M. NELSON.

Received June 15, 1920.

It is well known that the starches as they are obtained ordinarily from the plants have a certain amount of fat associated with them. It has been assumed generally that this fat can be removed by solvents, and that its presence is a contamination of the starch with other constituents which occur intimately associated with the starch in the plant.

In the manufacture of glucose commercially from corn starch an insoluble product known as "refinery mud" occurs in the sugar liquor after the hydrolysis, and is separated by filtration. This refinery mud as recovered contains about 50% of fat, chiefly the higher fatty acids, and after washing and other treatment is sold as soap stock.

Considering the process employed in the commercial hydrolysis of starch it is improbable that the source of this fatty material can be attributed to extraneous matter accompanying the starch from the kernel, since its presence is observed only during or after the destruction of the starch by hydrolysis. The occurrence of free fatty acids during the hydrolysis and disruption of the complex starch molecule leads to the interesting question of whether the fatty material constitutes an inherent part of the starch itself.

The present article is an account of an attempt to answer this question. and the results obtained lead to the following conclusions.

I. The major part of the fatty material present in starch cannot be removed by solvents before hydrolysis.

II. Hydrolysis of corn starch freed of extraneous fat liberates fatty acids.

III. The liberated fat is principally palmitic acid, but an unsaturated substance of unknown structure also occurs with it.

IV. The fat is liberated when hydrolysis has reached the erythrodextrin stage.

V. It is possible to obtain from starch residues containing relatively large amounts of fat combined with carbohydrate.

VI. The palmitic acid apparently is attached indirectly to the carbohydrate, but directly to the unsaturated component.

VII. Starches from other sources than corn also contain combined fat.

I. Extraneous Fat Accompanying the Starch.

The corn starch used was the best alkali-washed product available in the open market. A 82.26 g. sample of this material was extracted, first with ether, then with petroleum ether and finally with carbon tetrachloride. The duration of the extraction in each case was 36 hours. The amount of soluble matter, chiefly fat, obtained by means of each successive solvent was

Solvent.	%.
Ether (dry)	0.057
Petroleum ether	0.012
Carbon tetrachloride	0.046
Total	0.115

Further extraction gave no weighable residues upon evaporation of the solvent.

The residues, obtained by evaporation of the solutions from the first extractions and the weights of which are given in the table above, were yellow and gummy. Upon solution in alcohol and titration with alkali, the combined residues gave an acid value[1] of 95.1. A comparison of this acid number with 186.0, that of the fat described under II, indicates the presence of considerable foreign matter, probably nitrogeneous in character.

Purification of the Corn Starch.—Since starch is separated mechanically from the other substances which occur with it in the plant,[2] the separation is never complete, even after repeated treatments. For this reason, it is necessary to resort to other methods of removing the remaining impurities,[3] chiefly nitrogeneous. The presence of the latter is indicated both by the nitrogen content 0.06% (Kjeldahl method), and the presence of dark yellow particles when the starch, stained with iodine, is examined under the microscope.

Removal of the Nitrogenous Material and Extraneous Fat.—About 500 g. of dry powdered corn starch was placed in a 3-liter round-bottom flask provided with a reflux condenser, then enough 95% alcohol added to make a thick paste and finally 500 cc. of 90% alcohol containing 0.23 g. of hydrogen chloride per cc. After refluxing on the water bath for $^3/_4$ hour with continuous agitation, the contents of the flask was filtered through a Büchner funnel and the residue washed, first with hot 95% alcohol and finally with several portions of ether.

The purified starch obtained in this way was clean and white. When stained with iodine, it showed under the microscope no indications of protein, and the granules appeared to be still intact, although slightly enlarged, with evidence of incipient rupture at the hilum. That no profound change in the starch had occurred was shown also by the fact that when a sample of this starch, treated with alkali to neutralize the hydrochloric acid which still adhered, was gelatinized by stirring into

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[1] Mg. of potassium hydroxide neutralized by one g. of the fat.

[2] Commercial method, T. B. Wagner, *J. Soc. Chem. Ind.*, 28, 343 (1909).

[3] Composition of corn kernel, THIS JOURNAL, 25, 1166 (1903); and Porst, *Eighth Inter. Cong. App. Chem.*, 12, 205.

boiling water it gave a "thick boiling" paste which is characteristic of unchanged or "raw" starch. The amount of hydrochloric acid adhering was determined by drying the purified starch at 40° and then suspending in water and titrating with standard alkali, and was found to be 0.52%. By means of Kjeldahl determinations, the nitrogen content was found to have been decreased in the process of purification from 0.06 to 0.02%.

When the purified starch was stained with iodine and examined under the microscope a stratified structure of alternating dark blue and transparent concentric rings, was observed. This is in accord with previous observations of Duclaux[1] and others and indicates a layer structure of the starch granules, which might be of importance in connection with the question of the presence of 2 kinds of starch material in the granules, as held by Baker and Sherman and others.[2]

The starch purified by the latter method contains no extraneous fat. Eighty g. of dried starch was extracted in a Soxhlet for 40 hours with dry ether. Upon evaporation of the ether extract no weighable residue remained, showing the starch to be free from extraneous fat.

In order to make sure that no free fat was adsorbed so firmly to the starch that it could not be removed by the above method of extraction the following procedure was employed.

An ether solution of fat, previously obtained from hydrolyzed starch, was thoroughly mixed with finely powdered purified starch and this mixture, containing the starch in suspension, evaporated, then heated on the water bath with stirring. This fat-impregnated starch was then extracted for 10 hours in a Soxhlet with absolute ether and the amount of fat determined.

SAMPLE, 20.0 G.

	Fat added. G.	Fat recovered. G.
1	0.4566	0.4501
2	0.4035	0.4057
3	0.1400	0.1465

In Numbers 1 and 2 the fat added was much in excess of total fat usually found, while in 3 the amount was comparable with the usual fat content of the original starch.

On hydrolysis of these starch samples with aqueous hydrochloric acid, after the added fat had been removed by extraction, the usual amount of fatty material was recovered, as in II.

II. Liberation of Fatty Acids.

When the starch freed from extraneous fat as described in I is hydrolyzed, fat is liberated, exceeding in amount the extraneous fat extracted from the original starch.

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[1] Duclaux, *Ann. Inst. Pasteur,* 9, 836 (1895).

[2] THIS JOURNAL, 38, 1885 (1916).

Fat by Hydrolysis.—One hundred cc. of conc. hydrochloric acid was added to 200 cc. of boiling water, and immediately upon addition of the acid a starch suspension of 25 g. of starch in 100 cc. of water, was poured slowly into the boiling acid solution with continuous stirring and heating. The mixture soon liquefied and the starch was hydrolyzed with the liberation of an insoluble, flocculent material. The heating was discontinued when a drop of the liquid no longer showed color with iodine, and the mixture was allowed to cool. It was then poured on a large filter paper, allowed to drain, and the residue washed with cold water until free from hydrochloric acid. The paper and residue were dried at 50° in an air-bath, placed in a thimble and extracted in a Soxhlet for 3 hours. After removal of the solvent from the extract, by evaporation on the steam-bath, the flask and the remaining residue were dried and weighed.

Both ethyl ether and petroleum ether were used in the above. The former seemed to give slightly higher results and always carried with it more coloring matter, besides a small amount of reducing sugar, while the latter gave a cleaner product but it was found difficult to get rid of the last traces of the solvent.

Four samples of purified starch were subjected to the above treatment and the fat liberated by hydrolysis determined and given below.

SAMPLE, 25 G. OF STARCH.

	Solvent.	Extraction.	Fat by hydrolysis. %	Acid number.
1	Petroleum ether	Dry	0.56	181.3
2	Petroleum ether	Dry	0.49	186.5
3	Petroleum ether	Wet	0.54	...
4	Ethyl ether	Dry	0.64	184.7

Wet extraction with ethyl ether of the hydrolyzed starch liquor necesitated drying the ether layer due to the relatively large amount of water taken up by it. As this entails some loss, and further since in the presence of fat, reducing sugar passes into the ether layer, only extraction of dried fat should be attempted with this solvent.

The experiment corresponding to the data marked 3 in the above table was carried out slightly differently, in that the liquor resulting from the hydrolysis was extracted directly with petroleum ether, without first filtering or drying the residue.

The fat obtained by the hydrolysis of the starch will hereafter be designated as "fat by hydrolysis" to distinguish it from the small amount of extraneous fat, extracted directly from the starch.

Gelatinization and destruction of starch granule does not affect combined fat. In order to make sure that none of the fat obtained by the hydrolysis of the starch, the amounts of which are given in the table in

Part II, was held mechanically as extraneous fat between the layers in the starch granule, the latter were destroyed by gelatinization. One hundred parts of dry powdered starch were added to 80 parts of a 50% aqueous solution of ammonium thiocyanate to which had been added previously 40% of its weight of alcohol.[1] The gelatinized paste thus obtained was stirred with an excess of acetone which precipitated a white amorphous starch containing no granules. Practically all of the ammonium thiocyanate was then removed by repeated washing with acetone and alcohol and the dried product finally extracted with ether. A sample of this ether-washed starch contained no directly extractable fat, but did contain 0.41% of "fat by hydrolysis" and the latter had an acid number of 182.7. Since the amount of fat and its acid number agree very well with the values in the above table for starch in the form of granules, it is evident that the "fat by hydrolysis" cannot be attributed to retention of fat between the layers in the granules. Had this been the case then when the granules were destroyed the fat would have been removed by the acetone and alcohol, and the fat obtained upon subsequent hydrolysis of the amorphous material would have been much lower than 0.41%.

III. Nature of the Fatty Material Liberated by the Hydrolysis of Maize Starch.

The fatty material obtained by the hydrolysis of the starch as described under II, is semi-crystalline, forms soap with alkali, produces grease stains on paper and has a "tallow"-like odor which becomes more pronounced on heating.

In order to obtain more definite data as to the exact nature of the fatty material, a much larger quantity was necessary than could be obtained by the hydrolysis of batches of starch in ordinary chemical laboratory apparatus. Therefore, the "refinery mud" mentioned in Part I was used.[2] This mud corresponds to the flocculent precipitate which remains after acid hydrolysis of the starch in the method for "fat by hydrolysis." The commercial production of glucose from starch is simply this aqueous acid hydrolysis modified to fit large scale production.

Due to the fact that the mud is removed by filtration in iron filter presses, a considerable amount of iron soap is formed from the action of the fatty acids on the apparatus. A proximate analysis of this "refinery mud" shows the following.

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[1] *J. Soc. Chem. Ind.*, 28, 213 (1909).

[2] The authors wish to thank Dr. C. E. G. Porst for procuring from the Corn Products Refining Company the starch and "refinery mud" used in this investigation, and for his valuable suggestions concerning the determination of the amount of combined fat.

	Per cent.
Moisture	29.5
Protein	10.9
Ash	3.5
Red. sugar	2.4
Fat	48.8
Remainder	Undetermined

The fat content is high because included in this are other substances, especially iron soaps which dissolve with the fat, but these probably do not amount to more than 2.0% of the total extractable matter.

When the fat is first recovered it is a light yellow mass with an odor suggesting furfural, but on standing exposed to air it soon darkens and becomes gummy. After a few days the odor is typical of oleic acid which has been exposed to the air for a time.

Recovery of Fat from the Refinery Mud.—A kilo of this mud was thoroughly mixed with about a liter of low boiling petroleum ether and then poured into a 2-liter round-bottom, short-neck flask connected with a spiral condenser. The flask was heated on a water bath while vaccum was applied to the system, water and petroleum ether distilled over together and separated into 2-layers in the receiver. The ether layer was removed and returned to the flask. On distilling over the ether repeatedly the water was removed from the mud without undue exposure of the fat to the air and in addition the drying was uniform throughout the mass. Finally the last suspension of the starch in the petroleum ether was filtered through a Büchner funnel under suction and the ether distilled off, leaving the crude fat in a dark brown mass whose surface showed, as the fat became cold, a peculiar crystalline structure. This crude fat was dissolved in boiling alcohol and repeatedly treated with bone black and then recrystallized from alcohol until, on cooling, a perfectly white crystalline fatty acid separated. Several more crystallizations were made until the product showed no iodine number. A weighed sample of this final product was dissolved in neutral alcohol and titrated with standard alkali.

Subs., 0.2788, 0.5000: NaOH required, 0.0437, 0.0739. Found: Mol. wt. (monobasic acid): 254.8, 256.5.

The iodine value for this material was zero.

A silver soap was prepared by slightly over-neutralizing the free fatty acid with ammonia and then adding silver nitrate solution until no further precipitate formed. The precipitate was filtered off, washed free of salts, dried, and a weighed portion ignited in a tared porcelain crucible. A residue of silver resulted which was weighed and from this value the molecular weight of the substance calculated as a monobasic acid.

Subs., 0.212: Ag, 0.0061.
Calc. for palmitic acid: 256.6. Found: 268.3.

The acid, after remaining in an ice box for several hours, melted at

61.6°, with a rate of heating of about 1° per minute. Lewkowitsch gives 62.6° as the melting point for palmitic acid. The anilide of our acid melted at 90.2° which is the melting point given for the anilide of palmitic acid. The substance, upon combustion, agrees in composition with that of palmitic acid.

Calc. for palmitic acid: C, 74.92; H, 12.54. Found: C, 75.00; H, 12.36.

The freshly isolated fat mentioned in II, however, has a melting point between 38° and 43°, an acid number of 186, and an iodine number of about 92, while palmitic acid, as pointed out above, has a melting point of 62°, an acid number of 219, and a practically zero iodine number. There is, therefore, present in the fat, liberated in the hydrolysis of the purified starch, besides the palmitic acid an unsaturated constituent of relatively low acidity.

In order to get some insight into the nature of this other constituent, the lead salts were made according to the usual method and the ether soluble portion (the lead salts of certain unsaturated acids are soluble in ether) decomposed with hydrogen sulfide. The liberated fatty material was liquid at ordinary temperature and had an iodine number of 136.0. On cooling, some solid separated, leaving a light yellow liquid. The solid was removed from the liquid and dried between filter paper and was apparently palmitic acid, since it melted at 62° and had an acid number of 202. The light yellow liquid remaining was highly unsaturated, had an iodine value of 136, and showed practically no acidity. It was insoluble in cold aqueous alkali, coagulating as a gummy mass, showed the presence of small amounts of reducing sugar when treated with Fehling's solution, and gave no test for nitrogen by the sodium fusion method, but did show the presence of small amount of phosphorus, and gave no residue on ignition. This material will be referred to again as X in the latter part of the article.

IV. Liberation of the Fatty Acids at the Early Stages.

Erythrodextrin of the Hydrolysis of the Starch. Hydrolysis by Mineral Acids.—Fifty g. of the purified starch, suspended in water, was treated with 3 *M* hydrochloric acid, and when the erythrodextrin stage of hydrolysis, indicated by plum color with iodine, was reached, the operation was arrested, and the mixture poured into an excess of 95% alcohol. The alcohol caused a separation of the dextrin, which was removed by filtering and then washed with alcohol and ether. The combined alcohol-ether filtrates and washings were evaporated, the residue remaining extracted with ether and the extract evaporated, weighed, and found to amount to 0.53% of the original starch. The dextrin was hydrolyzed and the "fat by hydrolysis" from this was found to be negligible. When it is recalled that the "fat by hydrolysis" from the original starch is between 0.5 and 0.6% (see table under II) it becomes evident from these results that practically all the fat is liberated in the early stages of hydrolysis of the starch by aqueous acids. By repeating the above procedure with various concentrations of hydrochloric and nitric acids the same results were obtained except that the lower concentrations of acid seemed to favor the formation of insoluble retrograded starch which resisted further hydrolytic action. It was found, however, that a short treatment with 10% aqueous sodium carbonate solution rendered the retrograded starch soluble so that acid reagents could act in the usual way to give glucose.

Diastatic Hydrolysis.—The starch was hydrolyzed by means of diastase also instead of by acid. It was thought that possibly the fat might be liberated at a later stage in the hydrolysis than the erythrodextrin when the enzyme was used. The procedure was practically the same as in the acid hydrolysis except that in order to secure optimum conditions for the diastatic action, the hydrogen ion concentration was adjusted according to the directions of Sherman, Thomas and Baldwin.[1] Two experiments were carried out and in each case free fat was obtained. In one case the hydrolysis was interrupted at the erythrodextrin stage and the alcohol-ether residue similar to that described for acid hydrolysis, amounted to 0.19%. In the other case the hydrolysis was allowed to continue until a test portion gave practically no color with iodine, and then the liberated fat amounted to 0.41% of the original starch. It therefore appears, as far as one can judge by means of the iodine color, that at least some fat is liberated at the erythrodextrin stage when starch is hydrolyzed by the diastase just as was observed when acid was the hydrolytic agent.

V. Cleavage of Starch into Products of Relatively High Fat Content.

(A). Hydrolysis or Cleavage of Starch by Low Hydrogen-Ion Concentration in the Presence of Bacillus Aceto-ethylicum.—One hundred g. portions of starch were gelatinized by stirring into 2 liters of boiling water containing 2 g. of ammonium phosphate and 0.5 g. of magnesium sulfate as nutriment for the bacteria.[2] Starch purified as described above formed in this way a very limpid paste.[3] The last traces of foreign material such as cell fragments still present, settled and were removed by the decantation of paste through a layer of cotton. The decanted paste was then placed in a 5-liter flask and the hydrogen ion adjusted to approximately 10^{-8} by adding acid or alkali until a test sample showed no pink color with phenolphthalein and no yellow with phenol red.[4] The

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[1] Sherman, Thomas and Baldwin, This Journal, 41, 231 (1919).

[2] Schardinger, *Centr. Bakt.*, 22, 98 (1909).

[3] Small, This Journal, 41, 113 (1919).

[4] Lubs and Clark, *J. Bact.*, 4, 107 (1919).

flask was then stoppered with cotton, and the contents sterilized at 15 pounds steam pressure for one hour, cooled to 40° and inoculated with bacillus *aceto-ethylicum*,[1] and allowed to remain in an incubator at 40° until there was no more apparent action. A very limpid liquid, containing a small amount of insoluble material, resulted. This was filtered and the residue obtained was washed with hot water and allowed to drain. The residue then was stirred into an excess of absolute alcohol, the alcohol filtered off and the material dried *in vacuo* at 40°. In this way a gray powder was finally obtained which was digested with boiling ether, filtered through a Büchner funnel and washed with several small portions of ether to remove any fat which might have been freed in the fermentation. The residue thus obtained produced a plum color with iodine and showed no starch granules under the microscope.

Three such residues, ranging in weight from 10 to 15 g., were hydrolyzed by acid as in II and were found to contain still a considerable quantity of fat. The values given below were calculated on the dry weight of the residues.

No.	Fat of hydrolysis. %
1	1.6
2	3.8
3	2.2

(B). Hydrolysis or Cleavage of Starch by Low Hydrogen Ion Concentration without Addition of Aceto-ethylicum.—On allowing solutions, prepared for inoculation as above, to stand, a separation into layers was noticed, an upper clear and a lower turbid one. The latter was similar in appearance to retrograded starch. This observation led to the carrying out of the above partial hydrolysis of the starch without the addition of the salts or *aceto-ethylicum*, the procedure otherwise being identical with that in (A). After standing for about 6 hours a rather complete settling of the insoluble portion had taken place. The residue obtained by this latter method differed from that described in (A) in that it was more voluminous and had the appearance of retrograded starch. It was removed by filtration and treated in a way analogous to the procedure employed for the residue in (A).

Three 100 g. portions of purified starch containing 0.52 g. of "fat by hydrolysis" were analyzed by this method.

Residue No.	Residue from 100 g. of starch G.	"Fat by hydrolysis" in residue. %
88	5.0	5.5
89	8.1	3.6
90	8.0	3.3

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[1] The authors wish to thank Dr. J. H. Northrop for the culture of the *Bacillus aceto-ethylicum* and directions for applying it to starch. This is the bacteria used by Northrop, Ashe and Morgan for the production of acetone from starch and glucose See *J. Ind. Eng. Chem.*, 11, 723 (1919).

A sample of residue No. 88 gave on ignition an alkaline ash of 0.28%, which showed the presence of phosphorus and magnesium, while residue itself showed 0.04% of phosphorus.

Since these residues contained as high fat content as those described in (A), the method of preparation in (B) is to be perferred due to its being simpler. The fat content of the residues from both methods, (A) and (B), being about 6 times that of the original starch, this appears to offer an avenue to the isolation of a simpler compound and information concerning the structure of the fat-carbohydrate linking. Work is now in progress on this particular phase of the problem. That the fat in the residue might be occluded in the residue, is very improbable on account of the method employed in precipitation of the residue by alcohol and ether, both of which are good fat solvents. The argument that the residue material was so insoluble as to prevent the solvents from coming into contact with the fat and hence the latter being retained, although free, in the residue, can have very little justification in the light of the following experiment.

Two g. of residue No. 90 was refluxed for one hour with 20 cc. of 0.1 *M* alkali. This treatment gave a slightly opalescent liquid similar in appearance to colloidal starch. On pouring the liquid into an excess of alcohol a precipitate was formed which gave a blue color with acid iodine solution, indicating unchanged starch. The precipitate was filtered, dried and extracted with boiling alcohol and ether, and upon analysis showed 1.9% of "fat by hydrolysis" with an acid number of 175.7.

By this alkali treatment the residue was brought into solution again, and if the fat had been free fatty acid it would have been removed completely, yet the results showed that only 1.4 of the 3.3% fat present in the residue was removed. The reason why the 1.4% was removed can be explained most satisfactorily by assuming that the fat is present in the original residue as ester and that under the conditions of the above experiment the saponification of ester by the alkali was not complete.

Fat not Accounted for in Residue Described in B.—It is evident that only about $^1/_2$ of the total combined fat in the original starch remains as such in the residue No. 89. The aqueous filtrate, obtained in the preparation of this residue, was extracted with ether to make sure that no free fat was present, and subjected to acid hydrolysis. In this way, the filtrate was found to contain 0.085 g. of fat still combined with the soluble starch contained in the filtrate. Subtracting the sum of the combined fat held in the residue and aqueous filtrate, 0.292 + 0.085 or 0.38 g., from 0.56 g., the "fat by hydrolysis" in the original 100 g. of starch, gives 0.18 g. of fat which must have been liberated in the process and lost by being extracted by the alcohol-ether treatment. Qualitative test of the filtrate with Fehling's solution showed reducing sugar, and iodine test indicated erythrodextrin.

Decomposition of the Starch by Alcohol Solution of Hydrogen Chloride.—In the preparation of some methyl glucoside in this laboratory by the method described by Fischer,[1] maize starch was heated in an autoclave with an absolute methyl alcohol solution of hydrogen chloride. An insoluble residue, similar in appearance to the sediments described above, together with an oily liquid floating upon the surface of the alcoholic solution, were formed. This residue and the oily liquid were examined in the hope that further light might be cast upon the way the fat is combined within the starch.

Since the reaction of the starch with the alcoholic hydrogen chloride had taken place in a copper autoclave, there was some contamination with copper salts. It was necessary to remove the latter by washing with glacial acetic acid before the residue could be examined. The residue showed microscopically only flocks of amorphous material, which produced a red color with iodine similar to that from erythrodextrin. The "fat by hydrolysis" in this residue was 0.56% which is practically the same as in the original starch (see table under II). It is of interest in this connection to compare these results with those obtained in the aqueous acid hydrolysis. Although the iodine color of the various cleavage products of starch can not be considered absolutely reliable, it serves to show roughly that a change has taken place in the starch molecule. Comparing this color reaction of the material from the aqueous hydrolysis with that obtained from the alcoholic-hydrochloric acid treatment, the following facts can be set down.

In the aqueous hydrolysis (see Part III) as soon as there was any change in the starch complex, noted by the iodine test, the entire amount of bound fat was liberated. In the alcoholic cleavage, although apparently all the starch had undergone a change as shown by the red color with iodine and by the amorphous condition of the residue as revealed by the microscope, the erythrodextrin-like residue retained the same quota of fat as is present in the original starch. It would seem, therefore, from these rather limited data that the cleavage of the starch molecule takes place at different linkings according to the method used, and furthermore it serves as additional evidence that the fat is an inherent part of the starch molecule.

When the above alcoholic filtrate is evaporated and extracted with ether a dark brown oil is obtained. It was non-acidic, decolorized bromine, was insoluble in cold alkali but on warming practically all of it dissolved and gave a soapy solution which reduced Fehling's solution. Apparently this substance is the unsaturated constituent "X," mentioned in Part III.

Treatment of Residue Containing Relatively a Large Amount of Fat,

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[1] Fischer, *Ber.*, 28, 1151 (1895).

with Absolute Alcohol-hydrogen Chloride.—Since the residue from (A) and (B) still contained carbohydrate very similar to starch itself, and cleavage with hydrolytic reagents and the bacillus was apparently impossible, it occurred to us that treatment with alcoholic hydrogen chloride might offer a means of breaking down this still complex compound to a simpler one. Accordingly the following experiment was made.

Five g. of residue No. 99 was refluxed for 50 hours with 160 cc. of absolute alcohol containing 1.971 g. of hydrogen chloride. After this treatment there remained 2.24 g. of apparently unattacked starch-like residue which gave a red color when tested with iodine instead of the purple color given by the original sample. Analysis of this sample, after washing with ether, showed 3.2% of "fat by hydrolysis" referred to the weight of the dry product, a fat content essentially the same as that of the original sample No. 89 (see table) and therefore indicating that only about half of the original sample had been affected by the treatment. On partial evaporation of the alcoholic solution containing the glucoside, there appeared on the surface small droplets of dark brown oil. These were removed by solution in ether; and on evaporation of the ether a product remained which was similar in properties to the unsaturated liquid called "X" described above.

VI. The Fatty Acid is Combined Indirectly to the Starch.

(A) Saponification of Fat Liberated by Acid Hydrolysis.—A sample of 0.3058 g. of fat liberated by aqueous acid hydrolysis was refluxed for one hour with 5 cc. of *M* alcoholic sodium hydroxide, while as a blank analysis 5 cc. of sodium hydroxide was given exactly the same treatment. After refluxing, the flasks were cooled and titrated back with 0.05 *M* sulfuric acid.

Cc. of 0.05 *M* Sulfuric Acid Required.

Blank	48.9
Sample	38.0
Difference	10.9

This was equivalent to a saponification number of 199.5. Another portion of same sample gave an acid number of 182.3, while that of palmitic acid is 219.1.

(B) Saponification of Fat Liberated by Diastatic Hydrolysis.—A sample of 0.1290 g. of fat liberated by diastatic hydrolysis was dissolved in petroleum ether and 10 cc. of 0.1 *M* alcoholic sodium hydroxide added. The mixture protected from carbon dioxide by a soda-lime tube was allowed to remain at room temperature for 18 hours. Back titration of the excess alkali required 5.1 cc. of 0.05 *M* sulfuric acid, indicating therefore a saponification number of 212.7. The acid number of the same sample was 147.8.

It is evident that the fat from both methods of hydrolysis of the starch contains combined fatty acid or an ester. This ester has suffered more hydrolysis when acid instead of diastase was used in decomposing the starch. In the light of these data, very likely the unsaturated constituent present in the fat, labeled "X," is combined with the palmitic acid and accounts for the presence of the ester.

The fact that the palmitic acid, which is a mono-basic acid, is linked as an ester to the unsaturated compound ("X") precludes the possibility of direct carbohydrate fatty acid union, and since it has been shown that the entire fatty material (fatty acid and unsaturated substance "X") is combined with the carbohydrate and only liberated by hydrolysis, the substance "X" must serve as a connecting link between the acid and the carbohydrate.

Starches from other sources than corn also contained combined fat.

Samples of various representative starches were purified as described under Part I and the "fat by hydrolysis" determined. In the following table are enumerated the results of these analyses. Fifty g. samples were used, except in the case of potato starch.

Starch.	"Fat by hydrolysis."	Acid No.	Iodine No.
Corn	0.61	182.5	92.5
Rice	0.83	283.4	84.7
Sago	0.11	151.0	..
Cassava	0.12	168.0	..
Potato (200 g. sample)	0.04	109.4	..
Horse chestnut	0.56	21.9	..

From the above results it is evident that corn starch is not unique in having combined fat, but that starches of widely differing genera also contain combined fatty material.

We are greatly indebted to the Harriman Research Laboratory, New York City for grants in the aid of this investigation.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE CHEMICAL RESEARCH LABORATORY, UPJOHN COMPANY.]

THE RAGWEED POLLEN PROTEINS.

BY FREDERICK W. HEYL AND HARRIS H. HOPKINS.[1]

Received June 21, 1920.

In considering any drug from a pharmaceutical point of view, two distinct schools of thought are always in evidence. First, the progressive school which is largely dominated by chemistry and to whom pharmacy owes much in the matter of the isolation or preparation of pure or crystalline principles. Secondly, there is the conservative group, dominated

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[1] Holder of The Upjohn Coöperative Fellowship at Kalamazoo College (1919–1920). This paper is based upon the thesis presented by Mr. Hopkins to the Faculty of Kalamazoo College, in partial fulfillment of the requirements for the degree of Master of Science.

by the simpler pharmaceutical methods and favoring the preparation of galenical extractives. It is well for us to understand that however desirable the progressive results due to chemical investigation in all cases may be, that there are a number of drugs (*e. g.*, ergot and digitalis) the actions of which we do not comprehend, and for which it were well if the pharmacist adopted and the clinician used, a strictly galenical product until the chemist has first worked out the problem involved. Where the pharmacist attempts to precede the chemist, as has been done with both the drugs mentioned, there arises a chaotic condition which actually retards the advance of knowledge.

Ragweed pollen is such a drug. The uncertain state of our knowledge does not justify the preparation or use of pure principles from this drug, even though at present we may view the albumin fraction as the constituent of chief interest. In the texts we find pollen toxalbumin classified with the albuminous substances ricin, abrin, and crotin on the basis of their similar activity in producing antitoxic substances in the animal body. This classification is due to the work of Dunbar,[1] who perhaps succeeded in showing that he could produce a pollen antitoxin using rye pollen, but it need not necessarily hold for ragweed pollen.

It has been shown that rye pollen toxin which is extracted with water will withstand autolysis in the presence of the proteases of pollen. Kamman[2] claims that this increases its activity 100 fold, whereas, on the contrary, artificial digestion with trypsin leads to the loss of activity exactly as in the case of ricin. Kamman noted a loss of activity for rye pollen toxin when it was allowed to stand in the presence of alcohol and attributes this to the coagulation of the albumin. On the other hand, he states that his product was thermostabile, a finding which is difficult to understand if the activity resides in the coagulable albumin fraction.

The conclusive work of Osborne, Mendel and Harris[3] on ricin leads to the thought that in an analogous manner the pure pollen albumin is probably the so-called toxin in this case, but when we find, not 40% as in the rye pollen, but only 1–2%, we feel more than ever the logic of adhering to the galenical extract until the required information shall have been gained. In the case of Kamman's so-called "pollentoxin," the usual protein reactions (except the biuret) were lacking and it is evident that Kamman's thought is influenced by the work of Kyes[4] and of Faust,[5] who have established the non-nitrogenous, thermostabile nature of the neurotoxic constituent of cobra venom. This substance "ophiotoxin,"

[1] *Zur Ursache und specifischen Heilung des Heufiebers*," *München*, 1903.

[2] *Biochem Z.*, 46, 151 (1912).

[3] *Am. J. Physiol.*, 14, 259 (1905).

[4] *Biochem. Z.*, 4, 99 (1907); 8, 42 (1908).

[5] *Arch. expt. Path. Pharm.*, 56, 236 (1907).

($C_{17}H_{26}O_{10}$) is probably combined as an ester or salt with the albumin-like substances which are present, and with which it can be precipitated by saturation with ammonium sulfate. As is frequently the case, it is known that the native substance is more stable and has greater activity than the isolated fraction owing to the protective action of the protein moiety.

As has been previously[1] shown, the aqueous extract from pollen when precipitated with alcohol or when saturated with ammonium sulfate yields a small quantity of a coagulable albumin and a larger quantity of substance which was formerly classified as a proteose. The analytical results reported in this paper show that the albumin is a normal protein except that it is incomplete and lacks histidine and perhaps tryptophane. But the "proteose" or non-coagulable part of this fraction differs from the corresponding ricin proteoses or any other substances previously described in this fraction.

We have analyzed by the Van Slyke process 2 "proteose" products. The first was the most soluble part precipitated at 5/10–10/10 saturation with ammonium sulfate and was found to contain only 5.43% nitrogen. A second sample represented the entire fraction and was further purified by dialysis and it contained 6.0% nitrogen. These samples are possibly mixtures or uncoagulable combinations of the albumin and a non-nitrogenous moiety, there being a higher percentage of protein in the entire fraction than in that precipitated at higher saturations. On the basis of the nitrogen content these products correspond to a mixture or compound containing 38.3% and 35.1% of the albumin, respectively. Recalculating our base and tyrosine analysis we can make the following comparisons.

	Calc. for albumin × 0.383.	Found entire proteose.	Calc. for albumin × 0.351.	Found soluble proteose.
Arginine	2.36	2.08	2.15	1.48
Histidine	0.00	0.00	0.00	0.00
Lysine	3.36	4.48	3.07	3.70
Tyrosine	1.08	1.10	0.98	0.78

The stability of these substances is remarkable and it is difficult to decide definitely whether we have here an ester, a salt-like substance or a mixture of albumin with a nitrogen-free substance.

We have analyzed the pollen glutelin, which is the predominant protein, and found it to differ from the water-soluble albumin in that histidine is present among the bases and that it is therefore more complete. We have in pollen, therefore, a series that may represent 3 stages of protein development.

Native compound proteose (N = 5.4%) ⟶
Albumin(-histidine) ⟶ glutelin.

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[1] This Journal, 41, 670 (1919).

Experimental.

1. **Proteose.**—The aqueous extracts of ragweed pollen, after the removal of coagulable albumin by heating and filtering, contain an appreciable quantity of proteose-like material which can be precipitated by saturation with ammonium sulfate. As we observed considerable loss of material by dialysis, we thought we might procure a representative analysis on the material which had not been subjected to this treatment. The material[1] precipitated at 5/10–10/10 saturation was therefore redissolved in water and reprecipitated with alcohol. In this condition a considerable quantity of ammonium sulfate was present in the final product. It was, therefore, redissolved and a slight excess of barium hydroxide solution was added and the ammonia was removed at 40°. The precipitation was then made quantitative and after removal of the barium sulfate, the proteose solution was evaporated to dryness in a weighed flask.

The subsequent analysis gave such low results that we proceeded to study the dialysed sample[2] of the entire proteose product obtained in the first pollen extraction, which had been purified by a lengthy dialysis. The results were of the same nature and prove the conjugated nature of this substance. Both products gave a strong Molisch test. The fact that the analysis of the second product gave higher results than the first indicates the admixture *in the total proteose* of more protein. This is, of course, precipitated at lower saturations and is less extensive in the first sample.

(*a*) A sample of the undialyzed proteose (which had been prepared by precipitation between 5/10–10/10 saturation with ammonium sulfate) weighing 4.4258 g., and equivalent to 3.3595 g. ash and moisture-free, was hydrolyzed for 48 hours with 100 cc. of 20% hydrochloric acid. (Amino N = 4.48 and 4.39%.) The hydrolysis solution was subjected

Analysis of Proteose, 5/10–10/10.

	Found.		Average.	Parts per 100.
Total Nitrogen	5.45	5.42	5.43	100.00
Amide N	0.45	....	0.45	8.29
Humin N	0.56	....	0.56	10.31
Arginine N	0.48	....	0.48	8.84
Cystine N	0.00	....	0.00	0.00
Histidine N	0.00	....	0.000	0.00
Lysine N	0.71	....	0.71	13.08
Mono Amino N	2.47	2.55	2.51	46.22
Total Filtrate N	3.08	....	3.23[a]	...
Non Amino N	....	....	0.72	13.26

[a] Calculated.

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[1] *Loc. cit.*, p. 679.

[2] *Ibid.*, p. 676.

to the Van Slyke process, with the results tabulated below. These results are corrected for the solubilities of arginine and lysine phosphotungstates.

(*b*) A sample of dialyzed proteose (0 — 10/10 saturation with ammonium sulfate) weighing 3.1765 g. and equivalent to 2.7099 g. ash- and moisture-free, was hydrolyzed by boiling with 100 cc. of 20% hydrochloric acid for 24 hours. (Amino N = 5.6 and 5.35%.) The results tabulated below were obtained by the Van Slyke process and were corrected for the solubilities of arginine and lysine phosphotungstates.

Analysis Proteose, 0/10 to 10/10.

	Found.		Average.	Parts per 100.
Total Nitrogen	6.00	6.01	6.00	100.00
Amide N	0.35	....	0.35	5.83
Humin N	0.57	....	0.57	9.50
Arginine N	0.67	....	0.67	11.17
Cystine N	0.00	....	0.00	0.00
Histidine N	0.00	....	0.00	0.00
Lysine N	0.86	....	0.86	14.33
Mono Amino	2.92	2.92	2.92	48.67
Total filtrate N	3.37	3.64	3.55[a]	....
Non amino N	....	....	0.63	10.05

[a] Calculated.

2. **Glutelin.**—This protein was prepared by alkaline extraction from the first sample of pollen studied.[1] Of this material, 3.75 g. (Moisture = 18.59%; ash = 0.98%) equivalent to 3.0161 g. was hydrolyzed by boiling with 100 cc. of 20% hydrochloric acid for about 48 hours. (Amino N = 9.09 and 9.12%.) For the check analysis 2.0856 g., equivalent to 1.6774 g. moisture- and ash-free protein, was used. In calculating the results tabulated below the values have been corrected for the solubilities of all the phosphotungstates. We have persistently encountered low results in the determination of the total nitrogen of the filtrate from the phosphotungstates and this is a calculated value. (Found = 6.97%.)

Analysis Glutelin.

	Found.		Average.	Parts per 100.
Total Nitrogen	12.88	13.10	13.00	100.00
Amide N	1.30	1.14	1.22	9.40
Humin N	0.84	0.90	0.87	6.69
Arginine N	1.51	1.52	1.52	11.69
Cystine N	0.12	....	0.12	0.92
Histidine N	0.44	0.60	0.51	3.92
Lysine N	1.47	1.27	1.37	10.54
Mono amino N	6.92	7.33	7.12	54.77
Total filtrate N	7.20	7.55	7.37[a]	....
Non amino N	0.28	0.22	0.25	1.92

[a] Calculated.

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[1] *Loc. cit.*, p. 676.

3 **Albumin.**—The sample analyzed was prepared from the second and third pollen extractions by coagulation. Of this 3.1976 g. (moisture = 10.99; ash = 0.0), equivalent to 2.8462 g., was hydrolyzed by boiling with 100 cc. of 20% hydrochloric acid for about 48 hours. (Amino N = 12.16 and 12.38%.) In the table given below the total nitrogen of the filtrate from the phosphotungstates is calculated by difference, and a solubility correction is made for only arginine and lysine phosphotungstates.

Analysis of Albumin.

			Parts per 100.
Total Nitrogen	15.68	15.63	100.00
Amide N	1.42	...	9.05
Humin N	0.47	...	3.00
Arginine N	1.98	1.99	12.63
Cystine N	0.00	...	0.00
Histidine N	0.00	...	0.00
Lysine N	1.68	...	10.71
Mono amino N	9.49[a]	...	60.52
Total filtrate N	10.13[b]	...	....
Non amino N	0.64	...	4.08

[a] If the usual solubility correction is used this figure should read 9.31% corresponding to 59.37% of the total nitrogen. The non-amino N would then correspond to 0.82% = 5.23% of the nitrogen.

[b] Calculated.

Percentage of Basic Amino Acids and of Tryptophane.—Recalculating the results described above, the hexone bases found may be tabulated. We have furthermore determined the tyrosine present by the colorimetric method of Folin and Dennis.[1]

The absence of histidine in the proteoses and the albumin is so complete that it is impossible to detect it even with the diazo test in the base fraction.

Percentage of Amino Acids in the Ragweed Pollen Proteins.

	Proteose 5/10–10/10.	Proteose (entire) dialysed.	Glutelin.		Albumin.	
Arginine	1.48	2.08	4.69	4.70	6.15	
Histidine	absent	absent	1.69	2.30	absent	
Lysine	3.70	4.48	7.66	6.6	8.76	
Tyrosine	0.78	1.10	4.7		2.79	2.83
Tryptophane	absent	absent	absent		absent	

The above table summarizes the results of this study.

KALAMAZOO, MICH.

[1] *J. Biol. Chem.*, 12, 239 (1912).

[CONTRIBUTION FROM THE CHEMICAL RESEARCH LABORATORY, UPJOHN COMPANY.]

SOME CONSTITUENTS OF VIBURNUM PRUNIFOLIUM.

BY FREDERICK W. HEYL AND CHARLES BARKENBUS.[1]

Received June 21, 1920.

The drug "black haw" has been used clinically since about 1870, and at the present time it retains considerable prestige as an anti-spasmodic in menorrhagia and dysmenorrhea. In this sense it is generally spoken of as a uterine sedative.

It does not fall within the scope of this work to discuss the clinical reports upon this drug, but since this subject has received no small amount of attention it appears that a chemical study might be of some assistance on this question. Our present information is based largely upon the work of Van Allen[2] and Sherman[3] who report the presence of (1) a brown resinous body of a bitter taste from which it was impossible to separate the sugar; (2) a greenish-yellow resin, or neutral substance of bitter taste, slightly soluble in water, freely so in alcohol and which was called viburnin; (3) valeric acid; (4) a tannic acid; (5) oxalic acid; (6) citric acid; (7) malic acid; (8) sulfates; (9) chlorides of calcium, magnesium, potassium and iron; (10) some alkaloidal material. Viehoever[4] found that the tannins of the Viburnums gave a green color or precipitate with ferric salts. He also isolated valeric acid and made the copper, zinc, and mercury salts for microscopic identification. A trace of butyric acid was considered to be present.

Black haw is officially described in the latest pharmacopeia as the dried bark of *Viburnum prunifolium*, "without the presence or admixture of more than 5% of wood or other foreign matter." This description has probably completely altered the nature of the pharmacopeial drug because it had previously been defined as the dried bark of the root. We do not know of any experimental reasons for this change and hold that such alterations are unjustifiable unless at least some chemical data can be produced to substantiate the similarity. Our sample of black haw consisted of the dried root bark of the authentic drug and was carefully inspected by our colleague Dr. L. H. Harvey to whom our thanks are due. It was collected in Michigan, and was picked over by hand, so that the examination was conducted upon a selected sample.

The proximate analysis showed that the drug contained 7.1% moisture and 7.3% ash. Ligroin extracted 7.1%; ether, 10.4%; alcohol, 18.7%.

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[1] Holder of The Upjohn Coöperative Fellowship at Yale University (1919–1920). This paper is based upon the thesis presented by Charles Barkenbus to the Faculty of the Graduate School of Yale University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Van Allen, *Am. J. Pharm.*, 52, 439 (1880).

[3] Sherman, *Repts. Royal Coll. Phys. Lab. Edinburgh*, 6, (1897).

[4] Viehoever, *J. Am. Pharm. Assoc.*, 7, 944 (1918).

The alcohol-insoluble residue had the following composition: crude fiber, 23.3%; pentosans, 16.1%; protein, 2.4%; starch 5.5%; dextrin, 0.5%. The alcoholic extract in which our interest centers contained sucrose, 0.3%; invert sugar, 1.8%, and tannin, 2.0%. When the alcoholic solution was poured inno water a resin was obtained to the amount of 4.6%. This value when taken in conjunction with 7.1% of ligroin soluble (or 10.4% ether-soluble material) indicates the presence of a very considerable amount of material which while being extracted by these volatile solvents in the native state, does not make its appearance later in the water insoluble resin as might be expected.

Other products found in the alcoholic solution and soluble in water besides the sugars and tannin, include formic, acetic and valeric acids; a non-glucosidic, acidic resin soluble in amyl alcohol which readily yields acetic and valeric acids (6.5%) upon saponification; and a second acidic resin which was not extracted by the amyl alcohol procedure, but which yielded 8.1% of acetic acid upon saponification. Traces of salicylic acid and of a hydrocarbon (m. p. 53–54°) resulted upon saponification of this material. While Bourquelot's[1] method appeared to give positive results as to the presence of a glucoside, our exhaustive examination of this solution proved negative in this respect. A trace of amorphous alkaloid is present.

The resin insoluble in water was extracted successively with ligroin, ether, chloroform, ethyl acetate and alcohol. The fat in the ligroin extract yielded a very large amount of unsaponifiable matter, and the chief part of this was a rosin-like solid that could not be distilled. A trace of a mixture of hydrocarbon and a higher alcohol (m. p. 65–72°) was present and also a beautifully crystalline phytosterol, $C_{27}H_{46}O$, that melted at 186–187° and formed an acetate melting at 223–224°. This is a new phytosterol. $[\alpha]_D = +115°$. A small amount of a white crystalline alcohol (m. p. 303°) was found here. Formic, acetic, caproic, caprylic, myristic, palmitic, oleic and linolic acids were identified in the fat. The absence of valeric acid here is interesting.

The ether extract of the resin yielded a phytosterolin, $C_{33}H_{56}O_6$, that melted at 290°. The acetate melted at 168°. The chloroform extract of the resin consists of an acidic resin that yields valeric acid upon saponification, as does the ethyl acetate soluble resin (18%). The alcohol-soluble resin yielded no valeric, but large amounts of acetic acid upon hydrolysis.

Our chief interest in these results centers in the various different forms in which acetic and valeric acids are present including not only the free acids but the water soluble complex esters, and the resinous esters insoluble

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[1] *Arch. Pharm.*, 245, 172 (1907).

in water. A fluid extract of this drug offers these acids for assimilation in a great variety of combinations.

Some of these valeric ester combinations remind us, in connection with their possible value, of certain synthetic valerates, such as Neobornyval (borneol isovaleryl glycolic acid ester) or Gynoval, (isovaleric ester of isoborneol) with which they probably share the advantage of passing the stomach, and requiring alkaline media for the liberation of the valeric acid. In fact it becomes incomprehensible from a chemical point of view why a large number of simple and synthetic valerates should remain out of the realm of dispute and the discussion should appear to center upon the Viburnums, one of which has already been deleted from the pharmacopeia.

Experimental.

A. Proximate Analysis.—Quantitative extractions were made on the air-dried drug after grinding and sieving.

Solvent.	%.
Ligroin (50–60°)	7.05
Ether	10.46
Ether (110°)	9.82
Alcohol	18.72

The proximate analyses, using the official methods, gave the results tabulated below.

	%.		%.
Moisture	7.09	Protein	2.40
Starch (Diastase)	5.51	Ash	7.32
Pentosans	16.13	Dextrin	0.52
Crude fiber	23.25	Tannin (Hide Powder)	1.97

Concerning this proximate analysis it is to be observed that the sum of the above quantitative determinations of the alcoholic-insoluble plant constituents does not account for this fraction which should amount to 74.2%.

Alcohol-soluble carbohydrates were determined as follows. 250 g. was extracted with ether, and the fat-free drug was then exhausted with boiling neutral 95% alcohol. The combined alcoholic extracts were concentrated under diminished pressure to a small volume and 800 cc. of water was added. Then an excess of basic lead acetate solution was added and the precipitate was filtered off and thoroughly washed with water. The excess of lead was removed from the filtrate with hydrogen sulfide. In the presence of calcium carbonate the filtrate from the lead sulfide was concentrated at 40–45° to 50 cc. This was transferred to a 250 cc. volumetric flask, diluted with 50 cc. of thymol water and 6.25 cc. of 0.5 N sodium dihydrogen phosphate solution was added. Enough 0.5 N hydrochloric acid was added to make the solution just acid to methyl orange. It was finally made up to exactly 250 cc. and one drop of toluene was added. This solution showed a rotation of —9.1° V.,[1] at 22° in a 2 dcm. tube. By the Munson and Walker process, 5 cc. gave 0.1953 g. of cuprous oxide, equivalent to 1.79% of invert sugar.

Action of Invertase.—200 cc. of the above solution was treated with 0.25 g. of invertase. After 3 days the reading in a 2-dcm. tube was constant at —11.25° V.,[2] at 22°. 5 cc. gave 0.2180 g. of cuprous oxide. Sucrose, by reduction = 0.19%: by Clerget's formula = 0.34%.[3]

Action of Emulsin.—100 cc. of the above solution was plunged into a boiling, water bath for 10 to 15 minutes to inactivate the invertase. The solution was cooled to room temperature and 0.5 g. of emulsin was added. After 4 days the reading in a 2-dcm. tube was constant at —6.75° V., at 22°. 5 cc. gave 0.258 g. of cuprous oxide. These results indicate inconclusively the presence of a small amount of glucoside, the amount of glucose liberated is calculated to be 0.34%.

Viburnum was examined for the presence of alkaloids and was found in fact to contain traces of such material. An alkaloidal assay was conducted by the process which is official for *Hyoscyamus*,[4] and 15 g. yielded residues weighing 0.0393 g. (0.0398 g.) which were feebly alkaline and required 1.2 cc. of 0.02 *N* acid (1.1 cc.). When the titration was completed it was evident that these residues were conspicuously contaminated with resin, and the acid-soluble part was found to weigh 0.0207 g. (0.0197 g.) This corresponds to about 0.14% of the drug. The acid solutions gave a positive test with Mayer's reagent.

As this finding was unexpected we repeated the assay. By exhausting 100 g. of the drug with 95% alcohol, concentrating the combined extracts to 100 cc. and pouring this into a mixture of 10 cc. of *N* sulfuric acid +190 cc. of water, we obtained an acid solution of the alkaloids. The last traces of alcohol were removed by further distillation at low temperatures and the solution was made quantitatively to 250 cc. Of this 200 cc. of the clear acid fluid was exhaustively extracted with ether and then with chloroform. The solution was then rendered ammoniacal but no precipitation could be observed. The solution was exhausted with ether and then with chloroform but the extracts were not alkaloidal and had in fact an acid reaction. The solution was then exhausted with amyl alcohol, first at room temperature, and then at about 90°. The cold extraction yielded a trace of alkaloidal material. It required between 0.6 and 1.1 cc. of 0.05 *N* acid, and gave a positive test with Mayer's reagent. The hot amyl acoholic extraction likewise required 0.44 cc. of 0.1 *N* acid. The

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[1] Valenta number.

[2] All polariscopic readings were corrected by proper controls.

[3] As described later the drug contains more sucrose than found here and it is probable that the prolonged alcoholic extraction in the presence of valeric and acetic acids inverted a considerable part.

[4] U. S. Pharmacopeia, IX, p. 225.

ammoniacal liquor was re-acidified, centrifuged to remove resinous precipitation and then precipitated with an excess of Mayer's reagent and it was evident that most of the alkaloid remained in this solution.

The various alkaloidal fractions were united in an acid solution and precipitated with Mayer's reagent. The washed precipitate was suspended in water and decomposed in the usual manner. The filtrate from the mercuric sulfide was concentrated. It yielded a dirty brown solution of a feebly basic nature that contained nothing crystalline. When injected into guinea-pigs it was not fatal but did produce a marked reaction characterized by dyspnea, stupor and some paralysis of the hind quarters. This condition lasted about an hour.

B. Complete Examination of Alcoholic Extract.—For this purpose 29.48 kg. was exhaustively percolated with cold methyl alcohol. The percolate (177.9 liters) was concentrated under diminished pressure to 4.74 liters, giving a dark green viscid syrup. This was shaken into 50 liters of distilled water. On standing for several days a green viscid resin separated but a brown amorphous solid remained suspended in the aqueous layer which was decanted. The resin was washed with water, and the solutions combined. The resin amounted to 1358 g. or 4.6% of the drug.

The Examination of the Water Soluble Constituents.—The aqueous solution was concentrated to a volume of 12 liters under reduced pressure. The acid distillate was rendered alkaline and concentrated to a small volume acidified and steam distilled, and this distillate was extracted with ether, which extracted 53 g. of liquid acid. These were fractionally distilled and collected in 4 fractions (1) 140–155°, (2) 155–165°, (3) 165–170°, (4) 170–175°. The first fractions were small while the chief fraction consisted of pure valeric acid which was further identified by the silver salt.

Calc. for $C_5H_9O_2Ag$: Ag, 51.37. Found: 51.31.

The lower-boiling fractions contained small quantities of acetic acid. Fraction 1 was converted into the silver salt and the most soluble part as well as the less soluble part were analysed.

Found: Ag, 57.0, 51.5.

The steam distillate from which valeric acid had been extracted yielded smaller quantities of acetic acid.

Calc. for $C_2H_3O_2Ag$: Ag, 64.6. Found: 64.0.

The concentrated main solution was freed from the brown amorphous material by filtration, and was then extracted repeatedly with ether. This fraction (39.4 g.) separated upon concentration a small quantity of phytosterolin (0.2 g.). It melted at 280°. Subsequent examination of the ether yielded nothing definite.

Chloroformic extractions of the aqueous layer yielded about 30 g. of a green smear from which nothing was isolated.

The water solution was now repeatedly exhausted with warm amyl alcohol of which the first extraction (after washing several times with water) was concentrated to a dark brown syrup, which proved to be miscible with water. It was, therefore, diluted with 1.5 liter amyl alcohol and repeatedly washed in a mechanical shaker to remove soluble sugars, but after many extractions the aqueous layer continued to give a positive test with Fehling's solution. The washed amyl alcoholic solution was concentrated under reduced pressure to a syrup, and the last traces of the solvent removed by blowing steam through. The residue was taken up in 60% alcohol and made up to a volume of 1000 cc. (133.8 g.) When an aliquot of this solution (250 cc.) was hydrolyzed by refluxing for 8 hours with 5% sulfuric acid, there was an increased reducing action by Fehling's test but it was impossible to prepare an osazone from this hydrolysis mixture in the usual manner.

250 cc. (33.5 g.) was heated in the presence of 10% of potassium hydroxide, the alcohol was removed by distillation and then after acidifying and subjecting to steam distillation a quantity of a mixture of valeric and acetic acids were obtained equivalent to 18.1 cc. of *N* sodium hydroxide solution. These acids were identified as silver salts.

Ether soluble acids found: Ag, 51.5. Water soluble acids found: Ag, 62.6.

Considering these to be mostly valeric acid this indicates the presence of 6.5% in ester form.

The acid mixture from which these volatile acids had been steam distilled was examined but nothing isolated.

The total amount of material extracted by amyl alcohol weighed 663 g., equivalent to 2.2% of the drug. These amyl alcohol extracts gave a greenish-black coloration with ferric chloride.

The aqueous liquid which had been extracted with ether, chloroform and with amyl alcohol was freed from the latter by a vigorous steam distillation and then divided into 2 equal aliquots. One-half was precipitated with an excess of basic lead acetate, and the chocolate brown precipitate that separated was filtered off after several days. The precipitate was suspended in water and decomposed with hydrogen sulfide but it contained nothing of interest except for the separation of a small quantity of calcium oxalate and a larger amount of tannin. The solution with ferric chloride gave a dark green coloration that turned to a black precipitate and it gave a heavy precipitate with gelatin solution.

The filtrate from the lead tannate was freed from lead with hydrogen sulfide and concentrated at 40–45° to a volume of 800 cc. This thick cherry-red syrup was allowed to stand for weeks but nothing crystalline separated. It was then taken to dryness and exhausted with alcohol but these solutions failed to crystallize under any conditions.

All this material was united, the alcohol was removed, and then the residue was taken up in water and made to exactly 1000 cc. with a little toluene.

This solution gave no precipitate with phosphotungstic acid, nor with mercuric acetate solutions.

From 6.5 cc. of the solution we obtained 1.47 g. of *d*-phenyl glucosozone which melted at about 207°.

A trace of pentose sugars was found, since 10 cc. gave 0.0457 g. of phloroglucide (0.03%.)

Inasmuch as the preliminary test for glucoside by Bourquelot's method had indicated the possible presence of such a substance here, we subjected this fraction which had been purified by the removal of 2.2% of the drug by amyl alcohol to a second quantative investigation.

10 cc. of syrup (147 g. drug) was diluted to 100 cc. and 10 cc. (14.7 g.) gave 0.5987 g. of total solids dried at 100°, and 0.0175 g. ash.

5 cc. (7.35 g.) gave 0.2053 g. of Cu_2O = 0.0946 g. of invert sugar.

5 cc. inverted, gave 0.3850 g. of Cu_2O = 0.0783 g. of sucrose.

The solution (1000 cc.) therefore contained approximately 598.7 g. of solids, of which 17.5 g. was ash; 189.2 g. was invert sugar and 156.6 g. was sucrose. The unaccounted material amounted to about 241.6 g. In other words the total solids amounted to 4.07% while the invert sugar equalled 1.29% (1.2) and the sucrose 1.07% (0.94).

In order to find out whether a part of the unaccounted for material might be a glucoside, we repeated the analysis by the biological method. It will be remembered that this solution no longer contains the amyl alcohol soluble fraction which had a high reducing action on Fehling's solution. For this purpose a solution was prepared containing 16.9 cc. of the syrup (250 g. drug) +150 cc. thymol water +6.25 cc. of 0.5 *N* sodium phosphate solution and sufficient 0.5 *N* hydrochloric acid to make the solution just acid to methyl orange. The final volume was exactly 250 cc.

(*a*) *Direct.* Rotation in a 2-dcm. tube at 21° = —1.37° V. 5 cc. gave 0.1383 g. of Cu_2O = 0.0627 g. of invert sugar = 1.25%.

(*b*) *Action of Invertase.* 200 cc. of the solution + 0.25 g. of invertase after standing 5 days gave a reading of —5.1° V. in a 2-dcm. tube at 21.5°. 5 cc. gave 0.2171 g. of Cu_2O. Sucrose, by reduction = 0.7%; by Clerget's formula = 0.75%.

(*c*) *Action of emulsin.* 100 cc. of the solution was plunged into a boiling water bath for 10 to 15 minutes, cooled to room temperature and 0.5 g. of emulsin added. The reading was difficult to take but averaged —3.5° V. at 22° in a 2-dcm. tube. 5 cc. gave 0.239 g. of Cu_2O.

This change in rotation again indicates the liberation of glucose and there is an increase of 0.0219 g. of Cu_2O (for 5 g. of drug). This is equivalent to 0.182 g. of glucose per 100 g. of viburnum.

It was now attempted to remove the sugars by fermentation[1] and

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[1] Fischer and Thierfelder, *Ber.*, 27, 2031 (1894).

200 cc. of syrup (119.7 g. of solids) containing 36.5 g. of invert sugar and 31.3 g. of sucrose was diluted and titrated to alkalinity with *N* potassium hydroxide solution using phenolphthalein, and then one drop of phosphoric acid was added. To this solution 300 cc. of yeast decoction was added for nutrient material. This solution was filtered through porcelain and the sterile filtrate was inoculated with yeast.[1] It fermented rapidly and was clarified with lead subacetate, filtered and concentrated to 250 cc. after removing the excess of lead.

The material left was an uncrystallizable resin, characterized by an ester-like structure rather than a glucosidic one. When prepared in the dry condition it was not hygroscopic; had a bitter taste and had some reducing action upon Fehling's solution.

17.8 g. was heated upon the steam bath with 25 cc. of 6 *N* sodium hydroxide solution for about 6 hours, acidified and steam distilled. The distillate required 24.0 cc. of 1 *N* potassium hydroxide solution for neutralization, equivalent to 8.1% of acetic acid. (Ag, 63.5%).

A further quantity of the original syrup was fermented as above described and after clarifying with lead subacetate and subsequent removal of the excess of this reagent with hydrogen sulfide, the solution was concentrated, poured upon purified sawdust and dried. This was fractionally extracted with absolute ethyl acetate, and then with absolute alcohol and many fractions separately concentrated, but nothing crystalline was found beyond a few straggling needles in the first ethyl acetate fraction.

All the fractions were united, dissolved in water, and concentrated to remove traces of alcohol and ethyl acetate and then hydrolyzed in the presence of 10% sodium hydroxide solution.

The solution was acidified and steam distilled, to remove quantities of valeric and acetic acids. The acid residue in the flask was agitated with large volumes of ether, which in turn was fractionally extracted with solutions of ammonium carbonate, sodium carbonate, and sodium hydroxide. From the first of these a small quantity of salicylic acid was isolated that melted at 153–154° and gave a violet coloration with ferric chloride. From the ether solution of the neutral substances a quantity (0.2 g.) of a hydrocarbon was isolated. After several crystallizations from alcohol the melting point was elevated from 48–51° to 53–54°.

Calc. for $C_{27}H_{56}$: C, 85.2; H, 14.7. Found: C, 84.5; H, 14.5.

The material appears to be heptacosane.[2]

An acid hydrolysis yielded nothing interesting.

The Examination of the Resin.—The resin (1358 g.) was dissolved in

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[1] We are indebted to Dr. Ralph E. Lee of the Fleischmann Company for kindly supplying this material.

[2] The possibility of contamination presents itself because of the difficulty of accounting for this substance here.

wood alcohol and poured upon purified sawdust and dried. The entire material was extracted with the following results:

	G.
Petroleum ether (40–60°)	348
Ether	104
Chloroform	245
Ethyl Acetate	365
Alcohol	168
Total	1230

During the extraction 128 g. had become insoluble, through alteration, possibly of the nature of oxidation.

The Ligroin Extract.—This extract, amounting to 348 g., was dissolved in ether and extracted with 10% sodium hydroxide solution. The alkaline solution was acidified and shaken with ether, whereupon a precipitate insoluble in either layer separated and produced an emulsion which was broken by filtration. The green solid that separated (1.0 g.) was hydrolyzed with dil. alcoholic sulfuric acid in the presence of chloroform, whereupon most of the material became converted into a brown amorphous product, but from the chloroform solution a residue was obtained that crystallized gelatinously from ethyl acetate after treating with boneblack and concentrating. With great difficulty this substance was finally obtained as beautiful white silky needles (0.1 g.) from absolute alcohol. It melted at 303° to a clear oil and perhaps belongs to the class represented by oleanol.[1] We attempted to acetylate this product by heating with acetic anhydride in the presence of pyridine but this did not proceed smoothly and we obtained a mixture of substances. From the reaction mixture upon cooling a separation of small plates that melted at 340–350° took place. Upon concentrating gradually a syrup finally resulted which could be crystallized from alcohol. On recrystallization, needles were obtained that melted at 176–178° and effervesced at 190°. We attempted no analysis on account of these small fractions.

The ether solution of acidic substances was extracted with solutions of ammonia carbonate, sodium carbonate, and sodium hydroxide. The sodium carbonate extracted a quantity of free acids and these were studied later. The other solvents yielded nothing crystalline.

While shaking with sodium hydroxide solution, the neutral layer separated 2.0 g. of material from which phytosterolin melting at 280° was readily isolated.

The ether solution of the neutral substances was saponified by boiling for 8 hours with 10% alcoholic potassium hydroxide and the unsaponifiable material separated with ether.

Examination of the Unsaponifiable Matter.—The dried solution

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[1] *J. Chem. Soc.*, 93, 891 (1908).

yielded 176 g. of a brownish-red semi-solid mass. It was dissolved in absolute alcohol and a trace (0.05 g.) of a mixture of hydrocarbon and higher alcohol separated that melted at 65–72°. The solution was concentrated sharply and after prolonged standing 13 g. of fine needles separated. This was subjected to a systematic fractional crystallization and the fractions analyzed.

Found: (I, m. p. 182°) C, 83.9; H, 11.6: (IV, m. p. 181°) C, 83.7; H, 11.4.

The results indicate the presence of a predominant amount of phytosterol agreeing in composition for that required by the common formula $C_{27}H_{46}O$.

The material was acetylated and the resulting acetyl derivatives fractionally crystallized from ethyl acetate and alcohol. The top fraction melted at 223–224°. It was saponified with alcoholic potassium hydroxide, and the recovered phytosterol after recrystallization now melted at 186–187° and had a specific rotation in chloroform of +115°.

Calc. for $C_{27}H_{46}O$: C, 83.9; H, 11.9. Found: C, 83.9; H, 11.5.

This alcohol when dissolved in chloroform and acetic anhydride gave a play of colors upon the addition of sulfuric acid resulting in red, purple and finally brown. When moistened with concentrated sulfuric acid it assumed an orange-red color which disappeared upon dilution with water. These color reactions are similar to those described by Power and Tutin[1] for oleasterol.

From the mother liquors of the acetate that melts at 223–224°, a quantity of an acetate was obtained that melted at 200–203°. It was hydrolyzed and an impure phytosterol fraction was obtained. It was repeatedly crystallized but did not melt sharply at 168–172°. It showed a specific rotation of +96.7° and probably consisted largely of the same material as the pure compound first described. (C, 83.3; H, 11.5.)

The alcoholic mother liquors were subjected to a fractional distillation and we obtained a non-distillable solid and brittle residue amounting to about 125 g. The material that distilled was recovered as follows.

Fraction I. (b. p. 100–180° at 28 mm.) This was an orange limpid liquid with aromatic odor and weighed 2 g.

Fraction II. (b. p. 180–210° at 25 mm.) A thick syrupy liquid weighing 5.7 g.

Fraction III. (b. p. 210–250° at 25 mm.) This was a dark red viscid liquid which solidified to a varnish-like mass on cooling.

It should be pointed out that 35.9% of the ligroin extract consisted of the non-distillable unsaponifiable resinous matter as this is unusual.

Examination of the Volatile Fatty Acids.—The alkaline solution from which the above described unsaponifiable matter had been extracted with ether was acidified and steam distilled, and the volatile fatty acids

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[1] *Loc. cit.*

were likewise recovered from the acids that occurred free in the fat. The distillate was made alkaline and concentrated, acidified and extracted with ether. These acids were separated by means of their silver salts which were fractionally precipitated.

Fraction I. Calc. for $C_{14}H_{27}O_2Ag$: Ag, 32.24. Found: 31.94.
Fraction II. Calc. for $C_8H_{15}O_2Ag$: Ag, 43.03. Found: 42.5.
Fraction III. Calc. for $C_6H_{11}O_2Ag$: Ag, 48.3. Found: 48.4.

This material, therefore, consists of a mixture of caproic, caprylic and myristic acids.

The aqueous liquid from which the above described acids had been ether-extracted consisted chiefly of formic acid with a trace of acetic acid.

Examination of the Non-Volatile Fatty Acids.—The acid mixtures which had been steam distilled were cooled and extracted with ether and the fatty acid fractions were united. 50 g. was distilled, and the distillate collected in 2 fractions; (*a*) b. p. 195–230° at 23 mm. weighing 21.5 g., showed an iodine number of 23.8, (*b*) b. p. 230–265° at 23–60 mm. weighed 11.5 g. and had an iodine number of 82.0. The residue in the distillation flask was considerable.

The distillates were united and the solid and liquid acids were separated by the lead salt method. From 23 g. there was obtained 7 g. of liquid acids (30%) while 14.8 g. of solid acids (64%) was recovered.

The solid acids were prepared in larger quantity and material having an iodine number of 15.5 to 19.3 was obtained and this was subjected to a systematic fractional crystallization. The top fractions were palmitic acid (m. p. 60–61°).

Calc. for $C_{16}H_{32}O_2$: C, 75.0; H, 12.5; N. V.,[1] 219.1. Found: C, 75.0; H, 12.35; N. V., 219.2.

The lower fractions consisted essentially of palmitic acid with a small amount of myristic acid. The fourth fraction melted at 49°.

Calc. for $C_{14}H_{28}O_2$: C, 73.7; H, 12.3; N. V., 246.1. Found: C, 74.1; H, 12.2; N. V., 221.4.

The liquid acids were prepared in larger quantities and converted into their methyl esters by the method of Phelps and Phelps[2] and of these 102 g. were distilled. These boiled at 185–280° at 15 mm., the lower fractions contained some palmitic ester. The unsaturated esters boiled chiefly at 205–280° at 15 mm.

Calc. for $C_{17}H_{33}COOCH_3$: C, 77.0; H, 12.2; iodine No., 85.1. Calc. for $C_{17}H_{31}COOCH_3$: C, 77.55; H, 11.6; iodine No., 172.8. Found: C, 77.7; H, 11.5; iodine No., 95–106.1.

The liquid acids, therefore, consist of linolic and oleic acids.

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[1] Neutralization value.

[2] *Am. J. Sci.*, **24**, 194 (1907).

The Ether Extract of the Resin, upon standing deposited 25.5 g. of a green solid. From this precipitate phytosterolin was readily obtained by crystallization from dilute pyridine. It melted at 290°.

Calc. for $C_{33}H_{56}O_6$: C, 72.3; H, 10.2. Found: C, 72.6; H, 10.4.

The material gave the characteristic color tests and was converted into its acetyl derivative that melted at 168°.

A systematic examination of the ethereal filtrate yielded nothing crystalline.

The Chloroform Extract of the Resin was divided into several parts, one of which was systematically examined by extraction with the usual alkaline solutions, but nothing was isolated. When subjected to acid hydrolysis with dil. alcoholic 5% sulfuric acid it was shown to be non-glucosidic, but no definite products resulted.

This extract is characterized by its ester-like structure and readily yielded valeric acid upon alkaline hydrolysis. It amounted to 7.2% of the resin and was identified as silver valerate. (Ag, 51.5%) No acetic acid was found.

The hydrolysis solution from which valeric acid had been removed by distillation was examined, but with the exception of a minute quantity (0.05 g.) of a crystalline product that melted at 99–102° nothing was found. This material occurred in the ammonium carbonate extract of the ether soluble fraction.

The Ethyl Acetate Extract of the Resin could not be directly crystallized. It constantly underwent spontaneous alteration leading to the precipitation of increasing amounts of insoluble amorphous material. The insoluble material proved to be soluble in alcohol but was not crystalline. Acid hydrolysis gave no crystalline products but an hydrolysis with 10% alcoholic potash yielded large quantities of valeric acid. Calculated on the basis of titration values found in the steam distillate it amounts to 18.5% of the resin that remained soluble in ethyl acetate. It was readily identified as the silver salt. (Ag, 51.6%.) This resinous material is an acidic resin.

The Alcohol Extract of the Resin was systematically examined but yielded nothing of interest except when subjected to alkaline hydrolysis it yielded large quantities of acetic acid (Ag, 64.4%) and practically no valeric acid.

KALAMAZOO, MICH.

NEW BOOKS.

Elektrochemisches Praktikum. By DR. ERICH MÜLLER, Professor and Director of the Laboratory of Electrochemistry and Physical Chemistry; with an introduction by Dr. Fritz Foerster, Geheimer Hofrat, Professor and Director of the Laboratory of Inorganic Chemistry, both at the Technische Hochschule, Dresden. Second Edition. 240 pages, 24 figures, 31 diagrams. Theodor Steinkopff, Dresden, 1919. 23 × 15 cm.

This excellent manual of electrochemistry deserves a much wider recognition in this country than it now enjoys. Although written by Dr. Müller, it had its origin in a set of laboratory exercises prepared jointly with Dr. F. Foerster, for a class in electrochemistry at the Technische Hochschule in Dresden. The book contains directions for some 70 experiments, one-half of which deal with electrochemical theories and one-half with applications of these theories. The principles involved in each experiment are brought out clearly by a preliminary discussion and the directions for the execution of the experiments are straightforward and complete. They have evidently survived the ordeal of actual use. In connection with the experiments are given references to the excellent text-book of Foerster "Elektrochemie der waesserige Loesungen," Second Edition.

The experiments illustrating the applications of electrochemistry cover electroanalysis, electroplating, the preparation of inorganic and organic substances by electrolysis, the preparation of inorganic substances by electrothermal methods. Even these experiments are not mere directions for securing the desired end, but in each case involve a careful study of the process itself. The experiments on the electrolysis of chloride solutions are especially illuminating and instructive.

The second edition differs but slightly from the first, the only important addition being a study of the current and energy capacities, the efficiency and the shelf-life of the dry-cell. ARTHUR B. LAMB.

A Treatise on Qualitative Analysis. Adapted for Use in Laboratories of Colleges and Technical Institutes. By FRANK CLOWES, D.Sc., Lond., AND J. BERNARD COLEMAN, A.R.C.Sc., Dublin. 9th Edition. 1920. J. & A. Churchill, London. pp. xiv + 400. $5.00 net.

The present edition of this well-known work has been "rewritten, recast and enlarged in order to adapt it to modern methods of teaching," besides having an altered style and size of paper which makes it conform to the Quantitative Analysis by the same authors. The tables for systematic analysis are so arranged across the page that it is not necessary to turn the book while the tables are being consulted. Besides the usual inorganic reactions for metals and acid-radicals, considerable space (pp. 174–240) is given to the reactions and detection of typical organic substances. There is evident a painstaking endeavor to make everything easy for the student by abundant cross references, but it is to be feared that their very multiplicity will defeat their purpose. The rather lengthy and detailed description of ordinary operations seems to be intended for a course without instructors, and aims at meeting conditions which do not prevail in this country. The space taken in a text-book (pp. 331–383) to describe in detail, "Laboratory Fittings, Apparatus, Chemicals, Reagents and Test Substances," would seem of more use to an instructor and supply-room man than to a student. The book will be of interest and value to industrial chemists as well as to students. The printing is good; the illustrations abundant, though some are antiquated. The methods of analysis are all tested by experience, though one notes the omission of several modern methods that are standard. That the book has an appeal to analysts and students is evidenced by the fact that nine editions have been printed since its first appearance. GEO. L. COYLE, S. J.

Die Bedeutung der Kolloide für die Technik. 3rd revised edition. By PROFESSOR DR. KURT ARNDT, Privatdozent at the Technische Hochschule, Berlin. Theodor Steinkopff, Dresden. 53 pp. 15 × 22 cm. $0.50.

The first edition of this little book appeared in 1909, and its purpose was to state in simple and non-technical language some of the very numerous instances in which colloids play important rôles in the industries. It fulfilled this purpose admirably, as its continued publication eloquently testifies.

The present (3rd) edition contains many additions, though it has wisely been kept a small and simple pamphlet. New chapters on flotation and electro-osmosis have been added.

While the author has not wholly avoided a somewhat encyclopedic form of treatment, he has achieved the difficult task of presenting a technical subject simply, clearly, and interestingly. ARTHUR B. LAMB.

Chemistry for Public Health Students. 1st Edition. By E. GABRIEL JONES, M.Sc., F.I.C., Lecturer in Public Health Chemistry in the Univ. of Liverpool. Deputy Public Analyst for the City of Liverpool. Methuen & Co., Ltd., London, 1920. ix + 244 pp. 13 × 19 cm.

This book is more than a manual and guide for laboratory procedure in public health chemistry, although such is the purpose it principally aims to serve. A considerable amount of material has been added to each chapter which will add to the student's general knowledge of the subject and enlighten him upon the application of laboratory findings. It is needless to say that extended discussion is not permitted by the size of the volume, and that amplification will be necessary in some sections, either in the form of class room instruction or collateral reading, if the student is to properly digest the material.

The style adopted by the author is one which makes for clarity and concise statement. Numerous side headings are used which enhance the value for continued use or for reference. Altogether the book is very readable and justifies the publication by bringing together within its covers a great many methods used in public health laboratories and much information in condensed form which is the stock in trade of the skilled public health analyst.

In general, the method of presentation is a separation of the important subjects, such as milk, alcoholic beverages, air and water, into separate chapters in which a few pages are given to general information on the subject. This is followed by the laboratory determination of different constituents. A summarized statement of the method is given, then a list of required apparatus and solutions and the detailed procedure. Frequent use is made of equations and examples of calculation.

The first two chapters of the book, some 25 pages, are given over to a discussion of the fundamental operations of quantitative analysis. It is evident that English experience in preparing students of public health chemistry has been much like that in America, in that it has found a majority unfamiliar with the principles and procedures which are the basis of the work which is to be undertaken. The author begins with detailed directions for the use of the balance and gives numerous rules and precautions to be observed in its manipulation. Full directions are then given for two typical gravimetric determinations. Under the head of volumetric analysis is a brief discussion of standard solutions, equivalent weights, normal solutions, indicators, acidimetry and alkalimetry. Greater space is devoted to the preparation and standardization of commonly used solutions of acids, bases and oxidizing substances. These serve as typical examples and care is taken to present equations and calculations. Procedures are also given to illustrate the use of the prepared solutions.

Twenty-five pages are devoted to the composition, analysis, and adulteration of milk. The composition of normal milk, the variations due to season, time of day, and methods of milking, come in for discussion. Excerpts are given from The Sale of Milk Regulations of the British Board of Agriculture. The procedures described for the estimation of fats, solids, gravity, nitrogen and lactose are characteristic of the attention given by the author throughout his book to the details and precautions of analysis.

There are certain omissions in this chapter which are apparent to one familiar with American practice. No mention is made of cream; the widely used Babcock method for fats does not appear, the Leffmann-Beam method evidently being more widely employed in England; the cotton-disc method for the rapid comparative estimation of sediment is not described.

A chapter is devoted to butter and margarine. In this there is a considerable discussion of the manufacture of margarine, the properties which distinguish it from butter, and the substances employed for adulteration of both of these products. Methods of analysis are given for the determination of water, fat, and salt, and for the detection of preservatives and foreign fats in butter.

There is a short chapter dealing with alcoholic beverages, and in Chapter VI ten pages are devoted to the composition and adulteration of certain articles of food, as condensed milk, cheese, lard, and honey, to the beverages tea, coffee, and cocoa, and to condimental substances, such as vinegar, pepper, and spices. Continuing in the same chapter, the author summarizes the microscopical appearance of certain food stuffs and briefly discusses food values and vitamines.

Out of 24 pages devoted to a chapter on food preservation and the detection of metallic poisoning in foods, 13 pages are given to the subject or arsenic and its detection. Justification of the use of this space is evidently found by the author in the epidemic of arsenical poisoning from beer which was brought to light in England in 1900. In this country experience has not shown any great danger existing to the public health from such a source.

The fore part of the chapter discusses 8 methods of preserving food and continues with the subject of chemical preservatives, quoting the work of Wiley and others in this field. Recommendations of the departmental Committee on Preservatives and Coloring Matters in Food made in 1901 are listed.

Water and water supplies receive attention in the 50 pages of Chapter VIII. The author devotes the first few pages to a description of the different sources of water and the quality of the supplies derived from them. Detailed directions are then given for taking samples of water for chemical analysis. Methods are given for the determination of free and albuminoid ammonia, oxygen absorbed, chlorine, nitrates, nitrites, total hardness, temporary and permanent hardness, and for the detection of poisonous metals. In some cases, qualitative as well as quantitative methods are given, and it is needless to say these do not always conform to the standard methods of water analysis of the American Public Health Association, but rather suggest a choice of methods which has merit from the standpoint of instruction. The author is to be congratulated upon incorporating several pages of material on the interpretation of water analyses. This very important phase of the subject is too often omitted or neglected not only in the text-books but in the class room as well. In this connection several typical analyses are given from various sources and interpretation is made of the quality by the author.

The significance of algae and protozoa and of the microscopical examination in general is given in this chapter. Water softening is briefly discussed.

The Analysis of Sewage Effluents is the subject of a short chapter, in which modifications of some of the methods described under water analysis are given. The importance of suspended matter and of disssolved oxygen in sewage effluents is pointed out and methods for their determination are given. The chapter closes with the recommendations of the Royal Commission on Sewage Disposal (1912) in regard to the pollution of streams with sewage and sewage effluents.

One of the best chapters of the book is that dealing with air, to which 27 pages are devoted. Composition of normal outdoor air, the changes produced by respiration and combustion, and the detection of gaseous impurities are discussed in turn, and the author has given a very complete list of gaseous impurities liable to be encountered, particularly in the industries, together with methods for their detection and the permissible limits of their concentration. In connection with the subject of dust, extracts are given from the Report of the Committee appointed for the Investigation of Atmospheric Pollution (February, 1916).

The closing chapter is devoted to disinfectants, their action, detection and estimation. Directions are given in an appendix for the preparation of numerous solutions. Several useful tables will also be found here. Following these are 7 pages of questions and a bibliography of reference books.

This little book ought to prove helpful and useful not only to students but also to instructors of courses in sanitary chemistry and public health laboratory methods. It is unfortunate that more care should not have been given to certain details of publication. The uneven margins and careless trimming of leaves, which are conspicuous in the reviewer's copy, detract seriously from the true worth of the book.

MELVILLE C. WHIPPLE.

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REPORT OF THE INTERNATIONAL COMMITTEE ON ATOMIC WEIGHTS FOR 1920–21.

Received July 22, 1920.

Since the report of this committee for the preceding year was prepared, only a few new determinations of atomic weights have been published. They may be summarized as follows.

Fluorine.—Moles and Batuecas[1] have made 23 determinations of the density of methyl fluoride, CH_3F. For the weight of a normal liter of the gas they find, in mean, 1.54542 g. From this the molecular weight, 34.024 is deduced, and F = 18.996. This rounded off to 19, is the value already accepted.

Silicon.—Baxter, Weatherill and Holmes,[2] from analyses of silicon tetrachloride, find Si = 28.111. This determination, however, is not regarded by the authors as final. Its acceptance, therefore, must await confirmation, especially as the value is much lower than that given in the present table of atomic weights.

Lead.—The atomic weight of isotopic lead from thorium minerals has been determined by Hönigschmid.[3] For lead from Norwegian thorite he finds Pb = 207.88 to 207.92. For lead from Ceylonese thorianite,

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[1] *J. chim. phys.*, 17, 538 (1919).

[2] Baxter, Weatherill and Holmes, THIS JOURNAL, 42, 1194 (1920).

[3] Hönigschmid, *Z. Elektrochem.*, 25, 91 (1919).

Pb = 206.88 to 207.24. In thorianite there is evidently a mixture of isotopes. and perhaps also of normal lead.

Richards and Sameshima[1] have examined lead from a radioactive Japanese mineral. The values found for the atomic weight were 207.11, 207.12 and 207.15. For ordinary lead the corresponding value was 207.184. The Japanese material, evidently, contained very little isotopic lead.

Tin.—In two papers Brauner and Krepelka[2] give new determinations of the atomic weight of tin based upon analyses of the tetrabromide. In the first paper, which is preliminary, they find Sn = 118.70. In the second, by Krepelka alone, the value Sn = 118.699. This confirms the earlier determinations by Briscoe and by Baxter and Starkweather. The work of the last named chemists appears in full in the same number of the JOURNAL. It was noticed in our last report from a preliminary publication.

Tellurium.—From analyses of the hydride, TeH_2, Bruylants and Michielsen[3] find for tellurium the value Te = 127.73, 127.79, and 127.4. The last value they reject. As these determinations are preliminary they need no further consideration now.

Scandium.—Meyer and Schweig,[4] after a study of methods for the purification of their material, give determinations of the atomic weight of scandium by the usual sulfate method. They found Sc = 45.03–45.37, in mean 45.23, but conclude that the method is untrustworthy. Hönigschmid,[5] with some of the same material, prepared scandium bromide and determined its ratio to silver. In 18 concordant analyses he found Sc = 45.099, which may be rounded off to 45.1. This value is accepted by Meyer and Schweig, and should be adopted.

Samarium.—The atomic weight of samarium has been determined by Owens, Balke and Kremers[6] by analyses of the anhydrous chloride. From the mean of 18 concordant analyses, Sa = 150.43, in close agreement with the determinations by Stewart and James, 150.44, which was noticed in our report of last year.

Apart from the actual determination of atomic weights 3 papers relative to the reduction of the experimental data deserve attention. Guye,[7] in one paper, has discussed the application of Avogadro's law to this problem. In a second paper[8] he has examined the data relative to bro-

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[1] Richards and Sameshima, THIS JOURNAL, 42, 929 (1920).

[2] Brauner and Krepelka; Krepelka, *ibid.*, 42, 917, 928 (1920).

[3] Bruylants and Michielsen, *Bull. Acad. Belg.*, Classe des Sciences, Nos. 2–3, 119 (1919).

[4] Meyer and Schweig, *Z. anorg. allgem. Chem.*, 108, 303 (1919).

[5] Hönigschmid, *Z. Elektrochem.*, 25, 93 (1919).

[6] Owens, Balke and Kremers, THIS JOURNAL, 42, 515 (1920).

[7] Guye, *J. chim. phys.*, 17, 171 (1919).

[8] Guye, *ibid.*, 17, 141 (1919).

mine and silver, and concludes that Br = 79.92 and Ag = 107.87. The last figure differs from the value 107.88, as given in the table by only 0.01, which is quite within the limits of experimental uncertainty. The third paper, by Van Laar,[1] relates to the method of calculating atomic weights.

INTERNATIONAL ATOMIC WEIGHTS, 1921.

	Symbol.	Atomic weight.
Aluminum	Al	27.1
Antimony	Sb	120.2
Argon	A	39.9
Arsenic	As	74.96
Barium	Ba	137.37
Bismuth	Bi	208.0
Boron	B	10.9
Bromine	Br	79.92
Cadmium	Cd	112.40
Calcium	Ca	40.07
Carbon	C	12.005
Cerium	Ce	140.25
Cesium	Cs	132.81
Chlorine	Cl	35.46
Chromium	Cr	52.0
Cobalt	Co	58.97
Columbium	Cb	93.1
Copper	Cu	63.57
Dysprosium	Dy	162.5
Erbium	Er	167.7
Europium	Eu	152.0
Fluorine	F	19.0
Gadolinium	Gd	157.3
Gallium	Ga	70.1
Germanium	Ge	72.5
Glucinum	Gl	9.1
Gold	Au	197.2
Helium	He	4.00
Holmium	Ho	163.5
Hydrogen	H	1.008
Indium	In	114.8
Iodine	I	126.92
Iridium	Ir	193.1
Iron	Fe	55.84
Krypton	Kr	82.92
Lanthanum	La	139.0
Lead	Pb	207.20
Lithium	Li	6.94
Lutecium	Lu	175.0
Magnesium	Mg	24.32
Manganese	Mn	54.93
Mercury	Hg	200.6
Molybdenum	Mo	96.0
Neodymium	Nd	144.3
Neon	Ne	20.2
Nickel	Ni	58.68
Niton (radium emanation)	Nt	222.4
Nitrogen	N	14.008
Osmium	Os	190.9
Oxygen	O	16.00
Palladium	Pd	106.7
Phosphorus	P	31.04
Platinum	Pt	195.2
Potassium	K	39.10
Praseodymium	Pr	140.9
Radium	Ra	226.0
Rhodium	Rh	102.9
Rubidium	Rb	85.45
Ruthenium	Ru	101.7
Samarium	Sa	150.4
Scandium	Sc	45.1
Selenium	Se	79.2
Silicon	Si	28.3
Silver	Ag	107.88
Sodium	Na	23.00
Strontium	Sr	87.63
Sulfur	S	32.06
Tantalum	Ta	181.5
Tellurium	Te	127.5
Terbium	Tb	159.2
Thallium	Tl	204.0
Thorium	Th	232.15
Thulium	Tm	168.5
Tin	Sn	118.7
Titanium	Ti	48.1
Tungsten	W	184.0
Uranium	U	238.2
Vanadium	V	51.0
Xenon	Xe	130.2
Ytterbium (Neoytterbium)	Yb	173.5
Yttrium	Yt	89.33
Zinc	Zn	65.37
Zirconium	Zr	90.6

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[1] Van Laar, *J. chim. phys.*, 17, 266 (1919).

The only change in the table of atomic weights is in the case of scandium; from 44.1 to 45.1; which appears to be fully justified by the evidence.

Signed, F. W. CLARKE,
T. E. THORPE,
G. URBAIN.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NEW HAMPSHIRE COLLEGE.]

A NEW METHOD FOR THE DETERMINATION OF ZIRCONIUM.

BY MELVIN M. SMITH AND C. JAMES.

Received August 16, 1919.

The increased commercial development of zirconium and its compounds during the last two or three years has called for far more accurate determinations of the dioxide than nearly all the older methods would give. Heretofore, in practically every instance the study of the quantitative separation of an element, keeps ahead of its industrial application. It seems reasonable to state, in the case of the element under discussion, that, up to the present time, there has been only one method, that employing nitroso-phenylhydroxylamine (cupferron), which has given absolutely reliable results.

Sodium thiosulfate has probably been the precipitant most commonly employed until comparatively recently. This method separates zirconium from iron very nicely when carried out under the proper conditions. However, since thorium, aluminum, titanium and phosphoric acid were precipitated by this reagent also, the results obtained were often as much as several per cent. too high.

Precipitation as the phosphate by sodium phosphate in the presence of hydrogen peroxide possesses an advantage in that titanium is held up. A considerable excess of hydrogen peroxide must be present and a second precipitation is advised. Unfortunately the solubility of the phosphate is affected by sulfuric acid; the second precipitation involves several tedious operations and the precipitate is not any too well defined.

The cupferron method, which is an excellent one, precipitates both zirconium and titanium together, iron having been previously removed. The solution should have 10% of free sulfuric acid present. If the original material contains only a few per cent. of phosphoric acid, a negligible amount of the latter will be found in the precipitate. The amount of titanium dioxide present must be determined either colorimetrically by hydrogen peroxide or by zinc reduction and subsequent titration. Tantalum and columbium, which occur in some varieties of zirkite, are precipitated by cupferron in the presence of large amounts of conc. sulfuric acid. It is, therefore, necessary to make sure that these elements are absent.

The other methods described for the estimation of zirconium leave much to be desired.

While the cupferron method is a very good one, it is not very simple, and in addition the reagent is very costly. Having these facts ever in mind, the authors commenced a search for suitable reagents. Several interesting ones have been found and work upon one of them is described below.

It was noticed that when selenious acid was added to boiling solutions of zirconyl chloride made acid with hydrochloric acid precipitates of basic selenite would form even in very dilute solutions. The composition of the selenite probably varied according to the conditions of this experiment, as was noticed by Nilson in 1875. Selenious acid moreover gave no precipitates with solutions of aluminum, or the rare earths. In the case of ferric chloride a precipitate formed in nearly neutral solution but not in a dilute acid solution. This last observation appeared to be especially interesting for it is here that the cupferron method fails. Thorium is precipitated in dilute acid solutions of the chloride. However this element does not appear to occur in zirkite to any appreciable extent.

Purification of Zirconyl Chloride.—Crude zirconium hydroxide was dissolved in conc. hydrochloric acid and the solution evaporated. When the volume had been considerably reduced, a quantity of conc. hydrochloric was added and the whole allowed to crystallize. The crystals were then placed upon a Büchner funnel and well washed with 1 : 1 hydrochloric acid. The chloride was further purified by 2 more crystallizations from 1 : 1 hydrochloric acid. The material was then examined for both iron and titanium by adding ammonium thiocyanate and hydrogen peroxide to separate portions of a solution. In neither case could any coloration be detected.

Preparation of Selenious Acid.—This acid was prepared by treating selenium with conc. nitric acid until oxides of nitrogen ceased to be evolved. The solution was evaporated to dryness and the selenium dioxide purified by sublimation. The oxide was then dissolved in water and the solution diluted until the liquid contained approximately 12.5% of selenious acid.

Zirconyl Chloride Solution.—A certain amount of zirconyl chloride was weighed out and dissolved in distilled water so as to give about 8 g. of zirconium oxide per liter.

A comparison of the amount of oxide contained in 25 cc. of the solution was made by precipitating the zirconium by ammonium hydroxide, cupferron and selenious acid with the following results.

Ammonium Hydroxide.—25 cc. of zirconyl chloride solution was diluted to 100 cc. and ammonium hydroxide added to the boiling liquid until it smelled of ammonia. The resulting precipitate was filtered off, washed, dried, ignited to oxide and weighed. Two runs gave 0.2111 g. and 0.2107 g., respectively.

Nitroso-phenyl-hydroxylamine, Cupferron.—25 cc. of the solution was evaporated to fumes with 15 cc. of conc. sulfuric acid in a Kjeldahl flask. The cooled residue was taken up with water, diluted to 150 cc., cooled to 10° and precipitated with a 6% solution of the cupferron. The precipitate was filtered off, washed first with 10% hydrochloric acid and then with 5% ammonium hydroxide, after which it was dried, ignited and weighed. Two different portions gave 0.2102 g. and 0.2106 g., respectively.

Selenious Acid.—In the case of this reagent precipitations were made under varied conditions. For the first tests 25 cc. of the original solution was diluted to 100 cc., precipitated by the addition of about 20 cc. selenious acid solution and the whole heated to boiling. The precipitate was filtered off, washed with hot 2% hydrochloric acid, dried and ignited. Three results gave 0.2106 g., 0.2107 g. and 0.2105 g., respectively.

The next trials were made upon 25 cc. of solution diluted from 100 to 250 cc. in the presence of 5% of conc. hydrochloric acid. Under these conditions the figures yielded were 0.2109 g., 0.2106 g., and 0.2109 g. The filtrate was found to be free from zirconium, the ignited precipitate contained no selenium.

Sulfuric acid solutions are not suited to the use of the selenious acid reagent. The material should be in the form of the chloride and the free acid should not exceed 7% of hydrochloric acid (sp. gr. 1.200). Precipitation from 7% hydrochloric acid and washing with water containing 3% of hydrochloric acid gave good results, since no zirconium was found in the filtrate or wash water. The selenite appeared to be distinctly soluble in solutions containing 10% of free acid, as the following results show. 25 cc. of zirconium chloride solution was used in each experiment.

Hydrochloric acid. %	Zirconium oxide found. G.
0	0.2106
do	0.2107
do	0.2105
5	0.2109
do	0.2106
do	0.2109
10	0.2060
do	0.2044

Separation of Zirconium from Aluminum.—A solution of aluminum chloride was prepared by dissolving pure aluminum chloride in water. It was standardized by precipitating with ammonium hydroxide, washing and igniting to form the oxide. One cc. of the solution was equivalent to 0.0183 g. of aluminum oxide.

In order to find out whether the presence of aluminum would affect the determination of zirconium as the selenite, various portions of the solutions were mixed and diluted with 150 to 200 cc. of water. Hydrochloric acid was added to bring the concentration to 5%. The whole was then heated to boiling and precipitated by about 20 cc. of selenious acid. The precipitate was washed with a hot 2% hydrochloric acid solution. The aluminum hydroxide was precipitated from the filtrate by adding ammonium chloride and ammonium hydroxide in the usual manner. The results obtained were as follows.

Al_2O_3 taken. G.	Al_2O_3 found. G.	ZrO_2 taken. G.	ZrO_2 found. G.
0.0366	0.0360	0.2108	0.2106
0.1830	0.1831	0.2108	0.2106
0.7320	0.7326	0.2108	0.2107
0.1830	0.1831	0.04216	0.0421

Separation of Zirconium from Rare Earths.—Solutions of chlorides of the rare earths give no precipitates with a solution of selenious acid. Cerium should be in the cerous condition.

A solution of the chlorides of the rare earths was prepared and standardized. One cc. of the solution was equivalent to 0.0083 g. of oxides.

The operations were carried out in a manner similar to those described under aluminum. Although the rare earths might easily have been precipitated as the oxalates, no determination was made. The following figures were obtained.

Rare earth oxides taken. G.	ZrO_2 taken. G.	ZrO_2 found. G.
0.2490	0.2108	0.2108
0.0249	0.2108	0.2107

Separation of Zirconium from Iron.—These 2 elements may be easily separated by means of hydrogen sulfide in ammoniacal ammonium tartrate solution, sodium thiosulfate, etc. This involves the use of some additional method for the removal of such other elements as aluminum, the rare earths, etc. Ferric chloride made slightly acid with hydrochloric acid is precipitated by selenious acid. This precipitate is readily dissolved by hydrochloric acid, and it was found that in 5% hydrochloric acid solution ferric chloride is not precipitated by selenious acid.

A solution of ferric chloride was prepared and standardized by precipitation by ammonium hydroxide in the presence of ammonium chloride. One cc. of the solution was equivalent to 0.00222 g. of ferric oxide, Fe_2O_3.

Twenty-five cc. of zirconyl chloride solution, 20 cc. of ferric chloride solution and 7.5 cc. of conc. hydrochloric acid were mixed and diluted to about 150 cc. The liquid was then heated, precipitated by selenious acid and filtered. The precipitate was washed with a boiling 2% hydrochloric acid. The precipitate and paper were returned to the original beaker owing to the fact that iron could be seen in the zirconium selenite. A measured volume 1 : 1 hydrochloric acid was added and the mass heated carefully for a time. Water was then added until the hydrochloric acid content was reduced to 5%. Any zirconium that might have remained in solution was next thrown out by adding about 20 cc. of selenious acid. The insoluble selenite was removed, washed and ignited. The resulting oxide which possessed a reddish tint, weighed 0.2145 g. instead of 0.2111 g. A similar run involving the use of 10 cc. of ferric chloride gave 0.2128 g. of oxide, and another in which 5 cc. was employed gave 0.2115 g. of oxide. Although these results were far from encouraging, it was decided to see what one precipitation in very dilute solution would do, for in the operations described above it was noticed that the selenite never entirely dissolved in the strong acid, and that certain portions of the ignited precipitate was very red, while others were white.

Twenty-five cc. of zirconyl chloride, 10 cc. of ferric chloride and 20 cc. of conc. hydrochloric acid were mixed, diluted to about 400 cc. and precipitated by 30 cc. of selenious acid. The whole was then boiled and filtered. The precipitate was washed with 2 to 3% hydrochloric acid and ignited. This time the oxide weighed 0.2112 g. as compared with the standard figure of 0.2111. In the next experiment 25 cc. of zirconyl chloride, 20 cc. of ferric chloride and 40 cc. of conc. hydrochloric acid were diluted to about 750 cc. and precipitated by 40 cc. of selenious acid. The ignited oxide weighed 0.2125 instead of 0.2111 g. These results indicate that if the amount of iron oxide in the combined iron-zirconium oxides is about 20% there will be a very slight error. As the amount of iron decreases, the error will become less and finally disappear when the figure reaches about 10% oxide of iron. Since practically all commercial zirconia ore contains much less than this latter value, a single precipitation is sufficient. In certain special cases it might become necessary to repeat the operation or else to remove the iron by another method.

Separation of Zirconium from Titanium.—Selenious acid throws down titanium along with zirconium and it is necessary to make a correction for this. This may easily be carried out either colorimetrically by hydrogen peroxide when small amounts are present or by titration after reduction in the Jones reductor if larger quantities are found.

It was found that zirconium could be precipitated, in the cold or boiling, as the selenite, in the presence of an excess of hydrogen peroxide free from titanium. The filtration can be carried out much better in the cold, since the evolution of oxygen in the pores of the filter paper causes the precipitate to run through.

In order to test the accuracy of the separation, 25 cc. of zirconyl chloride solution and 5 cc. of titanium sulfate were mixed, diluted and precipitated by ammonium hydroxide in the presence of ammonium chloride. The hydroxides were filtered off, washed, returned to the original beaker and warmed with 10 cc. of conc. hydrochloric acid. After standing a short time an equal volume of water was added and the whole heated to boiling. The solution was diluted further, filtered and the residue of filter paper well washed. An excess of hydrogen peroxide was added, the liquid diluted to about 500 cc. and precipitated by an excess of selenious acid. The precipitate was filtered off and washed with water containing 2% of hydrochloric acid and a little selenious acid.

TiO_2 taken. G.	ZrO_2 taken. G.	ZrO_2 found. G.
0.0463	0.1022	0.1019
0.0463	0.1022	0.1016

Separation of Zirconium from Phosphoric Acid.—If phosphoric acid is present it will be precipitated along with the members of the iron group by ammonium hydroxide in the presence of ammonium chloride. Upon dissolving the precipitate in hydrochloric acid zirconium phosphate will remain insoluble and be lost if the paper pulp is filtered off. On the other hand if the phosphate is not removed the determination will be too high. If this substance is found, it must be collected, decomposed by fusion with an excess of sodium carbonate, boiled out with water, the residue washed, dissolved in hydrochloric acid and added to the main portion.

Determination of Zirconium in Zirconia Ore.—1.2408 g. of zirconia ore was fused with 12 to 15 g. of potassium hydrogen fluoride in a platinum dish. The potassium hydrogen fluoride was prepared by treating potassium fluoride with a slight excess of hydrofluoric acid and evaporating over a very small flame until a clear fused mass was obtained. After allowing it to cool, it was broken up. The mixture of zirconia ore and fluoride was carefully heated by a very small flame. When the mixture became fused it was stirred with a platinum rod, and the size of the flame was gradually increased. After the whole had become solid and white, it was heated over a powerful burner until it just fused to a clear liquid. The lowest possible temperature for this operation was always used. The cooled melt was next treated with about 50 cc. of 1 : 1 sulfuric acid, gently heated until nearly all water was removed, and then more strongly heated until abundant fumes were evolved. The cold residue was boiled with water, cooled and diluted to 250 cc. 100 cc. of this solution was diluted, boiled and precipitated by ammonium hydroxide in the presence of ammonium chloride. The hydroxides were filtered off and well washed. The filter paper and the precipitate were treated with 36 cc. of conc. hydrochloric acid and about 40 cc. of water, boiled, diluted to 700 cc. and precipitated by selenious acid.[1] The insoluble selenite was removed

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[1] If phosphoric acid is present, the insoluble phosphate must be filtered off and treated as mentioned under phosphoric acid.

by filtration, washed with 3% hydrochloric acid, dried and ignited. The resulting oxides weighed 0.4286 g. 50 cc. of the solution treated in a similar manner gave 0.2141 g. These quantities represented 86.36 and 86.40% respectively, of zirconium and titanium oxides.

Average by selenious acid	86.38%
By cupferron was	86.36%

0.2591 g. of another sample of zirconia ore gave 0.1939 g. of oxides of zirconium and titanium, or 74.84%, while the average given by cupferron was 74.70%.

The method described above was found to be very rapid, simple and accurate for the determination of zirconium. The reagent, selenious acid, is cheap.

The determination of thorium by means of selenious acid and the determination of tantalum and columbium by means of cupferron are being investigated at the present time.

DURHAM, N. H.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

TRANSFERENCE NUMBERS OF SODIUM AND POTASSIUM IN MIXED CHLORIDE SOLUTIONS. (PRELIMINARY PAPER.)

BY S. A. BRALEY AND J. LOWE HALL.[1]

Received January 2, 1920.

In a study of the equilibria existing between mixed salt solutions and liquid amalgams, Smith and Ball[2] have noted that, with equivalent mixtures of sodium and potassium chlorides in solution, the ion-fraction of the potassium gradually decreases with increasing total salt concentration. In other studies on sodium-strontium[3] and potassium-strontium[4] mixtures similar results have been obtained. Several explanations may be offered to account for this behavior and the present work has been carried out for the purpose of throwing some light upon the subject by comparing the calculated values (on the basis of the isohydric principle) with the determined values of the transference numbers at various equivalent salt concentrations.

G. M. J. McKay,[5] by the use of transference experiments in mixed solutions of potassium chloride and potassium sulfate, 0.2009 *N* with respect to each, has shown that the ratio of the ionization factors of the 2 salts in the mixture is 1.372, whereas the ratio as calculated from the

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[1] The authors wish to thank Dr. T. R. Ball for originally suggesting the problem and starting the work upon it.

[2] Smith and Ball, THIS JOURNAL, 39, 179 (1917).

[3] Smith and Braley, *ibid.*, 39, 1545 (1917).

[4] Smith and Rees, *ibid.*, 40, 1802 (1918).

[5] McKay, *ibid.*, 33, 308 (1908).

conductance of the solution on the basis of the isohydric principle is 1.275. Also, in general, calculations based on conductivity do not yield values in agreement with those obtained by other methods.

Many examples of the double salts in which the halides appear are known, such as K_2PtCl_6, $KCl.MgCl_26H_2O$, Na_3AlFe, $2NaCl.Al_2Cl_6$, the potassium iodide complexes with the iodides of cadmium, mercury, zinc, bismuth, etc. It is, therefore, not altogether rash to expect that the alkali halides form complexes with each other in solution, especially as their ions are known to be hydrated.[1]

On this assumption we would then have one of the metals showing a decrease of transference due to the back transference of the metal in the negative complex.

Theoretical.

The transference number of an ion in solution is

$$T\oplus = KC\oplus + U\oplus = K'C\oplus + \Lambda\oplus \qquad (1)$$

where $\oplus$ represents the ion.

But

$$C\oplus = C_{\text{salt}}\,\alpha_{\text{salt}} \qquad (2)$$

Also

$$\alpha = \Lambda/\Lambda_0. \qquad (3)$$

Therefore, the ratio of the transference numbers of the sodium and potassium ions in the solution will be

$$\frac{T_{\text{Na}}}{T_{\text{K}}} = K\,\frac{\Lambda\text{NaCl}/\Lambda_0\text{NaCl}.\Lambda_{\text{Na}}\oplus}{\Lambda\text{KCl}/\Lambda_0\text{KCl}.\Lambda_{\text{K}}\oplus}. \qquad (4)$$

Since equivalent ion conductances are known only at infinite dilution, it is necessary to assume, as McKay[2] does, that the ratio of these values for sodium and potassium ions is the same as at infinite dilution. Also, as Washburn[2] and McKay[2] both observe that in the case of 2 strong electrolytes in a mixed solution, ionization calculations based on total salt concentration agree quite closely with those based on the common ion concentration, the former will be used in the calculations. As viscosity corrections would be applied alike to numerator and denominator, they will be omitted.

The value of the proportionality constant K in Equation 4 may be readily calculated, for at infinite dilution the ratio $\frac{\Lambda\text{NaCl}/\Lambda_0\text{NaCl}}{\Lambda\text{KCl}/\Lambda_0\text{KCl}}$ becomes equal to one, hence $\frac{T_{\text{Na}}}{T_{\text{K}}} = K\,\frac{\Lambda_{\text{Na}}\oplus}{\Lambda_{\text{K}}\oplus}$, in which case K becomes equal to 1.17.

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[1] E. W. Washburn, *Tech. Quart.*, 21, 288 (1908).

[2] *Loc. cit.*

Materials, Apparatus and Method of Experimentation.

1. **Materials.**—(*a*) *Sodium and Potassium Chlorides.*—These salts were prepared by twice precipitating good commercial grades of the salts in aqueous solution with hydrogen chloride, centrifuging and drying in an electric muffle at about 750°. They were stored in glass-stoppered bottles, and again dried in the muffle in quantities as used.

(*b*) *Coulometer Materials.*—15 g. of crystalline c. p. silver nitrate was dissolved in 150 cc. of distilled water shortly before using. This amount of solution just conveniently filled both coulometers.

A pure grade of silver (99.9% fine) was used for anodes. The silver was melted on a bone-ash cupel by means of a blast lamp. A piece of heavy silver wire was inserted into the molten silver button, and the mass allowed to solidify.

A weighed platinum dish was used as a cathode.

(*c*) *Silver Chloride for Cathode.*—The silver nitrate solution from the coulometers used in the previous run was kept in a dark place to be used in preparation of silver chloride for the succeeding run. It was filtered, heated to boiling, and precipitated with a hot solution of a little more than the theoretical amount of sodium chloride. The adherent pasty precipitate was finely disintegrated with a glass spatula, washed by decantation 2 or 3 times, and finally transferred to a filter and thoroughly washed. The precipitate was then washed with some of the stock solution of mixed chlorides and transferred to the apparatus.

(*d*) *The Anode.*—The anode was prepared essentially as was the "Type B Anode" described by Washburn[1] for use in transference experiments.

2. **Apparatus and Method of Experimentation.**—(*a*) *Apparatus.*—The same transference apparatus was used as that used and fully described by E. W. Washburn[1] for the measurement of transference numbers in simple solution. The special coulometer stands were equipped with a glass rod support.

(*b*) *Method of Manipulation.*—Essentially the same procedure was followed as that described by Washburn.[1]

(*c*) *Pipets, Burets, and Weights.*—The pipets and burets used were calibrated by the Bureau of Standards and the weights were calibrated against a standard set and proper corrections applied.

(*d*) *Thermostat.*—A large Freas thermostat electrically controlled was filled with water to a depth sufficient to cover the horizontal section of the apparatus. The temperature was accurate to within a 0.1° and constant to within 0.01°.

3. **Analysis and Calculations.**—(*a*) *Analysis.*—Duplicate samples from the end portions and one from each of the 3 middle portions were transferred to small porcelain evaporating dishes for a sodium-potassium

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[1] *Loc. cit.*

determination. At the same time an entire duplicate set of samples was transferred to resistance glass beakers (600 cc. capacity) for a Volhard volumetric determination of chlorine. This analysis was used merely as a check on the total equivalents of salt as found by the chloroplatinate method.

The sodium-potassium determination was carried out by the chloroplatinate method as described by Ball,[1] with the exception that methyl alcohol (redistilled on a steam bath) was used instead of ethyl alcohol as a separating medium. Care was taken to allow the last traces of the methyl alcohol to evaporate, however, before washing down the filter with hot water and evaporating on the steam bath, as the alcohol exerts a strong reducing effect on the platinum salts when heated. The chloroplatinic acid was also prepared as described by Ball.

(*b*) *Calculations.*—The factor 0.3056 was applied to the weight of potassium chloroplatinate to obtain the potassium chloride. Ordinary transference calculations were applied using atomic weights as follows: Na = 23.0; K = 39.1; Cl = 35.46; and Ag = 107.88.

Experimental Data.

The following table shows the experimental and theoretical values obtained. The basis of comparison of the obtained and theoretical values is the ratio of T_{Na}/T_K, as shown in Equation 4. Conductance data of reliable character covering the range of concentration used, at 25°, were difficult to find. However, values for Λ determined by Kohlrausch at 18° were corrected to 25° and the values desired were obtained by careful graphical interpolation.

No values are given for the cathode portions as these results did not agree in the least with themselves or with the anode portions. No explanation can be offered at this time but the difference was probably due to manipulation in removing the portion from the silver chloride electrode or to some side reactions on the part of the electrode itself. This matter will be investigated and in this preliminary paper only the anode values will be considered.

TABLE I.

Temp. 25°.

	0.1 *N* KCl. 0.1 *N* NaCl.				0.2 *N* KCl. 0.2 *N* NaCl.				0.8 *N* KCl. 0.8 *N* NaCl.			
Infinite dilution.	T_{Na}.	T_K.	$\frac{T_{Na}}{T_K}$.	Calc.	T_{Na}.	T_K.	$\frac{T_{Na}}{T_K}$.	Calc.	T_{Na}.	T_K.	$\frac{T_{Na}}{T_K}$.	Calc.
.....	0.173	0.258	0.670	.....	0.176	0.265	0.665	.....	0.174	0.267	0.650	.....
.....	0.174	0.258	0.672	.....	0.177	0.263	0.673	.....	0.170	0.267	0.636	.....
.....	0.154[a]	0.228	0.674	.....	0.176	0.274	0.636	.....	.....	.....	.....	.....
.....	0.154[a]	0.228	0.674	.....	0.177	0.273	0.650	.....	.....	.....	.....	.....
Av., 0.802	0.174	0.258	0.673	0.776	0.176	0.268	0.656	0.760	0.172	0.267	0.643	0.700

[a] These two values at total concentration of 0.2 *N* are evidently low, but this is undoubtedly due to experimental error as the ratios are the same.

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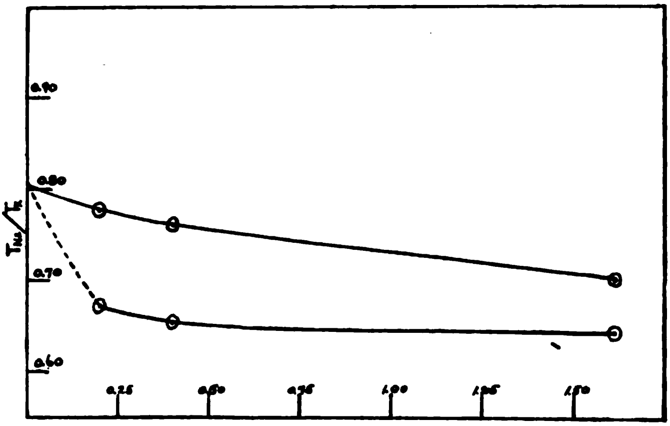
[1] *Loc. cit.*

It should be noted that a small difference in the transference numbers of the ions themselves makes a large error in the ratio, and because of this fact the checks on the observed ratios are very close and the difference between the observed and calculated values the more significant.

In Fig. 1 the calculated ratios and the observed ratios have been plotted against the total concentration. It is readily seen that while the theoretical ratio is always higher than the experimental the difference decreases as a function of the total concentration. Also, the experimental curve has been extrapolated to the theoretical value at infinite dilution for at this point all complicating factors would be removed and the theoretical value for a simple solution would be obtained.



Total Concentration in mols/liter.

Fig. 1.—Curves showing variation of T_{Na}/T_K with total concentration. Upper curve showing calculated values. Lower curve showing determined values.

These results indicate that, on the whole, more potassium was transferred than the theory would indicate, but that over the range studied, that is, form a total concentration of 0.2 N to 1.6 N that more sodium is being transferred proportionally than potassium, since over this range the 2 curves tend to converge with increasing concentration. In other words, from a total concentration of 0.2 N to 1.6 N the sodium gains "transference advantage" with increased concentration. Such an "advantage" may be due to the following possible causes—(1) a direct increase of the sodium ion fraction, (2) a relative increase of the sodium ion mobility, (3) the entrance of sodium in superior amounts into positive aggregates, and (4) a "back transference" of potassium in the form of a complex negative ion.

It is interesting to note that the first possibility is in accordance with the results obtained by Ball and Smith, and that the fourth possibility would indirectly lead to the same condition, for if potassium goes into complex negative ion formation, the simple sodium ion fraction is correspondingly increased. In connection with the second possibility, Washburn has found that the sodium ion is 50% more highly hydrated than the potassium ion. And because of the resulting more voluminous and unwieldly character of the sodium ion, which is further evidenced by its much lower ion conductance and transference number, it is reasonable to believe that its ion mobility would be slowed up more, with increasing viscosity, than the potassium ion mobility. This fact undoubtedly accounts for the very sharp break in the determined ratio when extrapolating from a total concentration of 0.2 *N* to infinite dilution, as it would be over this range that the hydration would take place to the greatest extent and so exceed the change due to the other factors. If this were the only factor entering, however, it should continue and the curves in Fig. 1 would continue to diverge; therefore, we must conclude that other factors have entered which overcome this one.

If we assume the formation of complexes in order to account for the results obtained, we of course have none other than a qualitative indication of their nature. In order to satisfy the results obtained in Smith and Ball's[1] work and in this investigation, the complex must be of such character as to involve an excessive transference of sodium and a diminution of the simple potassium ion fraction, both of which become more pronounced with increase of concentration above 0.2 *N*. Mention was made in the third possible cause given above of the possibility of sodium entering in superior amounts in positive aggregates. This condition might be satisfied by the possible interpolation of sodium chloride in place of the water of hydration of the potassium ion. But as a greater opportunity is afforded for the interpolation of potassium in the more highly hydrated sodium ion, and as the removal of free sodium chloride would cut down the sodium ion fraction rather than the potassium, this possibility is inconsistent.

The simplest complex formation possible is NaCl.KCl, which may be expressed either as $K(NaCl_2)$ or $Na(KCl_2)$, and which may ionize to either free potassium ion or free sodium ion. If it should be the first and ionize thus,

$$K(NaCl_2) \rightleftharpoons K^+ + NaCl_2^-,$$

the simple sodium ion fraction would be relatively decreased and a "back transference" of sodium would occur, both of which are contrary to results.

But if it should ionize thus,

$$Na(KCl_2) \rightleftharpoons Na^+ + KCl_2^-,$$

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[1] *Loc. cit.*

the sodium ion fraction would be relatively increased, and a "back transference" of potassium would occur, both of which conditions would give an additive tendency to explain the results obtained in both investigations, and which satisfy both the first and fourth possible causes mentioned.

Summary.

It has been shown that over a range of total concentration from 0.2 N to 1.6 N with equivalent mixtures of sodium and potassium chlorides a relatively higher amount of sodium is transferred than is called for by calculation, on the basis of the isohydric principle, from the conductance of the simple salt solutions.

The increase of sodium transferred, over this range of concentration, is roughly a linear function of the total salt concentration.

The results are in harmony with those of Smith and Ball,[1] according to which they find that the sodium ion-fraction increases with increase of total salt concentration over this same range of concentration.

The results may be explained on the basis of complex formation, the simplest form of which, in accordance with these results, may be expressed thus,

$$NaCl + KCl \rightleftharpoons Na(KCl_2) \rightleftharpoons Na^+ + KCl_2^-.$$

URBANA, ILLINOIS.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF COLUMBIA UNIVERSITY, No. 337.]

THE VISCOSITY OF LIQUIDS. IV. IDEAL MIXTURES OF THE TYPES ETHER-ETHER AND ESTER-ESTER.

JAMES KENDALL AND ALEXANDER HOLLAND WRIGHT.

Received April 27, 1920.

Previous attempts to derive a general equation for representing the viscosities of ideal liquid mixtures have been critically examined, and new lines of attack discussed, in earlier papers of this series. In the first article,[2] all existent formulas were tested by means of the available experimental data and a modification of an equation proposed by Arrhenius[3] was shown to give most satisfactory agreement. This equation may be written

$$\log \eta = x \log \eta_1 + (1 - x) \log \eta_2 \qquad (1)$$

(where η_1 and η_2 are the viscosities of the pure components, and the composition, x, is expressed in molecular fractions). Later investigation by Egner[4] has confirmed the approximate accordance of this formula with the results of experiment.

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[1] *Loc. cit.*

[2] Kendall, *Medd. K. Vetenskapsakad. Nobelinst.*, 2, No. 25 (1913).

[3] Arrhenius, *Z. physik. Chem.*, 1, 285 (1887).

[4] Egner, *Medd. K. Vetenskapsakad. Nobelinst.*. 3, No. 22 (1917).

On more detailed examination[1] of these experimental data, however, it was recognized that, in all systems studied, the differences between the physical constants of the pure components were entirely insufficient to afford a decisive test of the relative merits of the several formulas. Not only were viscosities, in general, only slightly different in value, but also variations in molecular weight and density were too narrow to permit definite conclusions on the proper method for representation of composition. Volume, weight and molecular units have all been suggested by different investigators, and the calculated curves for any one system were in most cases so closely clustered around the experimental curve that no real discrimination was possible.

Several selected systems, as nearly ideal as possible, were, therefore, made the subject of exact experimental study, all of the above mentioned factors being varied as widely as possible. It was found, in consequence, that *none* of the previously proposed formulas agreed even approximately with the experimental data (in one typical series the maximum divergences ran from 27 to 204%) although the logarithmic formula (1) was superior to any other. A new equation, of the form,

$$\eta^{1/3} = x\,\eta_1^{1/3} . + (1 - x) . \eta_2^{1/3} \qquad (2)$$

(η_1, η_2 and x having the same significance as in Equation 1) was suggested, which reproduced the observed values very accurately for the majority of the systems examined. In one case, however, the divergences were sufficiently pronounced to force the conclusion that this equation also possessed no general theoretical foundation.[2]

The present article continues the quest for the fundamental viscosity formula for ideal liquid mixtures by an examination of 2 additional series of systems. It was hoped that further accurate data for carefully chosen mixtures (as nearly as possible ideal and with components of widely divergent viscosities, densities and molecular weights) might enable us at least to narrow down still more the possible limits between which the true equation lies by the final rejection of formulas obviously beyond these limits, even if no ultimate success were obtained in establishing the ideal relation. In particular, it was desired to compare the relative merits of Formulas 1 and 2 more stringently than had been done in previous work.

Experimental.

The liquids selected were representative *ethers* and *esters*, 3 systems of each type (ether-ether and ester-ester) being examined.

As the starting point for each substance, standard preparations of reliable firms were taken, and subjected to careful purification. *Ethyl*

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[1] Kendall and Monroe, THIS JOURNAL, 39, 1787 (1917).

[2] The results obtained by the application of this equation to ideal solutions of solids in liquids were also not entirely satisfactory (see Kendall and Monroe, *ibid.*, 39, 1802 (1917).

ether was washed with small amounts of water, then with sodium carbonate solution, dried for several months over sodium and fractionated. *Phenetol* was fractionated under constant low pressure (about 20 mm.) by means of a specially devised form of apparatus[1] which allowed change of receivers without break of the vacuum. The fractionation was repeated until no further change in the physical constants of the product could be noted. *Diphenyl ether* was fractionated under low pressure and then fractionally crystallized several times. *Ethyl acetate* was washed with small amounts of water, then with sodium carbonate solution, dried over phosphorus pentoxide and specially fractionated. *Ethyl benzoate* was washed, dried over calcium chloride and fractionated repeatedly. *Benzyl benzoate* was very carefully purified[2] by successive fractionations under constant low pressure.

The portions employed possessed the following constants:

Liquid.	Freezing pt. ° C.	Boiling pt. (760 mm.) ° C.	Density 25°/4°.	Viscosity.	Spec. conductivity.
Ethyl ether.............	...	34.6	0.7139	0.002233	.....
Phenetol...............	...	170.1	0.9618	0.01158	.....
Diphenyl ether..........	27.05	..	1.0706	0.03864	.....
Ethyl acetate...........	...	77.15	0.8948	0.004239	$<1 \times 10^{-9}$
Ethyl benzoate..........	...	209.1	1.0431	0.02014	$<1 \times 10^{-9}$
Benzyl benzoate.........	19.4	323.0±0.2	1.1121	0.08504	$<1 \times 10^{-9}$

A comparison of these constants with those obtained by previous workers indicates that the more laborious methods of purification here adopted have been justified by the removal of final traces of impurities. Thus the benzyl benzoate employed by Kendall and Monroe[3] gave m. p., 18.8°: $\eta_{25°} = 0.08454$. The same workers obtained for ethyl benzoate $\eta_{25°} = 0.01990$. Since all likely impurities would tend to lower the observed viscosity, the present values are preferred. Previous accurate determinations for the remaining liquids are rare, the value $\eta_{25°} = 0.004193$ obtained by Dunstan[4] for ethyl acetate may, however, be cited.

With regard to the ideality of the mixtures examined, it must be admitted that the first liquids in each series (ethyl ether and ethyl acetate), in particular, are not perfectly normal liquids, but the similarity in the nature of the components of each system will be sufficient to render any deviations from ideality only slight.[5] No appreciable heat or volume

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[1] To be described in a later article (P. M. Gross and A. H. Wright).

[2] The difficulty of purifying benzyl benzoate has recently been discussed by the Earl of Berkeley, *J. Chem. Soc.*, **109**, 520 (1916).

[3] Kendall and Monroe, *loc. cit.*, p. 1796.

[4] Dunstan, *Z. physik. Chem.*, **49**, 590 (1904). The values obtained for phenetol and diphenyl ether by Sachanov and Rjachowsky, *ibid.*, **86**, 529 (1914) are by no means in such satisfactory agreement.

[5] The factors affecting ideality have been examined in detail by Hildebrand, THIS JOURNAL, **38**, 1452 (1916).

changes were noted on admixture of equivalent volumes of the 2 components in any one case.

Viscosity measurements were carried out with the use of the Bingham[1] type of viscometer, the experimental procedure and calculation of results being exactly as recorded in earlier articles of this series. Densities (which are required, for this method, only for use in a correction factor) are appended in the tables below to facilitate conversion of the results from molecular to volume units, but accuracy beyond the third place is not claimed.[2]

Results.

In the following tables, the first column gives the composition of the mixture in molecular units, the second its density, the third its absolute

SERIES A. MIXTURES OF DIETHYL ETHER AND PHENETOL.

Mol. % ethyl ether.	Density 25°/4°.	η (expt.).	η (calc.). Log eqn.	Percentage divergence.	η (calc.). Cube rt. eqn.	Percentage divergence.
100.00	0.7139	0.002233	....	...	....	...
90.04	0.7458	0.002674	0.002646	—1.1	0.002757	+3.0
83.03	0.7656	0.003057	0.002952	—3.4	0.003171	+3.7
74.85	0.7891	0.003494	0.003377	—3.3	0.003704	+6.0
68.82	0.8059	0.003866	0.003730	—3.5	0.004133	+6.9
60.48	0.8283	0.004406	0.004278	—2.9	0.004780	+8.5
55.79	0.8387	0.004809	0.004629	—3.8	0.005176	+7.6
51.06	0.8488	0.005154	0.004996	—3.0	0.005587	+8.3
45.01	0.8628	0.005713	0.005519	—3.3	0.006151	+7.7
35.16	0.8853	0.006667	0.006489	—2.7	0.007148	+7.2
30.26	0.8970	0.007152	0.007035	—1.6	0.007682	+7.4
25.23	0.9083	0.007856	0.007642	—2.7	0.008256	+5.1
18.55	0.9230	0.008671	0.008530	—1.6	0.009274	+7.0
9.75	0.9427	0.009993	0.009860	—1.3	0.01025	+2.5
7.45	0.9471	0.01027	0.01024	—0.3	0.01052	+2.4
0.00	0.9618	0.01158	....	...	....	...

SERIES B. MIXTURES OF DIETHYL ETHER AND DIPHENYL ETHER.

Mol. % ethyl ether.	Density 25°/4°.	η (expt.).	η (calc.). Log eqn.	Percentage divergence.	η (calc.) Cube rt. eqn.	Percentage divergence.
100.00	0.7139	0.002233	....	..	....	..
90.92	0.7601	0.003106	0.002893	— 6.8	0.003344	+ 7.3
78.26	0.8213	0.004552	0.004150	— 8.8	0.005433	+19.3
70.88	0.8554	0.005733	0.005122	—10.6	0.006978	+21.3
60.76	0.8974	0.007614	0.006835	—10.2	0.009539	+25.3
51.02	0.9311	0.009926	0.009022	— 9.0	0.01253	+26.0
42.45	0.9583	0.01258	0.01152	— 8.4	0.01563	+24.0
32.97	0.9862	0.01631	0.01509	— 7.5	0.01962	+20.2
21.93	1.0181	0.02153	0.02068	— 3.9	0.02505	+16.3
13.18	1.0387	0.02737	0.02654	— 3.0	0.03000	+ 9.6
7.04	1.0542	0.03158	0.03161	+ 0.1	0.03382	+ 7.0
0.00	1.0706	0.03864	....	..	....	..

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[1] Bingham, *J. Ind. Eng. Chem.*, 6, 233 (1914); Bingham, Schlesinger and Coleman, THIS JOURNAL, 38, 27 (1916).

[2] In a few cases the values given are interpolated.

viscosity. The viscosity calculated according to Equation 1 and its percentage divergence from the observed value are presented in the next 2 columns. Similarly the last 2 columns show the viscosity calculated from Equation 2 and its percentage divergence from the experimental results.

SERIES C. MIXTURES OF PHENETOL AND DIPHENYL ETHER.

Mol. % phenetol.	Density 25°/4°.	η (expt.).	η (calc.). Log eqn.	Percentage divergence.	η (calc.). Cube rt. eqn.	Percentage divergence.
100.00	0.9618	0.01158	...	...	...	...
90.06	0.9755	0.01309	0.01305	—0.3	0.01337	+2.1
81.27	0.9870	0.01451	0.01451	0.0	0.01510	+4.1
70.37	0.9993	0.01632	0.01654	+1.4	0.01745	+6.8
60.02	1.0111	0.01862	0.01879	+0.9	0.01990	+6.9
51.05	1.0206	0.02096	0.02088	—0.4	0.02218	+5.8
37.31	1.0346	0.02455	0.02460	+0.2	0.02602	+6.0
32.53	1.0396	0.02630	0.02611	—0.7	0.02748	+4.5
20.72	1.0510	0.03003	0.03012	+0.3	0.03127	+4.1
13.67	1.0573	0.03264	0.03277	+0.4	0.03363	+3.1
0.00	1.0706	0.03864	...	...	...	...

SERIES D. MIXTURES OF ETHYL ACETATE AND ETHYL BENZOATE.

Mol. % ethyl acetate.	Density 25°/4°.	η (expt.).	η (calc.). Log eqn.	Percentage divergence.	η (calc.). Cube rt. eqn.	Percentage. divergence.
100.00	0.8948	0.004239	....	...	....	...
89.92	0.9204	0.005188	0.004960	—4.4	0.005173	—0.3
79.77	0.9440	0.006178	0.005810	—6.0	0.006234	+0.9
69.89	0.9598	0.007247	0.006778	—6.4	0.007419	+2.4
59.98	0.9740	0.008478	0.007909	—6.8	0.008736	+3.1
50.44	0.9866	0.009851	0.009177	—6.8	0.01014	+3.0
39.73	0.9992	0.01157	0.01074	—7.1	0.01190	+2.9
31.31	1.0101	0.01292	0.01236	—4.3	0.01341	+3.7
20.88	1.0223	0.01514	0.01455	—3.9	0.01545	+2.0
12.16	1.0320	0.01704	0.01667	—2.2	0.01731	+1.5
00.00	1.0431	0.02014	....	...	....	...

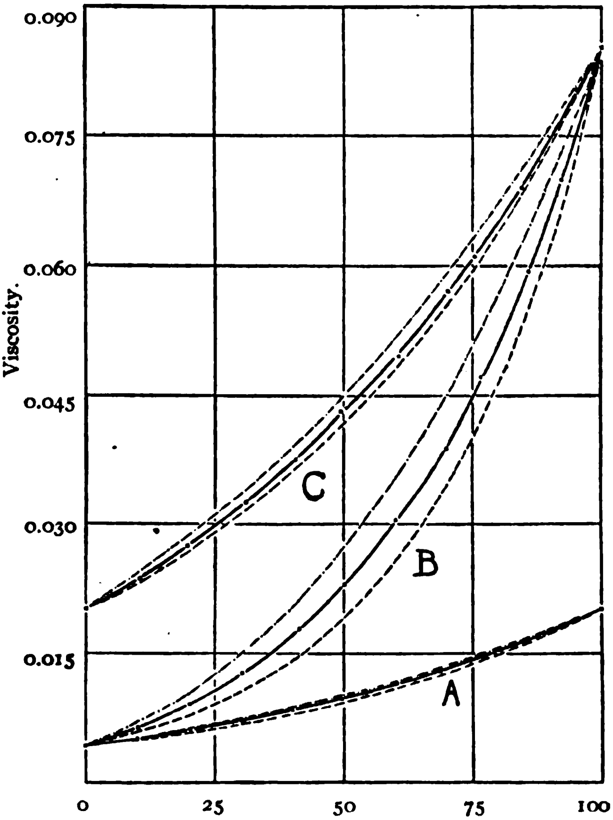
SERIES E. MIXTURES OF ETHYL ACETATE AND BENZYL BENZOATE.

Mol. % ethyl acetate.	Density 25°/4°.	η (expt.).	η (calc.). Log eqn.	Percentage divergence.	η (calc.). Cube rt. eqn.	Percentage divergence.
100.00	0.8948	0.004239	....	..	....	..
89.80	0.9394	0.006406	0.005756	—10.1	0.006876	+ 7.4
79.90	0.9720	0.009116	0.007746	—15.0	0.01032	+13.2
69.73	0.9988	0.01275	0.01051	—17.5	0.01489	+16.5
58.63	1.0247	0.01789	0.01467	—18.0	0.02122	+18.7
50.00	1.0454	0.02299	0.01900	—17.3	0.02724	+19.0
40.01	1.0625	0.03047	0.02570	—15.6	0.03536	+16.0
30.02	1.0778	0.03881	0.03460	—10.9	0.04528	+16.8
23.47	1.0867	0.04711	0.04210	—10.7	0.05258	+11.6
14.26	1.0975	0.05938	0.05520	— 7.0	0.06412	+ 8.0
7.84	1.1048	0.07003	0.06728	— 4.0	0.07307	+ 4.3
0.00	1.1121	0.08514	....	..	....	..

SERIES F. MIXTURES OF ETHYL BENZOATE AND BENZYL BENZOATE.

Mol. % ethyl benzoate.	Density 25°/4°.	η (expt.)	η (calc.). Log eqn.	Percentage divergence.	η (calc.). Cube rt. eqn.	Percentage divergence.
100.00	1.0431	0.02014	...	...	...	...
89.63	1.0524	0.02371	0.02339	—1.4	0.02426	+2.5
80.23	1.0603	0.02749	0.02678	—2.5	0.02845	+3.5
69.06	1.0683	0.03249	0.03146	—3.2	0.03402	+4.7
59.41	1.0760	0.03740	0.03616	—3.3	0.03938	+5.2
50.54	1.0825	0.04309	0.04109	—4.6	0.04478	+3.9
39.45	1.0910	0.04948	0.04821	—2.6	0.05219	+5.4
29.73	1.0967	0.05695	0.05546	—2.6	0.05933	+4.2
24.75	1.1005	0.06108	0.05960	—2.4	0.06323	+3.5
15.49	1.1053	0.06898	0.06825	—1.1	0.07091	+2.8
4.65	1.1104	0.08039	0.07961	—1.0	0.08069	+0.4
0.00	1.1121	0.08514	...	...	...	...

The results for the esters are also reproduced graphically in the diagram. It will be found, by reference to this diagram and to the tables above, that neither the logarithmic nor the cube root formula expresses the experimental results in a satisfactory manner. The experimental curve lies in all cases[1] between the 2 calculated curves, the logarithmic equation



A = ethyl acetate—ethyl benzoate.
B = ethyl acetate—benzyl benzoate.
C = ethyl benzoate—benzyl benzoate.
— x — Experimental.
— — — — Log. eqn.
— . — . — . — Cube root eqn.

[1] In one case (for the system: phenetol-diphenyl ether) the logarithmic formula is practically identical with the observed values, the average divergence being only 0.2%. The ratio between the viscosities of the 2 components, however, is smaller here than for any other system studied; the average divergence for the cube root equation is only 4.8%.

giving values consistently too low, the cube root equation giving values consistently too high. The maximum divergence for the 62 mixtures examined is —18.0% for the logarithmic equation, the average divergence —4.8%. For the cube root equation the maximum divergence is +26.0%, the average divergence +7.9%.

The divergences in each case become greater as the ratio between the viscosities of the 2 components of the mixture is widened. In the system ethyl acetate-benzyl benzoate this ratio is more than 20 to 1, the variation being greater than in any system hitherto studied. The divergences here are much larger than for the 2 remaining ester systems, as will be evident from the diagram.

Neither equation can, therefore, be claimed as the ideal formula. The 2 formulas, however, clearly do furnish us with limits within which this unknown relation may be confidently predicted to lie. All other previously proposed equations (such as fluidity formulas, or equations with weight or volume composition units) give hopelessly discordant values, as in the systems investigated by Kendall and Monroe.

The following brief mathematical analysis of the situation which thus presents itself is instructive. The original linear viscosity equation

$$\eta = x\eta_1 + (1 - x)\eta_2 \qquad (3)$$

is equivalent to the statement $d\eta/dx = k$. As indicated in previous articles[1] and also in the diagram here given, however, the experimental viscosity curve is not linear but considerably "sagged;" in other words $d\eta/dx$ increases as η increases. The fluidity formula of Bingham[2]

$$1/\eta = x/\eta_1 + (1 - x)/\eta_2 \qquad (4)$$

which is equivalent to the statement $d\eta/dx = k\eta^2$, errs in the opposite direction, indicating that $d\eta/dx$ does not increase so rapidly as η^2.

We should, therefore, expect some power of η less than the second to give approximate constancy for $d\eta/dx$. The logarithmic Equation 1 reduces, in point of fact, to the statement $d\eta/dx = k\eta$, while the cube root Equation 2 reduces to $d\eta/dx = k\eta^{4/3}$. The former gives results consistently low, the latter gives results consistently high. It would obviously be a simple matter, therefore, to devise an empirical formula, with an index for η lying between 1 and $^4/_3$, which would represent exceedingly well the experimental data for all of the systems investigated.

Such a procedure, however, would hardly ameliorate the present unsatisfactory status of the problem, for it is difficult to conceive how such a formula could possibly be invested with any theoretical significance. Since all efforts to substantiate a simple ideal equation from the experimental side have failed (all possible simple relations being put, indeed,

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[1] Kendall and Monroe, *loc. cit.*, p. 1788.

[2] Bingham, *Am. Chem. J.*, 34, 481 (1905); *Phys. Rev.*, 35, 407 (1912).

outside the pale of error limits) it would seem inadvisable to continue the attack until considerable progress has been made in neighboring sectors which will open up some weak point at present unsuspected. The conclusions drawn from an earlier article[1] may here be emphasized: "It may be, of course, that the true equation is so exceedingly complex (other factors, such as internal pressure, average molecular volume,[2] etc., entering into consideration) that it can never be arrived at except theoretically. Even in that case, however, the data presented in these articles will prove of immediate service in verifying or disproving any such theoretical equation as soon as propounded."

The difficulties confronting any attack from the theoretical side should not be minimized. First of all, an exact and comprehensive kinetic-molecular theory of liquids must be established.[3] Secondly, the nature of the forces conditioning the flow of molecules past one another in the interior of a liquid must be more intimately understood. An exhaustive physico-mathematical treatment of the forces involved must undoubtedly precede any real advances in this field, the fundamental importance of which is, at present, insufficiently realized both by physicists and by chemists. The valuable results attending recent work on the viscosities of gases[4] ought certainly to encourage similar efforts to advance our knowledge of viscosity in the liquid state[5] beyond its present chaotic condition.

Summary.

The viscosity curves for the following liquid systems have been determined with the use of the Bingham viscometer: (1) ethyl ether-phenetol; (2) ethyl ether-diphenyl ether; (3) phenetol-diphenyl ether; (4) ethyl acetate-ethyl benzoate; (5) ethyl acetate-benzyl benzoate; (6) ethyl benzoate-benzyl benzoate.

Although these mixtures are certainly very nearly ideal, yet the experimental data are not reproducible satisfactorily by means of any known simple formula. The logarithmic viscosity equation of Arrhenius and Kendall gives values uniformly a little low, the cube root viscosity equation of Kendall and Monroe gives values uniformly a little high. All other proposed formulas are altogether out of agreement with the figures of experiment.

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[1] Kendall and Monroe, *loc. cit.*, p. 1801.

[2] Tinker, *Phil. Mag.*, [6] 33, 430 (1917).

[3] A recent monograph by Kleeman ("A Kinetic Theory of Gases and Liquids," John Wiley and Sons, 1920) contains many new and exceedingly interesting suggestions on the physico-mathematical development of viscosity relationships from this standpoint.

[4] See, for example, Rankine, *Phil. Mag.*, 29, 552 (1915); *Proc. Roy. Soc. A.*, 91, 201 (1915), and earlier articles.

[5] A differentiation between viscous flow in liquids and in gases has been attempted by Bingham, This Journal, 36, 1383 (1914).

From a brief mathematical consideration of the results obtained, the conclusion has been drawn that further progress in this field must be preceded by fundamental advances on the theoretical side of the subject. The experimental work has, at present, reached as far as it can go alone in showing that all simple solutions of the problem hitherto proposed are certainly insufficient.

New York, N. Y.

[Contribution from the Denver Food and Drug Inspection Station, Bureau of Chemistry, U. S. Department of Agriculture.]

A COLOR TEST FOR OXALIC ACID.[1]

By Lewis H. Chernoff.

Received May 22, 1920.

Recently Sacher[2] suggested a color test involving the use of a dilute solution of a manganous salt. This is treated with sodium or potassium hydroxide solution and allowed to stand till the manganous hydroxide is partially oxidized by the air. On adding an aqueous solution of oxalic acid, drop by drop, the precipitate dissolves and a red coloration is produced. Reducing substances, also excess of oxalic or any other acid, prevent the color formation.

Dorronsoro and Fernandez[3] have observed a color reaction while working with pinene derived from Spanish oil of turpentine. When pinene was oxidized, a substance, supposed to be nopic acid. was produced which gave a *green* coloration with resorcinol and sulfuric acid. This substance was later identified as oxalic acid.[4]

The writer has confirmed this reaction with oxalic acid and has further developed it for use as a general test for oxalic acid. Under certain conditions described below, a *blue* color is obtained instead of green.

While resorcinol forms colorations with a great number of organic compounds, the colors are mostly red, pink or violet. When nitrates or nitrites are dissolved in conc. sulfuric acid and a crystal of resorcinol is added, a deep blue color is produced. If a little water is added, however, the color becomes brown to red. The writer is unaware of any other compound which gives a *blue* color *under the conditions described below*, although it is quite probable that such compounds exist. Some substances, such as carotin, xanthophyll, some terpenes, etc., give a *blue* color with sulfuric acid alone. It is best, therefore, in many cases to re-

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[1] Published by permission of Secretary of Agriculture, U. S. Department of Agriculture.

[2] Sacher, *C. A.*, 9, 2043 (1915).

[3] Dorronsoro and Fernandez, *Ibid.*, 9, 2522 (1915).

[4] Details of this reaction are not given in the abstract. The original article (*Anales. soc. españ. fis. quim, II*, 441–3 (1913)) was not available.

move the oxalic acid by precipitation as the calcium salt and to apply the test to the precipitate.

No *blue* color was obtained with some of the commoner natural acids, such as formic, acetic, lactic, tartaric, citric, malic, succinic and benzoic acids, neither did these acids interfere with the test for oxalic acid. Although tartaric acid gives a brilliant red color with resorcinol and sulfuric acid, it did not interfere with the *blue* oxalic color (until heated) in a mixture of 10 mg. of oxalic acid, 100 mg. of tartaric acid and 2 cc. of water.

Color Test for Oxalic Acid.—A few crystals of resorcinol are added to about 5 cc. of the unknown solution in a test-tube, and the mixture is warmed slightly to dissolve the resorcinol. It is then cooled and 5 cc. of conc. sulfuric acid is carefully and slowly poured in along the side of the tube so as to form a layer. A blue ring will be formed at the junction of the 2 layers, if oxalic acid is present. The color is best seen if held to the light in front of a sheet of white paper. Care must be taken that the mixture does not warm up appreciably. If the blue color does not appear in a few minutes, the mixture is shaken thoroughly, and, after cooling somewhat, 5 cc. more of sulfuric acid is added. Should the color still fail to appear, the mixed contents of the tube should be gently warmed over a flame (not boiled) when an indigo blue color will diffuse throughout the liquid. If the mixture be cooled with ice-water, the color will disappear only to reappear again on heating. If the mixture be boiled a few minutes, the color will turn a deep dark *green*, which will become a light yellow-green on cooling. If to the cold yellow-green solution an equal volume of sulfuric acid be added so as to form 2 layers, the *blue* color will again appear. It is believed that all these reactions taken together are characteristic of oxalic acid alone.

This test may be made sensitive to one milligram if the dry unknown substance be warmed with 2 drops of a 10% aqueous resorcinol solution and the sulfuric acid added drop by drop. The blue color then appears immediately. For very dilute solutions of oxalic acid or its salts, it is best to evaporate to a concentration of about 10%.

If interfering substances are present the oxalic acid may be precipitated in ammoniacal solution as the calcium salt, washed with water, and the test applied directly to an aqueous suspension of the salt.

DENVER, COLORADO.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, SYRACUSE UNIVERSITY.]

THE PREPARATION AND STUDY OF THE RARER ALKALI BROMATES. CESIUM BROMATE.

BY C. R. MCCROSKY AND HAROLD D. BUELL.

Received June 12, 1920.

Introduction.

The literature affords no reference to the preparation of the bromates of cesium and rubidium. Since it seemed plausible to expect that these salts could exist, as well defined crystalline bodies, it was thought worth while to attempt their preparation, and then to study some of their physical and chemical properties.

The preparation of cesium bromate is taken up in this paper. Later an effort will be made to prepare and study the properties of rubidium bromate.

Preparation of Bromic Acid.

This acid was made by the action of bromine upon silver bromate. Potassium bromate was dissolved in water, and silver nitrate added. The silver bromate precipitated from the warm saturated solution in the form of a fine white powder. This was well washed with water to free it from nitrates of potassium or silver and then treated, in a large amount of water, with liquid bromine as long as the color disappeared. Due to the slight solubility of silver bromate, amounting to 0.158 part in 100 parts of water, and also to the formation of the still more insoluble silver bromide, 0.000026 part in 100 parts of water, the reaction mixture was stirred constantly for 2 days or longer with the addition of bromine from time to time. The bromic acid solution was then decanted from the silver bromide and the excess bromine expelled by bubbling air through the solution.

According to Kammerer[1] the reactions indicated above proceed as follows:

$$KBrO_3 + AgNO_3 = AgBrO_3 + KNO_3$$

$$5AgBrO_3 + 6Br + 3\,H_2O = 5AgBr + 6HBrO_3.$$

One would conclude from Kammerer's work that all of the free bromine could be expelled, leaving pure bromic acid. But in our experience this was found impossible, the solution still being colored with a little bromine after bubbling pure air through it for 24 to 48 hours. It was apparent that there was a slow decomposition of the bromic acid. At any rate, the reaction proceeds slowly, and in expelling the excess bromine, only a small amount of bromic acid was lost.

Preparation of Cesium Hydroxide.

Cesium chloride was treated with an excess of sulfuric acid and the mixture heated until the fumes of sulfur trioxide ceased to come off.

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[1] Gmelin-Kraut, Vol. I, ii, 262 (1870).

The cesium hydrogen sulfate was dissolved in water, and a saturated solution of barium hydroxide added until a drop gave no precipitate of barium sulfate. The clear cesium hydroxide solution was kept in a platinum container.

Preparation of Cesium Bromate.

Cesium hydroxide was neutralized with bromic acid and then an excess of the acid added. The solution was evaporated somewhat and allowed to crystallize. Several yields of crystals were obtained each time the mother liquors were concentrated, and even the last yield of crystals showed no test for a bromide. As the mother liquor became concentrated, the liberation of bromine became quite pronounced, as only a 4.28% solution of bromic acid is stable under ordinary conditions.[1]

Examination of the Product.—The product was recrystallized from water and the resulting crystals were small but well defined. The crystals were dried at different temperatures, and each time the temperature was raised there was a slight loss in weight, without, however, any apparent loss of crystalline structure. Some of the substance was heated in a test-tube, whereupon marked decrepitation occurred, which indicated that water was held between the crystals, and probably accounted for the loss in weight when dried slowly. There was no visible deposit of water on the cold portion of the test-tube, thus indicating the absence of water of crystallization. Further heating caused the substance to melt and then decompose with the evolution of large quantities of oxygen. The residue gave the bromide test.

From the position of cesium in the periodic table the melting point of the bromate ought to be above that of potassium bromate, 434°. No comparison could be made between the chlorate, bromate, and iodate of cesium, as the melting points of the first and last salts mentioned apparently have not been determined. An apparatus for determining a temperature above 360° was not on hand, and only a rough estimation could be obtained. It was found that in melted anhydrous zinc chloride[2] potassium bromate fused several seconds before the cesium bromate.

Analysis of the Substance.—The samples of the salt were ground finely in an agate mortar. They were then dried for about 36 hours at 115° and at the end of that time became constant in weight.

Two methods of analysis were employed, the iodometric and a gravimetric method used by Harkins[3] and by Baxter.[4] The latter is based upon the reducing action of hydrazine hydroxide and the determination of the bromine as silver bromide.

The following set of results (Tables I and II) establish the identity of the

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[1] Gmelin-Kraut, Vol. I, ii, 262 (1870).

[2] McCrosky, This Journal, 40, 2 (1918).

[3] Harkins, *ibid.*, 33, 1810 (1902).

[4] Baxter, *ibid.*, 31, 209 (1900).

salt prepared as cesium bromate. In the first column are given the weights of cesium bromate taken. The second column shows the amounts of cesium bromate obtained by analysis of the weighed samples of Column 1. The third column is the difference between the amount obtained by analysis and the weighed sample.

TABLE I.

Iodometric Method of Analysis.

Samples of $CsBrO_3$ weighed. G.	Amt. $CsBrO_3$ obtained by analysis. G.	Difference. G.
0.1022	0.1023	0.0001
0.1100	0.1103	0.0003
0.1010	0.1012	0.0003
0.0960	0.0961	0.0001
0.1054	0.1064	0.0010
0.0992	0.0982	0.0010
0.1052	0.1047	0.0005
0.1079	0.1077	0.0002
0.1106	0.1107	0.0001

TABLE II.

Precipitation Method of Analysis.

Reduction with Hydrazine Hydroxide.[a]

Samples of $CsBrO_3$ weighed. G.	Amt. $CsBrO_3$ obtained by analysis. G.	Difference. G.
0.2866	0.2871	0.0005
0.0934[a]	0.0934	0.0000
0.1016	0.1013	0.0003

[a] *Ibid.*, 31, 209 (1900). Hydrazine hydroxide was used by Baxter for reducing iodic acid in determining the atomic weight of iodine.

The Solubility of Cesium Bromate.

The solubility of cesium bromate was determined at 30°. The temperature of the bath in the thermostat varied from this only by 0.2° to 0.3° during the determinations. The method employed was essentially that used by Buchanan,[1] About 5 hours was allowed for the salt to come into equilibrium with the solvent, before the saturated solution was withdrawn for analysis. This solution was weighed and then carefully evaporated to dryness until constant in weight.

TABLE III.

Solubility of Cesium Bromate in 100 g. of Water at 30°.

	G.
	4.484
	4.573
	4.525
	4.549
	4.483
	4.577
Average	4.53

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[1] Buchanan, *J. Ind. Eng. Chem.*, 12, 448 (1920)

Summary.

As a result of this investigation the following facts have been established.

The preparation of cesium bromate is probably best carried out in acid solution.

Cesium bromate is a definite crystalline salt with no water of crystallization. Occluded water causes decrepitation.

Its melting point (not as yet determined) is above that of potassium bromate. After melting, it soon decomposes, giving a large amount of oxygen, and leaves a bromide.

The solubility of cesium bromate is 4.53 g. in 100 g. of water at 30°.

SYRACUSE, NEW YORK.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRINCETON UNIVERSITY.]

THE ELECTRO-ANALYTICAL SEPARATION OF NICKEL (COBALT) FROM ARSENIC.

BY N. HOWELL FURMAN.

Received June 24, 1920.

Introduction.

This investigation was undertaken at the suggestion of Dr. L. W. McCay, who first demonstrated the possibility of separating copper from quinquivalent arsenic in ammoniacal solution by means of the electric current.[1] A number of years ago he attempted the simultaneous separation of nickel and cobalt from arsenic by a similar method, but found that the results were always high, owing to the presence of arsenic in the deposits. The materials which he used in these investigations were specimens of smaltite and safflorite (arsenides of cobalt) which contained nickel.

The author has studied the action of the electric current upon ammoniacal solutions containing alkali arsenates and nickel alone, and finds that the nickel deposits are free from arsenic. On the other hand, when cobalt is deposited from an ammoniacal solution containing arsenates the deposit invariably contains arsenic in amounts ranging from 6.0–12.0 mg. per 0.1 g. of cobalt. If the 2 metals are deposited simultaneously they may or may not contain arsenic, for its presence depends upon the relative amounts of nickel and cobalt, and upon the absolute value of the concentration of the cobalt. For example, with a total volume of 100 cc. and a cathode surface of 55 $\overline{\text{cm}}^2$., the deposits were found to be free from arsenic when the relative amounts of the metals were 2.5 or more parts of nickel to one part of cobalt by weight, and the total weight of the mixed metals deposited was 0.1 g. When the 2 metals were present in a 1 : 1 ratio, from 0.5 to 1.0 mg. of arsenic was found in a 0.1 g. deposit of the mixed metals. If the concentration of the cobalt is increased, while the

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[1] McCay, *Chem. Ztg.*, 14, 509 (1890).

cathode surface is kept constant, it becomes increasingly more difficult to prevent the deposition of arsenic with the cobalt-nickel alloy. The separation described in this paper, therefore, finds practical application in the analysis of arsenical nickel ores in which cobalt *may be present*, but only in *small amounts*.

A detailed study of the electrolysis of ammoniacal solutions containing cobalt and alkali arsenates is in progress, and the results will be presented in a subsequent communication. Heretofore the electrolysis of alkaline solutions containing arsenates has not exhibited a reducing action upon the arsenic acid; upon this fact Covelli[1] has based a sensitive method for the detection of arsenious in the presence of arsenic compounds.

A search of the literature revealed the fact that the possibility of separating nickel from arsenic by the electrolysis of ammoniacal solutions containing the 2 elements was mentioned briefly in an early contribution from the Mannsfeld'schen Ober-Berg und Hütten-Direktion in Eisleben.[2] No experimental results were published, nor was the influence of cobalt upon the separation mentioned. Later observers either misinterpret or ignore this work. Thus Schweder[3] states, "The presence of *small* amounts of arsenic is not harmful in the electrolytic precipitation of nickel, according to experiments made in the Mannsfeld'schen Ober-Berg und Hütten-Direktion in Eisleben." Numerous later communications consulted all advise the removal of the arsenic by hydrogen sulfide before the deposition of the nickel.[4]

Experimental Part.

Solutions of nickel sulfate were prepared as needed by weighing out suitable quantities of hydrated nickel sulfate. The iron present was removed by repeated precipitations with ammonium hydroxide, and the resulting solution was diluted to a convenient volume. The solutions were standardized by precipitating the nickel in 25 cc. portions from ammoniacal solution by means of the electric current.[5] The material used

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[1] Covelli, *Chem. Ztg.*, 33, 1209 (1909).

[2] *Z. anal. Chem.*, 11, 14 (1872). "Attempts to obtain the nickel content of niccolite (Kupfer-Nickel) gave very satisfactory results. They prove that the separation of the arsenic need not precede the electrolytic estimation of the nickel, for one obtains the same results as if the arsenic had been previously removed. When the nickel deposited on the platinum, in the former case, is brought into the Marsh apparatus scarcely a trace of arsenic can be found."

[3] Schweder, *ibid.*, 16, 344 (1877).

[4] The extended list of references in "Electro-Analysis" by E. F. Smith, 1912 Ed., p. 126, many additional references cited in "Die Bestimmungsmethoden des Nickels und Kobalts," by H. Grossmann, as well as other communications listed in *Chemical Abstracts*, Vols. 1–12, were consulted.

[5] The details given in Smith's Electro-Analysis, p. 127 were followed closely. Stationary electrodes were used, the cathode being a platinum cone in the analysis of solution No. 1, and a Winckler platinum gauze in the case of solution No. 2.

was examined qualitatively and found to contain only a trace of cobalt.

NICKEL FOUND PER 25 CC. OF SOLUTION.

	G.	G.	G.	Average.
Solution No. 1	0.1029	0.1026	0.1027	0.1027
Solution No. 2	0.1782	0.1784	0.1783	0.1783

Test Separations.—In making test separations, aliquot portions of a standardized nickel sulfate solution were placed in a suitable vessel. Known amounts of arsenic were introduced, either by weighing out portions of previously analyzed di-hydrogen potassium arsenate (KH_2AsO_4), or by pipetting out aliquot portions of a solution of this salt.

Each solution electrolyzed contained 2 g. of ammonium sulfate and 15 cc. of ammonium hydroxide (sp. gr. 0.90) in a total volume of 100 to 125 cc. The current was allowed to act overnight (10 to 12 hours). The nickel was deposited upon a platinum cone, gauze or dish. The results of these separations are summarized in Table I.

TABLE I.

	Arsenic taken. G.	Nickel taken. G.	Current N. D$_{100}$. Amp.	Voltage.	Nickel found. G.	Difference. G.
1	0.0892	0.1027	0.46	3.3	0.1022	—0.0005
2	0.0849	0.1027	0.46	3.3	0.1028	+0.0001
3	0.0846	0.1027	0.55	4.2	0.1030	+0.0003
4	0.0899	0.1027	0.40	3.8	0.1030	+0.0003
5	0.1214	0.1027	0.55	3.5	0.1031	+0.0004
6	0.1072	0.2054	0.61	3.8	0.2055	+0.0001

After the nickel had been deposited and weighed the deposits were dissolved in nitric acid. The solutions of deposits 1 to 3 were combined, also those of deposits 4 to 6. The 2 resulting solutions were evaporated to dryness, the residues were taken up in as little nitric acid as possible, made ammoniacal and treated with magnesia mixture. After the solutions had been well shaken they were allowed to stand for some time but no crystals of magnesium ammonium arsenate were deposited. In both cases the introduction of 2 cc. of a standard arsenate solution (= 0.1 mg. of arsenic) gave an unmistakable precipitate of magnesium ammonium arsenate which could be converted into brown silver arsenate.

The Separation and Estimation of Both Nickel and Arsenic.

It is possible to estimate the amount of arsenic after the removal of the nickel, as the results in Table II will serve to show. The mode of procedure and conditions during electrolysis were similar to those described in the preceding section. After the removal of the nickel the arsenic was weighed in the form of magnesium pyroarsenate,[1] or as arsenic pentasulfide.[2]

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[1] Levol's method was used. Treadwell-Hall, "Quantitative Analysis," 1914. pp. 206–208,

[2] Method devised by L. W. McCay, *Am. Chem. J.*, 9, 174 (1887).

TABLE II.

	Nickel taken. G.	Nickel found. G.	Difference. G.	Arsenic taken. G.	Arsenic found. G.	Difference. G.
1.........	0.1783	0.1785	+0.0002	0.1623	0.1614[1]	—0.0009
2.........	0.1783	0.1784	+0.0001	0.4060	0.4071[1]	+0.0011
3.........	0.3566	0.3562	—0.0004	0.2403	0.2412[2]	+0.0009

Rapid Determination of the Nickel.—Nickel may be rapidly separated from arsenic by using the well-established methods involving rotating electrodes and high current densities. Solutions similar to those employed in the 2 preceding sections were used. Results of typical determinations are to be found in Table III. The cathode in this series of experiments was a platinum dish of 125 cc. capacity. The speed of anode rotation was from 600 to 800 per minute.

TABLE III.

	Nickel taken. G.	Nickel found. G.	Difference. G.	Arsenic taken. G.	Current $N. D_{100}$. Amp.	Voltage	Time for complete deposition. Min.
1..........	0.1783	0.1783	0.0000	0.4060	1.25	3.6	75
2..........	0.1783	0.1779	—0.0004	0.8120	1.25	3.8	60
3..........	0.3566	0.3564	—0.0002	0.4060	1.50	4.2	60
4..........	0.1783	0.1787	+0.0004	0.4060	3.75	8.6	25

Each deposit was tested in the manner previously described and was found to be free from arsenic.

Practical Test of the Method.—As a further test of the method a sample of niccolite (arsenide of nickel) was examined. The samples of the mineral were brought into solution by treatment with appropriate amounts of conc. nitric, hydrochloric, and sulfuric acids. After the excess of nitric and hydrochloric acids had been volatilized the small quantity of iron present was precipitated by the addition of ammonium hydroxide. The precipitate was freed from nickel by repeated precipitations with ammonia, after the ferric hydroxide had been dissolved in hot dil. sulfuric acid. The resulting ammoniacal solution of nickel was then electrolyzed, with the conditions as nearly as possible those described under "Test Separations." The mineral examined contained only a very small amount of cobalt. The per cent. of metal found by the electrolytic method was (1) 38.12, (2) 38.08, (3) 37.88. Previous examination of the material by Mr. F. K. Dimon, a former honors student, who used the excellent volumetric method of Moore,[1] had yielded (1) 38.10, (2) 37.74, (3) 37.97% of metal.

It is, of course, evident that copper, if present in such a mineral, will be deposited along with the nickel and cobalt. The amount of the copper may be readily determined by electrolyzing the nitric acid solution of the deposit.

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[1] Moore, *Chem. News*, 59, 160 (1889); 72, 92 (1895).

Summary.

Experimental results have been communicated which prove that nickel may be quantitatively separated from salts of arsenic acid in ammoniacal solution by means of the electric current.

The striking and radical difference between the behavior of cobalt and nickel when deposited from such solutions has been pointed out. This interesting property of cobalt is being made the subject of further study in order to determine why arsenic is always deposited with cobalt and not with nickel.

In conclusion the writer wishes to thank Dr. L. W. McCay for very valuable advice and suggestions during the progress of this work.

PRINCETON, N. J.

[CONTRIBUTION OF THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY.]

A STUDY OF THE VAPOR PRESSURE OF AQUEOUS SOLUTIONS OF MANNITE.[1]

BY J. C. W. FRAZER, B. F. LOVELACE AND T. H. ROGERS.

Received July 6, 1920.

Introduction.

The vapor pressure method offers certain advantages for the investigation of the colligative properties of solutions, and, though many efforts have been made to apply it to the study of aqueous solutions, the results have not been entirely successful. The fundamental importance of the knowledge of the vapor pressure of solutions is shown by its frequent use in thermodynamic formulas. In practice 2 methods, known as the dynamic and static methods, have been used. The first depends on the determination of the amount of the solvent required to saturate the same volume of air when in equilibrium with the solvent and solution, respectively, both maintained at the same constant temperature. This method has been used by Ostwald; the Earl of Berkeley[2] and his associates have investigated the various sources of error involved in this method and have made many improvements in the apparatus and details of manipulation. The recent work of Washburn[3] has been essentially an application of the apparatus of Berkeley.

Some time ago Frazer and Lovelace,[4] in spite of the failure of earlier workers, described an apparatus and manipulation by which accurate measurements of vapor pressure of aqueous solution by the static method could be made. Many of the errors which had previously been encoun-

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[1] The experimental part of this article forms the basis of a dissertation submitted by T. H. Rogers to the Johns Hopkins University.

[2] *Proc. Roy. Soc. A.*, 17, 156 (1906).

[3] Washburn, THIS JOURNAL, 37, 309 (1915).

[4] Frazer and Lovelace, *ibid.*, 36, 2439 (1914); *Z. physik. Chem.*, 89, 155 (1914).

tered in attempting to apply this method were eliminated by making it differential, comparing directly, by means of the Rayleigh manometer, the vapor pressures above the solution and the pure solvent when both were maintained in the same accurately regulated thermostat.

After preliminary work certain improvements were made in the temperature regulation and the method of stirring, and the method was applied to the study of aqueous solutions of mannite. After the elimination of certain other slight sources of error the method was extended to aqueous solutions of potassium chloride.[1]

The present paper is a repetition of the study of mannite solutions in the course of which an additional slight source of error was discovered and eliminated. The work on potassium chloride solutions was also repeated, the results of which will be the subject of a future communication.

Experimental.

Series I.—The apparatus used for this work was that described in the work on potassium chloride solutions.[2] The mannite used was carefully purified and the same sample used throughout. The experimental details were carried out in this series in practically the same manner as in the previous work. The solutions were subjected to a preliminary removal of air by repeatedly exhausting the space above the solution contained in a specially constructed flask as there described, and were further freed from air after they were introduced into the bath. Often the vapor was allowed to expand into an evacuated bulb as many as 25 times before the solution was sufficiently air-free to take observations. The test for air was made by measuring with the McLeod gage the residual pressure after the liter bulb, which contained the vapor from the solution, had been opened to the flask containing phosphorus pentoxide.

To insure equilibrium between liquid and vapor phase before testing, the solution was left open to the vapor bulb for 24 hours with intermittent stirring of the solution. When the test was made, it was observed that while practically all the vapor seemed to be absorbed in perhaps a half hour, a further slow absorption took place for a number of hours. At the end of about 12 hours the reading on the gage became constant and, if the pressure indicated was 0.0005 mm. or less, the test was considered satisfactory and the air present deemed negligible. While this behavior, especially the slowness of the absorption, occasioned surprise, its significance was entirely overlooked during this series.

Observations.—A careful study was made of the proper conditions for taking observations. In the light of the previous work it was obvious that an essential condition is that the temperature of the room should be

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[1] Lovelace, Frazer and Miller, THIS JOURNAL, 38, 515 (1916).

[2] *Loc. cit.*

fairly constant. As the work progressed, however, it was found unnecessary to provide for any special regulation of the temperature of the room, though it is necessary, of course, to prevent any sudden change. Under these conditions evaporation and condensation at the surface of the solvent and solutions are sufficiently rapid to prevent any disturbance in the pressure of the system caused by the slow fluctuations of the room temperature.

After removal from the bath the solutions were analyzed both by the use of the interferometer and by evaporating a weighed portion to dryness and heating the residue to constant weight at 130°. The results of the 2 methods accorded well.

Table I gives in brief the results of this (preliminary) investigation of the lowerings of mannite solutions of 10 different concentrations. Column 1 gives the concentrations expressed in mols (O = 16) of solute per 1000 g. of solvent. Column 3 gives the lowerings produced in mm. of mercury at the prevailing room temperature. For the sake of comparison, Column 2 gives the lowerings found by Mullikin[1] expressed similarly. His data have been extrapolated over a slight range in order to get values corresponding to the concentrations in Column 1.

Column 4 shows the theoretical lowerings of these solutions as calculated from Raoult's law, and under the same conditions as the values in Columns 2 and 3. Column 5 gives the deviations from Raoult's law of the values found in this series.

Table I.

Comparison of the Values Obtained for the Lowering of Mannite Solutions.

M.	Mullikin.	Series I.	Calculated.	Difference.	Series II.
0.0995	0.0287	0.0280	0.0314	0.0034	0.0311
0.1993	0.0587	0.0585	0.0627	0.0042	0.0620
0.2985	0.0906	0.0882	0.0939	0.0057	0.0930
0.3984	0.1188	0.1221	0.1251	0.0030	0.1239
0.4986	0.1538	0.1533	0.1563	0.0030	0.1553
0.5968	..	0.1819	0.1867	0.0048	0.1869
0.6960	..	0.2127	0.2175	0.0048	0.2173
0.7958	..	0.2471	0.2489	0.0018	0.2491
0.8944	..	0.2740	0.2784	0.0044	0.2802
0.9941	..	0.3061	0.3088	0.0027	0.3108

Column 6 gives the values found in Series II (*vide infra*) extrapolated and expressed similarly.

The agreement of the results in Series I with those of Mullikin is fair, though in several cases there is greater deviation than the 0.001 mm. claimed as the accuracy of the method. However, the nearly constant deviation from Raoult's law was suspicious, especially in the concentrations where the best agreement would be expected. In order to make

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[1] R. Mullikin, *Dissertation*, Johns Hopkins Univ., 1916.

certain that the solutions measured were free from air another method of preliminary removal of air was devised. This will be described when the discussion of the results of Series II is taken up. It was found that solutions so prepared gave a lowering from 0.003 to 0.005 mm. greater than those recorded in Series I. Further, when tests for air were made on the solutions of Series II, the readings on the McLeod gage showed negligible air pressure after 20 minutes absorption by the phosphorus pentoxide. This difference in behavior was obviously due to the fact that the solutions of Series I were measured with an air pressure of 0.003–0.005 mm. The gage readings on air tests should have been made after the same length of time, 20 minutes, whereupon the air present would have been discovered. If the pentoxide is kept open for a longer time, adsorption of the residual air takes place slowly, both by the pentoxide and the glass surfaces[1] of the system. The agreement between Mullikin's results and those of Series I is better than might be expected since the solutions in Series I were measured with an air pressure of about 0.004 mm. But this residual amount of air pressure was practically the same in each case since the same methods of preparation of solutions were used and the same criterion adopted for testing the presence of air, the result being that nearly the same amount of air was left in practically every case.

Series II. Preparation of the Solutions.—In order that the solutions might be made up to a definite concentration it seemed best to have both solvent and solute free from air and mix the two in a vacuum. After several trials a method was found which accomplished this in a satisfactory manner.

The water is introduced into a 500-cc. flask A, Fig. 1, to which is sealed a length of 7 mm. glass tubing. A constriction *a* is drawn near the end of the tube and a short piece of rubber tubing fitted on the end. After boiling the water vigorously for 30–35 minutes, the rubber tube is suddenly pinched shut, at the same time removing the burner. The tube is then quickly sealed off at the constriction. The flask having been previously weighed, by weighing the sealed flask and tip the amount of water contained is determined.

A short length of tubing is sealed to the neck of a 300-cc. flask and another into the bottom, as shown in B, Figs. 1 and 2. An amount of solute corresponding to the weight of water prepared is introduced in the flask. After making a file mark on the tip, the tube of the flask containing the water is joined to one end of the flask B by means of a stout rubber tube, as shown in Fig 2, and the other end is connected to a vacuum pump. The solute is thus freed from air after several hours pumping. Finally the tube connecting to the pump is sealed off at *b* and the solute

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[1] Menzies, This Journal, 42, 978 (1920).

and solvent mixed by breaking the tip of the flask A inside the connecting rubber tube. After solution is effected, the rubber tube is pinched shut, the flask A removed and a specially constructed pipet, *p*, Fig. 3, put in its place. A file scratch is made on the other end of the flask now free and connection made to a mercury reservoir as shown. To introduce

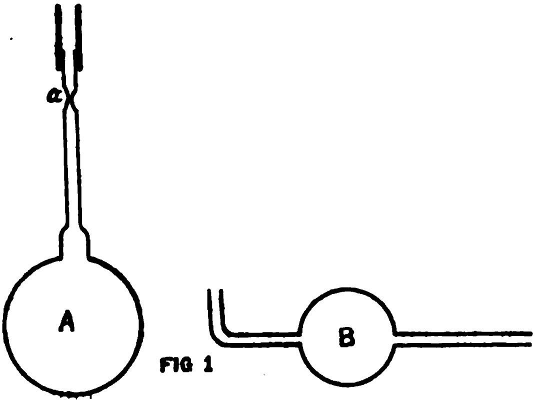

FIG 1

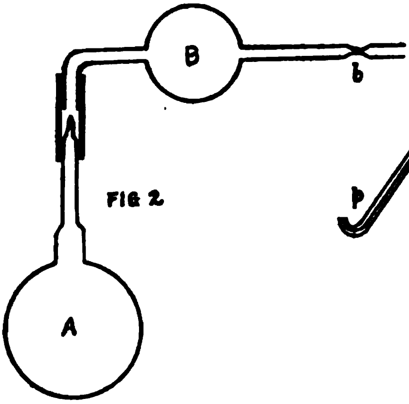

FIG 2

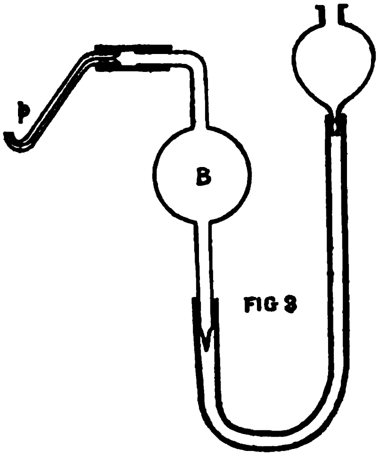

FIG 3

the solution this tip is broken under the mercury and the end of the pipet placed under the bottom of the tube which, dipping in mercury, leads up into the temperature bath.[1] Under pressure from the reservoir the solution flows out of the flask and bubbles up through the mercury to the reservoir in the bath.

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[1] See Fig. 1, This Journal, 38, 517 (1916).

Solutions prepared and introduced in this manner require only a few vapor expansions in the bath in order to remove the air completely. The use of rubber tubing for a connection in the apparatus cannot be conveniently avoided and no trouble from leakage was experienced after a good grade of antimony rubber tubing had been selected and care taken to wire the end. Absolutely complete removal of air in the preparation of a solution was not attempted, as there is always some air taken up in introducing, due to the slight amount of air trapped by the mercury column on the walls of the tubes leading up into the bath. The flask in which the water was boiled was steamed out thoroughly before using. After this a sample of water which had been boiled in the flask for 35 minutes was compared in the interferometer with a sample of conductivity water. The difference in density was found to be very slight and certainly not enough impurities were present to effect a lowering of the vapor pressure. In this work either conductivity water or distilled water, which compared favorably in the interferometer with conductivity water, was used throughout.

Observations.—The readings were taken under conditions as described in Series I. Frequently observations were attempted before the solutions were air-free, as in this way the rate of the removal of air could be followed. Hence these preliminary readings were not reliable and no results are recorded here unless the solutions had been shown to have less than 0.0004 mm. residual air pressure. The exact reading of the McLeod gage is unsatisfactory at this slight pressure, but it is safe to say that the maximum air pressure of a solution considered air-free was as small as this amount, while generally it was much less. At the time of making readings the residual air was certainly less, for the solution and solvent were subjected to a fresh vapor expansion just before observations were made.

Constant readings can be obtained within 15 minutes after opening a solution to an evacuated bulb. If appreciable air were present in the solution the deflection would not be constant, due to air coming out of the solution gradually. This phenomenon was actually observed in many preliminary observations on solutions known to contain air, when the readings would gradually drop. When the solution is once freed from air no trouble is experienced in getting a series of concordant measurements.

The observations were continued until at least 5 consecutive concordant sets were obtained. In these final measurements as recorded here no values have been discarded unless the data were unreliable for obvious reasons, such as the loss of the zero point, or a change in bath temperature. A few non-concordant values are bracketed. Some readings were taken while the solutions were being stirred at a variable speed and the deflections were found to be independent of the rate of stirring, so that practically all of the observations were made with constant speed stirring. The arrangement mentioned was such that the rate of stirring was changed over a wide range several times each minute, thus effectually preventing surface concentration.

The zero point of the measurement is given by the setting of the manometer when the limbs of this instrument are open to one another. This reading was always taken before and after each reading of the deflection. Sometimes due to the slight unsteadiness of the telescope mounting, the zero value was not checked. In such cases the deflection was taken again. If the 2 values checked, these 2 deflections together with the included zero point, were used to compute the lowering.

To calculate the lowering, the scale deflection, s, the distance between the points of the manometer, d, and the distance from the mirror on the manometer to the scale D, must be known. The lowering, h, is given by the expression[1] $h = d/2D\ s$ or, $h = ks$. This involves the assumption that $\sin \theta = {}^1/_2 \tan 2\theta$, where θ is the angle of tilt of the manometer. This assumption is found not to introduce an appreciable error in the case of the most concentrated solution investigated here. The value of d for the manometer was redetermined and the length, D, was frequently checked. The value of h thus calculated is the height of a column of mercury at room temperature, about 24°. This is corrected to the height of a column of mercury at 0°, which is the lowering $p_0 - p_1$.

Analysis.—After taking due precaution to keep the solution as near as possible to the original concentration in removing it from the bath, the exact concentration was determined. The Rayleigh-Zeiss interferometer served admirably for this purpose. With a 20 mm. cell a solution can be compared with a standard with as great an accuracy as that with which the standard can be prepared. By making a rough analysis and then preparing a standard of very nearly the concentration of the solution being analyzed the interferometer serves practically as a zero instrument. Often as a check the weighed portion of a solution was evaporated to dryness and the residue dried to a constant weight at 130°. These results accorded well with those from the interferometer method. No trouble was experienced in getting a constant weight of the mannite residue, a difficulty mentioned by Flügel.[2] The molar concentration was thus easily determined with an accuracy of 2×10^{-4} weight molar, which corresponds to a vapor pressure lowering of less than 0.0001 mm. The concentration was always expressed in terms of mols of mannite per 1000 g. of water, the weights being reduced to the vacuum standard, and 182.12 employed as the molecular weight of mannite.

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[1] THIS JOURNAL, 36, 2440 (1914).

[2] Flügel, *Z. physik. Chem.*, 79, 577 (1912).

Results.

0.09845 *M* Mannite.

Date.	Zero.	Reading.	Zero.	Deflection (mean).
11/8/16	1.1	7.2	..	..
	1.0	7.0	..	..
	0.95	7.1	0.95	..
	..	..	1.0	6.10
11/9/16	1.0	7.1	..	..
	1.05	7.05	1.05	..
	..	7.1	1.1	6.01
11/9/16	1.9	..	..	..
	1.8	7.9	1.9	..
	1.75	7.9	1.8	..
	1.8	7.95	1.7	6.11
11/10/16	0.95	7.0	..	..
	1.0	7.0	1.0	..
	..	7.0	0.95	6.02
11/11/16	2.0	8.1	..	..
	2.0	8.15	..	..
	..	8.0	2.05	..
	..	8.1	2.05	6.08
11/11/16	2.8	8.9	..	..
	2.8	8.95	2.8	..
	2.9	8.85	2.9	6.06

Average deflection.................................. 6.06 mm.

Lowering (corr. to Hg at 0°)........ = 0.0307 mm.

Maximum deviation............... = 0.0005 mm.

k = 0.005080

0.4938 *M* Mannite.

Date.	Zero.	Reading.	Zero.	Reading.	Deflection (mean).
12/1/16	290.05	320.1	..	..	...
	290.0	320.1	289.95	320.1	...
	290.05	320.05	289.95	320.15	30.15
12/2/16	..	320.7	290.45	320.6	...
	..	320.7	290.5	320.75	...
	..	320.7	290.5	320.75	30.22
12/2/16	290.8	321.0	..	..	...
	290.8	321.0	290.8	..	...
	..	321.0	290.85	..	30.19
12/2/16	290.4	320.55	..	..	...
	290.4	320.55	290.4	..	...
	..	320.5	290.4	..	30.13
12/3/16	290.0	320.35	..	..	...
	290.05	320.3	..	..	...
	..	320.3	290.0	..	30.31

Average deflection.................................. 30.20 mm.

Lowering (corr.)................. = 0.1542 mm.

Maximum deviation............. = 0.0007 mm.

k = 0.005109

0.9908 *M* Mannite.

Date.	Zero.	Reading.	Zero.	Deflection (mean)
11/17/16	2.95	63.9	..	...
	2.95	63.9	..	...
	..	63.85	2.9	60.95
11/18/16	2.1	63.05	..	...
	..	63.05	..	...
	..	63.05	2.1	60.95
11/19/16	1.15	62.1	..	...
	1.05	62.05	1.05	...
	..	62.05	1.05	60.99
11/20/16	2.95	64.0	2.9	...
	..	64.0	3.0	...
	..	64.0	3.0	61.04
11/20/16	2.65	63.7	..	...
	..	63.7	2.7	...
	..	63.6	2.65	60.99

Average deflection.................................. 60.98 **mm.**

Scale corrected.................................. 61.20 **mm.**

Lowering (corr.)............. = 0.3109 **mm.**

Maximum deviation......... = 0.0004 **mm.**

$k = 0.005080$

TABLE II.

Summary of Data.

G = g. of mannite per 1000 g. of water (*in vacuo*).

M = concentration in moles per 1000 g. of solvent.

s = scale deflection in mm.

p_0-p_1 = vapor pressure lowering in mm. mercury (mercury corr. to 0°).

$K = d/2D$

Calc. = lowering calculated according to Raoult's law.

Diff. = difference between calculated and observed lowerings.

G.	*M.*	*s.*	$p_0 - p_1$.	$k \times 10^{-6}$.	Calc.	Diff.	Mol. fract. $\times 10^{-4}$.	$\frac{p_0 - p_1}{n/N+n} = p_0$.	$\frac{p_0 - p_1}{M}$.	O. P.
17.930	0.0984	6.06	0.0307	5080	0.0311	0.0004	17.70	17.31	0.3113	2.343
36.004	0.1977	12.15	0.0614	5080	0.0622	0.0008	35.48	17.32	0.3108	4.703
53.951	0.2962	18.23	0.0922	5080	0.0931	0.0009	53.09	17.37	0.3133	7.040
71.917	0.3945	24.26	0.1227	5080	0.1239	0.0012	70.64	17.37	0.3107	9.392
89.938	0.4938	30.20	0.1536	5109	0.1547	0.0011	88.18	17.42	0.3111	11.78
108.243	0.5944	36.56	0.1860	5109	0.1858	—0.0002	105.9	17.55	0.3129	14.27
108.498	0.5958	36.63	0.1863	5109	0.1862	—0.0001	106.2	17.55	0.3128	...
126.283	0.6934	42.50	0.2162	5109	0.2164	—0.0002	123.4	17.56	0.3118	16.61
144.357	0.7927	48.71	0.2478	5109	0.2469	—0.0009	140.8	17.60	0.3126	19.07
162.332	0.8913	54.86	0.2791	5109	0.2772	—0.0019	158.0	17.66	0.3131	21.50
162.485	0.8922	55.20	0.2792	5080	0.2775	—0.0017	158.2	17.65	0.3129	...
180.451	0.9908	61.20	0.3096	5080	0.3076	—0.0020	175.4	17.65	0.3124	23.88

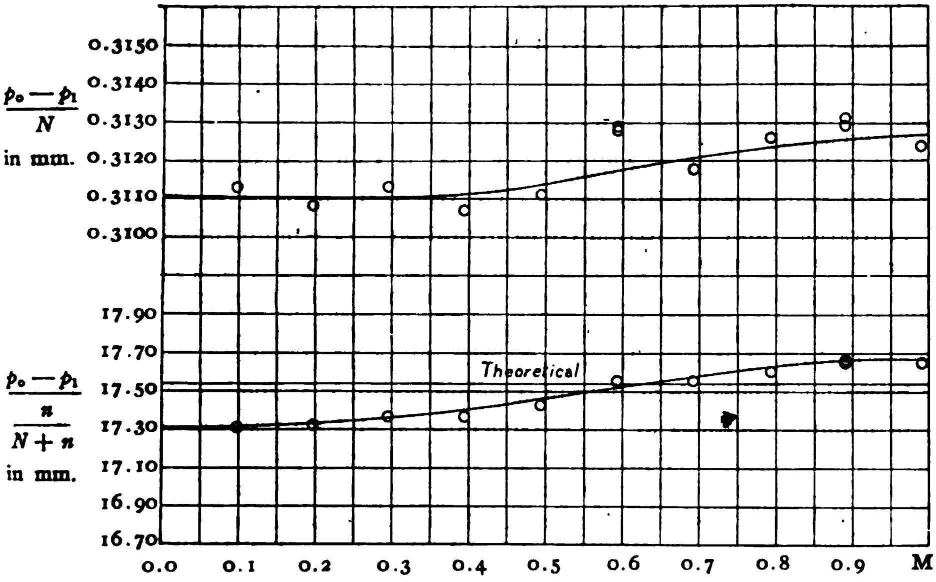
Above, the complete data for 0.1, 0.5 and 1.0 molar concentrations are given. A table summarizing all the results for the 12 concentrations studied is shown; the detail data for 9 solutions are omitted for the sake of brevity.

Discussion of Results.

Accuracy of the Method.—Significant errors arising from a variation in the temperature are hardly possible, as no variation could be detected by a sensitive Beckmann thermometer for days at a time. The chance errors of observation are very small as will be seen by a consideration of probabilities. Three readings at least were always made of the zero point and of each deflection. The average error of the zero-point setting was about 0.03 mm. and that of the deflection reading 0.04 mm. scale deflection. This gives an average error of each measurement of $\sqrt{(0.03)^2 + (0.04)^2} = 0.05$ mm., or for 5 observations, 0.01 mm. scale deflection. The probability that a given series of observations will be within this range is about $^4/_7$. In other words, under the conditions of the work, 4 times out of 7, the error of the observation of the lowering will be within 0.01 mm. scale deflection, corresponding to 0.00005 mm. actual lowering. However, this does not represent at all the accuracy of the method, for there may be certain constant errors whose relative values are additive in calculating the final error. 1. There may be a slight amount of air present. 2. There is a possibility that the surface concentration of the solution is not entirely overcome by stirring the solution during the reading. Altogether it is evident that the method is limited in its accuracy by these factors and not by errors of observation; *viz.*, (*a*) measuring the deflection and (*b*) analyzing the solution. The 2 separate determinations at 0.6 and at 0.9 *M* with the greater variation in the latter case of only 0.0002 mm. serve as a striking confirmation. It is believed that the values in Table II are correct within 0.0006 mm.

Raoult's Law.—Table II shows a summary of the results and gives the deviation from Raoult's law, the validity of which has been supported from theoretical considerations by van Laar, G. N. Lewis and others. In calculating the theoretical lowering the equation $\frac{p_0 - p_1}{p_0} = \frac{n}{N + n}$ was used, where p_0 is the vapor pressure of the pure solvent at the same temperature, p_1 the vapor pressure of the solution, n the number of moles of solute, and N the number of moles of solvent. p_0 has been accurately determined by Holborn and Henning and by Scheel and Heuse, who give the value 17.539 mm. The agreement of lowerings thus calculated with experimental values is much closer than when the old form of Raoult's law is used, $\frac{p_0 - p_1}{p_0} = \frac{n}{N}$. It will be seen from Col. 1, Table II that the observed values are increasingly smaller than those calculated until a maximum positive deviation is reached at about 0.4 *M*. At about 0.6 *M* the calculated and observed values are the same, and it is not until a higher concentration is reached that there is a marked negative deviation from Raoult's law. However, although the deviation in the range 0.1 to 0.8 M is never much greater than the 0.0006 mm. claimed as the accuracy of the method, it must be emphasized that the results are relatively accurate enough to allow us to draw some conclusions from these deviations.

In order to facilitate comparison and to magnify the deviations the value of the lowering may be divided by the concentration. Hence it is often the custom to examine vapor pressure results in the light of the molecular lowering value, $(p_0 - p_1)/M$, and for that reason this value has been plotted against concentration in Fig. 4 (upper curve). However, this function has no theoretical significance, as will be seen; since



Conc. in Mols. per. 1000 g. of water.

Fig. 4.—Upper Curve—Molecular lowering of Mannite solutions at 20° C. Lower Curve—The ratio of the vapor pressure lowering to the Molar Fraction.

$$p_0 - p_1 = p_0 \frac{n}{N + n}$$

the molecular lowering,

$$\frac{p_0 - p_1}{n} = \frac{p_0}{n + N}.$$

The function, $p_0/N + n$, is a decreasing one, with respect to n. It seems that it is often thought that molecular lowerings should be constant, but for an ideal solution the molecular lowering curve is concave downward, only slightly, however, in dilute solutions. Thus it is evident that conclusions drawn from the molecular lowering curve may be misleading.

It is more logical to calculate the value of the lowering divided by the mol fraction, which, according to Raoult's law, is a constant, *viz.*, the vapor pressure of water at the temperature in question.

$$\frac{p_0 - p_1}{\frac{n}{N + n}} = p_0.$$

This function has a real meaning. The value of this function is plotted against concentration in Fig. 4 (lower curve). An examination of the curve gives one a clear and accurate idea of the behavior of mannite solutions. The smoothness of the curve in the dilute region, where a difference of 0.001 mm. would bring a value quite out of line, indicates the normal character of aqueous mannite solutions up to 0.5 *M*, above which slight irregularities begin. The rise in the curve in the higher concentrations may be attributed to hydration. It is unfortunate that we are limited in further investigation by the solubility of this substance.

Von Babo's Law and the Heat of Dilution.—The temperature coefficient of the vapor pressure of solutions is of interest, and for this purpose comparison of the results at 20° with those at other temperatures will be made. There are no data of sufficient accuracy on the vapor pressures of mannite solutions at other temperatures, and we resorted to indirect comparison by means of boiling-point and freezing-point data. Loomis[1] found that the molecular freezing-point lowerings of mannite solutions are perfectly constant. The accurate freezing-point work of Adams,[2] using very dilute solutions, has shown Loomis to be slightly in error, but this is negligible for the present comparison. The most concentrated solution measured by Hall and Harkins,[3] using Adams' method, was 0.1197 and they confirmed closely the lowering found by Loomis. Recently Braham[4] has determined the lowering of 2 concentrations of mannite solutions, obtaining value slightly higher than those of Loomis.

The relation between the freezing-point lowering and the vapor pressure of a solution is[5]

$$ln \frac{p_0}{p} = -\frac{M}{R}\int_{T_F}^{T_0} \frac{L_F dT}{T^2},$$

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[1] Loomis, *Z. physik. Chem.*, 32, 599 (1897).

[2] Adams, THIS JOURNAL, 37, 481 (1915).

[3] Hall and Harkins, *ibid.*, 38, 2658 (1916).

[4] Braham, *ibid.*, 41, 1707 (1919).

[5] This expression is often deduced simply from the equation of Clausius-Clapeyron for the variation of the vapor pressure of water with the temperature and a similar one for ice, since at the freezing-point of a solution its vapor pressure is equal to that of ice.

where L_F is the latent heat of the solvent and T_0 and T_F are, respectively, the freezing-points (absolute) of solvent and solution. Assuming that L_F is independent of temperature the right-hand member becomes $\frac{ML_Ft}{RT_0T_F}$, where t is the lowering. However, it is known that the heat of fusion decreases with lowering temperature and it is necessary to introduce a slightly different expression to take care of this. This variation is fundamentally the variation of the specific heat of ice, and Jüttner[1] puts, $L_F = L_0 + a(T_F + T_0)$, where L_F and L_0 are the heats of fusion at T_F and T_0 and $a = S - S'$, the difference between the specific heats of water and ice at T_F. This gives the expression

$$ln\,\frac{p_0}{p_1} = \frac{M}{R}\left[\frac{L_0}{T_0}\,\frac{t}{T_F} + a\,ln\left(1 + \frac{t}{T_F}\right)\right]. \qquad \text{(I)}$$

He calculated the values of $ln\,p_0/p$ for mannite solutions using $L_0 = 80.7$ and $a = 0.504$ cal. The heat of fusion and the specific heat of ice have since been accurately determined by Dickinson and Osborne,[2] who obtained $L_0 = 79.67$ $\text{cal}_{15°}$ and $S' = 0.5052$ $\text{cal}_{15°}$. Recalculating, using these figures, $R = 1.985$ and $S = 1.007$, values about 1.5% lower are obtained and are given in Column 4 of Table III.

Callendar[3] has treated this question similarly but has included also the variation of the specific heats with temperature. The expression is

$$ln\,\frac{p_0}{p} = \frac{ML_0t}{RT_FT_0} + \frac{1}{T}\int_{T_0}^{T_F}(S-S')dT - \int_{T_0}^{T_F}(S-S')\,\frac{dT}{T}.$$

The specific heat of water is not known accurately below 0° but the integrals are solved by making different assumptions as to the variation of $S - S'$ with temperature. Nernst[4] states that this varies inversely with the temperature just below 0°. Callendar's final expression on this basis is

$$ln\,\frac{p_0}{p'} = \frac{ML_0t}{RT_FT_0} + \frac{aM}{R}\left(\frac{t}{T_F} + \frac{T_0}{T_F} + ln\,\frac{T_F}{T_0}\right). \qquad \text{(II)}$$

Values calculated by this equation differ only slightly from those from Equation I, and are given in Column 5 of Table III. It was also found that the simplified expression, proposed by Callendar

$$ln\,\frac{p_0}{p'} = \frac{ML_0t}{RT_0^2} = 0.9695t$$

gives values practically identical with those of his rigid expression, since t is never greater than 1°.

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[1] Jüttner, *Z. physik. Chem.*, 38, 110 (1901).

[2] Osborne, *Bur. Standards Sci. Paper*, 248 (1918).

[3] Callendar, *Proc. Roy. Soc. A.*, 80, 446 (1908).

[4] Nernst, *Trans. Faraday Soc.*, 6, 117 (1910).

Vapor pressure ratios may be obtained from boiling-point elevation values by application of the same fundamental equation, but a surer method is to find the atmospheric pressure from the boiling temperature of the pure solvent. This becomes p_1 the vapor pressure of the solution, when the boiling temperature is raised slightly above that of the solvent. Then the vapor pressure of the pure solvent for that final temperature is found by the use of tables. This gives p_0 and p_1 at the same temperature. Jüttner has calculated the values of $ln\ p_0/p_1$ from Beckmann's[1] data which are given in Column 7 of Table III, while the observed values of the present authors are given in Column 6.

TABLE III.
Comparison of Vapor Pressure Ratios at 20° with those Obtained from Freezing-and from Boiling-Points.

			$ln\ p_0/p_1$			
	F. pt. lowering, t.		0° — t.			
M.	Obs.	Calc.	I.	II.	20°.	100° + t'.
0.1013	0.1874	0.1857	0.00181	0.00182	0.00180	...
0.131	..	..	...	...	0.00233	0.00235
0.2061	0.3807	0.3776	0.00368	0.00369	0.00366	...
0.268	..	..	...	...	0.00479	0.00451
0.2709	0.505	0.4962	0.00488	0.00490	0.00481	...
0.5323	0.9835	0.9737	0.00950	0.00953	0.00945	...
0.537	..	..	...	...	0.00957	0.00951
0.546	1.019	1.005	0.00985	0.00988	0.00974	...
0.801	..	..	...	...	0.01438	0.01448
1.018	..	..	...	...	0.01902	0.01915

The calculated values of t, given in Column 3, are obtained, using Callendar's equation, from the values of $ln\ p_0/p_1$ determined experimentally at 20° by the authors, assuming that this function is the same at the freezing-point or is independent of temperature. Von Babo's law states that the relative lowering of vapor pressure is independent of the temperature. And Kirchhoff's equation for the heat of dilution is a quantitative statement of the deviations from Von Babo's law.

$$H = RT^2\, \partial/\partial T\ (ln\ p_0/p_1).$$

H is the heat of dilution and is here defined as the heat which must be added to keep the temperature constant when one gram of solvent is added to an infinite amount of solution. Von Babo's law is thus a special case of Kirchhoff's equation and merely states that

$$\partial/\partial T\ (ln\ p_0/p_1) = 0.$$

Hence the function $ln\ p_0/p_1$ is a very convenient one to use in dealing with the variation of vapor pressure with temperature.

It is seen that the calculated freezing-point lowerings are slightly smaller than the observed, which deviation is roughly proportional to the concen-

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[1] Jüttner, *Z. physik. Chem.*, 6, 459 (1890).

tration. Von Babo's law does not hold exactly, therefore, and the $ln\ p_0/p_1$ curve for 0° lies slightly over that for 20° and the heat of dilution is negative. The $ln\ p_0/p_1$ values at 100° lack smoothness as the lowest concentration is somewhat out of line, but the smoothed curve lies under the 20° curve for the lower concentrations (below 0.8 *M*), showing a decrease in $ln\ p_0/p_1$ from 0° to 20° to 100°. For the lowest concentration the values of this function agree quite closely for 0°, 20°, and 100°, which means a very small (negative) heat of dilution. Pratt[1] has measured the heat evolved when solutions of mannite are diluted, but the data are empirically expressed and do not admit of quantitative comparison. However, his observations are in qualitative agreement with the deduction as regards sign and order of magnitude of the heat by dilution. The mean heat of dilution between 0° and 20° for a 0.5 *M* solution is roughly —0.5 cal, using the data in Table III and Kirchhoff's equation. For the concentrations 0.8 and 1.0 *M*, the $ln\ p_0/p_1$ at 100° are greater than those at 20°, indicating that the heat of dilution changes sign with increasing concentration, a not unusual phenomenon. It is significant that this takes place in the same concentration as that in which the deviation from Raoult's law is marked.

Vapor Pressure and Osmotic Pressure.—The relation between osmotic pressure and vapor pressure has been discussed by a number of authors, using different methods and resulting in a number of equations which differ only slightly according to the conditions and definitions chosen. The integral equation of A. W. Porter[2] covers all of these and is an expression for solutions of any compressibility and under any hydrostatic pressure. Introducing the limits corresponding to the conditions, neglecting compressibility and using the gas law for the vapor pressure he obtains.

$$\text{O. P.} = \frac{RT}{V_s} ln \frac{p_0}{p_1}.$$

V_s is the increase in volume when one gram of solvent is added to a large amount of solution, and is a function of the density.[3] This was found to be a correction of about 0.1%. The calculated values of the osmotic pressure are given in Column 10, Table II. Final direct measurements of the osmotic pressure have not been made, but will be the object of a future investigation.

Summary.

1. The vapor pressure lowerings of aqueous mannite solutions have been determined over the range of its solubility.

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[1] *J. Franklin Inst.*, 185, 663 (1918).

[2] Porter, *Proc. Roy. Soc. A.*, 79, 519 (1907).

[3] Gouy and Chaperon, *Ann. chim. phys.*, [6] 12, 384 (1887).

2. The presence of dissolved air as a source of error has been eliminated by a new method of preparing the solutions.

3. A mean deviation from Raoult's law of only 0.0006 mm. is observed up to 0.8 *M* concentration.

4. By comparison with freezing-point lowerings it is found that $ln\ p_0/p_1$ decreases with the temperature or, the heat of dilution is a small negative value for concentrations up to 0.5 *M*. Comparisons with boiling-point determinations show that this changes to a positive quantity in the higher concentrations.

BALTIMORE, MD.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA.]

THE THERMODYNAMIC PROPERTIES OF THE IONS OF SOME STRONG ELECTROLYTES AND OF THE HYDROGEN ION IN SOLUTIONS OF TENTH MOLAL HYDROCHLORIC ACID CONTAINING UNI-UNIVALENT SALTS.

BY HERBERT S. HARNED.

Received July 8, 1920.

Introduction.

In two earlier communications[1] from measurements of the electromotive forces of cells of the types

$H_2 \mid MeCl(c)$ in $HCl\ (0.1) \mid$ saturated $KCl \mid$ calomel electrode and
$Hg \mid HgCl \mid KCl\ (c + 0.1) \mid KCl\ (0.1) \mid HgCl \mid Hg$
$H_2 \mid KCl\ (c)$ in $HCl\ (0.1) \mid HgCl \mid Hg$,

the author has shown that the hydrogen ion activity of 0.1 *M* hydrochloric acid as measured by this method is increased by the addition of salts to the acid. On account of the difficulties attending the calculation of the electromotive forces of the cells

$$H_2 \mid MeCl\ (c) \text{ in } HCl\ (0.1) \parallel^{2} HCl\ (0.1) \mid H_2$$

from the above data, due largely to the present incomplete knowledge of liquid junction potentials, and a distrust of some of the earlier interpretations of the results, this investigation has been extended with the object of obtaining the complete thermodynamic data at 25° for the last mentioned series of cells containing potassium, sodium, and lithium chlorides. In this manner, the so-called "neutral salt effect" has been studied in a more searching manner from the thermodynamic point of view.

From the point of view of the theory of solutions a number of important contributions have been made comparatively recently. The first in importance of these is the hypothesis of complete dissociation of strong

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[1] THIS JOURNAL, 37, 2460 (1915); 38, 1986 (1916).

[2] Double bar indicates that liquid potential has been eliminated.

electrolytes as developed by Milner,[1] Ghosh,[2] Bjerrum,[3] Brönsted,[4] and others. A second, which may be looked upon as a corollary of the first, is the hypothesis of the independent activities of ions, first clearly proposed and used by MacInnes.[5] During the course of the present investigation, a large quantity of data have been obtained which, along with the data recently obtained by others, will contribute evidence of the validity of both of these hypotheses within narrow limits of error, and, for this reason, Part II of this paper will consist in the proof and application of these principles to the calculation of the activity coefficients of the ions of single electrolytes. Since the greater part of this investigation consists of complicated numerical calculations, a more detailed discussion of these hypotheses will be reserved until later sections.

PART I. GENERAL THEORY AND MEASUREMENTS.

(1) General Theory and Nomenclature.

Throughout this work, the system and nomenclature of G. N. Lewis[6] have been employed. The activity ξ can be defined by the equation

$$\bar{\mathrm{F}} = \delta \mathrm{F}/\delta n = RT\ ln\ \xi + i \qquad (1)$$

where $\bar{\mathrm{F}}$ is the partial molal free energy, (Gibb's chemical potential. See Brönsted)[7] or the partial derivative of the free energy with respect to mass, F is the free energy, i a constant, R the gas constant, and T the absolute temperature.

If we refer $\bar{\mathrm{F}}$ in any state to its value in some chosen standard state, $\bar{\mathrm{F}}_o$, we have

$$\bar{\mathrm{F}} - \bar{\mathrm{F}}_o = RT\ ln\ \xi/\xi_o = RT\ ln\ a \qquad (2)$$

where ξ_o is the activity in the standard state, and a is "the relative activity," a term used by Lewis. If the arbitrary state is so chosen that $\bar{\mathrm{F}}_o = 0$ and $\xi_o = 1$, then

$$\bar{\mathrm{F}} = RT\ ln\ a \quad \text{and} \quad \mathrm{F} = RT\ ln\ a \qquad (3)$$

and

$$\Delta \mathrm{F} = \mathrm{F}_2 - \mathrm{F}_1 = RT\ ln\ a_2/a_1 \qquad (4)$$

$$\Delta \mathrm{F} = \mathrm{F}_2 - \mathrm{F}_1 = RT\ ln\ \xi_2/\xi_1 \qquad (5)$$

Where ΔF is the increase in free energy.[8]

In a similar manner, we may relate $\bar{\mathrm{F}}$ to the partial molal heat content function $\bar{\mathrm{H}}$ by the equation

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[1] Milner, *Phil. Mag.*, [6] 23, 551 (1912); 25, 743 (1913); 35, 352 (1918).

[2] Ghosh, *J. Chem. Soc.*, 113, 449 (1918); 113, 627 (1918); 113, 707 (1918).

[3] Bjerrum, *Z. Elektrochem.*, 24, 321 (1918); *Z. anorg. Chem.*, 109, 275 (1920).

[4] Brönsted, *ibid.*, 42, 761 (1920).

[5] MacInnes, *ibid.*, 41, 1086 (1919).

[6] Lewis, This Journal, 35, 1 (1913).

[7] *Loc. cit.*

[8] The function F in Lewis' system always equals the Gibb's function ξ: that is, $\xi = e - t\eta + pv$.

$$\bar{F} = -RT\ ln\ w + \bar{H} + i \tag{6}$$

where w is the probability.[1] By the same reasoning as the above

$$\Delta F = -RT\ ln\ w_2/w_1 + \Delta H \tag{7}$$

where ΔH is the increase in heat content function. ΔH can be computed from the ξ and w functions by

$$\Delta H = RT\ ln\ \xi_2/\xi_1 + RT\ ln\ w_2/w_1. \tag{8}$$

In very dilute solutions ΔH is small, and hence the probability ratio will approach the reciprocal of the activity ratio.

In order to evaluate ΔH from measurements of ΔF, it is necessary to determine ΔF at different temperatures and express ΔF as a function of T, then substitute this value in the fundamental thermodynamic equation

$$\frac{d\ (\Delta F/T)}{dT} = -\frac{\Delta H}{T^2} \tag{9}$$

or the equivalent expression

$$\Delta H = \Delta F - T\ d\Delta F/dT, \tag{10}$$

perform the differentiation, and, from the numerical equation thus obtained, make the required calculations. In cases where ΔF cannot be conveniently expressed as a function of T, an approximation can be made by determining the temperature coefficient of free energy at the desired temperature and substituting this value for $d\Delta F/dT$ in Equation 10.

For the sake of brevity, the following system of nomenclature has been adopted for the 5 cells most frequently referred to in the calculations. The cells are

Type 1. H_2 | MeCl (c) in HCl (0.1) | HgCl | Hg.

Type 2. Hg | HgCl | MeCl (0.1) ||[2] MeCl (c_1) | HgCl | Hg (where $c_1 = c + 0.1$).

Type 3. Hg | HgCl | MeCl (0.1) | Me in Hg | MeCl(c_1) | HgCl | Hg.

Type 4. H_2 | MeCl (c) in HCl (0.1) || HCl (0.1) | H_2.

Type 5. H_2 | MeCl (c) in HCl (0.1) | sat. KCl | HgCl | Hg.

The electromotive forces of the above cells are denoted **E**(1), **E**(2), **E**(3), **E**(4), and **E**(5), respectively. Also, let $\mathbf{E}_0$(1) equal **E**(1) when $c = 0$; $\mathbf{E}_0$(4) equal **E**(4) when $c = 0$ and so on.

The relation between the decrease in free energy ($-\Delta F$) of transfer of ions, the activities of the ions and the electromotive forces of the above cells can be obtained from Equations 4 and 5; and the well known equation $(-\Delta F) = n\mathbf{EF}$, where **E** is the electromotive force in volts, **F** is 96,500 coulombs, and n is the number of Faraday equivalents transferred. The following equations are of importance and will be referred to frequently throughout this work:

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[1] H is the Gibb's function ξ that is, $\xi = e + pv$.

[2] The double bar indicates that the liquid junction potential has been eliminated.

$$(-\Delta F)_1 = F(E_0(1) - E(1)) = RT\, ln\, \frac{a_{H(s)}a_{Cl(c+0.1)}}{a_{H(0.1)}a_{Cl(0.1)}}\text{[1]} \qquad (11)$$

$$(-\Delta F)_2 = F(E(2)) = RT\, ln\, \frac{\sqrt{a_{Cl(c_1)}a_{Me(c_1)}}}{\sqrt{a_{Cl(0.1)}a_{Me(0.1)}}} \qquad (12)$$

$$(-\Delta F)_3 = F(E(3)) = RT\, ln\, \frac{a_{Cl(c_1)}a_{Me(c_1)}}{a_{Cl(0.1)}a_{Me(0.1)}} \qquad (13)$$

$$(-\Delta F)_4 = F(E(4)) = RT\, ln\, \frac{a_{H(s)}}{a_{H(0.1)}} \qquad (14)$$

$(-\Delta F)$ is the decrease in free energy attending the ionic transfers indicated in the right-hand members of these equations. In other words, the transfer of an ion from the more concentrated to the more dilute solution is accompanied by a decrease in free energy. Formula 12 is true for a cell of Type 2 if the liquid junction potentials have been computed by a thermodynamic formula such as $E_l = E_l(1 - 1/2n_c)$.[2]

Besides the above, there will be occasion to refer to the independent free energies and electromotive forces of transfer of the individual ions. The following equations and nomenclature will be adopted:

$$\left.\begin{aligned}(-\Delta F)_{Na} &= FE_{Na} = RT\, ln\, \frac{a_{Na(c_1)}}{a_{Na(0.1)}}\\ (-\Delta F)_{Li} &= FE_{Li} = RT\, ln\, \frac{a_{Li(c_1)}}{a_{Li(0.1)}}\end{aligned}\right\} \qquad (15)$$

An other function which will be employed frequently is the activity coefficient F_a, which is defined by the equation

$$F_a = a/c \qquad (16)$$

where c is the concentration of the electrolyte in equivalents per 1000 g. of solvent.

(2) Measurements of the Cells.

H_2 | MeCl (c) in HCl (0.1) | HgCl | Hg.[3]

These measurements are similar to those reported by the author in one of the earlier papers[4] where MeCl was potassium chloride; but since, in the present instance, the temperature coefficients are desired, all the results are new. The technique of the hydrogen and calomel half-cells and their combinations has been carefully described by many recent

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[1] $a_{H(s)}$ refers to the activity of the hydrogen ion in HCl (0.1) + MeCl (c) solutions.

[2] This formula has been used in the earlier papers by the author (*loc. cit.*).

[3] As far as the author is aware, these results are the only ones on this type of cell in which the acid concentration has been kept constant and the salt concentration varied. Loomis, Essex and Meacham (THIS JOURNAL, 39, 1133 (1917)), and Ming Chow (*ibid.*, 42, 497 (1920)) have measured cells of the same type in which the total ion concentration was kept constant but not the concentration of the acid.

[4] *Loc. cit.*

workers, including Acree,[1] Harned,[2] Ellis,[3] Lewis, Brighton and Sebastian,[4] and others and need not be described in great detail in this paper. Considerable care was exercized throughout the work. All the materials employed were carefully purified. Four times distilled mercury was used. The calomel paste was made from this mercury. The solutions of salt in the acid were made up at 25° by weighing both the salt and a carefully analyzed portion of the constant-boiling-point hydrochloric acid distillate and diluting to the mark on a carefully calibrated flask.[5] In the following table of data, concentrations are expressed in both mols of salt per liter and mols per 1000 g. of water.

The design of the cell employed was similar to that described by Ellis and previously used by the author. The calomel paste for the calomel half-cell was washed by decantation 7 or 8 times with the solution to be employed, then stirred by rotation in a thermostat at 25° for one or two hours, and finally allowed to stand 3 or more days in a thermostat at 25° before being introduced in the cell. For further details, the earlier papers may be consulted. When made up, each cell was kept in a thermostat for one week and measurements taken from time to time at the different temperatures employed. When made up in this manner, excellent constancy was maintained throughout this period of time. The final values were the mean of the readings taken at the temperatures designated. The deviations from this mean were rarely more than 0.01 of a millivolt. Table I contains the final data at 18, 25 and 30°. The values of the complete cell are believed to be reproducible to within ±0.2 of a millivolt throughout the entire series; and the temperature coefficients to within ±0.005 millivolt. Column 1 contains salt concentration in mols per liter, and Column 2 salt concentration in mols per 1000 g. of water. The column headed p contains the actual pressures of the hydrogen in the hydrogen half-cell, computed from the barometric pressure and the vapor pressure of the solution at the concentration and temperature designated. The values under E are the observed electromotive forces at the temperature designated, and $E(cr)$ are these electromotive forces corrected so that they equal the electromotive forces of the cells at just one atmosphere hydrogen pressure at the temperature indicated. The method of making this correction is described in detail in the earlier papers. The concen-

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[1] Acree, *Am. Chem. J.*, 46, 632 (1911).

[2] Harned, This Journal, 37, 2460 (1915).

[3] Ellis, *ibid.*, 38, 737 (1916).

[4] Lewis, Brighton and Sebastian, *ibid.*, 39, 2245 (1917).

[5] In the earlier communication, the salt was dissolved in HCl (0.1) and diluted to the mark with same. No correction was made at that time for the acid dilution due to the volume occupied by the salt. In cases of the higher concentrations of salt, this correction is considerable.

tration of the acid used was 0.1000 mol per liter, or 0.1004 mol per 1000 g. of water.

TABLE I.

Cells, H_2 | KCl (c) in HCl (0.1) | HgCl | Hg.

(1).	(2).	p_{18}.	E_{18}.	$E_{18}(cr)$.	p_{25}.	E_{25}.	$E_{25}(cr)$.	p_{30}.	E_{30}.	$E_{30}(cr)$.
0.0000[a]	0.0000	738	0.39749	0.39785	732	0.39851	0.39898	737	0.39923	0.39963
0.2000	0.2018	737	0.37329	0.37357	727	0.37366	0.37424	718	0.37374	0.37446
0.2000	0.2018	...	...	...	728	0.37366	0.37421	...	...	...
0.5000	0.5086	746	0.35697	0.35722	735	0.35697	0.35736	729	0.35671	0.35734
1.0000	1.0346	751	0.34043	0.34057	750	0.34012	0.34029	740	0.33968	0.34001
1.0000	1.0346	759	0.34056	0.34058	750	0.34014	0.34032	741	0.33972	0.34004
2.0000	2.134	757	0.31680	0.31686	748	0.31580	0.31618	739	0.31530	0.31566
2.0000	2.134	746	0.31665	0.31690	739	0.31588	0.31624	730	0.31519	0.31571
3.0000	3.309	744	0.29702	0.29727	737	0.29591	0.29631	728	0.29503	0.29557
3.0000	3.309	750	0.29738	0.29751	732	0.29606	0.29651	730	0.29534	0.29576
Cells, H_2 | NaCl (c) in HCl (0.1) | HgCl | Hg.										
0.1000	0.1003	751	0.38207	0.38222	743	0.38273	0.38298	743	0.38298	0.38338
0.2000	0.2014	746	0.37297	0.37319	739	0.37341	0.37379	730	0.37354	0.37408
0.3600	0.3636	...	...	...	740	0.36208	0.36243	...	...	...
0.5000	0.5061	750	0.35556	0.35570	741	0.35555	0.35587	730	0.35531	0.35585
0.6000	0.6085	...	...	...	745	0.35118	0.35142	...	...	...
0.9000	0.9183	752	0.34046	0.34062	749	0.34024	0.34044	732	0.33973	0.34018
1.000	1.023	752	0.33736	0.33745	745	0.33690	0.33716	736	0.33649	0.33688
1.200	1.243	...	...	...	743	0.33089	0.33119	...	...	...
1.800	1.871	750	0.31567	0.31581	743	0.31491	0.31521	734	0.31428	0.31473
1.985	2.078	...	...	...	748	0.31055	0.31079	...	...	...
2.000	2.094	755	0.31082	0.31088	749	0.31001	0.31021	736	0.30923	0.30962
2.565	2.711	754	0.29774	0.29794	736	0.29671	0.29696	738	0.29599	0.29635
3.000	3.202	732	0.28744	0.28789	743	0.28658	0.28688	716	0.28537	0.28612
3.452	3.726	760	0.27814	0.27814	750	0.27691	0.27709	738	0.27593	0.27630
Cells, H_2 | LiCl (c) in HCl (0.1) | HgCl | Hg.										
0.4165	0.4203	...	...	...	729	0.35814	0.35867	...	...	...
0.8342	0.8485	745	0.33906	0.33929	738	0.33881	0.33919	734	0.33854	0.33898
1.668	1.727	738	0.31203	0.31241	730	0.31144	0.31196	720	0.31084	0.31152
2.503	2.636	755	0.28858	0.28865	748	0.28773	0.28795	739	0.28693	0.28730
3.336	3.579	747	0.26559	0.26579	741	0.26452	0.26485	738	0.26369	0.26407
4.171	4.556	742	0.24238	0.24269	733	0.24107	0.24154	726	0.24003	0.24061

[a] The value of the cell without salt (c equals 0.0000) is the mean of 4 determinations.

PART II. ACTIVITY COEFFICIENTS.

Throughout the entire discussion and all the calculations which follow, the assumption has been made that all the electrolytes employed are completely dissociated over the entire concentration range.

(1) **The Hypothesis of the Independent Activities of Ions.**—MacInnes[1] first clearly proposed and used the following hypothesis which may be summed up in a general way by the two postulates.

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[1] *Loc. cit.*

1. The activities of the cation and anion of a solution of an electrolyte may differ from one another at a given concentration and temperature.

2. In solutions of the same strength (weight normal) and at the same temperature of different electrolytes possessing a common ion, the common ion will have the same activity independent of the ion or ions associated with it.[1]

If Postulate 2 is true, Postulate 1 will be true because the square roots of the activity products of different strong uni-univalent electrolytes have been observed to be different.

Postulate 1 has been suspected by numerous workers,[2] but had not been directly postulated and used before MacInnes' calculations; Postulate 2 as far as the author is aware, is entirely original with MacInnes.

The data obtained by the author in the earlier investigations along with the data presented in this paper can be used to test the validity of both of these postulates. Equations 11 and 14 are

$$\mathbf{E}_0(1) - \mathbf{E}(1) = \frac{RT}{\mathbf{F}} \ln \frac{a_{\mathrm{H}(s)}}{a_{\mathrm{H}(0.1)}} + \frac{RT}{\mathbf{F}} \ln \frac{a_{\mathrm{Cl}(c+0.1)}}{a_{\mathrm{Cl}(0.1)}}$$

and

$$\mathbf{E}(4) = \frac{RT}{\mathbf{F}} \ln \frac{a_{\mathrm{H}(s)}}{a_{\mathrm{H}(0.1)}},$$

respectively.

By subtracting (14) from (11), the relation

$$\mathbf{E}_0(1) - \mathbf{E}(1) - \mathbf{E}(4) = \frac{RT}{\mathbf{F}} \ln \frac{a_{\mathrm{Cl}(c+0.1)}}{a_{\mathrm{Cl}(0.1)}} \qquad (17)$$

is obtained. If Postulate 2 is correct, $\frac{RT}{\mathbf{F}} \ln \frac{a_{\mathrm{Cl}(c+0.1)}}{a_{\mathrm{Cl}(0.1)}}$ should be the same at a given concentration in solutions containing each of the different salts; that is to say, the chlorine ion activity will be the same at a given salt concentration notwithstanding the fact that the cations differ.

In the earlier communication, an extended series of measurements was made of cells of Type 5 which contained potassium, sodium and lithium chlorides along with the 0.1 *M* hydrochloric acid in the hydrogen half-cell. At that time, it was thought that the potential between a solution of hydrochloric acid containing lithium chloride or sodium chloride and a saturated potassium chloride solution would be considerable. More recent work, particularly by Fales and Vosburgh,[3] show that the previous contentions are not true; nor are these liquid junction potentials calculable

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[1] This is a generalized statement of the hypothesis of MacInnes, who assumed that it was true of the chlorine ion in solutions of hydrochloric acid and potassium chloride.

[2] *E. g.*, Lewis, This Journal, 34, 1640 (1912).

[3] Fales and Vosburgh, *ibid.*, 40, 1291 (1918).

by either Planck's or Henderson's formulas. Fales and Vosburgh find that the liquid potential between saturated potassium chloride and 0.1 *M* hydrochloric acid is 0.0000 volt; between saturated potassium chloride and 1 *M* hydrochloric acid is 0.0000 volt. Planck's formula gives 0.0046 and Henderson's formula 0.0048 volt for the first of the above liquid potentials. On the other hand, in all cases, the liquid potentials are much smaller than those predicted in the previous communication, probably in no case amounting to over one millivolt. For the present, let the approximation assumption be made that the liquid potentials at the saturated potassium chloride salt in acid boundary are zero for all concentrations of salt. Then it is possible to compute E(4) from measurements of cells of Type 5 by using the expression $E(4) = E_0(5) - E(5)$. In Table II, Column 1 contains concentration of salt in mols per liter; Column 2, $E_0(1) - E(1)$ calculated from the data in Table I; Column 3, $E_0(5) - E(5) = E(4)$; and Column 4, $E_0(1) - E(1) - E(4)$, which by Equation 17 equals $\frac{RT}{F} \ln \frac{a_{Cl(c+0.1)}}{a_{Cl(0.1)}}$. The values of E(4) have been read off the electromotive force—salt concentration plots of the earlier results supplemented by some more recent observations at the higher salt concentrations. These results are thought to be reproducible to within ±0.2 of a millivolt.

TABLE II.

	(1). *c*(mols)liter.	(2). $E_0(1)-E(1)$.	(3). E(4).	(4). $\frac{RT}{F} \ln \frac{a_{Cl(c+0.1)}}{a_{Cl(0.1)}}$.
KCl..................	0.2000	0.0247	0.0003	0.0244
	0.5000	0.0416	0.0012	0.0404
	1.0000	0.0587	0.0033	0.0554
	2.000	0.0828	0.0104	0.0724
	3.000	0.1026	0.0192	0.0834
NaCl................	0.2000	0.0252	0.0011	0.0241
	0.5000	0.0431	0.0030	0.0401
	1.000	0.0618	0.0070	0.0548
	2.000	0.0888	0.0176	0.0712
	3.000	0.1121	0.0300	0.0821
LiCl..................	0.2000	0.0264	0.0020	0.0244
	0.5000	0.0452	0.0052	0.0400
	1.000	0.0661	0.0106	0.0555
	2.000	0.0966	0.0248	0.0718
	2.503	0.1110	0.0337	0.0773[a]

[a] Falls on the e. m. f., *c* plot of the potassium chloride and sodium chloride results.

There is excellent agreement, considering the sources of error due to the small liquid potentials, and to the quantity and nature of the data, between the values in Column 4 for the different salts at the same concentration. Throughout the entire range of concentration, the deviation is never greater than 1.3 millivolts. Hence, it may be said that the activity of the chlorine ion in these solutions is always the same within narrow limits at the same salt concentration and is not appreciably different when different ions are associated with the chlorine ion. This proves that Postulate 2 is correct to within narrow limits up to a concentration of 3.1 *N* chlorine ion, and confirms the truth of Postulate 1.

Postulate 3.—Another assumption made by MacInnes[1] is that at any given concentration of potassium chloride, the activities of the potassium and chlorine ions are the same. This assumption can be readily tested by the data in hand. In Table II, Column 4, $\frac{RT}{\mathrm{F}} \ln \frac{a_{\mathrm{Cl}(c+0.1)}}{a_{\mathrm{Cl}(0.1)}}$ will correspond to electromotive forces of cells of Type 2 containing potassium chloride if the activities of the potassium and chlorine ions are the same at a given concentration. This can readily be seen from Equation 12. Table III shows this correspondence. Column 1 gives the concentration of salt in mols per liter plus 0.1, the acid concentration; Column (2) gives

$$\frac{RT}{\mathrm{F}} \ln \frac{a_{\mathrm{Cl}(c+0.1)}}{a_{\mathrm{Cl}(0.1)}}.$$

taken from Table II, Column 4; Column 3 gives E_2 (Equation 12) for potassium chloride, obtained from the data of Harned;[1] and Column 4 gives the differences between the values in Columns 3 and 2.

TABLE III.

(1).	(2).	(3).	(4).
$c_1 = c + 0.1.$	$\frac{\mathrm{RT}}{\mathrm{F}} \ln \frac{a_{\mathrm{Cl}(c+0.1)}}{a_{\mathrm{Cl}(0.1)}}.$	E_2(KCl)	Diff.
0.3000	0.0244	0.0250	0.0006
0.6000	0.0404	0.0412	0.0008
1.1000	0.0554	0.0557	0.0003
2.100	0.0724	0.0720	—0.0004
3.100	0.0834	0.0825	—0.0009

The small magnitude of the differences in Column 4 is good evidence that in solutions of potassium chloride the activities of the potassium and chlorine ions are very nearly the same, if not identical, at any given concentration, and that this is true up to 3 *N* concentration. The differences in Column 4 might be very easily due to the error caused by the assumption made above, regarding the liquid potentials between the solutions and the saturated potassium chloride solution. The fact that this difference changes in sign with the concentration is evidence that the error is experimental, or caused by liquid potentials.

This evidence of the validity of the above 3 postulates, along with the evidence previously obtained by MacInnes, Ming Chow[1] and others, is considered sufficient for their adoption; and, in all the calculations which follow, these assumptions are employed.

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[1] *Loc. cit.*

(2) Calculation of the Individual Activity Coefficients of a Few Univalent Ions.

By use of Postulates 2 and 3, it becomes possible to calculate the individual ion activities from available accurate electromotive force measurements on cells with and without transference. The following table of the individual electromotive forces of transfer of the chlorine, potassium, sodium, lithium and hydrogen ions in concentrated solutions has been compiled from the data of the author[1] on cells of Type 2 with transference containing potassium chloride and sodium chloride, respectively; on cells without transference, Type 3, containing lithium chloride[2] and from cells of the type

$$H_2 \mid HCl\ (c) \mid HgCl \mid Hg,$$

measured by Ellis.[1] Thus, from Equation 12,

$$E_{Cl} = E_K = E(2)_{KCl} \qquad (18)$$

$$E_{Na} = 2E(2)_{NaCl} - E_{Cl} \qquad (19)$$

and, from Equation 13,

$$E_{Li} = E(3)_{LiCl} - E_{Cl} \qquad (20)$$

$$E_H = E(3)_{HCl} - E_{Cl}. \qquad (21)$$

In order to calculate the activity coefficients at concentrations from 0.1 to 3.1 from the electromotive force data by means of Equations 15 and 16, it is necessary to obtain the values of the activity coefficients in 0.1 *M* solutions. The best values available for the square root of the ion activity products of the electrolytes potassium chloride, lithium chloride and hydrochloric acid are given by Noyes and MacInnes[3] as 0.754, 0.779 and 0.823 at 0.1 *M*, respectively. The value of the same for sodium chloride has been taken to be 0.765. These values have been obtained from electromotive forces of concentration cells without transference at low concentrations on the assumption that at 0.001 *M* concentration, the activity coefficient and conductance viscosity ratio are equal. From the above, the activity coefficients, F_a, at 0.1 *M* of the potassium and chlorine ions will be equal to 0.754; $F_{a(0.1)}$ of the sodium ion may be obtained from $0.765 = \sqrt{0.754\ F_{a(0.1)}}$, and equals 0.775; likewise $F_{a(0.1)}$ of the lithium ion can be obtained from $0.779 = \sqrt{0.754 F_{a(0.1)}}$, and equals 0.815; and $F_{a(0.1)}$ of the hydrogen ion can be obtained from $0.823 = \sqrt{0.754\ F_{a(0.1)}}$, and equals 0.899. The results of the electromotive forces of transfer of the individual ions are given at round concentrations (mols per 1000 g. water) and have been read off the electromotive force-concentration plots of the electromotive forces E_{Cl}, E_K, E_{Na}, E_{Li} and E_H, calculated by Equations 18, 19, 20 and 21. Corresponding to each electro-

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[1] *Loc. cit.*

[2] MacInnes and Beattie, THIS JOURNAL, 42, 1117 (1920).

[3] Noyes and MacInnes, *ibid.*, 42, 239 (1920).

motive force is given the value of F_a, calculated by Equations 15 and 16. The temperature is 25 ± 0.01°.

TABLE IV.

(c_1).	$E_K - E_{Cl}$.	$F_K - F_{Cl}$.	E_{Na}.	F_{Na}.	E_{Li}.	F_{Li}.	E_H.	F_H.
0.1000	0.0000	0.754	0.0000	0.775	0.0000	0.815	0.0000	0.899
0.300	0.0250	0.665	0.0260	0.711	0.0274	0.771	0.0228	0.920
0.500	0.0365	0.639	0.0389	0.712	0.0427	0.860	0.0431	0.964
0.750	0.0459	0.599	0.0497	0.715	0.0541	0.894	0.0553	1.030
1.000	0.0524	0.578	0.0572	0.719	0.0640	0.980	0.0662	1.181
1.500	0.0619	0.556	0.0707	0.806	0.0795	1.192	0.0825	1.483
2.000	0.0689	0.547	0.0801	0.876	0.0931	1.519	0.0971	1.960
2.500	0.0747	0.550	0.0893	1.000	0.1048	1.880	0.1098	2.583
3.000	0.0796	0.556	0.0977	1.150	0.1168	2.540	0.1228	3.546

(3) The Calculation of the Activity Coefficients of the Hydrogen Ion at 25° in 0.1 *M* Hydrochloric Acid Containing Potassium, Sodium, and Lithium Chlorides at Concentrations up to 3 *M*.

The values of the electromotive forces E(4), of cells of Type 4 containing potassium chloride, sodium chloride, or lithium chloride, and the activity coefficient $F_a/0.1$ of the hydrogen ion of 0.1 *M* hydrochloric acid in the presence of the above 3 salts at the concentrations designated are given in Table V. This calculation was made using the accurate data obtainable on cells of Type 1 and Type 2. From Equations 11 and 14, we obtain

$$E_o - E(1)_c = RT\ ln \frac{a_{H(s)}}{a_{H(0.1)}} + E_{Cl(c+0.1)}.$$

Thus

$$E_o - E(1)_c - E_{Cl(c+0.1)} = E(4).$$

The values under E(4) in Table V were obtained at round concentrations by reading the values of $E_o(1) - E(1)_c$, calculated from the data in Table I, from the electromotive force-concentration plots, and subtracting from these $E_{Cl(c+0.1)} = E_{Cl(c_1)}$, obtained from Table IV.

TABLE V.

c.	E(4)KCl.	F_H(KCl).	E(4)NaCl.	F_H(NaCl.)	E(4)LiCl.	F_H(LiCl).
0.000	0.0000	0.899	0.0000	0.899	0.0000	0.899
0.300	—0.0001	0.895	0.0013	0.948	0.0023	0.985
0.500	0.0008	0.929	0.0025	0.989	0.0044	1.066
0.750	0.0015	0.953	0.0041	1.053	0.0073	1.191
1.000	0.0032	1.018	0.0064	1.152	0.0107	1.362
1.500	0.0062	1.144	0.0107	1.362	0.0171	1.748
2.000	0.0100	1.326	0.0167	1.681	0.0240	2.29
2.500	0.0139	1.542	0.0224	2.145	0.0311	3.02
3.000	0.0176	1.785	0.0279	2.66	0.0390	4.10

It is important at this juncture to note that the activity of the hydrogen ion in these solutions is different, depending on the added salt. Although the activity of the common ion has been shown to be identical in solutions of equivalent normality, this is not true of the hydrogen ion which is not common to both electrolytes. A further discussion of this so-called "neutral salt effect" will be reserved until a later section in which the increments of the heat content function of transfer of the hydrogen ion will be discussed.

(4) A General Formula for the Calculation of the Activity Coefficients of the Individual Ions of a Single Electrolyte.

The formula here used in calculating the individual ion activity coefficients is partly empirical and depends on the combination of the 2 equations

$$-\log f_a = \beta c^m \tag{22}$$

and

$$\log F_a/f_a = \alpha c \tag{23}$$

where f_a is the "ideal activity coefficient," F_a the observed activity coefficient computed from electromotive force data, c is the concentration in mols per 1000 g. of water, and α, β and m are constants.

Bjerrum[1] has deduced a particular form of Equation 22 for uni-univalent electrolytes, namely

$$-\log f_a = \beta\sqrt[3]{c} \tag{24}$$

from the following considerations and equations.

1. The hypothesis of complete dissociation.
2. The empirical equation relating the osmotic coefficient, f_o, with the concentration, namely

$$f_o = 1 - k\sqrt[3]{c} \tag{25}$$

obtained from the empirical equation of Noyes and Falk[2]

$$2 - i = k\sqrt[3]{c} \tag{26}$$

where i is the Van't Hoff factor.

3. The thermodynamic equation

$$f_o + c\,\frac{df_o}{dc} = 1 + c\,\frac{d\ln f_a}{dc} \tag{27}$$

which relates the osmotic coefficient with the activity coefficient. Since a correct theoretical treatment of these relationships has been presented by Bjerrum[3] and Brönsted,[4] no further comments are necessary. Equation 26 was shown by Noyes and Falk to hold within the error of experiment with the results then available for dilute solutions of electrolytes (from 0.001 M to 0.05 M), and, hence, Equation 24 will hold in very dilute solutions where abnormalities due to heats of dilution, hydration, etc.,

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[1] Bjerrum, *Meddel. K. Vetenskapsakad. Nobelinst.*, **5**, No. 16; *Z. anorg. Chem.*, **109**, 275 (1920).

[2] Noyes and Falk, This Journal, **32**, 1011 (1910).

[3] *Loc. cit.*

[4] Brönsted, This Journal, **42**, 761 (1920).

are not great. For this reason, Equation 24 can be used in calculating what the activity coefficient would be in solutions of higher concentrations if these abnormalities did not occur. f_a has, therefore, been termed the "ideal activity coefficient." β computed from the values of K in Equation 26 will differ for different types of electrolytes.

By using a different method Lewis and Linhart[1] have deduced the equation

$$-\log f_a = \frac{\beta'(\alpha' + 1)c^{\alpha'}}{2.303\, n'\lambda\alpha'} \qquad (28)$$

from the thermodynamic equation relating the activity and the freezing-point lowering, and an empirical equation relating the freezing-point lowering and concentration of electrolyte. α' and β' are constants, n' equals the total number of gram ions contributed by the electrolyte (thus, for NaCl, $n' = 2$; for $La_2(SO_4)_3$, $n' = 5$) and $\lambda = 1.858°$ or the molal lowering of the freezing-point. This equation for any given electrolyte can be reduced to the general form

$$-\log f_a = \beta c^m$$

since, for that electrolyte α', β', n', λ, in Equation 28 are constants.

Lewis and Linhart showed that electrolytes of similar type such as potassium chloride and sodium chloride or potassium iodate and sodium iodate would possess up to 0.01 M concentrations, identical f_a values, but that there would be large differences in f_a in these very dilute solutions between electrolytes of different types, such as sodium chloride, sodium iodate, copper sulfate, etc. From this consideration, the author has employed the general Equation 24.

The activity coefficients, F_a, as determined by the electromotive force method vary greatly from the values of f_a at the higher concentrations, and hence, it becomes necessary to seek a relation between F_a and f_a. Bjerrum[2] has made the only attempt to calculate on a theoretical basis the relation between the activity coefficients and the molal concentrations for single electrolytes. In Bjerrum's calculations, however, the hypothesis is made that the electromotive force method measures the activity of the non-hydrated ion. Since the effect of hydration on activity coefficients is at present little understood, since the ionic hydration values computed by this method are improbable (*e. g.*, for the lithium and hydrogen ion), and since thermodynamic data alone cannot decide the truth of such an hypothesis, it has been thought preferable to hold this idea in abeyance. In the second place, Bjerrum has employed the correction factor $\frac{55.5}{55.5 + 2c - (m_1 + m_2)c}$, for the volume correction due to hydra-

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[1] Lewis and Linhart, THIS JOURNAL, 41, 1951 (1919).

[2] *Loc. cit.*

tion. Here, m_1 and m_2 are the hydration values (the number of water molecules combined with an ion) of the 2 ions of an electrolyte, respectively, and c is the concentration. For a highly hydrated electrolyte, this correction is considerable, amounting, for example in the case of lithium chloride, to 25% at 3 M concentration. Further, this correction factor would affect both the ions in the solution, and, if true, the activity coefficient of the chlorine ion would not be the same in solutions of the same concentration, independent of the ions associated with it. This contradicts both the hypothesis of MacInnes, and the data of the author (Table II).

On the other hand, the equation $\log F_a/f_a = \alpha c$ has been employed to relate the functions F_a and f_a. By combining Equations 22 and 23, the equation

$$\log F_a = \alpha c - \beta c^m \qquad (29)$$

is obtained, and in what follows this equation will be shown to express, within experimental errors, F_a as a function of the concentration in the concentration range 0.01 to 3.0 molal.

To determine the values of α, β, and m, from the observed results, an empirical method has been employed. By transposition of Equation 29, we obtain

$$-\log F_a/c + \alpha = \beta c^{m-1}$$

and, taking the logarithms of both members

$$\log [-\log F_a/c + \alpha] = \log \beta + (m - 1) \log c. \qquad (30)$$

From Equation 30, it is clear that if α is known, the plot of $\log[-\log F_a/c + \alpha]$ against $\log c$ will be a straight line from which the values of β and

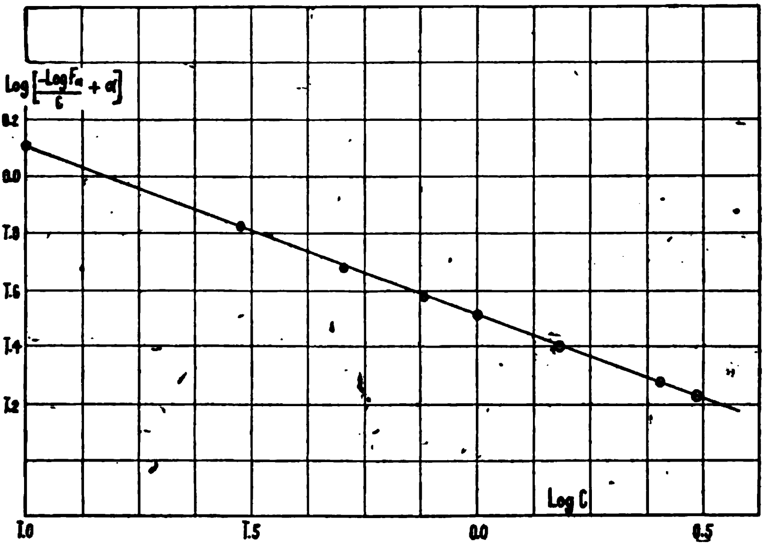

Fig. 1.

m can readily be read off. In order to determine these 3 constants, the above plot was made, using different values for α until a straight line could be drawn through the points. In all cases of the individual ions, Equation 29 can be shown to hold within experimental error throughout the concentration range under consideration. In Fig. 1, the plot of $\log [-\log F_a/c + \alpha]$ against $\log c$ of the potassium ion is shown, and in Table VI a comparison of the observed values of the activity coefficients and the values calculated by Equation 29 are given for the potassium, sodium, lithium, hydrogen, and chlorine ions, along with the respective values of α, β, and m for each ion. The results of this calculation are quite satisfactory; the observed lithium ion results exhibit the greatest inconsistency.

TABLE VI.

	K^+, Cl^-.		Na^+.		Li^+.		H^+.	
c.	F_a(obs.).	F_a(calc.).	F_a(obs.).	F_a(calc.).	F_a(obs.).	F_a(calc.).	F_a(obs.).	F_a(calc.).
0.001	0.979	0.955	...	...	0.973	0.965	...	...
0.010	0.890	0.892	...	...	0.920	0.910	0.975	0.963
0.100	0.754	0.766	0.775	0.770	0.815	0.813	0.899	0.906
0.300	0.665	0.666	0.711	0.715	0.771	0.790	0.920	0.904
0.500	0.639	0.629	0.712	0.703	0.860	0.814	0.964	0.950
0.750	0.599	0.598	0.715	0.716	0.894	0.875	1.030	1.051
1.000	0.578	0.578	0.719	0.735	0.980	0.955	1.181	1.175
1.500	0.556	0.557	0.806	0.795	1.192	1.175	1.483	1.496
2.000	0.547	0.550	0.876	0.885	1.519	1.500	1.960	1.964
2.500	0.550	0.551	1.000	1.005	1.880	1.919	2.583	2.624
3.000	0.556	0.558	1.150	1.160	2.540	2.500	3.546	3.557

	α.	β.	m.
K^+	0.080	0.318	0.397
Cl^-	0.080	0.318	0.397
Na^+	0.175	0.309	0.385
Li^+	0.309	0.329	0.435
H^+	0.390	0.322	0.596

By use of Equation 29, the activity coefficients of the potassium, lithium, hydrogen and chlorine ions can be computed with accuracy down to concentrations approaching 0.001 molal. The observed results for concentrations of 0.01 and 0.001 molal are taken from Noyes and MacInnes.[1] β and m for the potassium, chlorine and sodium ions are nearly identical as was found by Lewis and Linhart; β and m for the lithium ion are near but not identical with the same for the potassium and sodium ions. The values of these 2 constants for the hydrogen ion differ greatly from the values obtained for the alkali metal ions and the chlorine ion. The values of α for the potassium, sodium and lithium ions are approximately in the ratios of the relative ionic hydration values as determined by Washburn.[2]

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[1] *Loc. cit.*

[2] See Harned, THIS JOURNAL, 40, 1462 (1918).

The α ratios are

0.080 : 0.175 : 0.309 or 4 : 8.7 : 15.4.

Washburn's results give the ratio

5.4 : 8.4 : 14.0.

The departure of the values of F_a from f_a is due in great part, at least to the effect of hydration. Reasons for the abnormal behavior of the hydrogen ion will be discussed in Part III.

Further, Equation 29 shows the minimum in the F_a–c plots. The potassium and chlorine ions show a minimum at 2 *M*, the sodium ion at 0.50 *M*, and the lithium ion at 0.3 *M*. The observed hydrogen ion F_a–c plot does not show a minimum at concentrations above 0.1 *M*, although Equation 29 predicts one at about 0.2 *M* concentration. It can easily be seen that the position of this minimum depends on the magnitude of α.

PART III. THE FREE ENERGY AND HEAT CONTENT INCREMENTS.

(1). The Decrease in Free Energy and Heat Content of the Cell Reaction $H_2 + 2HgCl = 2HCl\ (0.1) + 2Hg$ in the Presence of Potassium, Sodium and Lithium Chlorides.

From the data in Table I, the decrease in free energy (—ΔF) of the cell reaction at the temperature designated may be obtained by multiplying

TABLE VII.

c.	$(-\Delta F)_{18}$.	$(-\Delta F)_{25}$.	$(\Delta F)_{30}$.	$\left(\frac{d\Delta F}{dT}\right)_{25}$.	$(-\Delta H)_{25}$.
(1) KCl.					
0.0000	76785	77003	77129	29.0	68360
0.2018	72098	72228	72272	13.0	68354
0.5086	68943	68970	68967	1.5	68523
1.0346	65730	65678	65625	— 8.5	68211
2.134	61157	61029	60929	—20.0	66989
3.309	57397	57207	57063	—28.0	65551
(2) NaCl.					
0.1003	73768	73917	73993	18.5	68404
0.2014	72027	72142	72199	13.5	68218
0.5061	68653	68683	68679	2.0	68087
0.9183	65740	65705	65656	— 7.0	67791
1.023	65129	65072	65017	— 8.5	67605
1.871	60952	60836	60744	—17.3	65987
2.094	60000	59870	59754	—20.5	65979
2.711	57503	57315	57197	—25.0	64765
3.202	55564	55369	55221	—28.0	63713
3.726	53680	53478	53326	—30.0	62418
(3) LiCl.					
0.4203	...	69223	...	..	...
0.8485	65483	65463	65423	— 5.0	66953
1.7267	60294	60209	60124	—13.5	64232
2.636	55711	55575	55450	—21.0	61833
3.574	51297	51114	50966	—27.0	59160
4.556	46839	46618	46417	—34.0	56750

the electromotive force by 2 × 96,500. Only in a few cases was it possible to obtain $(\Delta H)_{25}$ by using the linear equation $(-\Delta F) = (\Delta F)_{25}(1 + \alpha(t - 25))$, substituting for $(-\Delta F)$ in Equation 9 and differentiating, because of the complicated nature of the variation of $(-\Delta F)$ with the temperature. For this reason, $\left(\frac{d\Delta F}{dT}\right)_{25}$ in the neighborhood of 25° was read off from a carefully drawn large scale $(-\Delta F)$, T plot and then $(\Delta H)_{25}$ was computed by Equation 10. The data is compiled in Table VII. $(-\Delta F)_{25}$ and $(-\Delta H)_{25}$ are given in joules. $\left(\frac{d\Delta F}{dT}\right)_{25}$ is given in joules per degree. An error of 0.01 of a millivolt in $\left(\frac{d\Delta F}{dT}\right)_{25}$ will cause an error of 596 joules. It is thought that the following values of $(\Delta H)_{25}$ are not in error by more than ±300 joules.

(2). $(-\Delta F)_{25}$ and $(-\Delta H)_{25}$ of Transfer of Two Gram Ions of Hydrogen and Two Gram Ions of Chlorine from (MeCl(*c*) in HCl(0.1)) to HCl(0.1).

By subtracting $(-\Delta F)_{25}$ and $(-\Delta H)_{25}$ at a salt concentration *c* from $(-\Delta F)_{25}$ and $(-\Delta H)_{25}$ at a zero salt concentration, $(-\Delta F)_{25}$ and $(-\Delta H)_{25}$ of transfer of 2 gram ions of hydrogen ion and 2 gram ions of chlorine ion from MeCl (*c*) in HCl (0.1) to HCl (0.1) will be obtained. (See Equation

TABLE VIII.

	c.	$(-\Delta F)_{25}$.	$(-\Delta H)_{25}$.
(1) KCl.			
	0.2018	4775	6
	0.5086	8033	37
	1.0346	11325	149
	2.134	15974	1371
	3.309	19796	2807
(2) NaCl.			
	0.1003	3086	—44
	0.2014	4861	142
	0.5061	8320	273
	0.9183	11298	569
	1.023	11931	755
	1.871	16167	2373
	2.094	17133	2381
	2.711	19688	3695
	3.202	21634	4647
	3.726	23525	5942
(3) LiCl.			
	0.4203	7780	...
	0.8485	11557	1407
	1.7267	16794	4128
	2.636	21428	6587
	3.574	25889	9200
	4.556	30385	11610

11). Table VIII contains these values of $(-\Delta F)_{25}$ and $(-\Delta H)_{25}$ of transfer in joules.

(3) General Considerations Regarding the Increment in Heat Content Function of Ionic Transfer.

The only accurate data available on $(-\Delta H)$ of transfer of an electrolyte from a solution of strength c_1 to a solution of strength c_2 by electromotive force measurements have been obtained by Ellis[1] on hydrochloric acid. It has been necessary, therefore, to calculate $(-\Delta H)$ of transfer of potassium chloride and sodium chloride from the heats of dilution, or the heat absorbed or evolved on changing the concentration from c_1 to c_2 and the partial molal heats of dilution of water at the concentrations c_1 and c_2.[2] This can be done as follows.

1. Start with infinite quantities of 2 solutions at concentrations c_1 and c_2, respectively, and let $c_1 > c_2$. Let x_1 equal the number of mols of water per mol of salt corresponding to c_1, and x_2 equal the number of mols of water per mol of salt corresponding to c_2. Let $\overline{H}$ equal the partial molal heat of dilution of water, $\overline{H}_{c_1}$ and $\overline{H}_{c_2}$, the partial molal heats of dilution of water at concentrations c_1 and c_2, respectively. Remove one mol of solute and x_1 mols of water from 1. $(-\Delta H) = 0$. Remove $(x_2 - x_1)$ mols of solvent from 2. $(-\Delta H)_1 = -(x_2 - x_1)\overline{H}_{c_2}$.

2. Dilute one mol of solute and x_1 mols of water with $(x_2 - x_1)$ mols of water. $(-\Delta H)_2 = Q = \int_{x_1}^{x_2} \overline{H}\, dx =$ heat of dilution from x_1 to x_2. Add one mol of solute and x_2 mols of solvent to 2. $(-\Delta H) = 0$.

3. Remove x_1 mols of solvent from 2. $(-\Delta H)_3 = -x_1\overline{H}_{c_2}$.

4. Add x_1 mols of solvent to solution 1. $(-\Delta H)_4 = x_1\overline{H}_{c_1}$. The total heat content change of transfer $(-\Delta H)$, will be the sum of the above heat content changes. This gives

$$(-\Delta H) = \int_{x_1}^{x_2} \overline{H} dx + x_1\overline{H}_{c_1} - x_2\overline{H}_{c_2}. \qquad (31)$$

In Table IX are given the values of $(-\Delta H)$ of transfer in joules at 25° for potassium chloride and sodium chloride from a solution of concentration c to 0.1 M, calculated by Equation 31. The heats of dilution of potassium chloride necessary for the calculation have been taken from the data of Bishop,[3] and the partial molal heats of dilution of water in potassium chloride solutions have been taken from Stearn and G. McP. Smith.[4] All data on the heats of dilution, etc. of sodium chloride have been taken

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[1] *Loc. cit.*

[2] This partial molal heat of dilution equals the change in heat content when one mol of water is added to an infinite amount of a solution of the designated concentration.

[3] Bishop, *Phys. Rev.*, **26**, 169 (1908).

[4] Stearn and Smith, THIS JOURNAL, **42**, 18 (1920).

from Randall and Bisson.[1] The data on hydrochloric acid in the last column have been obtained from Ellis' electromotive force measurements.

TABLE IX.

$(c + 0.1)$.	KCl. $(-\Delta H)_{25}$.	NaCl. $(-\Delta H)_{25}$.	HCl. $(-\Delta H)_{25}$.
0.1000	000	000	000
0.3000	— 355	— 300	420
0.5000	— 650	— 570	820
1.000	—1310	—1196	1820
1.500	—1900	—1780	2770
2.000	—2375	—2300	3720
2.500	—2810	—2690	4740
3.000	—3175	—3010	5710

No further reliable data sufficient for calculating $(-\Delta H)$ of transfer of other electrolytes were available.

In order to carry further the calculation of the thermodynamic data presented in this paper, another hypothesis will be necessary regarding $(-\Delta H)$ of transfer of the ions. If the heats of dilution from molal concentrations c_1 to c_2 of a number of electrolytes be compared,[2] the conclusion (at least approximate), may be drawn that the ions have a specific individual effect. Thus, hydrochloric acid has a high positive heat of dilution, and sodium and potassium chloride have negative heats of dilution. Further, solutions of other acids have a positive heat of dilution. Thus, wherever the hydrogen ion occurs, there is a positive heat of dilution. If, in the cases of sodium chloride, potassium chloride, and hydrochloric acid, the chlorine ion has the same heat of dilution irrespective of the cation associated with it, then the hydrogen ion will have a greater positive heat of dilution than either the sodium or potassium ion In a general qualitative way, this same principle is true for the heats of dilution of all electrolytes. A rough study of the data will arrange some of the common ions in the following order, those on the left having a positive heat of dilution and those on the right a negative heat of dilution.

$$H^+ > {}^1/_2Cu^{++}, {}^1/_2Zn^{++}, {}^1/_2Ca^{++} > {}^1/_2Sr^{++} > {}^1/_2Ba^{++} >$$
$$ {}^1/_2Mg^{++} > OH^- > NH_4^+, {}^1/_2SO_4^{--} > K^+, Na^+, Li^+, Cl^- > NO_3^-.$$

From these considerations, the following 2 hypotheses have for the time being been adopted.

1. The ions act independently of one another in respect to the heat content increment of transfer.

2. The potassium and chlorine ions produce identical heat content increments of transfer between the same concentration limits.

The first hypothesis is believed to be approximately true for all ions, and a very close approximation, at least, for the univalent ions of strong

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[1] Randall and Bisson, THIS JOURNAL, 42, 347 (1920).

[2] *E. g.*, the data of Pratt, *J. Franklin Inst.*, 185, 663 (1918).

electrolytes. The second hypothesis is probably true because the activity coefficients of the potassium and chlorine ions are identical or very nearly so, and because other evidence points to the conclusion that these ions behave alike as regards hydration.

By means of these 2 hypotheses, the values of $(-\Delta H)$ of transfer in joules at 25° of the potassium, sodium, hydrogen, and chlorine ions were calculated at round concentrations from the results in Table IX. The results of this computation are given in Table X.

TABLE X.

$c + 0.1$.	$(-\Delta H)_{25}(H^+)$.	$(-\Delta H)_{25}(Cl^-)$.	$(\Delta H)_{25}(K^+)$.	$(-\Delta H)_{25}(Na^+)$.
0.100	000	000	000	000
0.300	598	—178	—178	—122
0.500	1145	—325	—325	—245
1.000	2477	—655	—655	—541
1.500	3670	—950	—950	—830
2.000	4908	—1188	—1188	—1112
2.500	6095	—1405	—1405	—1285
3.000	7299	—1588	—1588	—1422

These results are approximations, and the error cannot be estimated. They will, suffice, however, to bring out the main points of the following discussion.

(4). $(-\Delta F)_{25}$ and $(-\Delta H)_{25}$ of Transfer of Two Gram Ions of Hydrogen Ion from a Solution of MeCl(c) in HCl(0.1 M) to HCl(0.1 M).

From the data in Table IV, the free energy of transfer of 2 gram ions of chlorine ion from a solution of concentration $(c + 0.1)$ M to 0.1 M can be easily obtained by multiplying E_{Cl} at a concentration $(c + 0.1)$ M by 2 × 96,500. $2(-\Delta H)_{25}$ for the chlorine ion at the proper concentration can be read off the heat content decrease-concentration plot of the results in Table X, Column 3. By subtraction of $(-\Delta F)_{25}$ and $(-\Delta H)_{25}$ of transfer of 2 gram ions of chlorine at a concentration $(c + 0.1)$ M, thus obtained, from $(-\Delta F)_{25}$ and $(-\Delta H)_{25}$ of transfer of 2 gram ions of hydrogen ion and 2 gram ions of chlorine from MeCl (c) in HCl (0.1M) to HCl (0.1 M), given in Table VIII, $(-\Delta F)_{25}$ and $(-\Delta H)_{25}$ of transfer of 2 gram ions of the hydrogen ion from MeCl (c) in HCl (0.1 M) to HCl (0.1 M) will be obtained. This calculation has been made and the data compiled in Table XI. The last column gives $(-\Delta H)_{25}$ of transfer of one gram ion of the hydrogen ion.

In Fig. 2, the values of $(-\Delta H)_{25}$ of transfer of the hydrogen ion taken from the last column of Table XI are plotted against the concentration of added salt. The plot denoted hydrochloric acid is the $(-\Delta H)_{25}$ concentration of acid plot for the hydrogen ion in solutions of hydrochloric acid, taken from Table X, Column 2. These plots are straight lines within the error of experiment.

TABLE XI.

	$c.$	$(-\Delta F)_{25}.$	$(-\Delta H)_{25}.$	$(-\Delta H)_{25}.$ (1 gram ion)
(1) KCl.				
	0.0000	000	000	000
	0.2018	—49	356	178
	0.5086	79	902	451
	1.0346	575	1519	759
	2.134	2097	3960	1980
	3.309	3886	6177	3088
(2) NaCl.				
	0.1003	40	131	66
	0.2014	37	492	246
	0.5061	366	1073	536
	0.9183	938	1899	949
	1.023	1181	2215	1108
	1.871	2827	4723	2361
	2.094	3256	4931	2465
	2.711	4615	6630	3315
	3.202	5718	8022	4011
	3.726	..	9582	4791
(3) LiCl.				
	0.8485	1579	2682	1341
	1.7267	3766	6353	3176
	2.636	6470	9507	4754
	3.574	..	12775	6388

It is first clear from the above plots that these increments of transfer are of the same order of magnitude whether the hydrogen ion is transferred from a solution of HCl (c + 0.1) to HCl (0.1), or from a solution

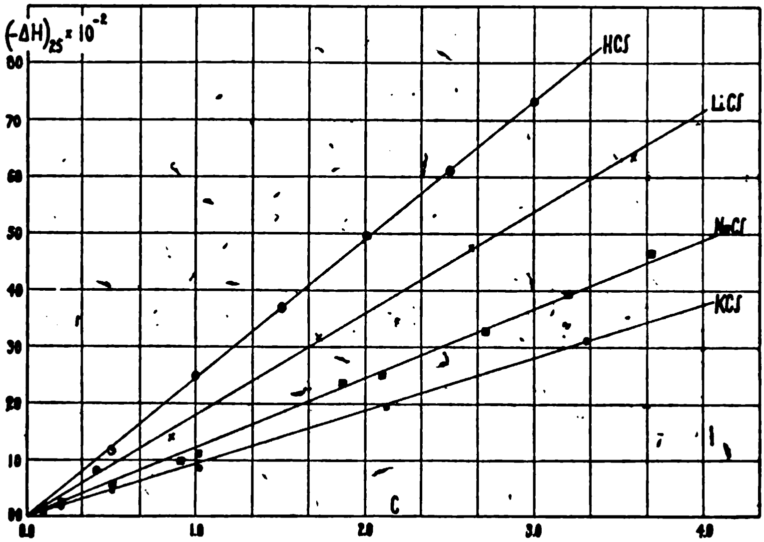

Fig. 2.

of HCl (0.1) + MeCl (c) to HCl (0.1). This points directly to the extremely important principle *that the decrease of heat content function of transfer of the hydrogen ion is a function of the total salt concentration or total ion activity, and not of the concentration or activity of the hydrogen ion.*

The following will clearly demonstrate this principle. In the first place

$$(-\Delta H)_{25} = Kc \qquad (32)$$

where c is the concentration of salt or hydrochloric acid added to 0.1 M hydrochloric acid, and K is a constant. Second, it is to be observed that, at a given concentration, the greater the activity of the ions of the single electrolyte added to the acid, the greater will be this decrease in heat content of transfer. The results tabulated in Table XII will roughly illustrate this relationship. Column 1 contains the values of K (Equation 32), or the slope of the plots in Fig. 2, Column 2, the sum ($\alpha_{Me} + \alpha_{Cl}$) of the values of the constant α of Equation 29 (Table VI) of both the ions added to the acid, and Column 3 contains the ratio $(\alpha_{Me} + \alpha_{Cl})/K$.

TABLE XII.

Electrolyte added.	(1).	(2).	(3).
KCl	920	0.160	1.74×10^{-4}
NaCl	1230	0.255	2.07×10^{-4}
LiCl	1800	0.389	2.16×10^{-4}
HCl	2420	0.430	1.98×10^{-4}

The approximate constancy of the values in Column 3 point to the conclusion that the decreases in heat content under consideration are functions of the total ion activities of the solutions.

This conclusion is also good indirect substantiation of the principle used by Bjerrum[1] and mentioned by Ming Chow[2] that "the activity coefficient, F_a/c, of uni-univalent ions of largely ionized substances is in general a function of the total salt or ion concentration, and not of its own concentration."

The above principles must have an important bearing on the phenomenon of the "neutral salt effect." In a previous communication,[3] the author has shown that the increase in velocity constant in hydrogen ion, and iodine ion catalysis, produced by the addition of a neutral salt (a chloride) is a function of the square root of the activity product of the ions of the added salt.[4] In other words, the "neutral salt effect" on catalysis in liquid systems was shown to be function of the total ion activity and not of the activity of the catalyzing ion.

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[1] *Loc. cit.*

[2] Ming Chow, THIS JOURNAL, 42, 447 (1920).

[3] *Ibid.*, "Neutral Salt Catalysis," 40, 1462 (1918).

[4] This was termed the chlorine ion activity at that time because the assumption of the individual activities of the ions was not known or used when that paper was written.

The question as to the underlying causes of this effect is an obscure one. The increase in activity of the hydrogen ion of hydrochloric acid by the addition of neutral salts has been assumed to be due, first, to the high hydration of the hydrogen ion,[1] second to the hydration of the ions of the added salts.[2] In view of the fact of the evidence in favor of the hypothesis of MacInnes, and the principle above relating to the decrease in heat content of transfer of the hydrogen ion, it is the belief of the author that these views will have to be modified or abandoned after a still deeper investigation of the phenomenon is made. The main point of interest is that the increase in activity coefficient of the hydrogen ion in solutions of hydrochloric acid on the addition of salts is probably due to this decrease in heat content function of transfer of the hydrogen ion caused by salt addition. Indirectly, ionic hydration will unquestionably have an effect. The fact that the hydrogen ion has a positive and the chlorine ion a negative decrease in heat content function of transfer indicates a fundamental difference in the behavior of these ions, and must receive an explanation before the problem of the "neutral salt effect" can be adequately solved.

Final Considerations.

The present investigation of the thermodynamic properties of concentrated solutions of strong uni-univalent electrolytes and their mixtures leads to verifications and conclusions which may be stated briefly as follows:

(1) The hypothesis of complete dissociation of strong electrolytes promulgated by Milner, Ghosh, Bjerrum and others is a good working hypothesis.

(2) The hypothesis of independent activity coefficients is also tenable.

(3) The hypothesis of MacInnes "that in solutions of the same strength of different electrolytes containing a common ion, the common ion will have the same activity independent of the ion or ions associated with it" is true or very nearly true for the chlorine ion in the solutions investigated in the present research.

(4) At a given concentration of a solution of potassium chloride, the potassium ion and the chlorine ion have the same activity.

(5) The activity coefficient of an ion is a function of the total ion concentration or activity, and not a function of its own concentration.[3]

(6) The hypothesis that the ions of strong electrolytes have independent heat content increments of transfer is probably a good approximation.

(7) It is also probable that the heat content increment of transfer of

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[1] Bjerrum, *loc. cit.*

[2] Poma, *Z. physik. Chem.*, 87, 197 (1914); 88, 671 (1914); Harned, *loc. cit.*; Thomas and Baldwin, THIS JOURNAL, 41, 1981 (1919).

[3] Bjerrum, *loc. cit.*; Ming Chow, *loc. cit.*

the potassium ion is identical with the heat content increment of transfer of the chlorine ion.

(8) The increment in heat content of transfer of an ion is a function of the total ion concentration or activity and not of its own concentration.

(9) The so-called "neutral salt effect" in hydrochloric acid—uni-univalent salt mixtures is probably due to the large decrease in the heat content function of transfer of the hydrogen ion caused by the addition of the salt and not to the high hydration of the hydrogen ion.

Summary.

(1) Measurements of the electromotive forces of the cells

$$H_2 \mid MeCl\ (c)\ \text{in}\ HCl\ (0.1) \mid HgCl \mid Hg$$

at 18°, 25°, and 30° containing potassium, sodium and lithium chlorides, respectively, have been made.

(2) Assuming the complete dissociation of the above electrolytes, it is shown that the hypothesis of the individual ion activities as postulated by MacInnes is true within narrow limits, and, that, at a given concentration of potassium chloride, the potassium and chlorine ion activities are identical within narrow limits.

(3) The individual ion activity coefficients of the hydrogen, potassium, sodium, lithium, and chlorine ions from concentrations 0.1 to 3 M have been computed.

(4) The activity coefficients of the hydrogen ion in solutions containing potassium, sodium, and lithium chloride up to 3 M concentration have been computed.

(5) It has been shown that the semi-empirical formula

$$\log F_a = \alpha c - \beta c^m$$

where F_a is the activity coefficient of the ion, c the concentration, and α, β, and m are constants, will express F_a as a function of c within experimental error from 0.01 to 3 M concentration.

(6) A table of the free energies and heat content decreases of the cell reaction

$$H_2 + 2HgCl = 2HCl\ (0.1) + 2Hg$$

in the presence of potassium, sodium, and lithium chlorides, respectively, has been compiled.

(7) On the assumptions that the ions have independent heat contents of transfer, and that, at a given concentration of potassium chloride, the potassium and chlorine ions possess identical heat contents of transfer from a solution of concentration c_1 to a solution of concentration c_2, it becomes possible to compute the decrease in heat content of transfer of the hydrogen ion from solutions of MeCl (c) in HCl (0.1) to HCl (0.1). The results of this calculation have been tabulated.

(8) The decrease in heat content of transfer of the hydrogen ion from MeCl (c) in HCl (0.1) to HCl (0.1) is shown to be a function of the total ion activity of the solution, and not of the activity of the hydrogen ion.

PHILADELPHIA, PA.

THE IONIZATION POTENTIAL OF HYDROCHLORIC ACID AND THE ELECTRON AFFINITY OF CHLORINE.[1]

BY PAUL D. FOOTE AND F. L. MOHLER.

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There are several means conceivable whereby a molecule of hydrogen chloride may be ionized.

1. The structure of the molecule might remain intact, the molecule as a whole losing an electron, as in the case of an atom of monatomic metal. This would require the existence of positively charged molecules of hydrogen chloride. The work of Aston[2] on positive ray analysis indicates that such *may be* the case. In discharge through phosgene containing hydrogen chloride, he found that ions were present of mass 35, 36, 37 and 38, and identified these as due to the 2 isotopes of chlorine and their corresponding acids.

2. We have shown[3] that in the case of hydrogen our experimental data lead to the conclusion that the hydrogen molecule may be ionized by dissociation into atoms and ionization of one atom. If hydrogen chloride were similar to hydrogen in this respect, the ionization might result in a positively charged hydrogen atom and a neutral chlorine atom. The work required to ionize thus a gram molecule of hydrogen chloride may be computed in the following manner.

Let Q_{HCl} = heat of formation of one gram mol. of HCl from the diatomic gases H_2 and Cl_2.

D_H = $^1/_2$ the heat of dissociation of a gram mol. of H_2 into monatomic hydrogen.

D_{Cl} = $^1/_2$ the heat of dissociation of a gram mol. of Cl_2 into monatomic chlorine.

Accordingly,

$$\begin{aligned} HCl + Q_{HCl} &= {}^1/_2H_2 + {}^1/_2Cl_2 \\ {}^1/_2H_2 + D_H &= H \\ {}^1/_2Cl_2 + D_{Cl} &= Cl \end{aligned}$$

Adding
$$HCl + Q_{HCl} + D_H + D_{Cl} = H + Cl.$$

The quantity $Q_{HCl} + D_H + D_{Cl}$ is the work required to dissociate a gram mol of hydrogen chloride into neutral monatomic hydrogen and

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[1] Published by permission, Director Bureau of Standards.

[2] Aston, *Phil. Mag.*, 39, 611 (1920).

[3] Mohler and Foote, *J. Opt. Soc. Am.*, 4, 49 (1920).

chlorine. To this must be added the work required to ionize a gram atom of hydrogen, J_H. We thus obtain for the work, J_{HCl}, necessary to ionize a gram mol. of hydrogen chloride, the following expression,

$$J_{HCl} = J_H + Q_{HCl} + D_H + D_{Cl}.$$

All the terms on the right are known. The ionization potential of monatomic hydrogen is 13.5 volts. To express this in kilogram calories per gram atomic weight we use the relation,

$$\text{kilogram calories} = 23.1 \times \text{volts}$$

whence

J_H = 312 kilogram calories
Q_{HCl} = 22 (Liddell's Handbook)
D_H = 45 (Langmuir)
D_{Cl} = 56 (Pier)

Thus, on adding, $J_{HCl} = 435$ kilogram calories per g. mol. ∞ 18.8 volts per molecule.

3. An atom of chlorine is believed to possess an affinity for an electron. That is, a neutral chlorine atom readily unites with an electron so that an amount of energy E must be expended on the negative ion to reduce it to a neutral condition. Until recently, no method was known for determining the magnitude of the quantity E. Born, Fajans and others[1] have lately arrived at a numerical estimate of E through a somewhat complicated and abstract process of reasoning. In order to make our discussion of this work clear, it is necessary to indicate briefly the method pursued by Born.

The compressibility of a crystal of a halogen salt of a monatomic metal may be fairly well explained quantitatively on the assumption that in addition to the ordinary Coulomb force of repulsion or attraction, between the charges on the ions forming the crystal structure, there exists between 2 ions a repulsive force, the potential of which is inversely proportional to the 9th power of their distance apart.

It is accordingly possible to compute the potential energy of the crystal system. The negative of this, U, referred to a mol of the crystal, is the work which must be done on a gram molecular weight of the crystal to convert it into free positive and negative ions. Born finds

$$U = \frac{Na}{4\delta}\,\frac{n-1}{n}$$

where a is a universal constant, N = Avogadro's number, $n = 9$ for alkali salts (except lithium, where $n = 5$), and δ is the grating space of the simple cubic crystal, *i. e.*, the distance between like atoms measured along the edge of an elementary cube. This is readily com-

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[1] See series of papers in *Verh. deut. physik. Ges.*, 1918 and 1919.

puted from the molecular weight, density, and Avogadro number. In this manner we may obtain a table of values of U for a large number of salts. The heats of formation Q of the salts are tabulated in any chemical handbook.

Let E = electron affinity in kg. cal. of the halogen atoms per g. atom.
J = ionization potential in kg. cal. of the neutral metal atoms per g. atom.
D = heat of dissociation per $^1/_2$ g. mol. of diatomic halogen gas.
D' = latent heat of sublimation of the metal per g. atom.

The work required to dissociate a gram atom of solid metal into free ions and electrons is accordingly $D' + J$, while the work required to dissociate $^1/_2$ g. mol. of diatomic halogen gas, in an atmosphere of electrons, into negatively charged ions is $D - E$. Hence, the heat of formation, for example, of sodium chloride crystal per g. mol. may be expressed as follows:

$$Q_{\mathrm{NaCl}} = -D'_{\mathrm{Na}} - J_{\mathrm{Na}} - D_{\mathrm{Cl}} + E_{\mathrm{Cl}} + U_{\mathrm{NaCl}}$$

The values of J for the alkali metals are known from our experimental work[1] to be accurately determined by the quantum relation $h\nu = eV$, where ν is the limit of the principal series of each metal in question. Born has shown that the value of D' for all the alkali metals is about 20 kg. cal. Hence, the above equation may be solved for E_{Cl}, the only unknown. Proceeding in a similar manner for other chlorides, it is found that the same value of E_{Cl} is obtained, thus substantiating the theory. The mean value of E_{Cl} per g. atom was computed as 119 kg. cal., or expressed in volts and referred to a single atom, 5.2 volts.

The second possible method for ionizing hydrogen chloride described above assumed the dissociation into hydrogen ion and neutral chlorine atom. If chlorine possesses an affinity for electrons, the chlorine atom might readily attach an electron to itself, since in the process of ionization, 2 electrons are present, the impacting electron and the electron ejected from the hydrogen atom. The ionization of hydrogen chloride would accordingly ultimately result in hydrogen ion and chlorine ion, but the energy disappearing when the chlorine atom becomes negatively charged would not by Method 2 have any effect upon the measured ionization potential of hydrogen chloride. Under such conditions, it should be radiated as a quantum of energy $eE = h\nu$, and the wave length, λ = 2400Å might be detected spectroscopically (if existing).

Born, Fajans, and others are of the opinion, however, that the gain in energy by the production of the negative chlorine atom assists in the ionization of hydrogen chloride. On this basis, the collision of an electron of sufficient velocity with the hydrogen chloride molecule, results in the immediate production of a positively charged atom of hydrogen and a

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[1] Foote, Rognley and Mohler, *Phys. Rev.*, 13, 59 (1919).

negatively charged atom of chlorine. A mechanical picture of the phenomenon readily suggests itself. The molecule of hydrogen chloride may be represented structurally by $H^+ — Cl^-$, and the ionization accordingly consists in a splitting apart of the 2 ions or in a disruption of the bond holding the 2 ions together. The work necessary to accomplish this, deduced in a manner similar to that outlined above, gives the following relation for the ionization potential:

$$J_{HCl} = J_H + Q_{HCl} + D_H + D_{Cl} - E_{Cl}$$

or

$$J_{HCl} = 312 + 22 + 45 + 56 - 119 =$$
$$316 \text{ kg. cal./g. mol. wt.} \backsimeq 13.7 \text{ volts/molecule.}$$

Born uses slightly different values for some of the above constants and obtains $J_{HCl} = 13.9$ volts, while Fajans computes 14.0 volts. This value is so close to the ionization potential of hydrogen, 13.5 volts, that every precaution must be taken to preclude the production of hydrogen by ordinary chemical reaction in the ionization tube.

Experimental.

The hydrogen chloride was generated by dropping hydrochloric acid into conc. sulfuric acid. This was passed through calcium chloride and a trap cooled to about —55° to eliminate water vapor, and then was allowed to stream through the ionization chamber. A similar trap was mounted between the ionization chamber and condensation pumps in order to reduce the vapor pressure of mercury. In a few cases the experiments were made with the vapor stagnant instead of streaming.

The ionization chamber was of the 4-electrode type, consisting of a hot wire with a cylindrical net surrounding it and at some distance a second concentric cylindrical net and outer cylinder. The electrodes were of platinum and hot cathodes of both platinum and molybdenum were employed since the latter could be operated at considerably higher temperatures and thus furnish a much larger electron current. The inleading wires were of tungsten sealed to Corning glass GT70–702P–Pyrex, and all metal joints were made either by welding or in some cases, by means of gold. Ordinary silver solder is readily attacked by the vapor.

The general methods of measurement have been discussed in papers on metallic and non-metallic vapors and gases.[1]

We were unable to show that hydrogen chloride possesses a resonance potential, a property exhibited by all of the other materials so far investigated. Two methods were employed to detect ionization.

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[1] Tate and Foote, *Phil. Mag.*, 36, 64 (1918); Bur. Standards *Sci. Paper*, 317; *J. Washington Acad. Sci.*, 7, 517 (1917); Foote and Mohler, *Phil. Mag.*, 37, 33 (1919); Foote, Rognley, and Mohler, *Phys. Rev.*, 13, 59 (1919); Mohler, Foote and Stimson, Bur. Standards *Sci. Paper*, 368; Mohler and Foote, "Non-Metallic Vapors and Gases." Bur. Standards *Sci. Paper* (in press); *J. Opt. Soc. Am.*, 4, 49 (1920).

1. The electrons were accelerated between the hot wire and inner net by a potential difference *V*. A portion of these passed through the net into the space between the 2 nets which were maintained at the same potential, and if of sufficient velocity, produced ionization. The positive ions diffused into the space between the outer net and cylinder which were connected through a galvanometer to a potential of such magnitude and sign that no electrons could pass through. The galvanometer accordingly showed zero deflection as the accelerating voltage was increased, until this reached the ionization potential, at which point an ionic current is observed.

2. The second method was that of Davis and Goucher, the details of which have been described in their paper.[1]

In order to correct for the velocity distribution of electrons, voltage drop along the cathode, polarization films, etc., velocity-distribution curves were obtained, using the apparatus as a 3-electrode tube, the outer net and cylinder being connected together. It is necessary to plot these curves on the proper coördinate scale, such that the galvanometer pos-

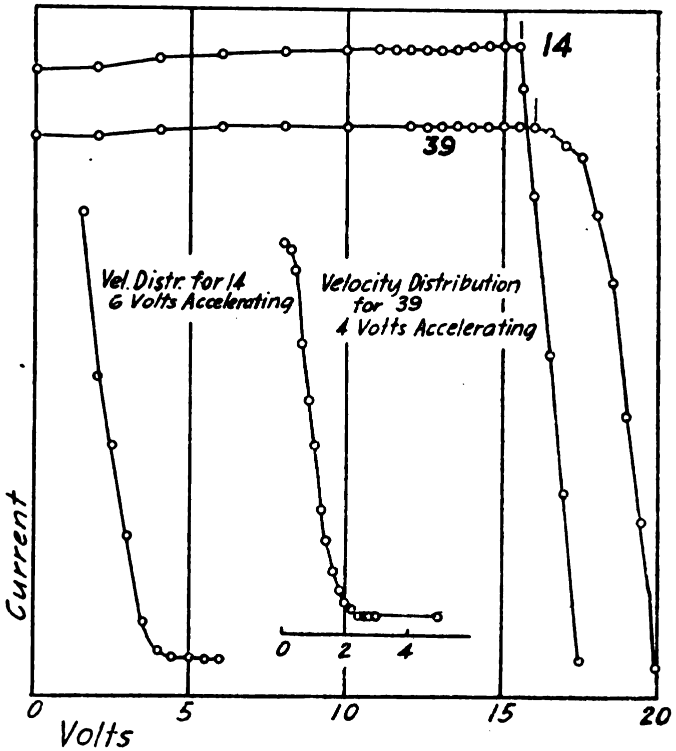

Fig. 1—Typical ionization and velocity distribution curves.

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[1] Davis and Goucher, *Phys. Rev.*, 10, 101 (1917).

sesses the same sensitivity to ions formed above the ionization potential and to electrons emitted much more copiously at low accelerating voltages with the 3-electrode tube. Typical curves are illustrated in Fig. 1.

Table I summarizes the data for hydrogen chloride, giving observed or applied potentials at ionization, initial potential corrections as determined by the velocity distribution curves, vapor pressure, and corrected values for the ionization potential. The final mean is 14.0 volts with a probable error of 0.2 volt. If we omit all data obtained on humid days when the electrical leaks were troublesome and use only those determined from curves 10, 14, 18, 21, 29, 34, 36, 38 and 40, the mean value is still 14.0 volts with a probable error of 0.1 volt.

TABLE I.

Ionization Potential of Hydrogen Chloride.

Curve.	Pressure. Mm.	Applied potential at ionization.	Initial potential.	Ionization potential.	Method.
2	0.15	13.0	—0.5	12.5	1
5	0.15	14.0	—0.7	13.3	1
10	0.33	16.0	—1.5	14.5	1
14	0.33	15.6	—1.5	14.1	1
18	0.45	16.0	—1.5	14.5	1
21	1.60	15.0	—1.5	13.5	1
25	0.20	15.6	—1.1	14.5	2
28	0.20	16.0	—1.1	14.9	2
29	0.25	14.0	—0.7	13.3	1
30	0.25	16.5	—1.0	15.5	2
31	0.25	14.0	—0.6	13.4	2
34	0.50	16.0	—2.0	14.0	1
36	0.40	15.2	—1.6	13.6	1
38	0.30	15.0	—1.2	13.8	1
39	0.30	16.0	—1.6	14.4	1
		Mean,	...	14.0 Volts	

As this value is close to that determined by us for atomic hydrogen, it is necessary to show that the ionization potential of hydrogen chloride was actually observed. If a liquid-air trap be connected to the ionization tube, thus condensing the hydrogen chloride, the characteristic ionization disappears, showing that the effect is not due to hydrogen produced by ordinary chemical reaction. This is illustrated in Fig. 2. A pressure of hydrogen chloride equivalent to 1.6 mm. of mercury was admitted to the ionization chamber and the apparatus sealed. With the trap maintained at —50°, Curve 21 was obtained. After some time the trap was cooled in liquid air and Curve 24, plotted to the same scale of sensitivity was secured. The pressure as shown by the manometer was 0.007 mm., about the order of magnitude of the vapor pressure of hydrogen chloride at this temperature. Only a trace of ionization is present, which may be accounted for by this small pressure of hydrogen chloride.

A further proof that the ionization was not due to hydrogen, which is produced to some extent from dissociation by the hot cathode, is the fact that no visible arc could be detected, even with ionization currents of a magnitude at which hydrogen shows a fairly brilliant discharge.

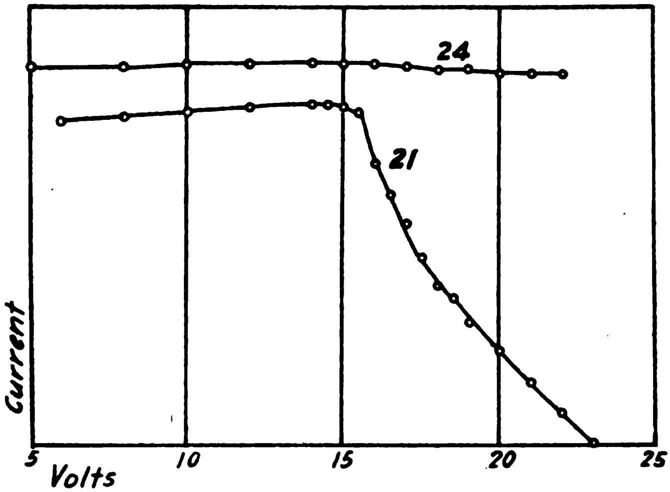

Fig. 2—Curve 21 obtained without liquid air; Curve 24 with liquid air.

A still further confirmation that the inelastic collisions taking place between the 2 nets did not occur with hydrogen is the fact that by the Davis and Goucher method no radiation could be detected below 14.0 volts, while at this voltage and at high pressure, thus permitting a rapid rate of recombination between hydrogen ion and chlorine ion, the radiation, measured photo-electrically, was pronounced. If many, collisions occurred with hydrogen, radiation would have appeared at 10.1 volts, the resonance potential of monatomic hydrogen.

We are, therefore, led to the conclusion that but one type of inelastic impact of electrons and molecules occurs in hydrogen chloride. This results in ionization, and the velocity of the impacting electron must be that developed in falling through a potential difference of 14.0 volts.

Conclusions.

The experimental results indicate that ionization of hydrogen chloride takes place according to Method 3, outlined above. The hydrogen chloride molecule consists of a positively charged hydrogen atom and a negatively charged chlorine atom bonded together, and the ionization simply disrupts this bond. The work necessary to ionize a gram mol of hydrogen chloride is accordingly the work of ionizing a gram atom of hydrogen plus the heat of formation of hydrogen chloride plus the heat of dissociation of 0.5 gram mol. of hydrogen plus the heat of dissociation of 0.5 gram mol of chlorine minus the electron affinity of a gram atom of chlorine. This, expressed in volts and referred to a single molecule is 13.7 volts, in excellent agreement with the experimentally determined value of 14.0 volts.

Our experiments accordingly afford a surprising confirmation of the theories of Born, Fajans and others, showing that their deductions on the magnitude of the electron affinities of the halogens from the grating energies of their crystalline salts is well founded. Were it not for the electron affinity of chlorine, hydrogen chloride would ionize at about 18.8 volts, far greater than the observed value. Hence, our value of 14.0 volts leads to an experimental determination of the electron affinity of chlorine expressed by the relation $E_{Cl} = 18.8 - 14.0 = 4.8$ volts.

Hydrogen chloride is known to possess no characteristic visible or ultra-violet spectrum, in agreement with natural consequence of the above observed peculiar type of ionization and the observed non-existence of a resonance potential. Any radiation emitted which is characteristic of hydrogen chloride would be produced by the union of hydrogen ion and chlorine ion, giving rise to a quantum of $h\nu = eV$, where V is 14.0 volts. The corresponding wave length in the extreme ultra-violet is $\lambda = 880$Å, radiation which might be observed, although the experimental difficulties would be considerable.

Since positively charged hydrogen atoms are formed on ionization of hydrogen chloride, we might expect that on recombination a portion of these atoms would attach electrons to themselves instead of chlorine ions, thus giving rise to the spectrum of monatomic hydrogen. Hydrogen atoms might combine to form molecules so that some molecular hydrogen is likely produced as a result of electronic impact in hydrochloric acid vapor. A high voltage discharge through hydrogen chloride shows the ordinary spectrum of hydrogen.

It is interesting to note that, as predicted by Haber, the attraction between a hydrogen nucleus and a halogen ion is about the same as the attraction between the hydrogen nucleus and the electron in the neutral hydrogen atom.

BUREAU OF STANDARDS,
WASHINGTON, D. C.

NOTE.

Correction.—In the article entitled "Reactions of β,β'-Dichloro-ethyl sulfide," appearing in the June, 1920, number of THIS JOURNAL, the following corrections should be made: on p. 1221, in the table, the boiling point should read, 222–3° *at 21 mm.*, and the melting point given as 101° should read, 171°; and on p. 1223, in the table, the boiling points should read, respectively, 173–5° *at 21 mm.*, 193–5° *at 22 mm.*, 223–3° *at 21 mm.*, and 170° *at 4 mm.* These errata should also appear in the Summary.

O. B. HELFRICH

[Thirty-Second Contribution from the Color Laboratory, U. S. Bureau of Chemistry.]

SYNTHESES OF *s*-XYLIDINE.

By Herbert L. Haller and Elliot Q. Adams, with optical measurements by Edgar T. Wherry.

Received April 27, 1920.

It is well known that *s*-xylidine is the only one of the isomeric xylidines absent from commercial xylidine. It has been prepared from *m*,4-xylidine by successive steps involving acetylation, nitration, saponification, deamination and reduction. As a starting point in the preparation of derivatives of quinoline, it became necessary to secure *s*-xylidine absolutely free from its isomers. Since, in its preparation from *m*,4-xylidine, the utmost care might fail to insure this, a synthesis starting with mesitylene was undertaken. Mesitylene was oxidized to mesitylenic acid, changed to the amide and finally converted to *s*-xylidine by means of Hofmann's reaction. The synthesis from *m*,4-xylidine, although consisting of as many steps as involved in the foregoing process, is more satisfactory for the preparation of considerable amounts of material on account of the consistently higher yields. We found it possible to eliminate one operation from the procedure given[1] for this synthesis.

Experimental Part.

I. The Preparation of *s*-Xylidine from Mesitylene.

Mesitylene was prepared in the usual manner by the condensation of acetone with the aid of sulfuric acid. We found that the directions of Orndorff and Young[2] gave the most satisfactory results. After steam distillation, the crude mesitylene was washed with alkali and water, dried over calcium chloride and distilled. To remove sulfur compounds the distillate was refluxed with sodium and redistilled. The portion which distilled up to 175° was subjected to fractional distillation, and the fraction boiling from 160° to 167° was oxidized to mesitylenic acid.[3]

Mesitylenic Acid.—Fifty g. of mesitylene, 80 cc. of conc. nitric acid (sp. gr. 1.47) and 240 cc. of water were heated under a reflux condenser for 22 hours on a sand bath. The solution was then cooled in ice and the precipitated solid removed by filtration. The crude mass was dissolved in alkali, and the alkaline solution extracted with ether. The filtrate was also rendered alkaline and extracted with ether. From these ether extracts 10 g. of mesitylene was recovered. The alkaline solution containing the mesitylenic acid was acidified with hydrochloric acid, filtered, and the precipitate subjected to steam distillation. To remove nitro com-

[1] C. Willgerodt and F. Schmierer, *Ber.*, **38**, 1472 (1905).

[2] W. R. Orndorff and S. W. Young, *Am. Chem. J.*, **15**, 249 (1893).

[3] R. Fittig, *Ann.*, **141**, 144 (1867). In this article the proportions of acid and mesitylene are not given, and the concentration of nitric acid used is higher than we have found desirable.

pounds, the product obtained by steam distillation was heated under a reflux condenser for several hours with tin and conc. hydrochloric acid, after which the undissolved solid was recrystallized from 50% alcohol. The yield was 9.7 g.

Mesitylenic Amide.—The conversion of mesitylenic acid to the acid chloride[1] was brought about by warming it gently with phosphorus pentachloride. After the phosphorus oxychloride had been distilled, the reaction mixture was poured into ice-cold conc. ammonia. The amide separated by filtration was washed with dil. ammonia, and recrystallized from water.

Conversion of Mesitylenic Amide with *s*-Xylidine.—The amide was verted to *s*-xylidine by means of sodium hypobromite. To a solution of 95 g. of sodium hydroxide in 400 cc. of water and cooled to 5°, 90 g. of bromine was added slowly. Forty g. of the amide was made into a paste with a 10% solution of sodium hydroxide. While the hypobromite solution was stirred, the amide was added slowly; finally the mixture was distilled with steam. The distillate was extracted with ether, the extract dried over calcium chloride and distilled. The yield of *s*-xylidine was 19 g.

The amine was converted into the acetyl derivative by heating it for half an hour on the steam-bath with an equal weight of acetic anhydride. The product was poured into water, the *s*-acet-xylide collected and recrystallized 6 times from 95% alcohol. The melting-point was 139.6° to 140.2°.

II. The Preparation of *s*-Xylidine from *m*-4-Xylidine.

To obtain *m*,4-xylidine, from commercial xylidine, it was treated with glacial acetic acid and the mixture allowed to stand for 24 to 48 hours.[2] The acetate which formed was filtered and recrystallized from ether. Acetylation was effected with acetic anhydride in the usual manner and the product was recrystallized from alcohol. The acet-nitro-xylide was prepared by adding the acet-xylide in small portions to "red" fuming nitric acid[3] (sp. gr. 1.55 to 1.57) while the mixture was stirred and the temperature was kept between 0° and 5°. After the addition of all the acet-xylide, the reaction mixture was poured into ice-water, the precipitated acet-nitro-xylide immediately filtered, washed well with water and recrystallized from alcohol.

We have found it possible to prepare the nitro-xylene directly from nitro-acet-xylide. For this purpose 50 g. of nitro-acet-xylide was added

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[1] R. Fittig and W. H. Brueckner, *Ann.*, 147, 47 (1868).

[2] W. R. Hodgkinson and L. Limpach, *J. Chem. Soc.*, 77, 65 (1900).

[3] Nitrous fumes were generated by dropping conc. sulfuric acid into a concentrated solution of sodium nitrite and were passed into C. P. fuming nitric acid (sp. gr. 1.50) to the point of saturation.

to 50 g. of sulfuric acid (sp. gr. 1.84) and heated at 125° for 15 minutes. The reaction product was poured into a mixture of 300 g. of 95% ethyl alcohol and 150 g. of conc. sulfuric acid, cooled to 5°, and then diazotized with 30 g. of sodium nitrite in conc. water soln. Copper powder was added to catalyze the reaction, after which the solution was distilled with steam. The yield of the nitro-xylene was 35 g. The nitro-xylene was recrystallized from alcohol.

To a solution of 150 g. of stannous chloride in 200 g. of hydrochloric acid (sp. gr. 1.19), the nitro compound was added in small portions. Heat was necessary to start the reaction. After the addition of all the nitro-xylene, the reaction mixture was heated on the steam bath for an hour, diluted, cooled, made alkaline, and distilled with steam. The yield of *s*-xylidine was 15 g.

The acetyl derivative was prepared and purified as already described for the *s*-acet-xylide from mesitylene. The melting-point was 139.6° to 140.2°. Samples of the 2 preparations and of their mixture were attached to the same thermometer and all 3 softened and melted within 0.1° of one another.

Optical Properties (by Edgar T. Wherry). When studied by the immersion method under the microscope, these preparations have identical properties, as follows.

Habit: plates, rather irregular in outline, and often overlapping. System: apparently monoclinic, with clinopinacoid prominent.

Refractive indices (D): $\alpha = 1.45$, β-indeterminate, $\gamma = 1.69$, $\gamma - \alpha = 0.24$.

As seen in polarized light, nicols crossed: Colors around 2nd order; the overlapping and stepped variation in thickness of the plates producing striking mosaic effects; elongation negative; extinction angle (on edges most frequently present) 12°.

In convergent polarized light, nicols crossed: Shows no definite interference figures, the optic normal being apparently perpendicular to the surfaces of the plates.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA.]

PARA CYMENE AS A SOLVENT.

BY A. S. WHEELER.

Received May 22, 1920.

Until the discovery was made that spruce turpentine, a by-product of the manufacture of spruce pulp by the sulfite process, consisted largely of *p*-cymene this hydrocarbon was not available as an ordinary solvent. The price is now so much lower that it shuold be placed on the regular list of solvents.

Cymene assumes an important position as a solvent because it is a hydrocarbon of high boiling-point and, where possible, is to be preferred to such colored solvents as aniline or nitrobenzene, or an ill-smelling solvent such as pyridine. Cymene boils at 176.5° and in point of availability comes next to xylene in the benzene series. It should be useful as a simple solvent or in mixed solvents and in molecular weight determinations where the elevation of the boiling-point method is employed. The solubilities of a variety of types of compounds in it have been determined and the results are given below. Owing to the method used the first group (Table I) are of moderate accuracy only.

Purification of Cymene.—Considerable work was done in searching for the best method of isolating the cymene from spruce turpentine. A very large yield was readily obtained from spruce turpentine made at Canton, N. C., where a moderate temperature was employed in digesting the spruce wood but this supply gave out and the spruce turpentine obtained from Erie, Pa., was a darker product and contained larger quantities of substances other than cymene.

The removal of sulfur dioxide was the first problem. Several methods were available: (1) extraction with water which is too slow and laborious; (2) the dioxide could be boiled out successfully, but explosions will sometimes occur; (3) shaking with dilute sodium hydroxide removes it, but produces a precipitate difficult to handle; (4) shaking with lime, 150 g. per 3000 cc., also causes a troublesome precipitate, although Andrews[1] has adopted this method; (5) hot air drawn through the turpentine readily removes the dioxide; (6) air of the ordinary temperature drawn through five gallons removes the sulfur dioxide completely in 10 hours. The volume diminishes 5%. This method needs no attention and is the best of any.

The turpentine was then submitted to distillation with super-heated steam, in apparatus arranged so that the vapors passed first through a 30% solution of sodium hydroxide and then into the condenser. As suggested by Professor R. H. McKee in a private communication, 3 fractions were collected : (1) 16%; (2) 50%; (3) 16%. The non-volatile residue made up the remainder of about 18%. In this laboratory we have obtained such an excellent yield of 2-bromocymene from pure cymene that I propose to test the quality of these fractions by brominating them.

To determine the next step in the purification, the following experiments were tried: the distillate was shaken (1) with a solution of sodium plumbate; (2) with a 0.5% solution of potassium permanganate; (3) it was boiled in a stream of hydrogen with copper chloride upon pumice stone; (4) it was boiled with metallic sodium; (5) it was shaken with conc. sulfuric acid. This acid attacks the impurities but also sulfonates the cymene even at ordinary temperature. We have completely sulfonated cymene at room temperature by shaking it for a week with conc. sulfuric acid. Schorger[2] states that pure cymene is not colored by sulfuric acid, but I have not been able to confirm this observation, neither

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[1] U. S. patent 1,314,920, *C. A.*, 13, 2765 (1919).

[2] THIS JOURNAL, 39, 2672 (1917).

has Professor McKee, according to a private communication. The distillate was purified by shaking it with a 5% solution of sodium hydroxide and then distilling it over metallic sodium. Young's most complex still head of 5 sections facilitated fractionation. Pure cymene boils at 176–176.5° and has a refractive index of 1.4905 at 12.5°.

These studies were carried out with the aid of Messrs. T. P. Dawson, J. S. Murray and R. H. Sawyer, senior students in Chemistry.

Solubility Determinations.

The following methods were employed to determine the solubilities given in Table I which are of moderate accuracy. For temperatures below 30°, the solid was shaken with the cymene for an hour, then allowed to stand somewhat longer when the solution was filtered into a dish of known weight. The temperatures were room temperatures. For solubilities at 30° the solid and cymene were placed in a tube immersed in a thermostat and stirred mechanically. The solution was drawn into another tube also in the thermostat. For solubilities at 100° a known

TABLE I.

Substance.	Temp. ° C.	Grams in 100 g. of cymene.	
Acetanilide	30	7.23	Dawson
Anthracene	25	1.57	Murray
	30	1.72	Murray
	100	9.24	Murray
	176	98.60	Murray
Antipyrine	30	2.09	Murray
Caffeine	25	0.76	Dawson
	30	1.10	Dawson
	100	1.74	Dawson
	175	15.58	Dawson
d-Camphoric acid	100	1.53	Dawson
Hexachloro-benzene	23.5	2.93	Sawyer
	100	16.77	Sawyer
	176	106.95	Sawyer
Naphthalene	30	14.22	Dawson
β-Naphthylamine	30	8.63	Dawson
o-Nitro-aniline	30	6.33	Dawson
m-Nitro-aniline	30	1.36	Murray
p-Nitro-aniline	25	0.83	Sawyer
Phloroglucinol	175	0.12	Dawson
Strychnine	30	0.71	Sawyer
	100	0.95	Sawyer
Tartaric acid	27	Insol.	Sawyer
	100	Nearly insol.	Sawyer
Thio-urea	25	Insol.	Sawyer
	100	Nearly insol.	Sawyer
Thymol	25	113.85	Dawson
Urea	27	Insol.	Sawyer
	100	Nearly insol.	Sawyer

weight of substance was placed in a test-tube which was heated by boiling water. Cymene was cautiously added from a buret until complete solution took place. An oil bath was used for higher temperatures. In all cases the solution was placed in a desiccator through which air was drawn. The evaporation was extremely slow and, in view of the danger of sublimation, the results are not as accurate as might be desired.

It was possible to attain greater accuracy in the case of acids since these could be titrated. The temperature adopted was 25°. A saturated solution was first made at 40° and this was placed in a thermostat carefully regulated to within 0.1°. The apparatus of Pawlewski[1] was used for stirring the solution and for transferring it under water. The solution and separated crystals were stirred for half an hour and then drawn over through a filter paper into the weighing tube. The solution was weighed and then transferred to a flask with the aid of a little alcohol. Water was added and the solution was titrated against 0.05 *N* sodium

TABLE II.

Normality of NaOH, 0.0486.

No.	Weight of sample. G.	NaOH. Cc.	Grams in 100 g. of cymene.
Benzoic acid.			
1	3.8445	39.9	6.545
2	4.1514	42.9	6.532
3	2.8170	28.97	6.500
Succinic acid.			
1	6.5898	0.475	0.020
2	4.8862	0.375	0.022
3	6.1368	0.425	0.020
Anthranilic acid.			
Normality of NaOH, 0.04676.			
1	4.7168	5.45	0.746
2	6.3264	7.25	0.740
3	9.3118	10.775	0.747
Citric acid.			
1	9.5310	1.05	0.036
2	10.9468	1.10	0.032
3	11.4490	1.50	0.034
Picric acid.			
1	4.6383	11.05	2.536
2	4.7848	11.40	2.618
3	5.6180	13.35	2.611
Phthalic acid.			
1	11.7587	0.80	0.026
2	12.1394	0.90	0.028
3	11.9753	0.75	0.024
Salicylic acid.			
1	5.5047	8.35	0.989
2	5.5831	8.45	0.986
3	6.9183	10.35	0.975

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[1] *Ber.*, 32, 1040 (1899).

hydroxide solution which had been standardized against benzoic acid.[1] Each acid was carefully purified. Benzoic acid was recrystallized from alcohol and then sublimed. Anthranilic, citric, picric, salicylic and succinic acids were recrystallized from hot water. Phthalic acid was recrystallized from hot water and also reprecipitated from its sodium salt.

These solubility experiments with the acids were carried out by H. M. Taylor, Senior student in Chemistry.

A Color Reaction.—In working with certain samples of cymene, it was observed that they turned red rather quickly when they contained *p*-anisidine in solution. The amount of *p*-anisidine used was small, about one part in 500. A study of this phenomenon developed the fact that a perfectly pure cymene does not change color, at least within 2 hours, if exposed to a moderate light. Impure cymene will turn pale yellow, deep yellow, pale red or deep red according to the degree of impurity or to the time of action. A strong light, especially sunshine, facilitates the development of the color. Coloration also occurs in the dark. It may be added that solutions of *p*-anisidine in other solvents also develop a color.

CHAPEL HILL, N. C.

[CONTRIBUTIONS FROM BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE.]

CRYSTALLINE CHLOROTETRACETYL FRUCTOSE AND RELATED DERIVATIVES.[2]

BY D. H. BRAUNS.

Received May 28, 1920.

The acetates of fructose have been obtained crystalline only by applying a principle which differs materially from the ordinary methods of acetylation. This principle consists in the action of acetylating agents on *finely powdered fructose at a low temperature* (*below* 0°).[3] The present communication deals with the use of these stable crystalline *acetates* as starting material for the preparation in the crystalline state of other derivatives of fructose.

Crystalline β-penta-acetyl or tetra-acetyl fructose in chloroform solution gives with phosphorus pentachloride and aluminum chloride a crystalline substance which has proved to be one of the isomeric forms (probably α-) of chloro-tetra-acetyl fructose. With phosphorus pentachloride alone it gives a good yield of another crystalline substance, supposed to be the β-isomer. It is to be regretted that the necessity of postponing further investigations has prevented the securing of definite proof of the

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[1] Bur. Standards *Bull.* 8, 643 (1912).

[2] The work described in this paper was done in the Carbohydrate Laboratory of the Bureau of Chemistry at the time when Dr. C. S. Hudson was Chemist in charge of that laboratory.

[3] "On a Crystallized *d*-Fructose-tetracetate," *Proc. Roy. Acad. Amsterdam*, 10, 563 (1907–1908).

possibility of preparing *two* isomeric chloro-tetra-acetyl derivatives of a sugar.

In continuation of the investigation of crystalline fructosides[1] crystalline β-ethyl fructoside and its tetra-acetate have been prepared and studied. While all attempts to obtain a crystalline α-form of methyl fructoside, either by enzymatic action or by fractional sublimation from Fischer's syrupy methyl fructoside, have been unsuccessful, it is noteworthy that the sublimation yields a crystalline β-methyl fructoside.

Experimental.

Crystalline β-penta-acetyl fructose was converted into chloro-tetra-acetyl fructose by the method which F. V. Arlt[2] used for preparing chloro-acetyl glucose.

Ten g. of β-penta-acetyl fructose was dissolved in 14 cc. of dry chloroform in an Erlenmeyer flask with glass stopper, cooled with ice-water, and there were added first 2.5 g. of aluminum chloride and then 6.5 g. of phosphorus pentachloride, the mixture being shaken at room temperature for an hour, occasionally warming the solution on the steam-bath. The reaction product was diluted with chloroform, quickly washed in a separatory funnel with small amounts of ice-water with addition of some sodium hydrogen carbonate, dried with calcium chloride and the chloroform quickly evaporated by means of a current of dry air passed over its surface in a large crystallizing dish. The residue was taken up with dry ether and the ether almost completely evaporated in a current of dry air. The chloro-tetra-acetyl fructose separated in long needles, which were filtered by suction and washed with small amounts of ether, or better with a mixture of petroleum ether and ether, as the crystals are very soluble in ether. The crystals may be recrystallized by evaporating the ether solution with a current of dry air. By placing a saturated ether solution in a stoppered bottle in the refrigerator and seeding the solution, large crystals separated overnight. Yield about 6 g., or about 60%. β-Fructose *tetra*-acetate has also proved in this case to be a valuable starting product as the same results are obtained as with the less available β-fructose *penta*-acetate.

To 60 g. of β-fructose tetra-acetate dissolved in 180 cc. of dry chloroform in a glass-stoppered Erlenmeyer flask and cooled with ice-water there were added first 15 g. of dry aluminum chloride and afterwards 38 g. of phosphorus pentachloride. The mixture was kept for half an hour at room temperature then shaken out with ice-water and treated as has been described for the first preparation. The yield was about 40 g. of chloro-tetra-acetyl fructose, or about 65%.

A few grams of chloro-tetra-acetyl fructose was also obtained by the

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[1] THIS JOURNAL, 38, 1216 (1916).

[2] Arlt, *Monatsh.*, 22, 144 (1901); see also Skraup and Kremann, *ibid.*, 22, 375 (1901).

following method, used by E. Fischer for obtaining chloro-tetra-acetyl glucose. 7 g. of β-fructose penta-acetate dissolved in 8 cc. of acetic acid saturated with hydrogen chloride, was made up to a volume of 25 cc. with glacial acetic acid and, after standing for half an hour, the mixture was poured into cold chloroform. The chloro-tetra-acetyl fructose was obtained by working up the chloroform solution in the manner already described.

This chloro-tetra-acetyl fructose is not a stable substance. It decomposes in a day in an open dish, and keeps only a little longer in a desiccator. The best way to preserve it for a longer time is in a tightly closed bottle in benzol solution in the refrigerator. In this way it can be kept for a few weeks. Before using, it was always recrystallized. Combustion (with lead chromate) gave the following data.

Subs., 0.2950: CO_2, 0.4991; H_2O, 0.1395.

Calc. for $C_6H_7O(C_2H_3O_2)_4Cl$: C, 45.83; H, 5.22. Found: C, 46.14; H, 5.29.

The quantitative estimation of acetyl was combined with the quantitative estimation of chlorine by the following method.

0.6000 g. of substance was saponified by shaking with 135.5 cc. of 0.1 *N* sodium hydroxide solution for 5 hours at 0° and titrating with 0.1 *N* sulfuric acid and phenolphthalein. For neutralization 53.39 cc. of 0.1 *N* sulfuric acid was required, hence 82.11 cc. of 0.1 *N* sodium hydroxide had been neutralized. An excess of silver nitrate solution was added to the warm neutral solution and the precipitate filtered on a weighed Gooch filter. 0.2310 g. of silver chloride was obtained, equivalent to 9.52% of chlorine in the substance. The 0.2310 g. of silver chloride had been formed from an amount of hydrochloric acid corresponding to 16.11 cc. of 0.1 *N* hydrochloric acid, hence in 0.6000 g. substance 82.11 — 16.11 = 66.0 cc. of 0.1 *N* solution or 66.0% of acetic acid is found. In a similar experiment of 5.5 hours duration, 9.52% of chlorine and 66.1% of acetic acid were found.

The theoretical quantities for chloro-tetra-acetyl fructose are 9.67% of chlorine and 65.5% of acetic acid.

In the filtrate from the silver chloride precipitate no chlorine could be detected by the copper oxide test.

The molecular weight was determined by the lowering of the freezing-point of benzene.

In 3 experiments 1.962, 4.037 and 6.548 g. of chloro-tetra-acetyl fructose per 100 g. of benzene gave the respective depressions 0.287°, 0.562° and 0.903°, from which the values 342, 360 and 362 are obtained for the molecular weight in comparison with the theoretical value 367.

The specific rotation was measured in chloroform solution.

2.0239 g. of twice-crystallized chloro-tetra-acetyl fructose was made up to 25 cc. with U. S. P. chloroform. The rotation, measured for a one-dcm. tube at 20° with sodium light, was 12.48 circular degrees to the left; hence $[\alpha]_D^{20} = -156.6$.

Beautiful large crystals were obtained once by keeping a saturated ether solution in the ice-box overnight. The rotation produced by 0.4351 g. in a similar solution was 2.80 circular degrees to the left, hence $[\alpha]_D^{20} = -160.9$.

Other values obtained from recrystallized preparations were always between the above specific rotations, therefore, the value $[\alpha]_D^{20} = -160.9$ is taken as the specific rotation of pure chloro-tetra-acetyl fructose.

The substance melts at 83°, is colorless and odorless, has a bitter taste and is easily soluble in the usual solvents excepting water and petroleum ether. It is decomposed by the air, even in a desiccator. When exposed to the air a pure preparation still gave the next morning after washing with an ether-chloroform mixture a weak test for chlorine, melted at 124° (unsharp) and had a specific rotation of —113°. After recrystallization from ether pure β-tetra-acetyl fructose was separated, identified by the melting-point and specific rotation. A nearly quantitative conversion into β-tetra-acetyl fructose was obtained by shaking 10 g. of *chloro-tetra*-acetyl fructose in ether solution with 10 g. of silver oxide and 5 cc. of water for a day. Eight g. of pure β-tetra-acetyl fructose was separated and the product was identified by melting-point and specific rotation. This reaction identified the substance as a fructose derivative. The following experiment seems to indicate that this chloro-tetra-acetyl fructose is an α-derivative.

Two g. of chloro-tetra-acetyl fructose was dissolved in 60 cc. of methyl alcohol and 4 g. of silver carbonate and 2 g. of silver oxide were added. The mixture was shaken for 1.5 days, filtered with the addition of some decolorizing carbon and gave on evaporation a colorless syrup which did not crystallize. Seeding with β-methyl-tetra-acetyl fructose was not effective in starting the crystallization. The syrup was dried in a vacuum desiccator in order to determine the specific rotation.

0.5423 g. of this dry syrup was dissolved in 25 cc. of chloroform and showed in a one-dcm. tube a rotation of 0.09 circular degrees to the left, hence $[\alpha]_D^{20} = -4.1$. Crystalline methyl-tetra-acetyl fructose has a specific rotation of —124.6.

E. O. v. Lippmann, in his book "Die Chemie der Zuckerarten," Vol. 1, p. 870, states that Kolli and Vachović mention chloroacetyl fructose;[1] it is said to be entirely analogous to chloro-aceto glucose. The translation of the original reference,[2] by the courtesy of Dr. E. Yanovsky, disclosed that the note made by v. Lippmann comprises all that could be found in the original literature regarding the preparation and properties of this compound. It is very probable that Kolli and Vachović, in the year 1880, in which Colley's "aceto chlor*glukose*" was known only as a syrup, have simply applied the method of Colley to fructose and have considered the syrupy reaction product as chloro-aceto fructose.

In one of the experiments for preparing chloro-tetra-acetyl fructose a small amount of large crystals separated on evaporation of the ether solution, which had an appearance and melting-point differing from those

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[1] *Chem. Zentr.*, 80, 613 must be *Chem. Zentr.*, 11, 613 (1880).

[2] *Proc. Russ. Phys. Chem. Soc.*, 12, 4–6 (1880); see also *Ber.*, 13, 2389 (1880).

of the chloro-tetra-acetyl fructose. Several experiments under different conditions were made in order to obtain this substance again, but were fruitless. At last it was found that if aluminum chloride is omitted the reaction produces a good yield of the new substance which is entirely different from the chloro-tetra-acetyl fructose which has been described. The explanation why this new compound has been formed the first time is obvious. Phosphorus pentachloride had been first added and after a short time (in which the new compound was formed) aluminum chloride.

Preparation of the Supposed β-Chloro-tetra-acetyl Fructose.

Sixty g. of β-tetra-acetyl fructose was dissolved in 180 cc. of dry chloroform in a glass-stoppered Erlenmeyer flask and cooled with ice-water. Forty g. of phosphorus pentachloride was added and the mixture was shaken occasionally, lifting the stopper now and then to release the excess pressure. After 15 minutes the phosphorus pentachloride had nearly disappeared, and the reaction product was shaken in a separatory funnel with ice-water with addition of small pieces of ice and afterwards of ice-water to which sodium hydrogen carbonate had been added. The chloroform solution was dried with calcium chloride and filtered, the chloroform evaporated and the residue mixed with absolute alcohol. Crystals separated directly and were filtered by suction and recrystallized from boiling absolute alcohol. In this way beautiful large crystals were obtained which resembled fructose tetra-acetate. The yield was about 35 g. or nearly 60% of the tetra-acetate used. The new compound is a stable substance, and analysis gives figures which agree with a chloro-tetra-acetyl hexose. Combustion (with lead chromate) gave the following data.

Subs., 0.3123: CO_2, 0.5275; H_2O, 0.1417.

Calc. for $C_6H_7O(C_2H_3O_2)_4Cl$: C, 45.83; H, 5.22. Found: C, 46.07; H, 5.08.

The quantitative estimation of acetyl showed that only very small amounts of chlorine are split off by alkali at 0°.

For this estimation 0.250 g. was saponified by shaking with 75 cc. of 0.1 *N* sodium hydroxide solution for 3.5 hours and titrated with 0.1 *N* sulfuric acid and phenolphthalein. The amount of acetic acid produced was found to be 68.8%. In a similar experiment of 4.5 hours duration the value 70.2% was found. The theoretical quantity of acetic acid in chloro-tetra-acetyl hexose is 65.5%.

The neutral liquid resulting from the saponification gave a slight opalescence with silver nitrate solution and the same liquid evaporated to a syrup gave a strong chlorine test with copper oxide.

A chlorine determination in the original substance gave the following data.

Subs., 0.2083: AgCl (Carius), 0.0806.

Calc. for $C_6H_7O(C_2H_3O_2)_4Cl$: Cl, 9.67. Found: 9.57.

The molecular weight was determined by the lowering of the freezing-point of benzene.

In 2 experiments 1.3115 g. and 2.6036 g. of chloro-tetra-acetyl hexose per 100 g. of benzene gave the respective depressions 0.190° and 0.360°, from which the values 345 and 361 are calculated for the molecular weight in comparison with the theoretical value 367. The specific rotation was measured in chloroform solution. 0.9900 g. of twice-recrystallized substance was made up to 25 cc. with chloroform and the solution gave a rotation in a one-dcm. tube at 20° with sodium light of 1.79 circular degrees to the right; hence $[\alpha]_D^{20} = +45.2$. After a third recrystallization from absolute alcohol 0.4274 g. of substance produced a rotation of 0.775 circular degrees to the right, hence $[\alpha]_D^{20} = +45.3$, which is taken as the specific rotation of the pure substance.

The melting-point of the pure substance is 108°. It is colorless, odorless, has no taste (or is very slightly bitter) and is less soluble in the usual solvents than the chloro-tetra-acetyl fructose described before. Though it is very probable that this new compound represents an isomeric chloro-tetra-acetyl fructose, the one of specific rotation—160.9 being the α- and the other of specific rotation +45.3 the β-form, only a few experiments for confirming this view could be performed on account of lack of time. The following experiment shows, however, that the new compound is very probably a fructose derivative and that no rearrangement of the fructose molecule has taken place. Seventy g. of crystalline barium hydroxide ($Ba(OH)_2 + 8H_2O$) was dissolved in one liter of water on the steam-bath and filtered into a bottle with a glass stopper. The solution was cooled with ice to about 5° and 20 g. of the new chloro derivative in powder form was added. After 1.5 hours shaking the substance had dissolved. The liquid was kept 0.5 hour longer in ice, was then saturated with carbon dioxide, filtered, shaken with silver carbonate and again filtered. The amount of sulfuric acid necessary to precipitate the dissolved barium acetate was calculated to be 218.1 cc. of N solution, since this amount is equivalent to the acetic acid that is obtained from 4 acetyl groups in chloro-tetra-acetyl fructose. After filtration and concentration *in vacuo* the solution could be filtered clear, and by carefully adding 0.1 N sulfuric acid to the filtrate, it was brought to the stage where it gave only a slight precipitate with sulfuric acid. On evaporating this solution in a vacuum desiccator a yellowish syrup was obtained which became gradually light brown. It was not possible to obtain crystals from this syrup. It reduced Fehling's solution readily, contained chlorine and gave a strong *Seliwanoff reaction* (a red color with hydrochloric acid and resorcin) *indicating the presence of a ketose.*

0.2394 g. of syrup was dissolved in 25 cc. of water and polarized in a one-dcm. tube, but no rotation could be detected. One g. of syrup gave with phenylhydrazine and sodium acetate about one g. of osazone. It was re-crystallized from methyl alcohol, the crystals giving a melting-point of 173°. The quantity was too small to recrystallize again.

The experiments indicate that the chlorine is much more strongly attached *in this compound than in the chloro-tetra-acetyl fructose which was first described.*[1]

Ethylation of β-Fructose Tetra-acetate.

Twenty g. of powdered fructose tetra-acetate, 75 g. of freshly prepared silver oxide and 128 g. of ethyl iodide were heated to 50° in a 300-cc. Erlenmeyer flask fitted with a reflux condenser. When the mixture heated up to boiling by the heat of the reaction it was cooled in cold water and the heating to 50° and cooling were repeated until heating by the reaction no longer took place. It was boiled afterwards for 2 hours under a reflux condenser on the water-bath, the ethyl iodide was distilled off and the residue extracted with ether. By evaporation of the ether, ethyl tetra-acetyl fructose was obtained in crystalline form. Yield, 16 g. of a nearly pure product. It was recrystallized from petroleum ether.

The specific rotation was measured in a chloroform solution. 0.5976 g. of once-recrystallized ethyl tetra-acetyl fructose was made up to 25 cc. with chloroform and the solution was found to read in a one-dcm. tube at 20° with sodium light 3.00 circular degrees to the left; hence $[\alpha]_D^{20} = -125.5$. After a second recrystallization from petroleum ether, 0.6016 g. of substance showed a rotation of 3.0 circular degrees to the left in a similar solution; hence $[\alpha]_D^{20} = -125.6$; and after a third recrystallization from petroleum ether 1.9968 g. of substance caused a rotation of 10.19 circular degrees to the left; hence $[\alpha]_D^{20} = -127.6$, which is taken as the specific rotation of pure β-ethyl tetra-acetyl fructose.

The substance melts at 83°. Combustion, ethoxyl and acetyl determinations gave the following results.

Subs., 0,2705, 0.2253: CO_2, 0.5082, 0.4225; H_2O, 0.1548, 0.1280.

Calc. for $C_6H_7O.OC_2H_5(C_2H_3O_2)_4$: C, 51.04; H, 6.43. Found: C, 51.24, 51.13; H, 6.40, 6.35.

An ethoxyl determination with 0.2489 g. of substance gave 0.1541 g. of silver iodide corresponding to 11.88% of OC_2H_5 group, whereas the theoretical amount is 11.97%. For the quantitative estimation of the acetyl group the substance was saponified by shaking 0.3000 g. with 75 cc. of 0.1 *N* sodium hydroxide solution at 0° for one hour and titrating with 0.1 *N* sulfuric acid, using phenolphthalein as an indicator. The amount of acetic acid was found to be 64.05%. In a similar experiment of 2 hours' duration, the value 63.99% was found, and in a third lasting 2.5 hours, the same value, 63.99% was obtained. The theoretical quantity for a tetra-acetyl ethyl fructose is 63.83%. Evidently the saponification is complete after one hour.

Preparation of β-Ethyl Fructoside.

The method of saponification is the same as that described for the preparation of β-methyl fructoside.[2] The barium hydroxide used was not pure and the ethyl fructoside obtained was not easily purified, as it was hard to obtain ash-free. It was recrystallized first from boiling alcohol and afterwards from water. In this way an ash-free prepara-

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[1] If we consider the theory of secondary valence it is probable that in the β-compound more chlorine valence is used for binding it to the second carbon atom than in the α-compound.

[2] THIS JOURNAL, 38, 1220 (1916).

tion was obtained. The specific rotation was measured in water solution.

1.0302 g. of β-ethyl fructoside, recrystallized from boiling alcohol, was made up to 25 cc. with water. A reading of 6.36 circular degrees to the left was obtained in a one-dcm. tube at 20° with sodium light; hence $[\alpha]_D^{20} = -154.3$. After a further crystallization from water, 0.7225 g. of substance made up in the same manner produced a rotation of 4.50 circular degrees to the left; hence $[\alpha]_D^{20} = -155.7$; and after a further recrystallization from water 0.4082 g. of substance made up in the same manner gave a rotation of 2.545 circular degrees to the left; hence $[\alpha]_D^{20} = -155.3$. This figure was taken as the specific rotation of pure β-ethyl fructoside.

β-Ethyl fructoside melts at 151°. The crystals are colorless, odorless and have a slightly bitter taste or no taste at all. The fructoside is easily soluble in water and hot alcohol. Its aqueous solution is not reduced by boiling with Fehling's solution. After hydrolyzing by boiling the aqueous solution with a mineral acid and neutralizing the cooled solution, it readily reduces Fehling's solution on boiling. This reaction proves, in connection with the analysis recorded below, that the prepared substance is an ethyl fructoside.

Subs., 0.2060: CO_2, 0.3487; H_2O, 0.1413.

Calc. for $C_6H_{11}O_5(OC_2H_5)$: C, 46.12; H, 7.75. Found: C, 46.16; H, 7.67.

An ethoxyl determination with 0.1669 g. of substance gave 0.1821 g. of AgI, corresponding to 20.93 of OC_2H_5. Calc., 21.16.

Preparation of β-Tetra-acetyl Fructose from α-Penta-acetyl Fructose.

α-Penta-acetyl fructose was prepared from β-tetra-acetyl fructose by the action of zinc chloride and acetic anhydride,[1] but the α-penta-acetyl fructose could not be converted into the β-penta-acetyl fructose. Recently, however, a method has been found for converting α-penta-acetyl fructose into β-tetra-acetyl fructose, and, therefore, with β-tetra-acetyl fructose as an intermediate product α-penta-acetyl fructose can be converted into the β-form. 5 g. of α-penta-acetyl fructose was dissolved in 500 cc. of hot water and the solution was heated for one hour in an autoclave at 106°. The solution was neutralized and shaken out with chloroform, the latter yielding on evaporation a crystalline substance which was recrystallized from ether. In this way 0.28 g. of β-tetra-acetyl fructose was obtained which was identified by melting-point and specific rotation.

Efforts to Prepare α-Methyl Fructoside Using a Biochemical Method.

Experiments were made to prepare the α-form of methyl fructoside biochemically. Bourquelot, Herissey, Bridel and Aubry[2] have prepared α-methyl glucoside and α-methyl galactoside in a pure crystalline condition in this way by means of bottom yeast (brewery yeast). As nothing was found in the literature regarding the application of this method to fruc-

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[1] THIS JOURNAL, 37, 2738 (1915).

[2] *Compt. rend.*, 156, 168, 491 (1913); *J. pharm. chim.*, [7] 9, 225, and 10, 202 (1914).

tose, according to the prescription of Aubry,[1] a macerate of bottom yeast was first prepared by washing and drying brewery yeast and macerating this dry yeast for 24 hours with 10 times the amount of water. Using this material, the results of the above investigation yielding α-methyl glucoside and α-methyl galactoside were confirmed.

To apply the same procedure to fructose 360 g. of methyl alcohol and 100 g. of fructose dissolved in 800 cc. of water were mixed in a bottle, 600 cc. of macerate of yeast was added and the volume made up to 2 liters. The rotation was determined at the beginning of the experiment and after one and three months.

The initial rotation in one-dcm. tube was found to be —4.2; after one month the rotation was —4.1, and after 3 months —4.1. As the change of rotation in within the limits of error it was concluded that bottom yeast does not act under the conditions of this experiment.

Other Efforts to Prepare α-Methyl Fructoside.

In order to obtain an equilibrium mixture of α- and β-methyl fructosides, β-methyl fructoside was treated with a 1% hydrochloric acid solution in methyl alcohol by dissolving in a 50 cc. volumetric flask one g. of β-methyl fructoside in 20 cc. of methyl alcohol, adding 4.2 cc. of 3.32 *N* hydrochloric acid in methyl alcohol and filling up to 50 cc. with methyl alcohol. The rotation was determined in circular degrees with a one-dcm. tube. The following negative rotations were obtained.

After 5 minutes —3.10, 0.5 hour; —3.03, 1 hour; —2.90, 18 hours; —1.60, 2 days; —1.32, 4 days; —1.10, 6 days; —1.02, 8 days; —1.02. At the end of the reaction the liquid had a yellowish color.

In a similar experiment in which 3.6% hydrochloric acid was used the time in which equilibrium was reached was diminished to about 2.5 days, and the resulting solution was colored dark brown. The solutions were worked up separately according to the direction of Fischer,[2] but no crystals could be separated from the resulting syrups.

By subliming Fischer's sirupy mixture of methyl fructosides in a high vacuum (cathode rays) a sublimate could be obtained in a crystalline state. By its chemical behavior and by its melting-point (120°) and specific rotation (—172.0°) it was identified as β-methyl fructoside. No other crystalline substance could be separated by this method.

WASHINGTON, D. C.

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[1] Aubry, *ibid.*, [7] 10, 202 (1914).

[2] *Ber.*, 28, 1160 (1895).

[Contribution from the Kent Chemical Laboratory of the University of Chicago, and the Otho S. A. Sprague Memorial Institute.]

AROMATIC MERCURI-ORGANIC DERIVATIVES.

By Morris S. Kharasch and Jean F. Piccard.[1]

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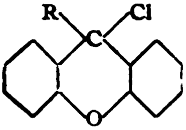
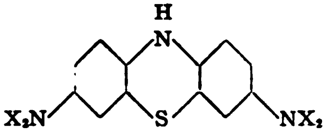
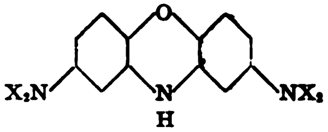
Introduction.

During the course of investigation of mercuri-organic derivatives undertaken for the Sprague Memorial Institute, the amount of data has accumulated to such an extent that it has been deemed advisable to publish some of the results thus far obtained. This paper contains some preliminary work on the preparation of a 6-membered atomic heterocyclic compound which contains a metal in place of a non-metal. In this case mercury was the metal experimented with. It was put in place of nitrogen in a ring of the azine type. Work is now being carried on to substitute mercury for oxygen, sulfur, and nitrogen, in the type of rings illustrated below.







A detailed study of the influence of different groups on the position taken by mercury when introduced into a substituted benzene nucleus is also under investigation.

The theory of mercurization will be published at a later date.

Experimental.

The Preparation of *m*-Bromo-dimethyl-aniline, $m\text{-}BrC_6H_4N(CH_3)_2$.—This compound was first prepared by Wurster,[2] by treating *m*-bromo-aniline with methyl iodide in a sealed tube. The method has the disadvantage that large quantities of *m*-bromo-dimethyl-aniline cannot be made in a single operation. Since we were not interested in obtaining pure *m*-bromo-dimethyl-aniline as such, but a pure *p*-nitroso-*m*-bromo-dimethyl-aniline, the following method was adopted. A quantity of *m*-bromo-aniline (75 g.) was suspended in water (900 cc.) and heated to about 80°. Sodium carbonate (300 g.) and dimethyl sulfate (300 g.) were then added in small portions, care being taken that the solution was always alkaline. The addition should take about 1.5 hours. After all of the dimethyl sulfate had been added, the solution was agitated for an hour and then subjected to steam distillation. The oil which came over was separated

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[1] The material presented here is used by Morris S. Kharasch in his dissertation presented in part fulfilment of the requirements for the degree of Doctor of Philosophy in the University of Chicago.

[2] Wurster, *Ber.*, 12, 1818 (1879).

from the distillate, the latter extracted twice with ether, and the portions combined. The ether solution was dried with sodium sulfate, the ether distilled off, and the oil distilled *in vacuo*. A colorless oil came over which, however, turned yellow on standing. Yield, 75 g.

The product thus obtained contains unchanged *m*-bromo-aniline, *m*-bromo-monomethyl-aniline and *m*-bromo-dimethyl-aniline. To separate these 3 substances, the usual method was employed. The oil was dissolved in 2.5 mols. of 20% hydrochloric acid, the solution cooled to 0°, and the calculated amount of sodium nitrite[1] dissolved in a little water was added in small amounts. The hydrochloride of the *p*-nitroso-*m*-bromo-dimethyl-aniline separated. The solution was then extracted repeatedly with ether until a sample test showed the absence of *m*-bromophenyl-methyl-nitrosamine in the latter.[2] The precipitate—the hydrochloride of the *p*-nitroso-*m*-bromo-dimethyl-aniline—was then filtered off and dried in a vacuum desiccator.

***p*-Nitroso-*m*-bromo-dimethyl-aniline,** $(CH_3)_2NC_6H_3BrNO$.—This compound was also prepared by Wurster, who gave its melting-point but no analytical data, owing to the fact that the compound decomposed when he tried to bring it to constant weight by drying it on the water-bath. The compound is also not recorded in Richter's Lexikon. It was thought, therefore, advisable to analyze it.

A quantity of the hydrochloride of *p*-nitroso-*m*-bromo-dimethyl-aniline (5 g.) was suspended in 75 cc. of water, cooled to 0°, 40 cc. of ether added, and enough carbonate to render the solution decidedly alkaline. The ether extract was then separated from the solution, and the latter extracted 3 more times with ether, 50 cc. being used each time. The ether extracts were combined, dried with sodium sulfate, and $^3/_4$ of the ether distilled off. The solution was then transferred to an evaporating dish and allowed to evaporate spontaneously. Beautiful long green needles were obtained which melted with decomposition at 148°.[3] For analysis the base was recrystallized twice from very small amounts of ether.

Subs., 0.1082: AgBr, 0.0886.
Calc. for $C_8H_{11}ON_2Br$: Br, 34.87. Found: 34.84.

***m*-Bromo-dimethyl-*p*-phenylene-diamine Dihydrochloride,** $BrNH_2C_6H_3N(CH_3)_2.2HCl$.—The hydrochloride of *p*-nitroso-*m*-bromo-dimethyl-aniline was reduced in the following manner. Twice the calculated amount of stannous chloride necessary for the reduction was dissolved in conc. hydrochloric acid, the solution diluted somewhat, warmed to 40°, and the *p*-nitroso-*m*-bromo-dimethyl-aniline hydrochloride, mixed

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[1] To avoid an excess of sodium nitrite, the oil was assumed to be pure *m*-bromo-dimethyl-aniline.

[2] Lieberman's nitrosamine test.

[3] Wurster also gave 148° as the melting-point of the compound.

with hydrochloric acid to the consistency of a thick paste, added to it in small portions. The reduction was practically instantaneous. The complex tin salt of the dihydrochloride of the *m*-bromo-dimethyl-*p*-phenylene-diamine separated. Enough water was then added to bring it back into solution, and the tin precipitated as stannic sulfide from the hot solution with hydrogen sulfide. Before being filtered the solution was diluted with an equal amount of water, warmed to 80°, and hydrogen sulfide passed through it for a half an hour longer. This procedure has been found very satisfactory, requiring very little time and precipitating the tin quantitatively in one operation. The water in the filtrate was distilled off *in vacuo*. The dihydrochloride of *m*-bromo-dimethyl-*p*-phenylene-diamine remained behind. It was purified by preparation of the free base and distillation of the latter *in vacuo*. The base was then dissolved in ether and dry hydrogen chloride passed into the solution. The dihydrochloride was precipitated. It was dried in a vacuum desiccator.

Subs., 0.1941: 16.80 cc. dry N_2 at 20° and 726.3 mm.
Calc. for $C_8H_{13}N_2Br.2HCl$: N, 9.81. Found: 9.64.

***m*-Bromo-dimethyl-*p*-phenylene-diamine,** $BrNH_2C_6H_3N(CH_3)_2$.—The free base was obtained by the method previously outlined. The oily distillate solidified on cooling in white, almost colorless, needles; m. p. 47.5°. The free base turned dark on exposure to light and air. When it was dissolved in dil. hydrochloric acid and the solution was saturated with hydrogen sulfide and treated with ferric chloride, an intensely blue coloration was produced.

Subs., 0.2749: AgBr, 0.2406.
Calc. for $C_8H_{11}N_2Br$: Br, 37.18. Found: 37.25.

***o*-Dibromo-Bindschedler's Green.**—The same method was employed as was used originally by Bindschedler for the preparation of Bindschedler's Green.[1] To a mixture of 2.15 g. of *m*-bromo-dimethyl-*p*-phenylene-diamine and 2 g. of *m*-bromo-dimethyl-aniline,[2] 2 g. of conc. hydrochloric acid in 50 cc. of water was added. The solution was cooled to —2° and oxidized by a solution of 2 g. of potassium dichromate and 0.6 g. of glacial acetic acid in 20 cc. of water. The oxidizing agent was added drop by drop. The flask was shaken continuously during the addition of the oxidizing agent. The dyestuff partly precipitated out. Sufficient water was then added to redissolve it, the solution heated to 40–50° and 5 g. of zinc chloride added to it. It was allowed to stand in ice-water for 2 hours longer and the precipitate collected on a filter, washed with a small quantity of cold water, then with alcohol, and finally with ether. It was dried in a vacuum desiccator. A dark amorphous powder was

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[1] Bindschedler, *Ber.*, 16, 864 (1883).

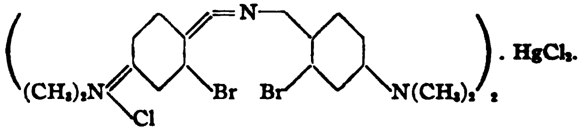
[2] Prepared by the method of Wurster, *ibid.*, 16, 864 (1883).

thus obtained which was slightly soluble in water, imparting to the latter an intensely green color. The yield was very good.

Subs., 0.3618: 27.40 cc. dry N_2 at 24.5° and 731 mm.
Subs., 0.4860: ZnO, 0.0382.
Calc. for $C_{32}H_{36}N_6Br_4Cl_2.ZnCl_2$: N, 8.25; Zn, 6.37. Found: N, 8.36; Zn, 6.31.

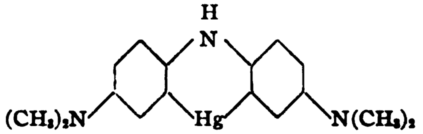
The analysis readily shows that in this case also 2 molecules of the dye combine with one of zinc chloride.

The mercuric chloride double salt was obtained by solution of the zinc chloride double salt in water at 40–50°, and addition of mercuric chloride. The structure of the compound thus obtained is expressed by the following formula,



Subs., 0.1373: HgS, 0.0278.
Calc. for $C_{32}H_{36}Br_4Cl_2.HgCl_2$: Hg, 17.17. Found: 17.47.

Work is also under way on the isolation of the leuco-dibromo-Bindschedler's Green, and the replacing in the latter of the 2 bromine atoms by mercury to give a compound of the following type,



which, when oxidized, would give a representative of a new class of organic mercury derivatives.

***m* - Bromo - phenylmethyl - nitrosamine,** *m*-$BrC_6H_4N(CH_3NO)$.—As previously stated, the methylation of *m*-bromo-aniline by the use of dimethyl sulfate gave rise to 2 derivatives, the mono-methyl and the dimethyl *m*-bromo-anilines. These 2 were separated by the use of sodium nitrite as given in detail in the preparation of *p*-nitroso-*m*-bromo-dimethylaniline. The ether extract of the acid solution contained the *m*-bromomethylphenyl-nitrosamine. The ether was distilled off and the oil subjected to steam distillation. The distillate was then extracted with ether, the solution dried with sodium sulfate, and the ether distilled off. When the sides of the crystallizing dish were cooled and scratched the oil solidified in feathery clusters of fine yellowish needles; m. p., 49°. Yield, 10 g.

Subs., 0.2049: AgBr, 0.1782.
Calc. for $C_7H_7ON_2Br$: Br, 37.17. Found: Br, 37.01.

The compound gives the characteristic Lieberman's nitroso-amine reaction and in the pure condition is very stable.

***p*-Nitroso-*m*-bromo-monomethylaniline,** $BrNOC_6H_3NHCH_3$. — The *m*-bromo-methylphenyl-nitrosamine was rearranged according to the method of Fisher and Hepp.[1] The nitrosamine (4 g.) was dissolved in ether (8 g.) and alcohol (16 g.), saturated with hydrogen chloride at 10°, added. A red coloration was produced after the addition of the alcohol. It took fully 2 days for the reaction to go to completion. A beautiful pink compound was obtained. This compound, the hydrochloride of *p*-nitroso-*m*-bromo-monomethyl-aniline, is very stable, much more so than the hydrochloride of the dimethyl-aniline derivative. It was kept 3 weeks in an open dish without changing color. Its melting-point was not sharp. At 140° it turned yellow, and at 168° melted with apparent decomposition. It hydrolyzed immediately to give the free base on suspension in water. The free base was isolated and purified by the same method as that given for *p*-nitroso-*m*-bromo-dimethyl-aniline.

Subs., 0.1055: 12.11 cc. dry N_2 at 20 and 736 mm.
Calc. for $C_7H_7ON_2Br$: N, 13.06. Found: 12.95.

The free base is green. It has no definite melting-point. It turns dark at 100° and explodes at 124°. An ether solution of the base is yellowish-green in thin layers and green in thick.

***p*-Nitroso-phenol-*o*-mercuric-chloride,** $HOC_6H_3(4)NO(2)HgCl$.—Three g. of *o*-phenol-mercuric chloride was gradually added to a solution of 0.42 g. of sodium hydroxide and 0.86 g. of sodium nitrite in 23 cc. of water. The solution was warmed to 30–40° and a few drops of 2 molar sodium hydroxide solution added to it until all of the *o*-phenol-mercuric-chloride had gone into solution. When finely powdered, it goes into solution rapidly in the given amount of sodium hydroxide.[2] It was cooled to —4° or —5° and 2.3 g. of conc. sulfuric acid in 6 cc. of water added very slowly. The flask was constantly shaken during the operation. The addition of the acid should take about 45 minutes. The solution first turned pink, due to the formation of the sodium salt of the *p*-nitroso-phenol-*o*-mercuric chloride, but it grew darker and darker in color as more of the acid was added. A dark-colored precipitate was also formed. After all the acid had been added, the solution was shaken for 15 minutes longer, and allowed to stand in a freezing mixture for 2 hours to complete the precipitation. The solution was then filtered and the residue, after being washed a few times with small amounts of cold water, dried in a vacuum desiccator over solid sodium hydroxide and soda lime. A beautiful bordeaux-colored compound was thus obtained which can be kept indefinitely over soda lime without decomposition. It can be recrystallized

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[1] Fisher and Hepp, *Ber.*, 19, 2991 (1886).

[2] It has also been found very advantageous to moisten the *o*-phenol-mercuric-chloride with a few drops of alcohol. It then dissolves in the alkali very readily—for very obvious reasons.

from xylene in which it is slightly soluble and also from anisol from which it separates in very small needles of a light brown color.

Subs., 0.1930: 6.72 cc. dry N_2 at 22° and 732.3 mm.
Subs., 0.1352: AgCl, 0.0547.
Calc. for $C_6H_4O_3NClHg$: N, 3.92; Cl, 9.92. Found: N, 3.90; Cl, 10.07.

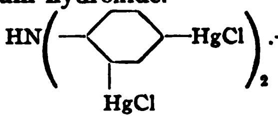
The compound, like *p*-nitroso-phenol, gives the Lieberman's nitrosamine test. It is partly soluble in ether, imparting to the latter an intensely green color. It behaves in all respects except solubility, like *p*-nitroso-phenol, of which it is a substituted derivative as noticed from the method of preparation. The mercury in *ortho* position to the hydroxyl group in phenol is known not to decrease the activity of the *para* hydrogen atom, as illustrated by the fact that it is possible to couple *o*-phenol-mercuric-chloride with diazo compounds.[1]

***p*-Nitroso-aniline-*o*-mercuric-chloride,** $NH_2C_6H_3(4)NO(2)HgCl$.—To 2 g. of *p*-nitroso-phenol-*o*-mercuric-chloride, 2.4 g. of ammonium chloride, 6.6 g. of dry ammonium acetate, and 0.2 g. of ammonium carbonate were added and the mixture warmed on the water-bath for $^1/_2$ hour with vigorous stirring.[2] It was then poured into 75 cc. of cold water, and allowed to stand $^1/_2$ hour. A slightly brown amorphous precipitate was obtained. It was filtered off, washed well with cold water until the washings gave no test for ammonia to Nessler's reagent and dried in a vacuum desiccator over sodium hydroxide. For purification, it was recrystallized from anisol.

Subs., 0.1431, 0.1311: (1) 9.80 cc. dry N_2 at 23° and 729.5 mm., (2) 8.90 cc. dry N_2 at 19° and 739.5 mm.
Subs., 0.1248: AgCl, 0.0530.
Subs., 0.1252: HgS, 0.0823.
Calc. for $C_6H_6ON_2ClHg$: N, 7.89; Cl, 9.98; Hg, 56.31. Found: N, 7.53; Cl, 10.18; Hg, 56.57.

The compound is slightly soluble in benzene and ether, coloring both green. An alcohol solution is reddish-yellow.

In the preparation of the above compound, smaller or larger quantities of the *p*-nitroso-phenol-*o*-mercuric-chloride sometimes remain unchanged. So it is always advisable to test the *p*-nitroso-aniline-*o*-mercuric-chloride by the Lieberman's nitrosoamine reaction for its presence. If the test is positive, the precipitate must be washed by decantation with a 2 molar solution of sodium hydroxide until the washings are colorless—the phenol derivative being soluble. It is then washed free from alkali with cold water and dried in a vacuum desiccator over sodium hydroxide.

Diphenylamino - tetramercuric - chloride, 

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[1] Dimroth, *Centr.*, 1901, I, 450.

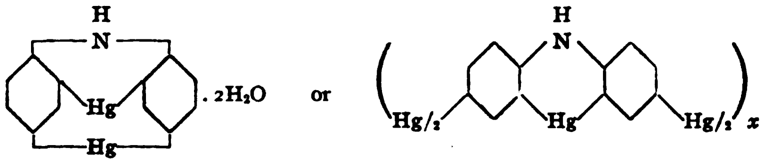
[2] Fisher and Hepp, *Ber.*, 20, 2475 (1887).

phenylamine (6.5 g.) was heated with mercuric chloride (2.7 g.) until the latter seemed to go into solution. A crackling noise was heard and the reaction went on of its own accord with the evolution of heat. The solution was first yellow, then brown, and finally dark brown. It was then poured into glacial acetic acid and boiled. The acid was decanted. The washing with glacial acetic acid was continued until the decanted liquid poured into water gave no precipitate, indicating that the product was free from diphenylamine. The filtrate was tested for mercuric chloride until the precipitate was washed free from it. A light yellow amorphous compound was thus obtained as a residue which, after being boiled with alcohol, was dried in a vacuum desiccator.

Subs., 0.8889: 10.20 cc. of N_2 at 21° and 734.2 mm.
Subs., 0.1940: AgCl, 0.1012.
Subs., 0.1699: HgS, 0.1426.
Calc. for $C_{12}H_7NCl_4Hg_4$: N, 1.26; Cl, 12.81; Hg, 72.26. Found: N, 1.28; Cl, 12.98; Hg, 72.10.

The compound is insoluble in all organic solvents. It does not melt when heated to 260°. When boiled with pyridine, it seems to undergo decomposition. This is probably a ring formation as large quantities of mercuric chloride are found in the pyridine. It is being investigated. From consideration of analogous cases the positions taken by the mercury are most likely *para* and *ortho* to the nitrogen. Thus, *p*-toluidine yields a mono-substitued derivative when treated with mercuric acetate or chloride, *o*-toluidine a di-substituted derivative, and *m*-toluidine a tri-substituted derivative. In these compounds mercury occupies the positions, relative to the nitrogen, *p*, *p-o*, *p-o-o*, respectively. Furthermore, the literature is abundant with instances of similar substitutions. In no case, however, has a mercury compound been prepared in which mercury would occupy a position *meta* to an amino nitrogen. We feel, therefore, in some way justified in assigning the above structure to the diphenylamine derivative.

3,3′-Mercuri-mercazine,



To 5 g. of diphenylamine-tetramercuric-chloride in 60 cc. of alcohol was added 10 g. of sodium thiosulfate in a little water. The precipitate turned dark immediately. The solution was warmed to 70° and kept at that temperature for 15 minutes, the whole being shaken during the operation. Sufficient water was then added to get a homogeneous solution, the solution boiled a few minutes and then filtered. The precipitate was washed with alcohol and then with ether, dried and then analyzed.

Subs., 0.1949: 4.60 cc. of dry N_2 at 21° and 730.2 mm.

Subs., 0.1478: HgS, 0.1142.

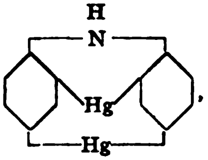
Subs., 0.3082: CO_2, 0.2739; H_2O, 2.09.

Subs., 0.2133: AgCl, 0.0008.

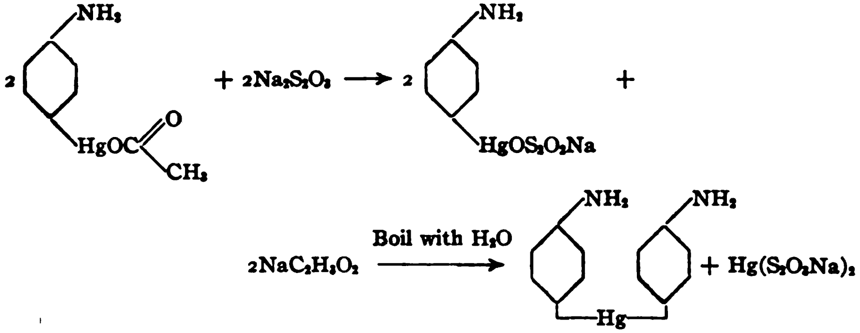
Calc. for $C_{12}H_{11}ONHg_2$: N, 2.33; C, 23.97; H, 1.83; Hg, 66.50. Found: N, 2.53; C, 24.22; H, 2.09; Hg, 66.60.

The compound is of a gray color, resembling finely precipitated metallic mercury. It is insoluble in all organic solvents. When heated to 100° in a vacuum, mercury distils over. The substance is unstable when treated with nitric acid. The product of nitration is soluble in sodium hydroxide with a red coloration.

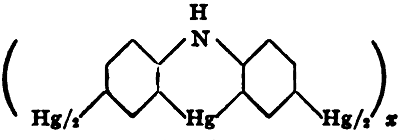
The structural formula of this compound is of great interest. The structure which suggests itself from the method of preparation is,



since from the work of Pesci[1] on aniline mercuri-acetate and similar compounds it is quite evident that the sodium thiosulfate acts in the following way



The intermediate compounds have been isolated by Pesci. On the other hand, the *para* mercury bridge would give rise to a 10-atom ring with respect to the nitrogen which would probably be extraordinarily unstable and, therefore, not likely to form. Then again, there is the possibility of the formation of a complex molecule of the type



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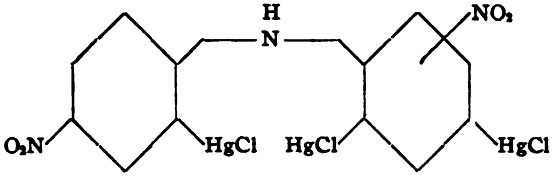
[1] Pesci, *Gazz. chim. ital.*, 29, I, 394 (1899).

We have not been able so far, however, to confirm either assumption, owing to the insolubility of the compound in all solvents.

***p,o,o'*-3-Mercuric-chloride-di-nitro(??)diphenylamine,**



To 5 g. of diphenylamine-tetramercuric-chloride 20 g. of a mixture of conc. nitric acid (2 parts sp. gr. 1.4), sulfuric acid (1 part), and water (one part) were added. It was warmed carefully for 2 minutes. The nitration took place with vigor. When the reaction had completed itself, the contents were poured into water, boiled, and the solution filtered. The residue was washed with alcohol and ether and dried in a vacuum desiccator.

Subs., 0.2491, 0.1732: (1) 10.00 cc. of dry N_2 at 20° and 728 mm.; (2) 6.60 cc. of dry N_2 at 21° and 740 mm.

Subs., 0.2518: CO_2, 0.1532; H_2O, 0.0159.

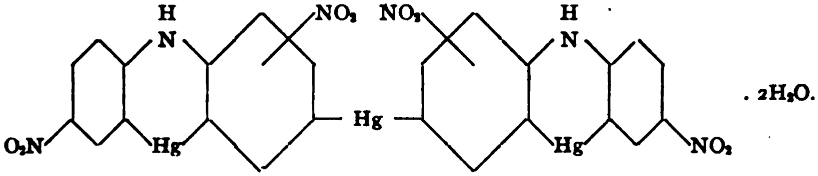
Subs., 0.2000: AgCl, 0.0900.

Subs., 0.1320, 0.1831: (1) HgS, 0.0954; (2) 0.1328.

Calc. for $C_{12}H_6O_4N_3Cl_3Hg_3$: N, 4.39; C, 14.93; H, 0.63; Cl, 11.03; Hg, 62.24. Found: N, 4.29; C, 14.72; H, 0.70; Cl, 11.13; Hg, 62.52.

The compound is of a light brown color. It is insoluble in all organic solvents. It is partly soluble in sodium hydroxide, giving the solution a red coloration.

Mercury-bis-3-di-nitro(?)-mercazine,



Starting with the above nitro compound, this compound was prepared by the same method as used for 3,3'-mercuri-mercazine.

Subs., 0.2248: 14.20 cc. of dry N_2 at 20° and 738.7 mm.

Subs., 0.1384: CO_2, 0.1218; H.

Subs., 0.1101: HgS, 0.0642.

Calc. for $C_{24}H_{10}O_{10}N_6Hg_3$: N, 7.09; C, 24.24; H, 1.52; Hg, 50.54. Found: N, 7.16; C, 24.01; H, 1.98; Hg, 50.26.

The compound is of a light brown color. It is insoluble in all organic solvents. When treated with sodium hydroxide, it gives to the latter a light red coloration. It resembles the other mercazine derivative in many respects. When heated in a vacuum to 100°, it loses mercury. Heated to 54° in a vacuum for fifteen minutes, it loses 5.22% of water.

Conclusions.

1. A few methods have been outlined for the preparation of a 6-atom heterocyclic ring containing mercury in place of a non-metal.

2. The preparations of a number of new derivatives of *m*-bromo-dimethylaniline, *m*-bromo-monomethyl-aniline Bindshedler's green, mercury derivatives of nitroso-phenol, nitroso-aniline, phenylamine and nitrodiphenylamine have been described. These compounds were obtained as a result of carrying out the above procedures.

Work on the problem is being continued.

CHICAGO, ILL.

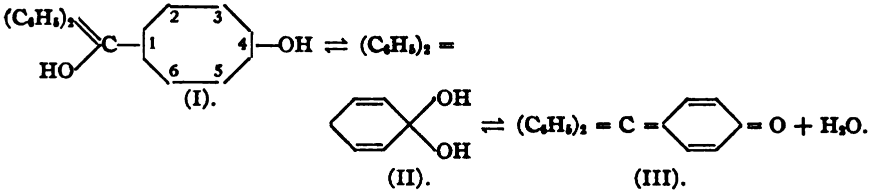
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN.]

TAUTOMERISM IN THE TRIARYL CARBINOL SERIES; DIPHENYL-4-HYDROXY-1-NAPHTHYL CARBINOL AND DIPHENYL-2-HYDROXY-1-NAPHTHYL CARBINOL.

BY M. GOMBERG AND F. W. SULLIVAN, JR.

Received June 15, 1920.

It has been shown in previous papers[1] from this laboratory that *p*-hydroxy-triphenyl carbinol exists in 2 tautomeric forms mutually convertible into each other, the benzenoid (I) and the quinonoid (II). The former, colorless, is converted into the latter, colored, by the agency of proper solvents, by heat, and by ultra-violet light. The quinonoid tautomer loses water on heating, to yield fuchsone (III). It is obvious that the benzenoid carbinol, on heating, should also yield the identical fuchsone, through the phase of temporary existence as the quinonoid carbinol. Such is really the case. Moreover, the benzenoid carbinol loses water much more slowly than the quinonoid tautomer does, a difference in behavior fully consistant with the constitutions assigned to the 2 carbinols, respectively.



(I). (II). (III).

Little is known as to how extensively this tendency to tautomerization is shared by substituted hydroxy-triaryl carbinols. Three possible variations of the occurrence of this phenomenon suggest themselves: first, as in the case of *p*-hydroxy-triphenyl carbinol itself, when the benzenoid and the quinonoid carbinol, as well as the fuchsone, all possess sufficient individual stability to permit the isolation of each in the solid state; second, when the equilibrium between the 2 carbinols is preëminently in favor

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[1] THIS JOURNAL, 35, 1035 (1913); 37, 2575 (1915).

of the benzenoid tautomer; the conversion of that into quinonoid requires then such energetic means that the reaction proceeds further and the fuchsone is produced; third, the equilibrium is largely or completely in favor of the quinonoïd carbinol; in such cases it becomes impossible to isolate the colorless carbinol, and the colored carbinol obtainable consists either wholly of the quinonoid tautomer or of that with some slight admixture of the benzenoid.

A knowledge of the factors that influence or determine in a particular carbinol the occurrence of the one or the other of these 3 possible tautomeric relationships should be of considerable interest, as this is intimately connected with the question of color-production in the triphenylmethane compounds, and also, in view of the contemporary discussion as to the "quinoncarbonium or oxonium" constitution of many dyes.[1]

At the present time our knowledge in this respect is very limited. It has been shown by Gomberg and Van Stone[2] that any of the groups CH_3, OCH_3, Br, Cl, in positions 3, or 3 and 5, in the hydroxylated nucleus (see Formula I), does not interfere with the stable existence of each of the 2 carbinols and fuchsone. On the other hand, even one NO_2 group in the same position prevents the stable occurrence of the quinonoid carbinol. The same is true, as has recently been found by P. Demont,[3] when the groups CH_3 and NO_2, Br and NO_2, or COOH and CH_3, are present in positions 3 and 5. Again, if the groups CH_3 or OCH_3 are present in position 2, *i. e.*, *meta* instead of *ortho* to the *p*-hydroxy groups, they have been found to impede tautomerization to such an extent that only the benzenoid carbinol and the fuchsone can be isolated.[4]

Thus, there are at present a number of hydroxy-triaryl carbinols on record of which all of the 3 components that constitute the tautomeric equilibrium are known; a still larger number are on record of which the stable existence of only 2 components is definitely established, a colorless carbinol and the fuchsone. But, strangely, there are no instances described in which the third possible variation has been observed; namely, the stable existence of a colored carbinol and the corresponding fuchsone. And yet the number of fuchsones described in the literature is quite extensive, although their formation has always been unforeseen since, in each case, the corresponding carbinol was sought. Bearing in mind the possible existence of a colored, in addition to the colorless tautomeric carbinol, it appeared to us probable that, in many instances, the existence of the colored carbinol had been overlooked; that, probably, the quinonoid carbinol,

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[1] Diethey, *Ber.*, 53, 261 (1920).

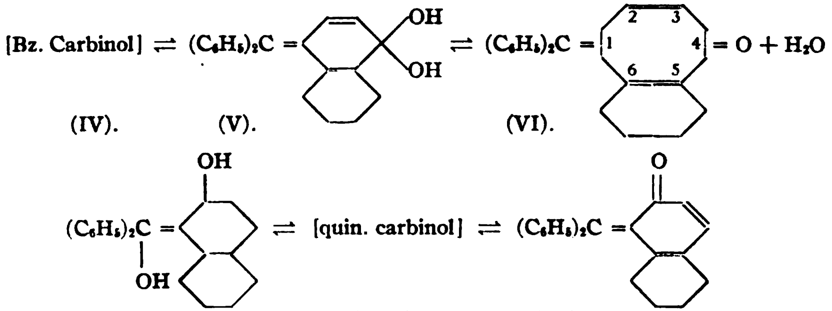
[2] Gomberg and Van Stone, THIS JOURNAL, 38, 1577 (1916).

[3] Demont, *Dissertation*, "Synthèse de quelques dérivés de la Parafuchsone, Fribourg," (Suisse) 1919.

[4] THIS JOURNAL, 39, 1674 (1917).

and not the fuchsone, was the first product of the reaction. When such a carbinol is dried for the purpose of analysis, or recrystallized from such solvents as benzene, acetic acid, etc., anhydrolysis would naturally take place and the carbinol would change to the fuchsone without becoming appreciably more intense in color.

With this idea in view, we subjected *p*-naphthofuchsone (VI) and *o*-1-naphthofuchsone-2- (IX) to a careful examination. Our surmise was verified; carbinols corresponding to these fuchsones were isolated, in the first case the quinonoid and in the second, the benzenoid tautomer only.



(IV). (V). (VI).

(VII). (VIII). (IX).

The statement that, in the case of the *p*-naphthofuchsone, only the quinonoid carbinol was obtained requires a modification. A definite answer to the question whether in a given instance both tautomeric carbinols exist is readily had, when the two tautomers happen to be clearly differentiated by the presence and absence of color, respectively, or by a distinct difference in the melting points, or by both. Equally definite is the answer in such cases when only the benzenoid carbinol is obtainable. But, on the other hand, when apparently only one carbinol is obtainable and that one possesses color, and is amorphous—as is usually the case—then it becomes difficult to give an unequivocal answer as to whether the substance under examination is the quinonoid carbinol alone or whether it contains an admixture of some of the benzenoid.

Occasionally[1] it may prove to be possible to establish the presence of some benzenoid tautomer in the colored substance when the latter is precipitated in part from an alkaline solution and in part from an acid solution. If the 2 samples, apparently alike in intensity of color, lose water at different rates, then certainly we are dealing with mixtures and not with a single tautomer. But when the 2 samples lose water at equal rates, the question is left open. If we may venture to assume that a quinonoid carbinol possesses an intensity of color near that of the corresponding fuchsone, then from the comparison of the 2 colored compounds an inference might be drawn as to whether the carbinol is wholly quino-

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[1] Gomberg and Todd, This Journal, 39, 2392 (1917).

noid or whether it contains some of the colorless tautomer. Such a comparison of the 2 solids would give at best only approximately correct results. A comparison of their solutions, while more certain, is not feasible, because the action of the solvent may induce partial tautomerization in an otherwise homogeneous carbinol.

It is obvious, then, that when only a colored carbinol is obtainable it often becomes difficult, if not impossible, to establish positively whether some of the benzenoid tautomer also is or is not present. This difficulty, however, is of no great moment to our problem. With the existence of the colored carbinol a demonstrable fact, it is clearly established that the formation of a fuchsone is dependent invariably upon the previous tautomerization of the benzenoid to the quinonoid carbinol.

The Condensation of Benzenone Chloride with α- and β-Naphthol.—This subject has been investigated by Clough,[1] who prepared *p*-naphthofuchsone and *o*-naphthofuchsone by the condensation of α- and of β-naphthol with benzophenone chloride. In the case of the former fuchsone he obtained a yield of only 15%, while he does not state the yield of the latter. Bistrzycki[2] also prepared *p*-naphthofuchsone by the condensation of benzilic acid with 1-hydroxy-2-naphthoic acid. Although the yields by this method are satisfactory, the method is quite complicated. Neither of these observers isolated the carbinols corresponding to these fuchsones. Carbinols isomeric with the two just mentioned have been prepared. Kaufmann and Egner[3] and Preizecker[4] prepared 1-hydroxy-2-naphthyl-diphenyl carbinol and 2-hydroxy-2-naphthyl-diphenyl carbinol by the action of phenyl-magnesium bromide on the esters of 1-hydroxy-2-naphthoic acid and 3-hydroxy-2-naphthoic acid, respectively.

***p*-Naphthofuchsone** (*Formula VI*).—Using a slight modification of the method given by Gomberg and Jickling for the preparation of *p*-hydroxy-triphenyl carbinol we obtained a quantitative yield of *p*-naphthofuchsone from benzophenone chloride and α-naphthol. Six g. of benzophenone chloride and 7.5 g. of α-naphthol were mixed in a flask protected from moisture by a tube of calcium chloride. After the reaction mixture had stood overnight, it was made slightly alkaline with dil. sodium hydroxide, decomposed with water and distilled with steam. The alkaline solution was decanted and the insoluble residue was dissolved in acetic acid, from which the fuchsone crystallized on the addition of water. The yield by this method was 7.8 g., or 100%. *p*-Naphthofuchsone is colored orange-yellow and melts at 179°. It gives a violet color with sulfuric acid.

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[1] Clough, *J. Chem. Soc.*, 89, 771 (1906).

[2] Bistrzycki, *Ber.*, 45, 1429 (1912).

[3] Kaufmann and Egner, *ibid.*, 46, 3779 (1913).

[4] Preizecker, *Monatsh.*, 35, 900 (1914).

3-Bromo-*p*-naphthofuchsone.—*p*-Naphthofuchsone was dissolved in glacial acetic acid in the proportion of 1 g. to 10 cc. and the calculated amount of a dil. solution of bromine in acetic acid was added. Gradually, bromo-naphthofuchsone separated as reddish-brown crystals, which melted at 176°. Yield, 70%. The compound gives an intense blue color with sulfuric acid.

3-Chloro-*p*-naphthofuchsone.—In a similar manner, but with the substitution of chlorine for bromine, chloro-naphthofuchsone was obtained as a bright red crystalline substance melting at 161°. The color produced with sulfuric acid is very similar to that produced by bromo-naphthfuchsone.

***o*-(1)-Naphthofuchsone-(2)** (*Formula IX*).—When β-naphthol and benzophenone chloride were mixed under the conditions given for the preparation of *p*-naphthofuchsone, condensation did not take place, but, under the influence of a catalyst, the reaction occurred, with the formation of the fuchsone. Six g. (1 mol.) of benzophenone chloride, 4.4 g (1.2 mols.) of β-naphthol and 4.1 g. (1.2 mols) of aluminum chloride were mixed in a flask and 50 cc. of carbon disulfide was added. The reaction mixture was protected from moisture with a tube of calcium chloride, and was allowed to stand overnight. Then it was boiled for one hour under a reflux condenser, decomposed with ice and distilled with steam. After the insoluble residue had been digested with dil. alkali, it was recrystallized from acetic acid; this gave 4 g. (a 50% yield) of brilliant orange red crystals of *o*-naphthofuchsone, melting at 198°. Clough gives the melting point as 194°, otherwise our observations agree with the properties of this compound as described by him. The fuchsone gives a green color with sulfuric acid.

Conversion into Carbinols.—In contrast with *p*-fuchsone it was found that *p*-naphthofuchsone and *o*-naphthofuchsone were quite insoluble in *N* alkali solution. The procedure finally adopted to dissolve the naphthofuchsones was to shake them overnight with 50% alcoholic 0.5 *N* sodium hydroxide. After solution was once effected dilution did not cause precipitation.

4-Hydroxy-1-naphthyl-diphenyl Carbinol.—*p*-Naphthofuchsone was dissolved in alcoholic sodium hydroxide and the solution was filtered. The clear liquid was diluted and stirred constantly while a solution of ammonium chloride was added. A very voluminous precipitate of the carbinol separated and was filtered after a short time. The carbinol was dried, but it could not be crystallized because it changed to the fuchsone in all solvents. The dried amorphous yellow powder obtained by precipitation was heated at 120°, and the moisture evolved was collected by passing it over calcium chloride and weighed.

Calc. for H_2O in $C_{23}H_{18}O_2$: 5.5. Found: (1) 5.6; (2) 5.8; (3) 6.0; Av., 5.8.

3-Bromo-4-hydroxy-1-naphthyl-diphenyl Carbinol.—According to the procedure given above, 3-bromo-4-hydroxy-1-naphthyl-diphenyl carbinol was obtained from bromo-naphthofuchsone as a canary-yellow powder. This carbinol also lost one molecule of water when heated to 120°

Calc. for H_2O in $C_{23}H_{17}O_2Br$: 4.4. Found: (1) 4.3; (2) 4.2.

3-Chloro-4-hydroxy-1-naphthyl-diphenyl Carbinol.—In the same manner as the preceding, 3-chloro-4-hydroxy-1-naphthyl-diphenyl carbinol was prepared from chloro-naphthofuchsone. It resembles the bromo-carbinol in appearance and, on heating, loses one molecule of water.

Calc. for H_2O in $C_{23}H_{17}O_2Cl$: 5.0. Found: (1) 4.6; (2) 4.6.

All these carbinols give the same colors with sulfuric acid as do the corresponding fuchsones. It was not found possible to isolate the benzenoid and quinonoid modifications. It is probable that the carbinols obtained consisted in each case largely, if not entirely, of the quinonoid tautomer.

2-Hydroxy-1-naphthyl-diphenyl Carbinol.—2-Hydroxy-1-naphthyl-diphenyl carbinol was readily prepared from *o*-naphthofuchsone in the same way that the preceding carbinols were prepared from their corresponding *p*-naphthofuchsones. It was found that the *o*-hydroxy carbinol was quite stable and could be crystallized from benzene and petroleum ether in the form of pure white plates, which give off water when heated, became red and melted slightly below the true melting-point of the fuchsone (194°). All efforts to convert this benzenoid carbinol to the quinonoid tautomer resulted in the formation of the fuchsone; even when heated to 150° with water in a sealed tube it suffered this change. Heated to 120° by itself, it becomes red, loses water and gives the fuchsone directly.

Calc. for H_2O in $C_{23}H_{18}O_2$: 5.5. Found: (1) 6.3; (2) 6.6.
Calc. for $C_{23}H_{18}O_2$: H, 5.52; C, 84.7. Found: H, 5.76, 5.92, C, 84.9, 85.2.

The behavior of this compound shows a distinct resemblance to that of *o*-hydroxy-triphenyl carbinol described by Baeyer.[1] It appears from the comparison of *ortho* and *para*-hydroxy-triphenyl carbinols with *ortho*- and *para*-hydroxy-naphthyl-diphenyl carbinols that in both cases the *ortho* isomer is more stable than the *para*, and that the substitution of the naphthyl for the phenyl group decreases the stability of the carbinol.

When *o*-naphthofuchsone was dissolved in alcohol to which a few drops of ammonia had been added, it was found that, on standing, feathery white crystals, presumably the ammonium salt, were formed. The same substance is readily prepared from the fuchsone by shaking the latter with alcohol saturated with ammonia. When the salt is heated in an open tube, it is converted into the fuchsone, but when it is heated in a sealed melting-point tube, it melts at 171°.

Hydrogen Chloride Addition Compounds of the Naphthofuchsones.—*p*-Fuchsone readily absorbs 2 mols. of hydrogen chloride when placed in

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[1] Baeyer, *Ann.*, 354, 167 (1907).

an atmosphere of the gas,[1] Similarly, when *p*-naphthofuchsone was placed in a porcelain boat and dry hydrogen chloride was passed over it, the absorption of the acid proceeded rapidly and was complete in 3 hours; the contents of the boat acquired the appearance of a black viscous mass. The absorption was somewhat more than that calculated for 2 molecules of hydrogen chloride. The boat was then placed in a desiccator over soda lime, but the loss in weight was only slight. Under diminished pressure about $^1/_3$ of the total acid was lost in the first 24 hours, and in 4 to 5 days all the acid was given up. *o*-Naphthofuchsone also absorbed hydrogen chloride, but it did not take up so large an excess over 2 molecules. It gave off its acid *in vacuo* much more slowly than the *para*-compound, and 23 days were required for elimination of 80% of the acid. It was found that chloro- and bromo-naphthofuchsones do not form additive compounds with hydrogen chloride.

Summary.

1. Improved methods of preparing *p*-naphthofuchsones and *o*-naphthofuchsones are described.

2. It was found that the fuchsones can be converted into their corresponding carbinols. The *para*-fuchsone gives the quinonoid almost entirely, while the *ortho*- changes to the benzenoid carbinol exclusively.

3. It was found that the influence of an hydroxy-naphthyl group is much greater than that of an hydroxy-phenyl group. In *p*-hydroxy-triphenyl carbinol, both tautomers are stable; in the *p*-hydroxy-naphthyl-diphenyl carbinol, the quinonoid only is stable. A similarly greater tautomerizing tendency was observed when *o*-hydroxy-triphenyl carbinol was compared with *o*-hydroxy-naphthyl-diphenyl carbinol; the former does not give the fuchsone on heating, while the latter does.

This investigation was done with the assistance of The National Aniline and Chemical Company Fellowship, and we wish to express our obligations for the generous aid we have thus received.

ANN ARBOR, MICHIGAN.

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[1] THIS JOURNAL, 37, 2585 (1915).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TORONTO.]

FRIEDEL AND CRAFTS' REACTION—NITRO-PHTHALIC ANHYDRIDES AND ACETYLAMINO-PHTHALIC ANHYDRIDES WITH BENZENE AND ALUMINUM CHLORIDE.

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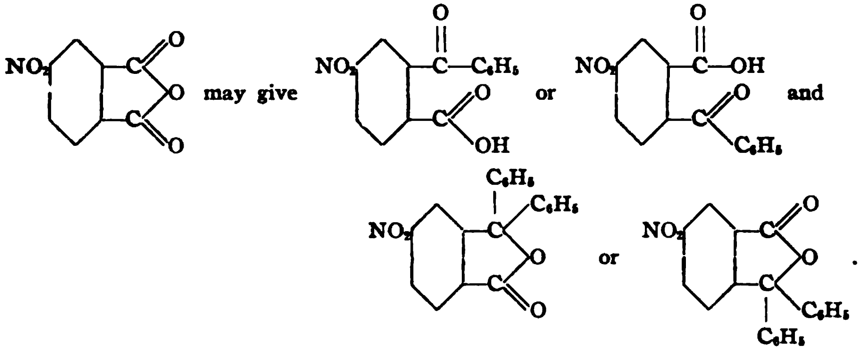
In Freidel and Crafts'[1] synthesis of *o*-benzoylbenzoic acid, phthalic anhydride is heated with benzene and aluminum chloride. This reaction has been studied quantitatively by Rubidge and Qua,[2] who state the conditions under which a 97% yield may be obtained and also the conditions which give a good yield of diphenyl-phthalide.

The object of the present research was to study this reaction when the 2 nitro-phthalic anhydrides and the 2 acetylamino-phthalic anhydrides were used. When a substituted phthalic anhydride is treated with benzene and aluminum chloride 2 acids and 2 derivatives of diphenyl-phthalide are possible. For example,



In most of the reactions studied the yields of the acids were poor, and in only one case was any attempt made to alter the conditions of the experiment in order to obtain the derivatives of diphenyl-phthalide.

The literature on this subject is confined to 2 papers by Rainer.[3] From 4-nitro-phthalic anhydride, this investigator obtained 2-benzoyl-4-nitrobenzoic acid identical with that obtained by Kliegl[4] from phenyl-nitrofluoren and 6-benzoyl-3-nitrobenzoic acid, m. p. 212°. Rainer also describes the reduction of the latter acid to 6-benzoyl-3-aminobenzoic acid, m. p. 193–4°. The products obtained separately by Rainer and Kliegl are identical with those obtained by the author from 4-acetylamino-phthalic anhydride.

In this work, the acetylamino-phthalic anhydrides were used instead

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[1] *Ann. chim. phys.*, [6] 14, 446 (1888).

[2] Rubidge and Qua, THIS JOURNAL, 36, 732 (1914).

[3] Rainer, *Monatsh.*, 29, 178; 29, 431 (1908).

[4] Kliegl, *Ber.*, 38, 294 (1905).

of the amino compounds because of the difficulty of preparing the amino anhydrides from the corresponding acids and also because of the general difficulty of using unprotected amines in the Friedel and Crafts' reaction.

Preparation of Nitro-phthalic Acids.—Several methods of preparing nitrophthalic acids have been described. Beilstein and Kurbatow[1] nitrated naphthalene and oxidized the product, Miller[2] nitrated phthalic acid and May,[3] Edinger,[4] and Poupold[5] obtained nitrophthalic acids by nitration of phthalic anhydride. Bogert and Boroschek,[6] using the latter method, increased the yield of 3-nitro-phthalic acid from 25% to 38% by renitration. In the method described below larger quantities of the mixed acids are used and renitration is unnecessary. A mixture of 125 g. of nitric acid (sp. gr. 1.5) and 125 g. of sulfuric acid (sp. gr. 1.834) was cooled and put in a 2-liter flask containing 50 g. of phthalic anhydride. The flask was heated gently on a water-bath until the temperature reached 75°, and then removed. Vigorous nitration began at about 80° and the flask was kept at about 100° for 3 hours, then allowed to cool, and the contents was poured into an equal volume of water. After standing overnight the precipitated acids were collected on a filter and the 3-nitro-phthalic acid was obtained by recrystallization of the product from hot water. The mother liquor was concentrated and 4-nitro-phthalic acid extracted with ether. The 4-nitro-phthalic acid may be purified by dissolving it in 95% alcohol and gradually adding benzene to the solution; but the method described by Bogert and Boroschek was found to give a purer product. This preparation gave a yield of 42% of the 3-nitro-phthalic acid and 47% of the 4-nitro-phthalic acid.

Preparation of 3-Nitro-phthalic Anhydride.—Bogert and Boroschek heated 3-nitro-phthalic acid for from 6 to 8 hours at 235–240° and obtained the anhydride in good condition. Kahn[7] gave 218° as the maximum temperature to be used. but later[8] used 230°. Bogert's experiment, repeated, gave considerable tarry material, and the product melted at 162–4°. The method finally adopted was to put the acid into a small flask and heat it in an air-oven at 215–7° (thermometer bulb in the melt) from 3 to 4 hours. When recrystallized from glacial acetic acid, the anhydride had a very pale yellow-brown color and melted sharply at 164°. Yield, about 89%. Quantitative determinations showed that at 215° the anhydride was slowly volatilized.

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[1] Beilstein and Kurbatow, *Ann.*, 202, 217 (1880).

[2] Miller, *ibid.*, 208, 223 (1881).

[3] May, *Inaug. Dissertation*, Frieburg, 1880.

[4] Edinger, *J. prakt. Chem.*, [2] 53, 382 (1895).

[5] Poupold, *Inaug. Dissertation*, Basle, 1897.

[6] Bogert and Boroschek, This Journal, 23, 743 (1902).

[7] Kahn, *Ber.*, 35, 472 (1902).

[8] *Ibid.*, 35, 3859 (1902).

Preparation of 4-Nitro-phthalic Anhydride.—A quantity of 4-nitrophthalic acid was heated in a small flask, in an air-oven, at 165–8°, for about 3 hours. The product, when cooled, was at first a brown gummy mass, but it slowly crystallized on standing. It was recrystallized first from acetyl chloride and then from glacial acetic acid. M. p., 114°. Yield, 80%. This anhydride is volatile at 165°.

Preparation of the Mono-ethyl Esters of 3-Nitro-phthalic Acid.—A solution of 3-nitro-phthalic acid in absolute ethyl alcohol was saturated with hydrogen chloride and boiled for one hour under a reflux condenser. The ester, when recrystallized, melted at 110°. This ester is 2-carbethoxy-3-nitrobenzoic acid.[1]

When 3-nitro-phthalic anhydride was dissolved in absolute ethyl alcohol and boiled for 5 hours, the isomeric ethyl ester, 6-carbethoxy-2-nitrobenzoic acid, was formed.[2] M. p. 156–7°.

Preparation of 3-Acetylamino-phthalic Anhydride.—As interest lay only in the acetyl derivative of the amino-phthalic anhydride, it was found more convenient to prepare this compound directly from the hydrochloride of the amine. Bogert and Jouard[3] obtained the hydrochloride of 3-amino-phthalic acid by reduction of the nitro acid with stannous chloride and recrystallization of the product from hot conc. hydrochloric acid. They also prepared the acetyl derivative from the amine and from the hydrochloride by using acetic anhydride, but gave no details.

Forty g. of 3-nitrophthalic acid was finely powdered and gradually added to 325 cc. of stannous chloride solution (150 g. of stannous chloride, 250 cc. of conc. hydrochloric acid and 50 cc. water) while the mixture was stirred thoroughly. The temperature of the reducing solution was kept at about 22° and the acid went slowly into solution. A short time after complete solution was affected the hydrochloride was precipitated slowly as a white voluminous substance. After several hours the precipitate was collected and the filtrate saturated with hydrogen chloride, which produced more of the precipitate. The product was recrystallized from hot conc. hydrochloric acid and dried, *in vacuo,* over both sulfuric acid and sodium hydroxide. Miller[4] states that he obtained a double tin salt by reduction of 3-nitro-phthalic acid with stannous chloride and based his formula on a chlorine determination; later[5] he modified this to conform with additional analyses. Bogert and Jouard state that they found no trace of a double salt. In one of our preparations this double salt was obtained, and investigation showed that the temperature was the controlling

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[1] *Ann.*, **208**, 223 (1881).

[2] THIS JOURNAL, **23**, 746 (1901).

[3] Bogert and Jouard, *ibid.*, **31**, 485 (1909).

[4] Miller, *Ber.*, **11**, 994 (1878).

[5] *Ann.*, **208**, 223 (1881).

factor; at about 22°, no tin salt was obtained, but when the reducing solution was allowed to become hot (sometimes 75° was reached) the double salt was found.

Twenty g. of the dry hydrochloride was dissolved in 80 cc. of acetic anhydride and boiled for 5 minutes. The acetylamino-phthalic anhydride crystallized when the solution was cooled, and was recrystallized from alcohol. M. p. 185–6°. Yield, 55%, calculated from the nitro compound.

Preparation of 4-Acetylamino-phthalic Anhydride.—The direct reduction of 4-nitro-phthalic acid with stannous chloride gives a double tin salt. When tin is precipitated by hydrogen sulfide this compound is converted into aminobenzoic acid with loss of carbon dioxide. Several indirect methods of preparing the amino acid have been proposed,[1] the one used below is that given by Bogert and Renshaw.[2]

The acid ammonium salt of 4-nitro-phthalic acid was converted into the imide and the nitro-imide reduced with stannous chloride. The amino-phthalimide, when boiled with ammonia, gave the ammonium salt of amino-phthalic acid from which the free acid was liberated by addition of hydrochloric acid. The 4-amino-phthalic acid was dissolved in acetic anhydride, boiled for a few minutes, allowed to cool and the acetylamino-phthalic anhydride filtered off. The product, recrystallized from ethyl acetate and acetyl chloride, did not have a sharp melting-point (203–6°). The yield was less than 10%, calculated on the acid ammonium salt.

3-Nitrophthalic Anhydride with Benzene and Aluminum Chloride.

Because of the slight solubility of the anhydride in benzene, a larger excess of this reagent was used. A mixture of 100 cc. of benzene and 6.5 g. of 3-nitro-phthalic anhydride (finely powdered) was put in a 300-cc. flask attached to a reflux condenser and boiled for a few minutes on the water-bath. After cooling the product, 9.0 g. of powdered aluminum chloride was added slowly while the flask was shaken at intervals. The mixture darkened rapidly and soon assumed a deep brown color. Then it was heated on the water-bath until hydrogen chloride ceased to escape, which usually required about 4 or 5 hours. When the mixture became cold, 80 cc. of 10% hydrochloric acid was added and the excess of benzene was distilled with steam. The solution was cooled to 15° and filtered to remove the black gummy mass. The filtrate, evaporated to half its volume and extracted twice with ether, gave 3-nitro-phthalic acid equivalent to 55–60% of the anhydride used.

The black residue from the reaction was thoroughly agitated with a warm 5% solution of sodium hydroxide and filtered from the insoluble

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[1] *Ber.*, 34, 4352 (1901); *J. Chem. Soc.*, 87, 1269 (1905).

[2] Bogert and Renshaw, THIS JOURNAL, 30, 1137 (1908).

portion. The filtrate contained the 2 possible benzoyl-nitrobenzoic acids as sodium salts, from which the free acids were obtained by the addition of 5% hydrochloric acid. The hydrochloric acid was added very slowly and at intervals of several hours; otherwise the precipitate was a gummy mass which made subsequent operations difficult. The 2 constituents of this precipitate have different solubilities in cold 95% alcohol, but the separation by acetic acid was found better than fractional crystallization from alcohol.

Hot 80% acetic acid dissolved one of these constituents and only a trace of the other. The acetic acid solution was filtered while hot, water was added until a faint cloudiness appeared, and after the solution had stood overnight, the precipitate was filtered off and dried. It softens at 140° and melts, with decomposition, at 158–61°. The portion insoluble in acetic acid melts with decomposition at 217–21°.

Identification of the Portion Insoluble in Acetic Acid.—*Hydrolysis.*—The finely divided substance was added to molten potassium hydroxide contained in a nickel dish and the temperature was kept a few degrees above the fusion point for from one to two hours. Then the mass was dissolved in water, acidified with hydrochloric acid, washed, and kept in a vacuum-oven at 100° until the residue had a constant melting-point, 146–8°—that of *o*-nitrobenzoic acid. The sublimate was benzoic acid.

Synthesis.—(A convenient method of preparation.) Ten g. of 2-carbethoxy-3-nitrobenzoic acid was dissolved in 15 cc. of thionyl chloride and kept at 60–70° until hydrogen chloride and sulfur dioxide were no longer given off. The excess thionyl chloride was then removed by distillation under reduced pressure. The resulting acid chloride is a light brown crystalline substance, is soluble in benzene and in ether, melts at 76–7°. To a solution of 8.4 g. of the acid chloride in 50 cc. of benzene, 9 g. of powdered aluminum chloride was added slowly. When the initial reaction had ceased, the flask was heated on the water-bath until the evolution of hydrogen chloride ceased. After acidification, the benzene was distilled with steam and the precipitate saponified with alcoholic potassium hydroxide. Water and hydrochloric acid were added which caused the precipitation of a light brown crystalline substance that melted with decomposition at 220–1° and was identical with the substance described above as insoluble in acetic acid. Yield, 45%, calculated on the acid chloride used.[1]

This method of synthesis and the products of hydrolysis leave no doubt that the acid is 6-benzoyl-2-nitrobenzoic acid.

Calc. for $C_{14}H_9O_5N$: N, 5.16. Found: 5.10.

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[1] Mr. M. E. Smith is working on the use of ester acid chlorides in Friedel and Crafts' reaction, in this laboratory.

The acid is soluble in alcohol, acetone, and in pyridine and slightly soluble in ether and in benzene.

Identification of the Portion Soluble in Acetic Acid.—*Hydrolysis.*—The products of hydrolysis by potassium hydroxide were *m*-nitrobenzoic acid and benzoic acid.

Synthesis.—The acid was made from 6-carbethoxy-2-nitrobenzoic acid, according to the method described above. The acid chloride obtained is a yellowish oily liquid miscible with benzene and with ether. It decomposes above 100°. The acid obtained melted with decomposition at 157–60°, was identical with the above portion soluble in acetic acid, and is 2-benzoyl-3-nitrobenzoic acid. It is very soluble in acetone and slightly soluble in ether, in alcohol and in water.

The yields of benzoyl-nitrobenzoic acids obtained when 3-nitro-phthalic anhydride reacts with benzene and aluminum chloride are very low. From 6.5 g. of the anhydride about 3.8 g. was recovered as 3-nitro-phthalic acid and about 1.7 g. of a black resinous substance insoluble in sodium hydroxide and also insoluble in the usual organic solvents. Approximately 0.7 g. of 6-benzoyl-2-nitrobenzoic acid and 0.6 g. of 2-benzoyl-3-nitrobenzoic acid were obtained. Various modifications were made in the method but neither the use of freshly distilled aluminum chloride, nor the addition of carbon disulfide as a diluent, nor an excess of aluminum chloride produced any better yields. If heat was applied longer than 5 hours the resinous product increased and the recovered 3-nitro-phthalic acid decreased, but the yield of benzoyl-nitrobenzoic acids was not improved.

4-Nitro-phthalic Anhydride with Benzene and Aluminum Chloride.

The method used was similar to that described for 3-nitro-phthalic anhydride. Separation of the 2 benzoyl-nitrobenzoic acids was made by the use of methyl alcohol as described by Rainer. One isomer, 6-benzoyl-3-nitrobenzoic acid, m. p. 212°, recrystallizes from the methyl alcohol while the more soluble isomer, 2-benzoyl-4-nitrobenzoic acid, m. p. 164–5°, is obtained by concentrating the alcoholic solution. With 6.5 g. of 4-nitro-phthalic anhydride dissolved in 100 cc. of benzene and 9 g. of aluminum chloride, about 0.8 g. of 6-benzoyl-3-nitrobenzoic acid and 0.5 g. of 2-benzoyl-4-nitrobenzoic acid were produced while 50% of the anhydride was recovered as 4-nitro-phthalic acid. The brown resinous substance, insoluble in sodium hydroxide, formed in the reaction, gave positive test for nitrogen and left a small ash on ignition.

3-Acetylamino-phthalic Anhydride with Benzene and Aluminum Chloride.

A mixture of 6.8 g. of 3-acetylamino-phthalic anhydride and 50 cc. of benzene was placed in a 200 cc. flask and boiled under a reflux condenser for several minutes. This solution was cooled and 9 g. aluminum chloride was slowly added while the contents of the flask was shaken thoroughly to prevent caking. The reaction was carried out on the water-bath until hydrogen chloride was no longer evolved, when 60 cc. of 10% hydrochloric acid was added and the benzene was distilled with steam. The distillation with steam removes the acetyl radical. The precipitate was shaken with a hot saturated solution of sodium carbonate and filtered from the brownish insoluble material. Slow addition of 5% hydrochloric acid to the filtrate gave a crystalline precipitate which, when recrystallized from ethyl alcohol, was white and melted at 193–4°. Yield, 51% calculated on the basis of the 3-acetylamino-phthalic anhydride used. The alcohol solution evaporated to dryness gave a small quantity of a pale yellow crysttalline substance which melted at 159–60° when recrystallized from water.

Identification of the Substance Melting at 193–4°.—*Hydrolysis.*—Hydrolysis with potassium hydroxide was not very successful; the only product that could be identified was benzoic acid.

Preparation by Reduction of the Nitro Compound.—To a solution of 2 g. of 2-benzoyl-3-nitrobenzoic acid in a small quantity of ammonia, 12 g. of ferrous sulfate and more ammonia were added. At first this was heated gently and then it was boiled for a few minutes. Six. g. of charcoal was added and it was boiled again for a few minutes before it was filtered. The black precipitate was boiled with water for about 10 minutes. After the residue had been removed the filtrate was boiled until all free ammonia was expelled; then powdered potassium alum was added, and the mixture was allowed to stand until it became cold. The precipitate formed was dried, boiled with 95% alcohol, and the solution filtered hot. The crystals separated from the cold alcoholic solution were identical with those obtained in the Friedel and Crafts reaction,

Calc. for $C_{14}H_{11}O_3N$: N, 5.81. Found: 5.74.

This substance melting at 193–4° is, therefore, 2-benzoyl-3-aminobenzoic acid. It is slightly soluble in water, in ether and in benzene, and soluble in hot alcohol.

Identification of the Substance Melting at 159–60°.—As a very small quantity of this substance was obtained, it was not possible to make a nitrogen determination. On so small a scale, fusion with potassium hydroxide was not successful, but the substance was prepared from 6-benzoyl-2-nitrobenzoic acid by the method described above. Since this acid is soluble in hot water, the aluminum hydroxide was filtered from the hot solution. Crystals separated from the cold solution gave a melting-point of 159–60°. Therefore, this pale yellow substance is 6-benzoyl-2-aminobenzoic acid. It is insoluble in benzene but soluble in alcohol, in ether, in acetone, and in hot water.

Identification of the Substance Insoluble in Hot Sodium Carbonate Solution.—This brown material from the Friedel and Crafts reaction is very soluble in alcohol, in ether and in benzene. It was purified from solution in alcohol to which water was added carefully until a slight turbidity appeared; after several hours, a few pale salmon-colored crystals appeared; these melted at 130°. Some hours later, an orange-colored amorphous powder (m. p. 86–89°) was obtained from the alcoholic solution. Efforts to obtain a product with a sharper melting-point were without success.

In this Friedel and Crafts reaction, two diphenylamino-phthalides might be formed which we may call diphenyl-3-amino-phthalide and diphenyl-6-aminophthalide. The experiment was repeated under conditions shown by Rubidge and Qua to be favorable to an increased production of phthalides. Thus, 6.8 g. of 3-acetylamino-phthalic anhydride, 50 cc. of benzene and 9 g. of aluminum chloride were heated on the water-bath for 7 hours; then 10 cc. of acetic anhydride was added and the heating was continued for another 7 hours. The principal product obtained was an orange-colored gummy substance which, when crystallized from alcohol, was identical with the previous product, m. p. 86–9°. No trace of the substance melting at 130° was found. This compound is either diphenyl-3-amino-phthalide or diphenyl-6-amino-phthalide.

Calc. for $C_{20}H_{15}O_2N$: N, 4.65. Found: 4.47.

The yield of this phthalide was 11% in the original experiment and 31% when acetic anhydride was used, calculated on the basis of 3-acetylamino-phthalic anhydride.

4-Acetylamino-phthalic Anhydride with Benzene and Aluminum Chloride.

A mixture of 5 g. of 4-acetylamino-phthalic anhydride (crude) and 50 cc. of benzene was boiled for a few minutes, then cooled and 6.75 g. of aluminum chloride was added slowly while the mixture was well shaken. The reaction was carried out at 80–85° until hydrogen chloride was no longer evolved, and the solution was then allowed to cool. To this product 50 cc. of 10% hydrochloric acid was added and the excess of benzene was distilled with steam. When cold, the residue was filtered, boiled with a saturated solution of sodium carbonate and the solution filtered from the small quantity of gummy insoluble matter. Hydrochloric acid was added slowly to the filtrate and a pale yellow precipitate was obtained which, when washed with ice-water and dried, melted at 183–4°. Separation of the 2 benzoyl-amino benzoic acids was accomplished by fractional crystallization from water. After 3 recrystallizations, 2 fractions were isolated, one melting at 193–4° and the other, at 195–6°(with decomposition).

Rainer[1] obtained a benzoyl-aminobenzoic acid by reduction of "*o*-benzoyl-*m*-nitrobenzoic acid;" it melted at 193–4°. This is identical with one of the acids obtained from the above reaction and is 6-benzoyl-3-

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[1] *Monatsh.*, 29, 431 (1908).

aminobenzoic acid. Kliegl[1] reduced "*o*-benzoyl-*p*-nitrobenzoic acid" (which he obtained from phenylnitro-fluoren) and isolated a product which melted at 195° with decomposition. This isomeric compound is 2-benzoyl-4-aminobenzoic acid and is the other acid obtained by the Freidel and Crafts reaction.

Summary.

1. The reactions of aluminum chloride and benzene with 3-nitro-phthalic anhydride, 4-nitro-phthalic anhydride, 3-acetylamino-phthalic anhydride and 4-acetylamino-phthalic anhydride, respectively, have been studied and the 2 possible derivatives of benzoylbenzoic acid have been obtained in each case.

2. In only one reaction was a derivative of diphenyl-phthalide isolated and, in this instance, Rubidge and Qua's method for increasing the yield of phthalide gave good results.

3. Seven new compounds have been prepared:

	M. p.
6-Benzoyl-2-nitrobenzoic acid	220–21° (decomp.)
2-Benzoyl-3-nitrobenzoic acid	157–60° (decomp.)
6-Benzoyl-2-aminobenzoic acid	159–60°
2-Benzoyl-3-aminobenzoic acid	193–4°
Diphenyl-?-amino-phthalide	86–9°
2-Carbethoxy-3-nitrobenzoyl chloride	76–7°
6-Carbethoxy-2-nitrobenzoyl chloride	Oil

4. Detailed directions are given for the preparation of several of the compounds used in the experiments and an improved method for the preparation of the benzoyl-3-aminobenzoic acids.

This research was done under the direction of Professor F. B. Allan. The author held a studentship from the Honorary Advisory Council for Scientific and Industrial Research.

TORONTO, CANADA.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN.]

TAUTOMERISM IN THE TRIARYL-CARBINOLS: MONO-PARA-HYDROXY-DIPHENYL-α-NAPHTHYL CARBINOL.

BY M. GOMBERG AND N. A. LANGE.

Received June 17, 1920.

In a preceding paper[2] it has been shown that in the monohydroxy-triaryl carbinols, the naphthyl nucleus exerts a much more pronounced tautomerizing influence than does the phenyl nucleus when each carries an hydroxyl group; while *p*-hydroxy-triphenyl carbinol is stable both in its benzenoid and its quinonoid modification, *p*-hydroxy-naphthyl-diphenyl carbinol (I) is not stable in its benzenoid form, but spontaneously changes

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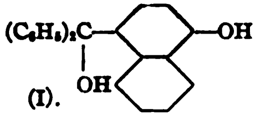
[1] *Ber.*, 38, 296 (1905).

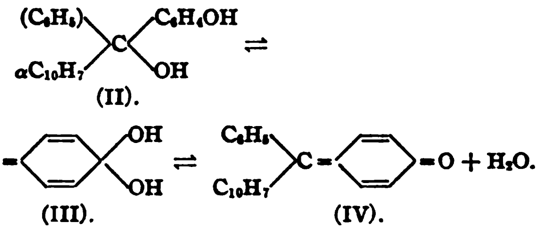
[2] Gomberg and Sullivan, THIS JOURNAL, 42, 1864 (1920).

into the quinonoid. We have now prepared a carbinol isomeric with (I), namely, mono-*p*-hydroxy-diphenyl-naphthyl carbinol (II), wherein the hydroxyl group is situated in the phenyl and not in the naphthyl ring. We find that, in spite of the separateness of the hydroxyl group from the naphthyl nucleus, the latter nonetheless still exerts a noticeably greater favorable influence upon the quinoidation of the carbinol than is exerted by a phenyl nucleus. The benzenoid tautomer (II) spontaneously changes into the quinonoid tautomer (III), which, on heating, readily gives the corresponding fuchsone (IV).

The carbinol, obtained under diverse circumstances, is invariably colored and is amorphous. Whether it is entirely free from the colorless, benzenoid, tautomer seems impossible at present to determine. Judging, however, from the intensity of its color as compared with that of the fuchsone, one would infer that some benzenoid carbinol must be present.

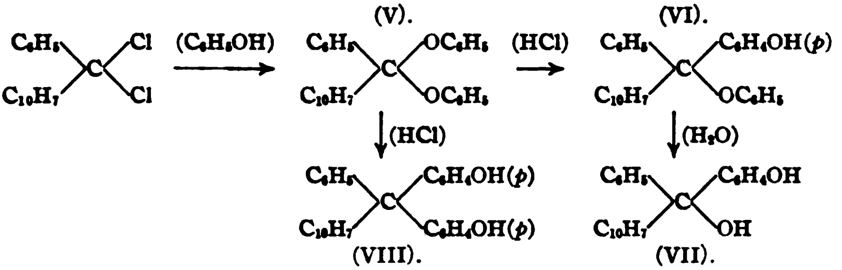


(I).



The demonstration of the existence of the quinonoid tautomer of *p*-hydroxy-diphenyl-naphthyl carbinol adds another instance in support of the generalization that the colored fuchsones—which are the mother substances of the triphenyl-methane dyes—are but the final step in the chain of reactions: benzenoid carbinol ⟶ quinonoid carbinol ⟶ fuchsone. It may yet prove possible to adduce direct experimental evidence of similar tautomerization in the formation of the dyes themselves.

The carbinol under consideration has been prepared by the condensation of α-naphthyl-phenyl-ketone chloride with phenol. The condensation was found to proceed in the same manner as described for the condensation of benzophenone chloride with phenol.[1] Here again, the mechanism of the reaction is



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[1] Gomberg and Jickling, THIS JOURNAL, 37, 2575 (1915).

Depending upon the conditions of procedure, the result of the condensation is the diphenoxy-compound (V), or the carbinol (VII), or the tetraaryl-methane derivative (VIII).

α-Naphthyl-phenyl-ketone Chloride, $(C_6H_5)(C_{10}H_7) : C : Cl_2$.—α-Naphthyl-phenyl ketone, prepared by the method of Montague,[1] and the calculated quantity of phosphorus pentachloride, were heated at 100° until the reaction mixture was liquid and the pentachloride had gone into solution. The phosphorus oxychloride was removed by distillation under reduced pressure at a temperature of 100°, which left the ketone chloride as viscous brown liquid. This was then poured into low boiling petroleum ether and the solution was boiled for a short time with charcoal and filtered. On standing, small colorless needles of the ketone chloride separated. A second crystallization from petroleum ether yielded practically pure chloride. The yield was 60%. On heating, the chloride begins to soften at about 86° and melts at 92°. Attempts to purify the chloride by distillation under reduced pressure were not successful because of its decomposition at elevated temperatures.

Calc. for $C_{17}H_{12}Cl_2$: Cl, 24.7. Found: 24.3.

Phenyl-α-naphthyl-diphenoxy-methane, $(C_6H_5)(C_{10}H_7) : C :- (O.C_6H_5)_2$.—Six g. of phenol was dissolved in 30 cc. of dry benzene and the solution heated to boiling under a reflux condenser; to this boiling solution, protected from moisture by a calcium chloride tube, 7 g. of ketone chloride, dissolved in 30 cc. of benzene, was added in small portions during the course of several hours. This solution was kept boiling until hydrogen chloride was no longer evolved. After the solution was cooled ammonia was added to neutralize any hydrogen chloride still in solution, and the mixture was then distilled with steam in order to remove the excess of phenol. The solid residue was digested with cold *N* sodium, hydroxide solution, and then boiled with a small quantity of alcohol which removes the yellow color caused by the presence of a small amount of the fuchsone. Finally, the product was purified by recrystallization from amyl alcohol, which formed white crystals that melt at 169–70°. The yield was 80–85%. The substance is readily soluble in benzene, chloroform, carbon tetrachloride, carbon disulfide, acetone; is fairly soluble in ether, ethyl acetate and amyl alcohol, and is slightly soluble in petroleum ether and in alcohol. On treatment with aqueous solution of acids, the diphenoxy compound hydrolyzes to give the ketone and phenol. When placed in an atmosphere of dry hydrogen chloride, it is converted into phenol and the fuchsone described below.

Calc. for $C_{29}H_{22}O_2$: C, 86.53; H, 5.51. Found: C, 86.31; H, 5.33.

α-Naphthyl-phenyl-quinomethane, $(C_6H_5)(C_{10}H_7) : C : C_6H_4 : O$.—Eight g. of ketone chloride and 13.5 g. of phenol were placed in a round-

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[1] *Rec. trav. chim.*, **26**, 280 (1917).

bottom flask and protected from moisture by a tube of calcium chloride. The reaction was allowed to proceed for 12 hours at room temperature, when the mixture was heated to about 50° for one hour. The contents of the flask were distilled with steam in order to remove the excess of phenol. This caused the fuchsone to remain as a dark red viscous liquid, which gradually solidified on standing. On recrystallization from dil. alcohol, yellow crystals are obtained which melt at 169–70°. The yield was 85–90%. The fuchsone is readily soluble in chloroform, carbon tetrachloride, benzene; is fairly soluble in alcohol, acetone, ethyl acetate, and only slightly soluble in petroleum ether.

Calc. for $C_{23}H_{16}O$: C, 89.61; H, 5.23. Found: C, 89.67; H, 5.32.

The fuchsone dissolves in sulfuric acid with a deep red color. On treating the fuchsone with an aqueous solution of sodium hydroxide, it is converted into the carbinol as described below.

4,4'-Dihydroxy-triphenyl-α-naphthyl Methane, $(C_6H_5)(C_{10}H_7):C(C_6H_4OH)_2$.—Four g. of the ketone chloride and 30 g. of phenol, previously saturated with dry hydrogen chloride, were heated at 110° for 24 hours. The contents of the flask were protected from moisture by a tube of calcium chloride. After the excess of phenol had been removed by steam distillation, the semi-solid residue, while still warm, was poured into 500 cc. of a 5% sodium hydroxide solution and thoroughly stirred to break up all lumps. After it had stood for about $^1/_2$ hour the white precipitate was removed from the alkaline solution by filtration, and washed with water. The precipitate was recrystallized several times from glacial acetic acid by careful addition of water to the hot solution. The crystals were dissolved in ether, and the solution was boiled with charcoal, filtered and evaporated to dryness. Another recrystallization of the solid residue from acetic acid gave white microscopic needles, which begin to soften at 206° and melt with decomposition to a red liquid at 209–10° (uncorr.). The yield was 15–20%. The compound is readily soluble in ether, methyl or ethyl alcohols; is fairly soluble in chloroform, carbon tetrachloride, *m*-xylene, toluene, benzene or acetic acid; is very slightly soluble in 10% sodium hydroxide solution and insoluble in petroleum ether. For analysis it was dried one hour at 110–5°.

Calc. for:		Found:	
$C_{29}H_{22}O_2$:	C, 86.53; H, 5.51	Sample A—	C, 88.71; H, 5.14
$C_{29}H_{22}O_2$ $0.5H_2O$:	C, 88.55; H, 5.34		C, 88.82; H, 5.24
$C_{29}H_{22}O_2H_2O$:	C, 90.62; H, 5.20	Sample B—	C, 88.41; H, 5.23
			C, 88.74; H, 5.06

Apparently the dihydroxy compound has been produced first, but on subsequent treatment, in the process of purification, it has suffered dehydration. From the fact that it is still somewhat soluble in sodium hydroxide solution, it must be concluded that the dehydration has occurred between 2 molecules of the tetra-aryl-methane compound, and not within one molecule through the destruction of both phenolic hydroxyl groups.

Diphenyl-α-naphthyl Carbinol, $(HOC_6H_4)(C_6H_5)(C_{10}H_7):C.OH$. — The fuchsone was dissolved in a small quantity of alcohol and then heated to boiling with *N* sodium hydroxide solution until the color of the solution had changed from red-yellow to a very light yellow. This solution was diluted with an equal volume of water and the carbinol was precipitated as a light yellow amorphous material upon the addition of a saturated solution of ammonium chloride. Attempts to recrystallize the carbinol from the common organic solvents were not successful. The method previously employed[1] for the isolation of the colored and colorless tautomers of a similarly amorphous carbinol was not successful in this case, because of partial dehydration of the carbinol to form the fuchsone when it is dissolved in acetic acid. Whether precipitated from an alkaline solution or from acid solution, the carbinol looks equally intense in color, loses water at about the same rate and readily changes to the fuchsone. However, the sample from dil. acetic acid, presumably quinonoid, begins to soften and turn red at 70°, while the sample from an alkaline solution, and presumably containing some benzenoid carbinol, begins to soften and turn red at 87°.

Thus, it has been demonstrated that a naphthyl group exerts a stronger tautomerizing influence than a phenyl group; also, that in this case as well, similarly to those described in previous papers, the formation of fuchsone is preceded by the intermediate stage, namely, the formation of the quinonoid carbinol.

ANN ARBOR, MICHIGAN.

[CONTRIBUTION FROM THE BUREAU OF PLANT INDUSTRY, U. S. DEPARTMENT OF AGRICULTURE.]

A MOSAIC DISEASE OF CABBAGE AS REVEALED BY ITS NITROGEN CONSTITUENTS.[2]

BY S. L. JODIDI.
(With the coöperation of S. C. Moulton and K. S. Markley.)

Received June 23, 1920.

Introductory.

It is generally accepted in plant hygiene that only healthy and vigorous plants, as a rule, yield maximum returns. Hence, it goes without saying that measures looking to the amelioration of our cultivated plants will, of course, lead to crops superior both in quality and quantity. This object may be attained by finding proper remedies for the existing plant

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[1] Gomberg and Todd, THIS JOURNAL, 39, 2392 (1917).

[2] Presented before the Division of Biological Chemistry at the Chicago Meeting of the American Chemical Society, September 6–10, 1920.

diseases, on the one hand, and by selecting and breeding improved and immune varieties on the other. However, the fact that the development of improved and disease-resistant varieties through selection and breeding will require very much time and labor and the further consideration that a plant variety immune from one disease is not necessarily immune from other diseases, renders it advisable, if not imperative, along with the cultivation of improved and immune varieties, to study plant diseases with the object in view of finding suitable means for combating the latter.

Though its organs are somewhat modified as storage organs, the cabbage plant (*Brassica oleracea*) has essentially the important nutritive qualities which a leafy vegetable possesses. Thus, it compares favorably with seeds, roots, and tubers in regard to the content of the inorganic elements, calcium and sodium,[1] being richer in the water-soluble[2] vitamine B, and containing in addition also the fat-soluble[3] vitamine A. The culture of cabbage for sauerkraut is too well known to dwell here upon this subject. At any rate, the desirable qualities of cabbage as food naturally suggest the necessity of doing away with a disease which is marked by a few symptoms chief among which is dwarfing of the affected plants and change of their color. While the leaves of normal cabbage plants have a healthy green color, those of diseased plants show a yellowish, *metallic* color between the veins, only the spaces nearest to the veins being green. At the same time the affected leaves are *brittle*, their margins being frequently of a uniform yellow color. Coupled with this is the comparatively poorly developed root system and the stunting of the diseased plants, all of which leads to poorer crops of inferior quality. Inasmuch as the cabbage disease under consideration has several symptoms in common with the spinach blight described in a previous[4] paper, the idea suggested itself to apply to this work the methods used in the spinach investigation with certain necessary modifications.

It is a pleasure here to acknowledge the highly appreciated help and cooperation of the Office of Cotton, Truck and Forage-crop Disease Investigations, as well as of the Virginia Truck Experiment Station.

Experimental.

Twelve perfectly healthy cabbage plants were taken in April, 1918, from the Lambert farm at Ocean View Road, Va., to which another dozen of equally normal plants[5] secured from the Cooper farm at Norfolk, Va.,

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[1] McCollum, Simmonds and Pitz, *J. Biol. Chem.*, 30, 18 (1917).

[2] Osborne and Mendel, *ibid.*, 41, 456 (1920).

[3] *Ibid.*, 37, 195 (1919).

[4] Jodidi, Moulton and Markley, THIS JOURNAL, 42, 1061 (1920).

[5] We owe our gratitude to Prof. T. C. Johnson, Director, Virginia Truck Experiment Station, for assistance in selecting the cabbage plants.

were added. At the same time from 25 to 30 diseased cabbage plants were selected from the Lambert farm. The healthy and diseased plants were separately dried, first at room temperature and finally in an electric drying oven at 50°, to be then powdered, passed through a 40-mesh sieve and transferred to sealed jars.

Description of Methods.—The *total nitrogen* was determined by Kjeldahl's method modified to include the nitrogen of nitrates.

The *ammoniacal nitrogen* was estimated according to Grafe's method *in vacuo* as described in a previous[1] paper.

The estimation of *nitric*, *nitrous* and *protein* nitrogen was carried out essentially according to the description given in the last mentioned paper.

The proportion of *acid amide*, *humin*, *basic* and *non-basic* nitrogen was determined according to Hausmann's[2] method as applied by one[3] of us to soil investigations.

TABLE I—SHOWING THE PROPORTION OF TOTAL AMMONIACAL,[a] AND NITROUS NITROGEN IN THE CABBAGE.

Healthy cabbage material.	Total nitrogen. Oven-dried cabbage. %.	Nitrites. %.	Diseased cabbage material.	Total nitrogen. Oven-dried cabbage. %.	Nitrites. %.	Ammoniacal nitrogen. Oven-dried cabbage. %.	Ammoniacal nitrogen. Total nitrogen. %.	Ammoniacal nitrogen. Soluble nitrogen. %.
Leaves..........	4.91	0.0	Leaves	3.72	Present	0.180	3.75	5.51
	4.86	0.0	......	3.73	...	0.180	3.75	5.51
	4.97	...	......	3.71	...	...	..	..
(Sample A)......	4.85	...	(Sample A)	3.74	...	...	..	..
	4.85	...	......	3.73	...	...	..	..
	4.85	...	......	3.75	...	...	..	..
Leaves..........	4.70	0.0	Leaves	3.73	Present	0.168	3.49	5.12
(Sample B)......	4.76	...	(Sample B)	3.72	...	...	..	..
	4.71	...	......	3.74	...	...	..	..
Leaves..........	4.83	0.0	......	3.71	...	0.171	3.55	5.21
(Sample C)......	4.82	...	......	..	...	...	..	..
	4.75	...	......	..	...	...	..	..
Roots...........	2.46	...	Roots	2.22	...	...	..	..
	2.37	...	......	2.22	...	...	..	..
(Sample A)......	2.27	...	(Sample A)	2.13	...	...	..	..
	2.38	...	......	2.11	...	...	..	..
	2.37	...	......	2.25	...	...	..	..
Roots...........	2.44	...	Roots	2.25	...	...	..	..
(Sample B)......	2.44	...	(Sample B)	2.20	...	...	..	..
	..	...	......	2.19	...	...	..	..

[a] The proportion of ammoniacal nitrogen in the healthy cabbage was not estimated because of lack of material.

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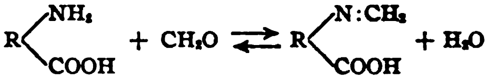
[1] Jodidi, Moulton and Markley, THIS JOURNAL, 42, 1063 (1920).

[2] *Z. physiol. Chem.*, 27, 95 (1899); 29, 47, 136 (1900).

[3] Jodidi, S. L., THIS JOURNAL, 32, 396 (1910); 33, 1226 (1911); 34, 94 (1912).

The estimation of the *amino acid* portion in what constitutes the basic and non-basic nitrogen, as well as the determination of the nitrogen of *polypeptides*, was effected according to the methods applied to spinach.[1] Inasmuch as the reaction of amino acids with formaldehyde is reversible in accordance with the equation



$$R\genfrac{}{}{0pt}{}{\diagup NH_2}{\diagdown COOH} + CH_2O \rightleftharpoons R\genfrac{}{}{0pt}{}{\diagup N:CH_2}{\diagdown COOH} + H_2O$$

Amino acid. Methylene amino acid.

care was taken, on carrying out the formol titration, to add 10 more cc. of formaldehyde in each case to make sure that the reaction from left to right was complete. The results obtained are presented in Tables I to IV.

TABLE II—SHOWING THE PROPORTION OF NITRIC NITROGEN IN THE CABBAGE.

	Nitric nitrogen.				Nitric nitrogen.		
Healthy cabbage material.	Soluble nitrogen. %.	Total nitrogen. %.	Oven-dried cabbage. %.	Diseased cabbage material.	Soluble nitrogen. %.	Total nitrogen. %.	Oven-dried cabbage. %.
Leaves..........	12.45	8.48	0.41	Leaves	4.08	2.06	0.08
(1st sample).....	12.45	8.48	0.41	(1st sample)	3.98	2.01	0.08
Leaves..........	12.65	8.62	0.42	Leaves	4.53	2.29	0.09
(2nd sample)....	12.86	8.76	0.42	(2nd sample)	4.53	2.29	0.09
Roots...........	...	6.63	0.16	Roots	..	4.80	0.11
	...	6.71	0.16	....	..	4.76	0.10

TABLE III.—SHOWING THE PROPORTION OF PROTEIN IN THE CABBAGE.

	Protein nitrogen.			Corresponding protein.	
	Fresh cabbage. %.	Oven-dried cabbage. %.	Total nitrogen. %.	Fresh cabbage. %.	Oven-dried cabbage. %.
	Healthy Cabbage Material.				
Leaves...........	0.16	1.44	29.80	1.00	9.00
	0.16	1.43	29.62	1.00	8.94
	0.16	1.40	29.07	1.00	8.75
	0.16	1.43	29.57	1.00	8.94
Roots............	..	1.21	50.41	..	7.56
	..	1.22	51.09	..	7.62
	..	1.21	50.41	..	7.56
	Diseased Cabbage Material.				
Leaves...........	0.26	1.91	51.16	1.62	11.94
	0.26	1.92	51.37	1.62	12.00
	0.26	1.91	51.16	1.62	11.94
	..	1.43	65.05	..	8.94
Roots............	..	1.43	65.10	..	8.94
	..	1.42	64.71	..	8.87

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[1] S. L. Jodidi, E. H. Kellogg and R. H. True, *J. Agr. Research*, 15, 385 (1918); S. P. L. Sörensen, *Biochem. Z.*, 7, 45 (1907).

TABLE IV.—SHOWING THE DISTRIBUTION OF THE WATER-SOLUBLE NITROGEN IN CABBAGE.

Healthy cabbage material.	Acid amide nitrogen (plus ammonia nitrogen). %.	Humin nitrogen. %.	Basic nitrogen. %.	Non-basic nitrogen. %.	Peptide nitrogen. %.	Diseased cabbage material.	Acid amide nitrogen (plus ammonia nitrogen). %.	Acid amide nitrogen only. %.	Humin nitrogen. %.	Basic nitrogen. %.	Non-basic nitrogen. %.	Peptide nitrogen. %.
Results Expressed in Percentage of the Oven-Dried Cabbage Materials.												
Leaves (Sample A)....	0.88	0.14	0.49	0.76	0.60	Leaves (Sample A)	0.41	0.23	0.13	0.23	0.54	0.49
	0.84	0.15	0.52	0.76	0.60		0.41	0.23	0.13	0.23	0.63	0.40
	...	..	...	...	...		0.41	0.23	0.14	0.23	...	...
Leaves (Sample B)....	0.81	0.15	0.54	0.72	0.64	Leaves (Sample B)	0.35	0.182	0.15	0.28	...	...
	0.82	0.14	0.54	...	...		0.35	0.182	0.14	0.28	...	...
	...	..	...	...	...		0.35	0.179	0.15	0.28	...	...
Results Expressed in Percentage of the Total Nitrogen of the Cabbage Materials.												
Leaves (Sample A)....	18.24	2.90	10.12	16.00	12.38	Leaves (Sample A)	10.97	7.22	3.60	6.04	14.62	13.20
	17.37	3.01	10.84	16.02	12.40		10.99	7.24	3.46	6.15	17.29	10.59
	...	..	...	...	...		11.04	7.29	3.76	6.13	...	...
Leaves (Sample B)....	16.88	3.12	11.16	15.02	13.32	Leaves (Sample B)	9.45	5.95	4.09	7.44	...	...
	17.10	2.90	11.21	...	...		9.44	5.95	3.73	7.58	...	...
	...	..	...	...	...		9.34	5.79	4.14	7.44	...	...
Results Expressed in Percentage of the Soluble Nitrogen of the Cabbage Materials.												
Leaves (Sample A)....	26.77	4.26	14.86	23.48	18.18	Leaves (Sample A)	21.70	16.19	7.13	11.95	28.99	20.15
	25.92	4.50	16.17	22.76	18.20		21.76	16.25	6.84	12.18	34.27	20.97
	...	..	...	...	...		21.86	16.35	7.44	12.14	...	...
Leaves (Sample B)....	25.19	4.65	16.65	21.30	19.56	Leaves (Sample B)	18.60	13.48	8.06	14.64	...	...
	25.51	4.33	16.72	...	...		18.59	13.47	7.35	14.93	...	...
	...	..	...	...	...		18.39	13.18	8.15	14.64	...	...

Discussion and Interpretation of Experimental Data.

Inspection of Table I reveals the fact that under normal physiological conditions the percentage of total nitrogen in the leaves is very much higher than in the roots (up to 107%), whereas the difference in the nitrogen content of the diseased leaves and roots, while still high, is essentially smaller (about 70%). A comparison of the healthy and diseased materials shows that whereas the differences in the nitrogen content of the normal and diseased leaves are considerable, ranging as they do from 27 to 33%, the corresponding differences of the healthy and diseased roots are comparatively small (from 7 to 9%). As to the nitrites, they were found in the diseased materials only. Since the differences mentioned hold true for all of the samples examined, it seems safe to state that the *lower nitrogen percentage and the nitrite content of the affected tissues are characteristic of the cabbage disease under consideration.*

By referring to Table II, it will be noticed that when in health the leaves have a higher percentage of nitric nitrogen than the roots, whereas under pathological conditions the reverse is the case. How are these facts to be interpreted? While, *absolutely*, the percentage of nitric nitrogen in the diseased leaves and roots is smaller than in the corresponding healthy tissues, the nitrate ratio of the diseased roots to healthy roots is relatively very much greater than the nitrate ratio of the diseased leaves to healthy leaves. This can only be taken to mean that loss of nitrates occurs in the diseased cabbage, the loss taking place in a higher degree in the leaves than it does in the roots. The very striking difference in the nitrate content of all diseased tissues, on the one hand, and the healthy on the other, does not seem to leave any doubt but that the *lower nitrate content of the diseased plants is another characteristic feature of the cabbage disease.*

A glance at Table III shows that normally the cabbage leaves are richer in protein and protein nitrogen than the roots when calculated to the oven-dried cabbage. The apparent exception in the case of the total nitrogen may be explained by the fact that the percentage of total nitrogen is very much higher in the leaves (Table I) to which the protein nitrogen was calculated. These relations hold good also for the diseased cabbage. When, however, the healthy tissues are compared with the diseased, it is seen that the latter in each and every case have a higher protein and protein nitrogen content. It is easy to see why the latter is higher in the diseased plants than in the healthy when calculated on the *total* nitrogen, which is considerably *lower* in the diseased plants (Table I). Just why this content is also higher in the diseased tissues when related to the fresh and oven-dried cabbage needs further elucidation in view of the close relation of the proteins to the life functions of the plants. That the diseased tissues have a comparatively higher protein content seems to indicate clearly that no loss of protein nitrogen is caused by the disease. This is probably due to the fact that proteins, belonging practically to the least soluble among the nitrogenous compounds occurring in plants, offer the least points of attack by the nitrous acid, as was pointed out elsewhere.[1] Coupled with this is the more or less stunted condition of the diseased plants in which, while the proteins remain intact, other compounds such as nitrates, acid amides, amino acids, etc., are destroyed, at least in part, with the result that the protein in the diseased plants is calculated on a *smaller* quantity of tissue. Another interpretation suggests itself from a teleological standpoint. The diseased plants having lost a large portion of their nitrogen are making an effort to make good that loss. They accomplish it by converting whatever nitrogen has remained in them, into the highest and most useful form of nitrogen, namely, into proteins.

By examining Table IV it is evident that the proportion of acid amide, basic and non-basic nitrogen is higher in the healthy cabbage than in the diseased, the only exception being the percentage of non-basic nitrogen when calculated to the soluble nitrogen. This may be ascribed to the considerably higher protein nitrogen content of the diseased plants (Table III), and hence to their correspondingly *lower soluble nitrogen content* on which the non-basic nitrogen was calculated. Inasmuch as the differences noticed hold good for all of the materials investigated it seems justified to state that a *lower acid amide, basic and non-basic nitrogen content of the diseased tissues is also characteristic of the cabbage disease.*

As to the peptide nitrogen, the results, which are not conspicuous enough and run, moreover, in opposite directions, do not permit of any definite conclusion.

The proportion of humin nitrogen appears to be higher in the diseased cabbage plants than in the normal ones. Since, however, in Hausmann's nitrogen distribution method as applied here, the conditions of hydrolysis[2] as well as of distillation of the hydrolyzed and evaporated cabbage extracts with magnesium oxide[3] were identical, the amount of humin attributable to the acid hydrolysis must have been the same in the case of the various cabbage tissues, healthy and diseased. Hence, the larger percentage of humin nitrogen in the affected plants seems to be also characteristic of the cabbage disease and may perhaps have something to do with the change of color from green to metallic in the diseased tissues.

[1] Jodidi, Moulton and Markley, THIS JOURNAL, 42, 1069 (1920).

[2] Ordinarily the solutions obtained by repeated extraction of the cabbage materials with boiling hot, ammonia-free water were treated with enough conc. hydrochloric acid to make a 20% acid and boiled for 10 hours, using a reflux condenser.

[3] Jodidi, S. L. and S. C. Moulton, THIS JOURNAL, 41, 1526 (1919).

Nature of the Cabbage Disease.

Of plant diseases those which are brought about by the activity of microörganisms (bacteria, fungi) are the best known. They are firmly established not only because the organisms causing the disease have been isolated from the diseased tissues and identified, but also because, in a great many cases, the pure cultures of the organisms in question when inoculated into healthy plants produced a disease identical with that of the affected plants from which the pure cultures had been obtained. As an example of this type of (bacterial) diseases of which more than a hundred are known it may suffice to mention crown gall and cancer in plants caused by *Bacterium tumefaciens* and now so well known through the remarkable work of Smith[1] and his collaborators. To another type belong the so-called *virus* diseases the cause of which remains unknown, since attempts to isolate microörganisms from and to associate them with affected tissues thus far have proved futile. As examples of this type the mosaic disease of tobacco[2] (*Nicotiana tabacum*) and spinach[3] (*Spinacia oleracea*) may be cited, in both of which the disease may be communicated to normal plants by virus-bearing aphids or by inoculating the infective principle into healthy tissues.

So far as the cabbage disease is concerned, it is perfectly true that preliminary experiments looking to the establishment of its infective nature have thus far led to negative results. However, judging from the striking similarity of the analytical evidence presented with regard to the various nitrogenous compounds occurring in healthy and blighted *spinach* plants, on the one hand, and in normal and diseased *cabbage* plants on the other, and taking into consideration that spinach blight belongs to the type of mosaic diseases, it appears logical to relate the cabbage disease caused by denitrification to the latter type. So strikingly similar are the figures characteristic of diseased tissues in cabbage and spinach that it seems worth while to arrange the data on spinach in tabular form for the sake of convenient comparison (Table V). To be sure, when we compare Tables I, II, III and IV, on the one side, and Table V on the other, we find considerable distinctions, *e. g.*, in the nitrogen of nitrates, acid amides, proteins present in the cabbage and spinach plants under *normal* conditions. But the features characteristic of the mosaic disease of spinach, especially the smaller percentage of total, nitrate, acid amide, basic and non-basic nitrogen of the affected tissues hold good also for cabbage in practically every particular.

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[1] Erwin F. Smith, *J. Cancer Research*, **1**, 231 (1916); *J. Agr. Research*, **6**, 179 (1916); **8**, 165 (1917); also Bur. Plant Ind., *Bull.* 213 and 255.

[2] H. A. Allard, *J. Agr. Research*, **6**, 649 (1916); **10**, 615 (1917).

[3] THIS JOURNAL, **42**, 1061 (1920); *J. Agr. Research*, **14**, 1 (1918).

TABLE V.—SHOWING THE PROPORTION OF TOTAL, NITRIC, ACID AMIDE, HUMIN, BASIC, NON-BASIC AND PEPTIDE NITROGEN IN SPINACH.

Results Expressed in Percentage of the Total Nitrogen of the Spinach Materials.

Healthy spinach material.	Total nitrogen (in oven-dried spinach). %.	Nitric nitrogen. %.	Acid amide nitrogen. %.	Humin nitrogen. %	Basic nitrogen. %.	Non-basic nitrogen. %.	Peptide nitrogen. %.	Diseased spinach material.	Total nitrogen (in oven-dried spinach). %.	Nitric nitrogen. %.	Acid amide nitrogen. %.	Humin nitrogen. %.	Basic nitrogen. %.	Non-basic nitrogen. %.	Peptide nitrogen. %.
Leaves.......	4.98	3.42	10.12	3.05	11.10	13.98	6.25	Leaves	3.89	2.20	7.33	3.65	8.24	11.12	12.19
(Sample A)...	4.98	3.43	10.11	3.02	11.11	14.91	5.34	(Sample A)	3.83	2.20	7.31	4.31	9.31	12.62	8.98
	5.03	...	10.43	2.44	...	...	5.40		3.92	..	7.58	..	9.61	...	...
Leaves.......	4.90	3.83	...	..	...	...	6.10	Leaves..	3.79	2.82	...	..	...	...	...
(Sample B)...	4.82	4.02	...	..	...	...	...	(Sample B)	3.80	2.76	...	..	...	...	...
	4.90	..	...	..	...	...	...		3.80	..	...	..	...	...	...
Roots........	3.90	3.30	10.64	2.91	9.83	...	...	Roots	3.95	3.01	7.44	..	8.05	...	...
	3.90	...	10.78	3.10	9.31	...	...		3.92	3.02	7.51	2.40	8.13	...	...
	3.94	..	10.83	3.01	9.23	...	...		3.88	..	7.72	3.01	8.36	...	...
	..	...	...	..	...	...	...		3.89	..	...	..	...	...	...

Results Expressed in Percentage of the Soluble Nitrogen of the Spinach Materials.

Healthy spinach material.	Total nitrogen (in oven-dried spinach). %.	Nitric nitrogen. %.	Acid amide nitrogen. %.	Humin nitrogen. %	Basic nitrogen. %.	Non-basic nitrogen. %.	Peptide nitrogen. %.	Diseased spinach material.	Total nitrogen (in oven-dried spinach). %.	Nitric nitrogen. %.	Acid amide nitrogen. %.	Humin nitrogen. %.	Basic nitrogen. %.	Non-basic nitrogen. %.	Peptide nitrogen. %.
Leaves.......	..	6.87	21.20	6.34	23.10	26.15	12.54	Leaves	..	4.65	15.48	7.71	17.41	23.56	25.79
(Sample A)...	..	6.89	21.17	6.28	23.12	28.02	10.72	(Sample A)	..	4.65	15.42	9.11	19.67	26.76	18.99
	..	...	21.85	5.08	...	...	10.84		..	..	16.00	..	20.19	...	...
Leaves.......	..	7.69	...	..	...	...	12.24	Leaves	..	5.97	...	..	...	...	...
(Sample B)...	..	8.07	...	..	...	...	...	(Sample B)	..	5.84	...	..	...	...	...
Roots........	..	6.30	20.32	5.56	18.77	...	...	Roots	..	..	18.91	..	20.20	...	...
	..	..	20.58	5.91	17.78	...	...		..	..	19.10	6.02	20.40	...	...
	..	..	20.68	5.74	17.63	...	...		..	..	19.61	7.55	20.97	...	...

Summary and Conclusions.

The cabbage disease investigated is characterized by denitrification taking place in the affected tissues, whereby the nitrates are in part reduced to ammonia which is lost as such, and in part to nitrites which, reacting on the amino groups of the various organic compounds—acid amides, amino acids, etc.,—bring about the elimination of elementary nitrogen. This is the reason why diseased cabbage tissues have a smaller proportion of total, nitrate, acid amide, di-amino and mono-amino nitrogen, nitrites occurring in diseased tissues only.

Denitrification occurs in affected cabbage leaves in a very much higher degree than it does in the roots. This follows conclusively from the fact that while the differences in total, nitrate nitrogen, etc., of healthy and diseased leaves are large, those of normal and affected roots are considerably smaller.

There is a higher proportion of protein and protein nitrogen in the diseased cabbage tissues than in the normal. This is interpreted to mean that the affected plants possess the ability of building up proteins from the lower nitrogenous compounds, and that the protein nitrogen is not attacked by the nitrous acid, the protein and protein nitrogen being related in the diseased plants to a *smaller nitrogen content* and a *smaller quantity of tissue*.

Loss of nitrogen in the affected cabbage tissues is in itself an explanation of the cabbage disease. Thus, *e. g.*, one of its conspicuous characteristics, the dwarfing of the plants, is easily understood when we bear in mind that the nitrogenous compounds, such as acid amides, amino acids, and others, which are partly lost through denitrification, are the very materials out of which the plant is building up its tissues.

It seems not out of the question that the change of color from green to metallic in the diseased tissues may be due to a larger proportion of humin present, the lack of nitrogen perhaps coming also into play.

In the healthy cabbage samples the nitrogen is made up, in round figures, of 30% protein nitrogen, 7% di-amino[1] nitrogen, 10% mono-amino[1] nitrogen, and 13% peptide nitrogen, which means that at least 60% of the nitrogen compounds present in cabbage have direct nutritive value.

Under normal conditions the cabbage leaves have a higher percentage of total and nitrate nitrogen than the roots, which was shown to hold true also for the spinach[2] plant.

WASHINGTON, D. C.

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[1] The cabbage nitrogen consists of 10% and 16% of basic and non-basic nitrogen, respectively (Table IV), of which 63.14% and 64.23% were found by formal titration to represent diamino and mono-amino nitrogen, respectively.

[2] *Loc. cit.*

[CONTRIBUTION FROM THE COLLEGE OF PHARMACY, UNIVERSITY OF MICHIGAN.]

"SOME OF THE IMPORTANT CONSTITUENTS OF DIGITALIS."

BY WILLIAM J. MCGILL.

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Much work has been done in an effort to determine the comparative values of various extracts of digitalis obtained by the use of different solvents, especially alcohol and hot and cold water, as a direct result of Kraft's careful and painstaking research in which he was able to demonstrate the presence of an exceedingly labile water-soluble substance in the leaves of digitalis.[1] Though this substance, which he called "Gitalin," was afterward shown by Kiliani[2] to be a mixture and not a pure substance, the name used by Kraft is still employed to designate the water-soluble, chloroform-soluble glucoside found in the leaves.

By purely pharmacological methods, Straub[3] has attempted to determine quantitatively the total amount of active substances present in the leaves, and the fraction of this obtained by extraction. He arrives at the conclusion that the leaves contain approximately 1% of active glucosides, a much higher proportion than it is possible to isolate by chemical processes.

No attempt has been made to determine whether these various extracts are of reasonably constant composition as far as the glucosides they contain are concerned. It is possible to reach a conclusion as to the identity of the glucosides by chemical methods only, but it is surely far-fetched to assume that one can determine by tests on cats, frogs, or other animals, just what glucosides may be present in any given fraction of the drug. It therefore, would appear of some value to determine whether it is possible to obtain fractions of uniform composition, using the same methods of procedure on different samples of the drug, and if so, just which constituents will be present in a given fraction.

Since, as stated previously, it is impossible to isolate all of the active material, the use of a pharmacological method of testing the relative values of the different fractions obtained is necessary. The M. L. D. method on frogs appears to be the only one now in use which can be adapted to such an investigation where it is desired to run a large number of tests in as short time as possible. The average chemical laboratory is a poor place in which to keep the number of frogs required for the tests, so that this presented quite a problem. After reviewing the results obtained on goldfish by Pittenger,[4] it was decided to try this method as it seemed to be simpler to obtain and keep these on hand.

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[1] Kraft, *Arch. Pharm.*, 250, 118 (1912).

[2] Kiliani, *ibid.*, 252, 13 (1914).

[3] Straub, *Arch. exp. Path. Pharm.*, 80, 52–71 (1916).

[4] Pittenger, *J. Am. Pharm. Assoc.*, April, 1915; *ibid.*, 8, 893 (1919).

Some experiments were, therefore, carried out with goldfish, using the method given by Pittenger in his second paper and maintaining a constant temperature of 22°.

Tinc. used. Cc.	After 3 hours.
2.5	Alive
2.6	Alive
2.7	Alive
2.8	Alive
2.9	Alive
3.0	Dead
3.1	Dead
3.2	Alive
3.3	Dead
3.4	Dead[a]
3.5	Dead
3.6	Dead

[a] This fish appeared to be alive at the end of 3 hours but died a few minutes later.

The tincture tested 300% of the U. S. P. standard by the M. S. D. method on frogs, so that there is a wide discrepancy between these results and those reported by Pittenger, who sets the 3-hour M. L. D. on goldfish as 2.85 cc. of standard tincture. The fish used were fairly large, averaging 25 g. in weight, but Pittenger states in his earlier communication that the size of the fish does not affect the result. When adjusted to U. S. P. standard, the tincture used above gave the following results.

Tinc. used. Cc.	After 3 hours.
7.5	Alive
8.0	Alive
8.5	Dead
9.0	Dead
9.5	Dead

Since the method appeared to give fairly concordant results, and this was all that was desired, the question as to why there should be such a large discrepancy between the results by the 2 methods, was not investigated at this time.

The crude drug used in the investigation was all obtained from the Stearns Medicinal Plant Gardens, at the University of Michigan, and consisted of 3 lots, 2 of which were first-year plants, one 1918 crop, and the other 1919, the third being 1919 second-year plants. No special precautions were taken in handling and storing the leaves, the drying being carried out at ordinary temperature.

Before using, the leaves were ground to a coarse powder, and this was cleaned by sifting through an 80-mesh screen in a rotary sifting machine, all the material passing through being discarded. The siftings ran as high as 34% ash while the cleaned powder gave an ash content of 9 to 11%.

Cold Water Extract.

Two kg. of the coarsely powdered first-year 1919 leaves was treated with 10 liters of cold distilled water containing 5% of alcohol, and the mixture was agitated during 8 to 10 hours by means of an electric stirrer. Too violent agitation is to be avoided as it causes intense foaming. The watery extract was then pressed off, and the process repeated, the second extract being added to the first and the whole then evaporated to a third or a quarter of the original volume at a temperature not exceeding 30°. The results obtained by shaking out the total volume of aqueous extract with chloroform without the preliminary evaporation are much more satisfactory as regards the final yield of pure product, but it is almost impossible to handle such a large quantity of material in shaking out with the facilities of the ordinary laboratory. No matter which method is used, the addition of the small amount of alcohol used in the extraction seems advisable, in the first case to retard the development of molds during the evaporation, and in the second method, to prevent the formation of emulsions in the shaking-out process, something very difficult to avoid with a large volume of liquid containing a saponin. Experiments on a small scale indicate that the addition of such a small amount of alcohol has very little effect on the amount of active material extracted. The aqueous extract obtained by either method was then extracted with chloroform until the residue left upon evaporation of a small portion possessed only a faintly bitter taste.

The cold water extract prepared in this manner contained from 20 to 22% of extractive, calculated on the weight of crude drug used. The chloroform extract, however, contained only 1.4% of extractive. These results were checked by manipulating several 25-g. samples of the same crude drug as used above, using 250 cc. of H_2O.

Sample	Extract. G.	$CHCl_3$ Ext.	%.
1	5.15	0.36	1.44
2	4.9	0.35	1.4
3	4.7	0.29	1.16

The residue from the chloroform extract after complete removal of the chloroform, re-dissolved in water, in which it is still completely soluble, possesses an activity 10% less than that of the chloroform-insoluble fraction, measured on goldfish, as has previously been shown by Straub.[1] Whether this chloroform soluble fraction loses part of its activity through the treatment with this solvent has not been conclusively determined although according to Kraft, "Gitalin," of which this fraction appears, to be composed, is not affected by chloroform [2]

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[1] Straub, *Arch. exp. Path. Pharm.*, 80, 52–71 (1916).

[2] Kraft, *Arch. Pharm.*, 250, 126 (1912).

The residue is a light brown in color and soluble in all the ordinary solvents. In order to purify it, it is dissolved in chloroform and precipitated as an amorphous powder by allowing the chloroform solution to run slowly into an excess of petroleum ether, the method followed by Kraft in the preparation of "Gitalin." A pure product can be obtained only by repeating this procedure several times. Treatment with animal charcoal seems to have little effect in removing the color, besides involving considerable loss due to absorption.

About 0.4 g. of a pure white amorphous susbstance was thus obtained, melting at 152°. Tested with Kiliani's modification of Keler's reaction, it gave a reddish-violet ring, and a blue color gradually developed in the acetic acid layer. A small portion dissolved in alcohol, on the addition of half its volume of water gave a precipitate of small crystalline aggregates, melting at 73–75°, the melting-point given by Kraft for his "Gitalin-Hydrat."

An attempt was made to separate digitoxin from the product, using a mixture of methyl alcohol and chloroform as a solvent and adding ether to precipitate any digitoxin present, but nothing was obtained. No conclusion could be drawn from this as the amount available for experiment was too small.

The water-soluble, chloroform-insoluble fraction, which contains approximately 55% of the activity of the water extract was evaporated to dryness at a low temperature, the final drying being done *in vacuo* over sulfuric acid. The dry substance was treated several times with an excess of acetone, which dissolves a large amount of yellow coloring matter, in addition to the active glucoside. The powder remaining can be purified further by solution in methyl alcohol and precipitation by means of ether. It proved impossible to obtain a crystalline substance from the purified product, and no attempt was made to separate it into α-, β- and γ-saponin, as done previously by Kraft.[1] In much higher concentration than usually used for the tests on the fish, it had no effect, except to cause them to come continuously to the surface for air. Two cc. of a 10% solution injected intravenously into 250 g. guinea-pigs had no effect whatever on the animals. Tests made, using one cc. of a 2.5% suspension of washed red blood cells from sheep with amounts of a 5% solution of the saponin ranging from 0.1 to 1 cc., the solution made up to 2 cc. with physiological salt solution, showed no hemolysis after an hour's incubation at 37°. The saponin substance of digitalis seeds (amorphous digitonin), possesses hemolytic properties.

It was attempted by various means to purify the acetone extraction of the original chloroform residue, but no successful method was worked out. In every case, the product obtained was a dark-brown amorphous

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[1] Kraft, *Arch. Pharm.*, 250, 121 (1916).

substance which resisted all attempts at further purification and upon continued treatment with solvents became more and more insoluble in water. A product was obtained, however, which was approximately 50% more toxic to the fish than the purified "Gitalin."

Alcohol Extraction.

The leaves, after extraction with cold water, were dried at a low temperature and treated with 3 liters of 50% alcohol after thoroughly moistening them with the same solvent. The mixture was allowed to stand overnight at room temperature, the liquid pressed off and the treatment repeated. After the second extraction, a test made on a portion of the extracted powder showed it to be inactive. The united alcoholic extracts were then precipitated with lead acetate, filtered, the excess lead removed with sodium phosphate and the final clear solution evaporated under reduced pressure on the steam-bath to a volume of about one liter. A copious precipitate was formed which was filtered off, dried at a low temperature, powdered finely and exhaustively extracted with 100 cc. of chloroform, by heating it on the steam-bath under a reflux condenser for 15 minutes. The chloroform solution was then evaporated, the greenish-brown residue taken up in hot alcohol, in which it is completely soluble, and digested with animal charcoal. After filtering, the solution was evaporated, the residue taken up in chloroform, the chloroform solution poured into an excess of ether and the mixture allowed to stand overnight. A peculiarity of the crude substance obtained from the chloroform extraction seemed to be that animal charcoal decolorized it much more efficiently in alcoholic solution than when chloroform was used as the solvent.

The precipitate obtained amounted to about 1.5 g. of an amorphous substance. Upon recrystallizing it from hot alcohol, long plates were formed, which melted at 244°, and showed a marked play of color between crossed nicols. They gave Keller's digitoxin reaction.

Subs., 0.1805, 0.1911: H_2O, 0.1387, 0.1471; CO_2, 0.4225, 0.4470.

Calc. for digitoxin, $C_{34}H_{54}O_{11}$: C, 63.90; H, 8.52. Found: C, 63.83, 63.79; H, 8.6, 8.58.

The filtrate obtained after the evaporation of the original alcoholic extract of the leaves had only a slightly bitter taste, and as it was without action on goldfish in the ordinary dilutions it was discarded.

According to Kraft,[1] after the exhaustive extraction of the precipitate obtained by evaporation of the alcoholic extract, there remains an inactive, chloroform-insoluble glucoside which he called gitin. However, after repeated extraction of the chloroform insoluble residue with hot alcohol and subsequent evaporation and purification of the united alco-

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[1] Kraft, *Arch. Pharm.*, 250, 138 (1912).

holic extracts, nothing was obtained except a trace of an amorphous substance and a few crystals resembling those of digitoxin.

Hot Water Extract.

The constituents of the infusion of the leaves appeared of special interest to us in view of some experiments performed by R. A. Hatcher.[1]

Two kg. of 1919 first-year leaf was treated with 8 liters of boiling water, the mixture allowed to stand on the steam-bath for an hour with occasional agitation, the watery extract pressed off and the process repeated. The united extracts were then strained through cotton and evaporated on the steam-bath in a current of air to a thick liquid. Evaporation takes place very rapidly in this manner, and the temperature of the liquid does not rise above 70°.

Instead of adding a large excess of alcohol at this point, which was the method followed by Hatcher, only enough was added to thin the syrupy liquid obtained from the evaporation. The precipitate was then removed and the aqueous-alcoholic mixture shaken out 5 or 6 times with 100 cc. of chloroform. The chloroform solution was evaporated, the brown resinous substance remaining dissolved in 90% alcohol, treated with animal charcoal, filtered, evaporated, dissolved in chloroform, and the chloroform solution diluted with twice its volume of petroleum ether. After standing for 48 hours, the amorphous precipitate was filtered off. Tests on a small portion showed it to be partially insoluble in a small amount of alcohol. Accordingly, the substance was dissolved in 5 parts of a mixture of equal volumes of methyl alcohol and chloroform, a solvent used by Kiliani in some of his later work on the digitalis glucosides, and an equal volume of ether was added. Upon standing overnight, a white incrustation appeared at the edge of the liquid. After this crust was filtered off and an equal volume of ether added to the clear solution, the latter became cloudy, and, after 24 hours later, a small amount of white incrustation had again appeared. The total amount of this substance obtained amounted to about 0.75 g. Upon recrystallizing it from alcohol, long plates, which melted at 240–245°, were obtained, exhibited a play of color under crossed nicols and gave Keller's digitoxin reaction.

Subs., 0.1556, 0.1485: CO_2, 0.3638, 0.3475; H_2O, 0.1196, 0.1140.
Calc. for $C_{34}H_{54}O_{11}$: C, 63.90; H, 8.52. Found: C, 63.77, 63.83; H, 8.61, 8.56.

The methyl alcohol-chloroform-ether solution was evaporated to dryness and the residue crystallized from alcohol. The product appeared to be a mixture of an amorphous substance with crystals of very irregular form when examined under the microscope. Careful recrystallization from alcohol in which the crystalline portion of the precipitate seemed to be insoluble gave an amorphous substance melting very definitely at

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[1] A short summary appears in the *J. Am. Pharm. Assoc.*, 8, 913 (1919).

150–160°. Solution in a very small quantity of alcohol and the addition of an equal volume of water gave a precipitate of the smaller granular aggregates melting at 73–75° which had been obtained from the chloroform soluble portion of the cold water extract; further investigation of this fraction was not made because of the small amount of material available; we assumed it to be what Kraft designated as "Gitalin-Hydrat."

The crystalline portion of the precipitate from the methyl alcohol-chloroform-ether solution proved to be insoluble in practically all the ordinary solvents except dil. alcohol, and the crystals melted at 257°.

Subs., 0.1654, 0.1864: CO_2, 0.3864, 0.4352; H_2O, 0.1295, 0.1463.

Calc. for anhydrogitalin ($C_{28}H_{46}O_9$): C, 63.83; H, 8.8. Found: C, 63.70, 63.66; H, 8.76, 8.78.

The total yield of both amorphous and crystalline substance amounted to 1.1 g.

The activity of the chloroform-soluble portion of the infusion was approximately double that of the chloroform-insoluble portion. This latter, as in the case of the chloroform-insoluble fraction of the cold water extract, was evaporated, dried, and extracted with acetone, thus separating the saponins from the active glucoside. The same methods of purification were employed; but, as stated previously, no feasible means were found of getting the active substance in a pure condition.

The powder, after being extracted with hot water, was dried and extracted with 50% alcohol, the extraction and subsequent purification being carried out in identically the same manner as in the case of the cold-water extracted drug. The final purified product amounted to 0.9 g. of the long plates characteristic of digitoxin, melting at 244°.

All of these extractions were repeated with 2 other lots of drug, one consisting of 1919 second-year leaf, and the other 1918 first-year leaf, and closely tallying results were obtained. It should be borne in mind that little attention was paid to the yields obtained, the object being solely to get a pure product from the various fractions which could be positively identified. Care was taken to insure that the manipulation of each lot was the same as regards time, amount of solvent, etc.

Conclusions.

1. It is possible with careful manipulation and uniform methods of procedure to obtain crude fractions from the drug by means of various solvents which will have a reasonably constant chemical composition. In view of the difficulty of separating individual glucosides in a chemically pure state from these crude fractions, such an undertaking at present seems to have no commercial value.

2. The cold-water extract of the leaves contains either none or a very minute quantity of digitoxin, its activity being due entirely to a chloroform-soluble and to a chloroform-insoluble fraction. In view of the fact

that Kiliani reports that "Gitalin," made according to Kraft's process, is a mixture containing some digitoxin, this cold-water extract requires further investigation, especially as very little is known of the chloroform-insoluble portion.

3. The saponing substance of digitalis leaves, digitsaponin, is a totally inactive and non-hemolytic susbtance when purified. This disposes of one possible source of error in pharmacological tests on the leaf.

4. Hatcher's chloroform-soluble fraction of the infusion is a mixture of "Gitalin" and digitoxin. If the accepted theory that the cause of the deterioration of digitalis preparations is the water-soluble, chloroform-soluble substance or substances which we have designated as "Gitalin" is true, then such a fraction should also be unstable. Work is being continued on this point.

The writer is indebted to Dr. Henry Kraemer for his many suggestions, and for his assistance in obtaining the crude drug used in this investigation, which was obtained from plants grown by him at the Frederick Stearns & Co. Medicinal plant garden at the University of Michigan during 1918 and 1919.

ANN ARBOR, MICHIGAN.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES, COLUMBIA UNIVERSITY, NO. 338.]

A FURTHER STUDY OF THE PROCESS OF PURIFYING PANCREATIC AMYLASE.

BY H. C. SHERMAN, I. D. GARARD AND V. K. LAMER.

Received June 26, 1920.

In a recent paper from this laboratory[1] the proteolytic and amylolytic activities of some of the fractions obtained in the purification of pancreatic amylase were compared. The results showed that the attempts to purify pancreatic amylase by fractionation of pancreatin result in greatly concentrating both amylolytic and proteolytic activities in certain fractions, but also revealed large losses of both types of enzyme activity and indicated to us that the purification process should be studied in some detail in order that more light might be thrown upon the place and nature of the losses. Especially was it sought to determine in so far as practicable whether the loss of amylolytic activity which occurs, for example, when the partially purified amylase is dissolved and reprecipitated, is due to incompleteness of precipitation, to deterioration (inactivation) of the enzyme under such treatment, or conceivably to a change of amylase into protease or a shifting of amylolytic to proteolytic activity. Accordingly, the process of purification previously developed in this laboratory[2] was carried out with determinations of total solids and enzyme activity at

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[1] Sherman and Neun, THIS JOURNAL, 41, 1855–62 (1919).

[2] Sherman and Schlesinger, *ibid.*, 33, 1195–1204 (1911).

each step in the process where such determinations were feasible. The colloidal nature of the materials dealt with and the very great instability of the active enzyme[1] necessarily render conclusive results exceptionally difficult of attainment.

Effect of Alcohol and Ether upon the Activity of the Pancreatic Amylase.

Since the solutions to be withdrawn for testing at different stages in the purification process all contain alcohol and many of them contain ether, experiments were first made to determine what effect, if any, would be exerted upon the activity of the enzyme by alcohol or alcohol and ether in such amounts as might be introduced with the enzyme in the various solutions and mother liquors to be tested. For this purpose equal portions of the same amylase preparation were treated for the determination of "amylolytic power"[2] with and without the addition of alcohol or alcohol and ether. The substrate was made up in the usual way[2] and the alcohol or alcohol and ether added to it before it was placed in the 40° water-bath. Some of the ether was doubtless evaporated while the substrate was coming to the temperature of the bath and during the digestion, but this is equally true of the later experiments which these tests were intended to control. The results are shown in Table I.

TABLE I.—EFFECT OF ALCOHOL AND ETHER ON THE ACTIVITY OF PANCREATIC AMYLASE.

Per cent. alcohol by volume.	Per cent. ether by volume.	"Amylolytic power" shown by pancreatin.
0	0	259
0	0	273
0.1	0	280
2.0	0	280
2.0	0	274
5.0	0	258
2.0	2.0	270
2.0	6.0	258

Greater concentrations of alcohol and ether were used here than in the later experiments and since the observed variations in the enzyme activity are no greater than the usual experimental variations, it is concluded that these reagents, in the concentration used, are without effect on the activity of the enzyme.

Extraction of the Pancreatin.

In every case the extraction was made with 50% alcohol by grinding 20 g. of pancreatin with the alcohol in a mortar. In the first 2 preparations the pancreatin was ground with the bulk of the 200 cc. of alcohol, only a few cc. being retained to rinse the mortar, and the maceration filtered through a fluted filter, which filtration required nearly 2 hours. In the third prep-

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[1] Sherman and Schlesinger, THIS JOURNAL, 37, 1309 (1915).

[2] Sherman, Kendall and Clark, *ibid.*, 32, 1073–86 (1910).

aration the alcohol was used in portions of 75 cc., 75 cc., and 50 cc., and drawn off each time on a Büchner funnel with suction. In the fourth preparation two 100 cc. portions were used and each filtered with suction.

The result of these variations in the method of extraction was not very marked. Somewhat more of the solution was recovered in the later cases, but the more efficient extraction of solids did not result in more efficient extraction of the amylase. However, the use of suction reduces the time required for filtration very greatly. The factors are too variable to afford a constant time of filtration, but in the third experiment only 20 minutes was required.

Precipitation with Alcohol and Ether.

A mixture was made containing one part of absolute alcohol and 4 parts of anhydrous ether. In Preparations 1, 2 and 3 the filtered, 50% alcohol extract was added to 7 times its volume of this mixture and the whole was rotated somewhat and allowed to stand for 30 minutes in the ice-box in order to induce coagulation of the precipitate. At the end of this time a yellow viscous precipitate had stuck to the bottom of the jar. The liquid (Mother Liquor 1) which was still slightly turbid was decanted.

In Preparation 4 the ratio of acohol to ether was changed. The filtered extract (180 cc.) was poured into 4 volumes of 1 : 1 alcohol-ether mixture. After standing for 30 minutes only a small amount had settled out, and so 280 cc. of ether was added, which produced a precipitate of the usual appearance. In Preparation 5, as a result of Preparation 4, four and one-half volumes of 4 : 5 alcohol-ether mixture was used. The liquid became turbid but no precipitate formed until 2 additional volumes of ether had been added. The pancreatin used here was a different sample which was probably responsible for the different concentrations required. Two points seem to be established with respect to this precipitation; that ether is essential to the coagulation of the precipitate at this point, and that the exact concentration necessary for effective precipitation varies somewhat with different samples of pancreatin.

The viscous precipitate from the alcohol-ether mixture (Precipitate 1) was dissolved in 40 cc. of thrice distilled water and poured into 200 cc. of absolute alcohol. The resulting precipitate (Precipitate 2) was an amorphous solid but no longer viscous. It should be noted that a precipitate is now obtained with alcohol alone, although the presence of ether was necessary in the first precipitation. (See discussion on p. 1905.)

In each case an attempt was made to disperse Precipitate 2 in 250 cc. of 50% alcohol, preparatory to dialysis. At first a dispersion was obtained which was apparently uniform but, as has been reported,[1] whenever this was put to dialyze a precipitate settled out ("sac precipitate"). An investigation of this phenomenon disclosed the fact that, when all

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[1] Sherman and Neun, This Journal, 40, 1138 (1918).

lumps are broken up and Precipitate 2 disappears, the liquid contains a finely divided suspension, which will coagulate and precipitate if stirred for a few minutes. It was first noticed that this new precipitate (Precipitate 3) apparently ceased to come down after the first hour of dialysis. It was then found that if the precipitate were allowed to form in the beaker for 20 minutes before being placed in the sac and then filtered off, very little came down during the dialysis. Finally, prolonged stirring (15 minutes) failed to produce complete dispersion and when this mixture stood 45 minutes in the ice-box it became very turbid. Filtration of this suspension through hardened paper gave a clear liquid which did not become turbid on standing for 15 minutes in the ice-box. From these data it seems that Precipitate 2 cannot be dispersed completely in 250 cc. of 50% alcohol even though all the solids present were previously dissolved in less than 200 cc. of the same solvent. This point has not been investigated in the earlier work in this laboratory due to the fact that the object has always been to produce a highly active amylase and so this dispersion was made as quickly as possible to avoid deterioration. While the fine white suspension is only slightly visible, the loss of salts as dialysis begins hastens the coagulation, consequently the precipitate appears to form from a clear solution as dialysis proceeds. In all cases this precipitate[1] was filtered out before proceeding further.

This filtrate (250 cc.) was dialyzed against 3 successive 2-liter portions of 50% alcohol; the first for 16 hours, the second for 8 hours, and the third for 16 hours; in all 40 hours. The inner solution (Mother Liquor 3) measured 300 to 450 cc. and was filtered from Precipitate 3 unless that had already been removed. Some variations were made in this dialysis. In the first experiment a thin collodion sac was used and a test of the dialysates showed that they were both amylolytically and proteolytically active. In order better to avoid mechanical defects a heavier sac was made for the second dialysis. In the third experiment a medium sac was used and in all 3 cases some of the enzyme was found in the dialyzates. No maltose was present during dialysis in Experiment 1, 5 g. in Experiment 2, and 2 g. in Experiment 3. The effect of the maltose in reducing deterioration of amylase was not conclusively determined but does not seems very great.

Thirty cc. of the clear Mother Liquor 3 was removed for the determination of activity and solids and the remainder poured into an equal volume of a 1 : 1 alcohol-ether mixture, and allowed to stand for one hour. The mixture was then centrifuged and the precipitate (Precipitate 4) removed from the tubes with a steel spatula, and dried in an evacuated desiccator in the ice-box. In Preparation 3, Mother Liquor 4 was turbid and was

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[1] As previously noted, this precipitate, formerly referred to as "sac precipitate" or "sac settlings," is very active proteolytically.

allowed to stand overnight when it was centrifuged again (Precipitate 5). To Mother Liquor 5 was added more alcohol and ether and the mixture centrifuged. This gave Precipitate 6.

In Preparations 4 and 5 dialysis was omitted and the relative proportions of alcohol, ether and water were varied somewhat in view of our experience with Preparations 1 and 3. While a moderately active product was obtained, it was not so active as the best preparations which have been made in this laboratory. However, the time required to make a preparation was reduced from 3 days to one.

The amylolytic activity was determined in all cases by the method of Sherman, Kendall and Clarke,[1] except that in the case of the liquid dispersions the activity was calculated to one cc. and not to one mg.

Proteolytic activity was determined by a variation of the method given by Sherman and Neun.[2] The 100 cc. of digestion mixture was taken from the bath and poured into 25 cc. of a solution containing 200 g. of crystallized sodium sulfate per liter and then 5 cc. of 0.5 *M* hydrochloric acid was added. This mixture was then made up to 200 cc., filtered, and aliquots taken for the determination of nitrogen. The method of making the casein substrate was modified as follows in order to avoid some of the usual difficulties, especially the formation of lumps. 8 cc. of molar sodium hydroxide was added to 200 cc. of distilled water and the solution heated to 40°. 10 g. of casein was finely powdered and added slowly to the solution with constant stirring. The dispersion was then heated rapidly to 80° or 90° and filtered through a fluted filter paper. This gave

TABLE II.—DISTRIBUTION OF THE SOLIDS AND ENZYMIC ACTIVITY EXPRESSED AS PER CENT. OF THE TOTAL.

	Expt. 1.		Expt. 2.		Expt. 3.	
	Solids.	Amylolytic activity.	Solids.	Amylolytic activity.	Solids.	Amylolytic activity.
Residue	62.5	19.3	40.0	22.2	48.8	18.7
Mother liquor 1	4.3	0.7	5.0	0.1	6.4	2.1
Mother liquor 2	12.2	0.0	13.5	0.0	13.9	0.0
Mother liquor 4	2.0	0.6	1.3	4.3	1.6	0.2
Dialyzate 1	7.8	3.7	2.5	1.2	4.4	1.6
Dialyzate 2	1.8	1.5	0.6	0.6	1.7	0.5
Dialyzate 3	1.6	1.4	0.5	0.9	1.3	1.3
Precipitate 3	0.1	0.1	1.0	0.2	1.0	0.4
Precipitate 4	0.9	5.7	0.9	4.7	2.4	14.5
Washings	10.1	0.3	...	..	..	..
Total	102.9	33.2	64.3	34.2	81.2	39.3
Loss	...	66.8	35.7	65.8	18.8	60.7
Mother liquor 3	2.9	8.0	6.4	19.5	5.7	34.7

NOTE.—The "washings" given in this table consisted of some 50% alcohol used in the first experiment to wash the residue from the first filtration.

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[1] *Loc. cit.*

[2] Sherman and Neun, THIS JOURNAL, 38, 2203 (1916).

a clear dispersion which is made up to 500 cc., and 50 cc. used for each determination.

The distribution of the solids and enzymic activity of the pancreatin during its purification is shown in Table II.

Proteolytic activities of most of the fractions were also determined.

Discussion.

The phenomena observed in the various preparations show that Precipitate 3 ("sac precipitate") does not come down on account of any effect of the sac nor primarily as a result of the dialysis, but is formed by the coagulation of particles which are present as fine suspension. This coagulation will take place if the suspension is allowed to stand, but it is accelerated by dialysis. The fact that this fraction is insoluble in 250 cc. 50% alcohol while it was formerly dissolved in less than 200 cc. of that reagent is inexplicable as a case of true solution but perfectly regular when considered as a colloidal phenomenon, since substances present in the earlier dispersion are absent in the latter, having been removed by the intervening precipitations. This fraction, as has been stated in earlier papers, is a very active protease; in fact, it is the most active protease preparation of which we have knowledge. In this connection it should also be noted that the first product (Precipitate A) obtained by Sherman and Neun (*loc. cit.*) through alcoholic precipitation after the usual dialysis was a more active protease than the second one (Precipitate B). These results indicate that the protease fraction of pancreatin is more easily coagulated than the amylase. If this is so, a larger proportion of the protease should remain behind during dialysis. The protease not only dialyzes but also precipitates during the dialysis and so the activity of this precipitate must be combined with that of the inner solution in order to permit a proper comparison of the relative rates of dialysis of the amylase and protease originally present. Compared in this way, it was found that in each of our 3 experiments the protease remained in the dialyzing sac in larger proportion than did the amylase. It seems then that in the dispersed state the protease dialyzes more slowly and, therefore, presumably consists of larger particles than the amylase.

From 3 to 7% of the original amylase was found in the dialyzates. This amounts to from 10 to 20% of the total amylase accounted for, or on the average about $^1/_5$ of the amount remaining in the sac after dialysis. Such slow dialysis is enitrely consistent with the classification of the enzymes as colloidal substances, since it has often been found that some colloids do dialyze through collodion membranes.

The average of the first 3 experiments gave the amylase content of the residue as 20.0% of the original; Mother Liquors 1 and 2, and Precipitates 3, 7.1%; Mother Liquor 3, 20.0%. At the end of the dialysis, therefore, there remained 20% of the original total amylolytic activity, and 27.2% was present in the fraction separated before the end of the dialysis, in all 47.2%, leaving a deterioration of 52.8%. Of the 20.0% remaining after dialysis 10% was recovered in Precipitate 4 and Mother Liquor 4 and 10% deteriorated. We see then, that of the original amylolytic activity 62.8% was lost by deterioration and 37.2% was found in the fractions separated. Precipitate 3 is obtained from a volume of from 300 cc. to 500 cc. and Precipitate 4 from a volume of 600 cc. to one liter. This precipitation brings down about 35% of the solids present which represents from 25 to 70% of the amylolytic activity and from 30 to 80% of the proteolytic activity present. When the activity of the enzyme left in the Mother Liquor 4 is taken into account, the deterioration in the last precipitation amounts to from 20 to 60% of the amylase and from 6 to 50% of the protease present. The 2 main factors in this loss are the heating of the centrifuge and the fact that the precipitate cannot be removed quantitatively from the centrifuge tubes. In these experiments liquid air was not used for cooling the centrifuge, as in some of the work of Sherman and Neun, and the higher temperatures here encountered presumably increased the loss due to deterioration in solution and lowered the activities of the final precipitates.

It seems that precipitation with absolute alcohol is efficient in freeing an aqueous dispersion of the enzyme. Whether it precipitates nearly all of the enzyme or inactivates that which remains in solution is not certain, but from the results recorded in the previous paragraph it seems probable that the enzyme is fairly well precipitated and that the deterioration is no more largely due to the alcohol than to other causes, such as increased temperature. Alcohol cannot be used exclusively as a precipitant because it will not precipitate the first extract unless at least 50% of ether is present. The way in which the ether functions is not known since ether alone will not give the precipitate. The exact concentration of ether necessary varies with the composition of the original pancreatin and the thoroughness of the extraction.

The present experiments afford no convincing evidence as to whether or not amylase changes to protease. The difference in the rate of deterioration here observed may be due either to such a change or to greater instability of the amylase.

Summary.

1. Alcohol up to 5%, or alcohol-ether mixture up to 8% of the volume of the substrate did not materially affect the activity of the pancreatic amylase. Higher concentrations were not tested, as these are much above the quantities introduced with the enzyme in the experiments here described.

2. When 50% alcohol extracts of pancreatin were precipitated by alcohol-ether mixture as in our usual purification process, the residual

solution (Mother Liquor 1) contained about 1% of the active amylase and 2.5% of the solids of the original pancreatin, or about 5% of the solids originally extracted.

3. When the alcohol-ether precipitate was dispersed in water and mixed with absolute alcohol, 25% of the solids originally extracted remained in the filtrate (Mother Liquor 2) but this filtrate showed no amylolytic activity.

4. From 10 to 20% of the amylolytic activity accounted for was found in the dialyzates.

5. In the purification experiments here described about 50% of the amylolytic activity was lost by the end of the dialysis, about 45% in the final precipitation and separation, and about 5% was found in the final precipitate. By the use of liquid-air cooling it has been possible in other experiments to diminish the losses in the later stages of the process and considerably increase the proportion of active amylase recovered in the final product.

6. The precipitate which forms in the inner solution during dialysis (Precipitate 3, "sac precipitate") shows very high proteolytic and little or no amylolytic activity. This material, which was originally extracted by 50% alcohol, now precipitates from this solvent. The explanation of this fact is probably to be found in the removal, through the intervening purification process, of some substance or substances whose presence interferes with the coagulation of the protease or stabilizes its dispersion.

We are greatly indebted to the Carnegie Institution of Washington for grants in aid of this investigation.

New York, N. Y.

NEW BOOKS.

Cours de Chimie a l'Usage des Etudiants P. C. N. et S. P. C. N. Par R. de Forcrand. Deuxième Edition, Paris, Gauthier-Villars et Cie. 1918. Tome I, pp. VIII and 438; Tome II, pp. 528. 14 × 22 cm. Price of Vol. I, 15 francs.

The first edition of this book was reviewed in This Journal, 27, 790 (1905). The second edition has veen very considerably enlarged but retains the same general scope. The book is intended for use in the instruction of students who are candidates for the "Certificat d'études supèrieures de physique, chimie et sciences naturelles (or S.P.C.N.). It is intended to give the work covered, in 3 lessons a week for one academic year. If the material of this book is fairly mastered in that period it must represent far more intensive work than is done by American students. The first 75 pages give the fundamental principles, laws and nomenclature of the science. There are some advantages of such a method of approach, but a beginner would certainly find these pages difficult. About

200 pages are given to a detailed discussion of the metalloids and 150 to the metals, completing the first volume. In the second volume 326 pages are devoted to organic chemistry, 108 pages to qualitative and quantitative analysis, including organic analysis and gas analysis, and the last 90 pages to numerical problems.

Probably every text-book retains some errors and some survivals of points of view which have been outgrown in the progress of the science. On p. 101 we find Regnault's value for the weight of a cubic meter of hydrogen 89.5 g. instead of the more correct modern value, 89.87 g.

On p. 110 we find the surprising statement that up to a temperature of 180° there is a false equilibrium causing limited combination of oxygen and hydrogen such that at 180° 12/10,000 of the mixture appears as water. The combination increases above that temperature and at 900° it is complete and remains so to 1200°. Above that dissociation begins. Surely this does not agree with modern views. In several other places the author seems not to have very clear views with regard to the nature of chemical equilibrium.

The thermal relations of many chemical reactions are discussed throughout and while the author follows Berthelot too closely in many passages which imply that the heat of formation of a compound is a direct measure of the affinity of the elements of which it is composed, the emphasis placed upon thermochemical data constitutes one of the most valuable features of the book.

As an illustration of the tendency to consider thermal relations, the definition of an acid, p. 290, may be cited: After having stated that the heat evolved in the replacement of hydrogen by sodium is —2.3 calories for NaOH, 14.84 for NH_3, 22.3 for C_2H_2, 32.9 for H_2O, 69.3 for HCl, and 69.2 for HNO_3, an acid is defined as a compound which evolves more than 33 calories of heat when its hydrogen is replaced by sodium. The author calls attention, very properly, to the fact that such a definition is based on the convention that water is neutral and one might, if he preferred, call acetylene or hydrochloric acid as neutral. It might be of interest to consider whether the above definitions would coincide, practically, with the ordinary definition based on the hydrogen and hydroxyl ion content of an aqueous solution of the substance.

On page 298 we find the erroneous statement that pure water contains no ions. Closely connected with this error is the omission of any reference to the hydrolysis of salts of weak acids and weak bases.

The portion of the book devoted to organic chemistry is arranged logically, treating the hydrocarbons first, then of alcohols, phenols, aldehydes, ketones, acids, amines, etc. The selection of material is satisfactory.

While the point of view of the book as a whole is quite different from that of most American and German text-books, this very fact would make it well worth reading, especially for students who wish to improve their knowledge of scientific French. There is no index. W. A. NOYES.

Die Welt der vernachlässigten Dimensionen. By WOLFGANG OSTWALD. Fourth Edition. Theodor Steinkopff, Dresden and Leipzig, 1920. xii + 222 pp. 15 × 23 cm. $1.00.

The book is based on a course of lectures given by the author in the United States during the winter of 1913–14. The first edition was translated by M. H. Fischer, appearing under a different title. The first chapter deals with the fundamental phenomena of colloid chemistry. The author points out that colloidal solutions are 2-phase systems and he gives some of the methods of preparing such solutions. The second chapter is devoted to a discussion of the way in which the properties of a colloidal solution vary with the degree of dispersity. This brings in red and blue gold, the Brownian movements, ultra-filtration, the Tyndall phenomenon, the ultra-microscope, and cataphoresis. The changes of state of colloids form the subject of the third chapter. Under this rather misleading heading the author discusses the formation and swelling of jellies, adsorption, rhythmic banding, viscosity, and coagulation. In the fourth chapter, under scientific applications of colloid chemistry, we find references to filtration, analysis with borax bead, tests for natural honey, photography, rubber, dyes, indicators, catalysis, radio-activity, meteorology, agriculture, geology, physiology, and pathology. In the fifth chapter the author points out that the technical and practical applications of colloid chemistry include about everything that is interesting: cellulose, adhesives, water-glass, textiles, coffee, tea, beer, ink, rubber, oildag, lamp filaments, colored glass, ultramarine, pigments, cement, pottery, plaster, carbon steels and alloy steels, leather, dyeing, artificial silk, bakelite, vulcanized rubber, soap, cooking, asphalt, smoke, and sewage.

The author showed a large number of excellent experiments in his lectures. WILDER D. BANCROFT

Catalysis in Theory and Practice. By ERIC K. RIDEAL AND HUGH S. TAYLOR. 496 and XV pages, 37 figures, 14 × 22 cm. MacMillan, Ltd., London, England, 1919. 19 shillings.

It is surprising how completely we have lacked any comprehensive treatise on catalysis, a phenomenon recognized now for nearly a hundred years, and known to be as important as it is universal. There have only been the compilations of Gertrud Woker, in German, encyclopedic rather than illuminating; chapters in the larger text-books of physical chemistry, the best of which is one by Mellor, in his "Chemical Statics and Dynamics;" the brilliant popular articles by the late Robert Kennedy Duncan, and a number of special monographs on particular branches of the subject, particularly "Le Catalyse in Chimie Organique," by Sabatier.

The present volume is a long step toward a remedy of this deficiency. Its first 3 chapters of 74 pages contain an historical and theoretical introduction; the remaining 400-odd pages are devoted to the more important concrete instances of catalysis, classified under Oxidation, Hydrogenation, Dehydrogenation, Fixation of Nitrogen, Hydration and Hydrolysis, Dehydration, Organic Chemical Reactions, Ferments and Enzymes, Catalysis in Electrochemistry and in Analytical Chemistry, and Catalysis by Radiant Energy. The theoretical introduction is not as thorough or complete as might be wished; the discussion of induced reactions being particularly brief. This deficiency is certainly in part due to the unsatisfactory state of the subject itself, for which the authors can hardly be blamed, and in part to a wise limitation of the size of the book. Moreover, it is largely remedied by the thorough theoretical treatment accorded separately to each of the industrially important catalytic processes. The chapters on Hydrogenation, Fixation of Nitrogen, and Catalysis by Radiant Energy, are particularly good.

The wide scope of the subject is impressive. Devotees of colloid chemistry maintain that every branch of applied chemistry falls within their domain, but catalysis apparently has equally valid claims for universality. The authors have treated this wide and varied subject matter with clearness and perspicacity. Best of all, they have been able to master the separate subjects so well that the book is replete with suggestions for further research.

That, indeed, is the greatest profit which a scientific book can afford. When the facts in any particular field are gathered together, the gaps and loopholes in our knowledge become apparent and this stimulates investigation. Moreover, speaking chemically, to bring together significant facts within reacting distance is bound to accelerate the synthesis of generalizations. In such a sense, this book should prove to be one of the best examples of the phenomenon it describes. ARTHUR B. LAMB.

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[CONTRIBUTION FROM THE PHOENIX PHYSICAL LABORATORIES, COLUMBIA UNIVERSITY.]

A CALORIMETRIC PROCEDURE FOR DETERMINING THE HEATS OF SLOW REACTIONS. II. THE CALORIMETRY OF A SLOW REACTION: THE HEAT OF INVERSION OF SUCROSE BY ACID.

BY FREDERICK BARRY.

Received February 2, 1920.

In the calorimetry of slow processes, the fundamental necessity is the long-continued maintenance of a negligible or precisely measurable heat interchange between the reacting system and its environment. Of the 3 general methods of calorimetric practice, the merodiabatic,[1] the isothermal and the adiabatic, the last alone is adequate in all cases for the establishment of such condition.[2] The complicated corrections for thermal leakage characteristic of merodiabatic calorimetry are not uniformly applicable to evey type of system, and in precise measurement must be

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[1] The term merodiabatic, suggested by W. P. White [THIS JOURNAL, 40, 388 (1918)] applies to the customary method, in which measured thermal leakage occurs between the calorimeter and its environment.

[2] The advantages of the adiabatic method for the possible measurement of protracted processes has already been remarked, in a general way, (White, THIS JOURNAL, 40, 1891; Dickinson, Bur. Standards, *Bull.* 11, 207) but has not, in the writer's opinion, been sufficiently emphasized; and the method has not, apparently, been thus applied heretofore.

separately determined. In long-continued operations, their magnitude will be comparable with that of the heat actually measured, and will be affected by comparable errors of observation; while their uncertainty, due to unavoidable differences of manipulation in separate measurements and, in minor degree, to fluctuation in environmental (thermostat) temperature will become increasingly significant with the passage of time. This method, therefore, is inapplicable to the precise measurement of slow reactions. By the isothermal method, on the other hand, a practically constant environment having been established, accidental transfer of heat could be eliminated, or reduced to such magnitude and to such narrow and determinable range of fluctuation that it could be safely corrected for from the results of accessory measurements. With this procedure, furthermore, all kinetic data involved in the analysis of the process examined could be used without correction for the effect of temperature change, and the temperature coefficients of changes in total energy could be left out of consideration. The probable technical difficulties attending its general use, however, are great,[1] and are probably insurmountable in the case of slow reactions which are wholly or in part exothermal.

These considerations are sufficient to justify the choice of the adiabatic method for the calorimetry of any slow process except in special cases. This method makes possible the practical elimination of error in correction for transfer of heat, as does the isothermal method; but unlike the latter, it may easily be adapted to the measurement of thermal changes of whatever character. Its single disadvantage, due to changing temperature, is relatively unimportant, and necessitates merely the application of simple and precisely determinable corrections, of which, in familiar types of slow reaction, only that which affects the kinetic data is measurable.[2]

The following paragraphs describe an adiabatic procedure which, it is believed, will be found generally adequate for the precise calorimetry of slow reactions. For illustrative measurement, the inversion of sucrose by hydrochloric acid, a process which includes both endothermal and exothermal changes, has been chosen. The thermal effects involved in this reaction as experimentally conducted have been analyzed in a previous communication,[3] and the results of this preliminary inspection are here practically applied. The final results leave small doubt that the precision of this sort of measurement is not influenced by errors peculiar to adiabatic procedure beyond the limit set by the errors of precise mercury thermometry, and that in the determination of slow reaction heats, further improvements in accuracy will depend primarily upon a reduc-

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[1] See Richards and Rowe, *Proc. Am. Acad.*, 43, 477 (1908).

[2] See the following reference, pp. 1307, 1308.

[3] THIS JOURNAL, 42, 1295 (1920).

tion of the cumulative effect of small sources of uncertainty common to all calorimetry, which though usually insignificant, are exaggerated by the passage of time.

Calorimetric Apparatus: Dimensions and Heat Capacity.—In these measurements an adiabatic calorimeter was used, of the general type devised and subsequently developed by Richards and his co-workers.[1] The accompanying sketch (Fig. 1), drawn particularly so as to show the detail of the instrument as modified for the purpose of the present research, will serve also to recall the general construction, which is now too well known to require further description.

The calorimetric vessel was a cylindrical cup of copper, of a thickness equal to that of the jacket wall, heavily plated with gold and highly burnished. It was supported and held precisely concentric with the polished jacket wall by points of ivory cemented to a closely fitting and rigid frame of boxwood. The widths of the air gaps surrounding it were 40 mm. above, 10 mm. below and 6 mm. laterally. These dimensions do not conform to those calculated by White to be the most effective for general insulation;[2] the calorimetric construction, therefore—which was made in 1913, prior to the appearance of White's important paper—could in this respect probably be improved.[3]

The heat capacity of the whole assembled system, determined by a variety of considerations relative to desirable advantages in experiment, was about 1,000 gram calorie units. This capacity was large enough to make the temperature change from thermal leakage under established conditions very small, and to allow considerable nicety in manipulation; while, with the thermometers employed, it still permitted the detection

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[1] For examples see THIS JOURNAL, 37, 1004–1006; *Proc. Am. Acad.*, 49, 174ff, and references in first citation, p. 994.

[2] W. P. White, THIS JOURNAL, 40, 379 (1918); cf. *Phys. Rev.*, [2] 7, 682 (1916) and *ibid.*, [2] 10, 743 (1917).

[3] White's results indicate that considerably larger basal and lateral spaces might have been used, with corresponding diminution of air conduction. In these determinations, however, transfer of heat by radiation and conduction was relatively unimportant since in the corrections for imperfect adiabaticity, the single assumption was made that the total transfer of heat was proportional to the thermal head (see p. 1923). The really necessary precaution was to reduce transfer by convection as much as possible. The wide upper space necessary for proper manipulation was on this account considered dangerous, but in practice was shown to be not so, in confirmation of White's general conclusions. It is not to be forgotten, however, that in the case of nearly all slow reactions which involve a heat of mixture, sudden changes of temperature are likely to occur at the beginning, which might well make the consistent employment of such very wide air spaces disadvantageous. It will in general be sufficient for experimental purposes to make these spaces no wider than is necessary to prevent undue conduction and thus to avoid the always possible danger of eddying convection currents, excepting in special cases when only gradual temperature changes take place.

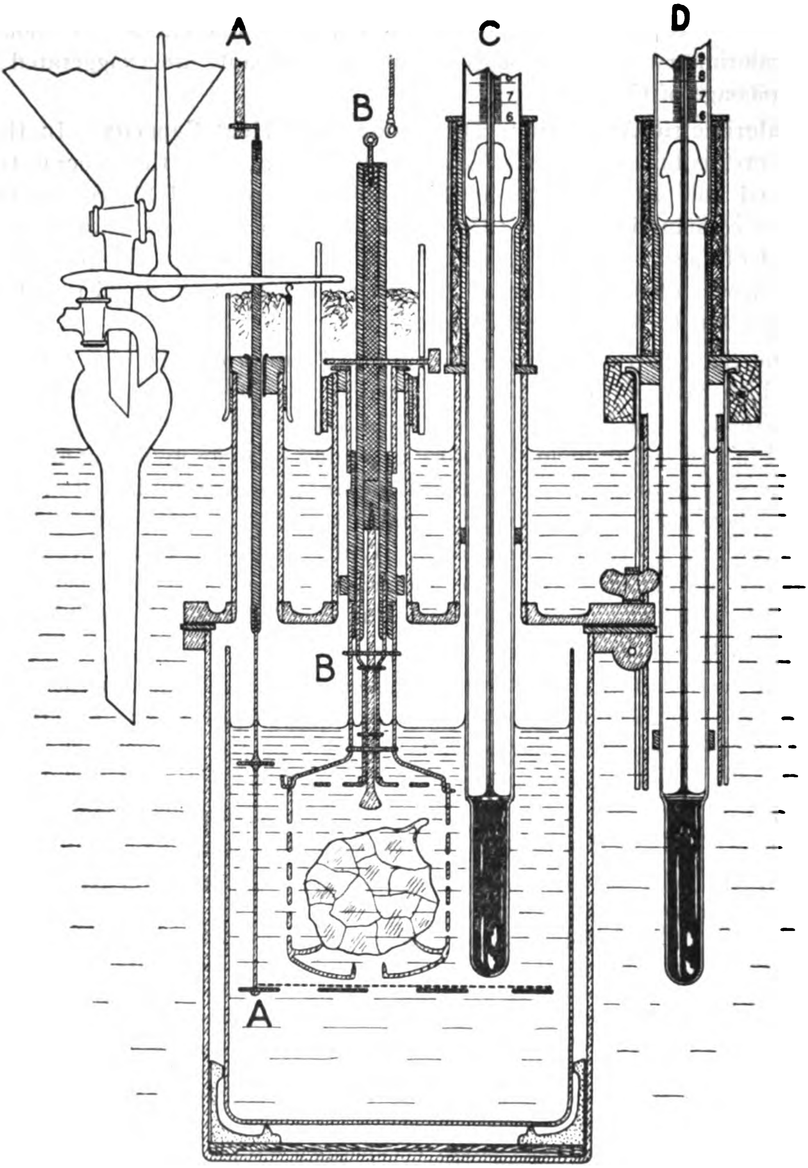

Fig. 1.

In this diagrammatic sketch, mercury, silver mirror surfaces and cement are in heavy black; gold- and nickel-plated copper in broken hatching; lead in cross hatching; vulcanite in heavy single hatching and soft rubber in light single hatching. Ivory, wool and wood will be recognized by characteristic markings. Glass is left unmarked.

Certain liberties have been taken with the section for the sake of clearness; the calorimetric thermometer, for instance, is actually not on the same diameter with the stirrer and mechanism chimneys, though it is here so represented.

of 0.5 calorie of thermal change. It was known in every determination to well within 0.5%, with negligible error of variation.

Constant Temperature Closet.—By the arrangements already described or suggested, the calorimetric system was well insulated from its surrounding bath. The bath in turn protected it as effectively as possible from the environment. There remained, however, unavoidable direct communication and consequent thermal leakage between the calorimeter and the outside air, through the thermometer, the stirrer, and the air in the stirrer chimneys. Such thermal interchange is never wholly eliminated nor made absolutely definable by any method of procedure; and the degree of uncertainty it introduces inevitably increases with the passage of time. As a prerequisite for the successful completion of the measurements under discussion, therefore, a closet had first of all been constructed, so designed that the temperature within it could be maintained for any desired time constant within narrow limits of variation. The essential features of this construction, including the thermostatic mechanism, by means of which its temperature was controlled, may merit future description. In this place it is sufficient to note that within it the temperature in the immediate neighborhood of the calorimeter could be held constant to ±0.1° for any desired interval of time, while that of the whole interior remained uniform and constant to within ±0.3°. By this means, while the bath was held within 0.01° of the reaction temperature, the unavoidable direct leakage was made measurably constant while the calorimeter was stirred, and quite negligible while it was held quiescent. It was sufficient that the temperature of the closet varied no more than 0.5° from the reaction temperature to accomplish this result.

Stirring Mechanism.—The calorimeter contents were agitated by a vertical reciprocating stirrer. This form possesses many advantages in experimental as distinguished from routine procedure over the rotating propeller. The latter is relatively ineffective in preventing thermal stratification unless it is held in a separate chamber so connected with the main calorimeter body that strong currents are made to flow through the connecting orifices;[1] and such a construction, which must be designed with care to ensure with a given arrangement of internal parts sufficient mixing, seems too unadaptable for use as a general laboratory appliance. In the present work, the reciprocating stirrer was in other respects preferable. Besides assuring quick and complete mixing, it made possible a thorough agitation with a minimum of eddying air convection such as would result from surface motion, and thus permitted

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[1] This type of stirrer has been designed and perfected at the Bureau of Standards. For a description of an apparatus which includes it see H. C. Dickinson, *loc. cit.*, Bur. Standards, *Bull.* 11, 210.

the relatively safe use of an open calorimeter vessel; its heating effect was probably smaller than that of an effective rotating stirrer would have been with the system employed; its adequate insulation was quite as certain; and though its motion was no more closely uniform than that of a propeller when the mechanism was in continuous operation, it was more precisely manageable when stirring was intermittent and slight. Finally, it assisted so materially in securing a rapid mixture of the reacting ingredients at the beginning of a measurement that on this account alone it could hardly have been dispensed with.[1]

The only obvious disadvantages of this kind of stirrer result either from irregular motion or from actual transfer of air by pumping; both of which effects can be minimized by proper construction. In these measurements, the outer calorimeter stirrer, which was a perforated ring and disk affair of usual design made of gold-plated copper (Fig. 1, AA), was suspended from the outer hanger by long thin rods of polished vulcanite which alone, during movement, entered and left the system. These moved through perforated stoppers at the chimney tops, the holes through which, only slightly larger than the rods, were lined with thin glass and insulated by fine wool held loosely over 20 mm. length above them by large glass tubes which capped the chimneys. The dimensions and adjustment of the stirrer were such that it moved with almost inperceptible lateral displacement, and very smoothly. The ring and disk, always submerged, each traversed a half of the liquid depth, and stirred most effectively the lowest layers where inhomogeneity was most likely. A no time did metal enter the chimneys, or vulcanite come in contact with the calorimeter liquid, the surface of which was only very slightly disturbed. The inner calorimeter stirrer (Fig. 1, BB), was similarly insulated, and was adjusted with similar care.

The external stirring mechanism was a miniature factory construction of steel shafts and crown pulleys easily adjustable to several convenient speeds and lengths of stroke; and was driven by a $^1/_4$ horse-power motor. All transmission was by flat belts 25 mm. wide. The stirring speed was thus made constant within the limits of constancy of the motor speed itself, and varied during a 10 or 12 hours' run no more than 2%. Absolute constancy, such as might have been provided by a synchronous motor, was unnecessary, since during measurement the actual speed could be and was easily measured at half-hour intervals, and corrected for this slight variability with sufficient precision. The mechanism was adjusted, in determination, to a speed of 55.0 to 56.0 strokes per minute over a traversed space of 40 mm., after it had been shown by test that 12 such strokes were sufficient to render a mass of water underlaid with dense, dyed sugar solution, of a volume equal to that which was to be

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[1] The process of mixing is described on p. 1917ff.

measured, apparently homogeneous in refracted light. The speed was invariable throughout a series of measurements; and the length of stroke was made the same in every experiment and invariable in each of these to within a millimeter, by suitable mechanism of adjustment. By a simple device, the inner stirring could be interrupted with ease at any stroke without interference of the bath stirring, which was continuous and always sufficiently rapid to prevent significant lag in the maintenance of thermal homogeneity.

Mechanism for Effecting Solution.—For reasons already discussed,[1] mixture was brought about in these determinations by dissolving dry sucrose in acid. It was obviously advantageous to use as large a mass of sucrose as could be conveniently accommodated by the calorimeter, and at the same time quickly enough dissolved. In order to effect a quick solution, it was necessary that the sucrose be delivered into the acid suddenly from above in such a way that it could not accumulate in any considerable mass at the bottom, and that during this operation the solid be scattered throughout the acid by rapid agitation. Provision against the gradual wetting of the sample while it was being held within the system during the long period in which thermal equilibrium was being established at the desired initial temperature also had to be provided. The final result of several attempts to meet these necessities was the apparatus designated BB in Fig. 1. The sample of very finely pulverized and very dry sucrose, about 35 g. in weight, was held in a fragile bulb of glass, weakened, and in the final determinations put under strain, by having been flattened in the blow-pipe into a roughly polyhedral shape, and sealed at a constricted part of the stem close to the body. Within the calorimeter, this bulb was held in a basket of gold-plated copper, so designed that when immersed in the calorimeter acid, this liquid would have free access to every part inside. The bulb rested on three chisel edges, immediately above a small crown of points which ringed a central orifice at the bottom. The basket hung from a stiff framework of gold-plated copper wire so reinforced that although light and easily detachable it nevertheless held the basket quite rigidly to a large vulcanite tube which supported the whole. This tube extended through the chimney designed to accommodate the mechanism, and was held concentrically within it by a detachable rubber ring, capped with a brass flange at the top, so that when the whole apparatus was assembled, the basket occupied a definite position just submerged beneath the calorimeter acid.

Attached to a smaller and considerably longer vulcanite tube weighted with lead, which could move freely within the larger one that held the basket, a chisel fashioned out of silver rod and heavily plated with gold

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[1] This Journal, 42, 1302 (1920).

was held suspended over the bulb by a removable pin which rested on the flange of the larger tube. This chisel was surrounded by a frame of wire, firmly attached to the vulcanite tube into which it was tapped, which carried at a point about 10 mm. above the cutting edge a perforated circular plate, designed to serve as a mixing stirrer within the basket. The entire chisel-stirrer construction could be operated rapidly by hand in such a way as to crush as well as stir the contents of the basket; and could also be attached to the stirrup of the external stirring mechanism by a small chain and pulley arrangement which was so adjusted that when connection was made the basket stirrer moved simultaneously with that in the calorimeter, but in opposition to it.

When it was desired to start the reaction, the chisel was allowed to fall upon the bulb; and this, now broken, was further crushed between the plate of the basket stirrer, operated momentarily by hand, and the sharp edges within the basket upon which it rested. The crown of points at the bottom effectively prevented the retention of sugar by any cup-shaped fragment. The basket stirrer was then attached to the stirring mechanism so that working in conjunction with the calorimeter stirrer, it effectively washed the basket free from all accumulations of solid. The greater bulk of the sugar slush thus formed fell upon the lower plate of the calorimeter stirrer, where it was held by a finely perforated piece of gold foil attached to the plate for this purpose, and was carried up and down through the acid by the motion of the stirrer.

In this way the solution of the sugar was made sufficiently rapid, and by careful routine manipulation, after a little practice, uniformly so.[1]

Thermometry.—The calorimetric thermometers used were closely similar instruments made to specification early in 1913. They were of a type previously found most suitable in work of this character; large bulbed mercury thermometers resembling metastatic instruments of the Beckmann type, which registered, however, the definite temperature range of 15–21° in 0.01° intervals. The length of a degree on each scale was more than 68 mm., so that by the use of a hand lens it was possible to read intervals of 0.0005° with a precision greater than that which is usual in reading 0.001° intervals on similar thermometers of the usual dimensions.

These instruments probably represented the limiting efficiency of mercury-in-glass thermometers. They showed very slight indication of capillary friction either on rising or on falling thread; their registrations

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[1] It is clear that the procedure here described or one closely similar may be used for the mixing of any solid sufficiently soluble, or of any liquid sufficiently dense with a reacting liquid, in analagous calorimetric processes. Simple modification would make it generally suitable for the mixing of liquids, excepting in cases where these would react with glass.

were never altered more than 0.0005° by tapping, and usually not at all; their threads were never found broken even after long-continued and violent agitation; and when read with a telescope to 0.0001°, both falling and rising threads showed a strictly continuous motion of the meniscus. If the precision of their standardization and the limit of calorimetric accuracy had justified the procedure, they might have been read accurately to ±0.0001° in this manner. They were very sensitive. The measured coefficient for external pressure, 0.000243° per millimeter for both instruments, was sufficiently large to make the influence of changing barometric pressure a source of possible error in the long-continued measurements. This effect, therefore, was always estimated, though as it happened no correction for it ever had to be applied. The lags of both instruments (determined in a simple manner which, because of its convenience, may merit future remark), were the same, the total lag under conditions of maximum convection being 30 seconds for both instruments, and independent of total temperature change within a range of 0.5°. This lag was insufficient to affect the present measurements excepting during the period of most rapid change, and had to be taken into consideration therefore, only in determining the form of the curves of solution (p. 1926).

The thermometers were standardized by comparison with normal instruments which had been made by Baudin and fully corrected to the hydrogen scale by the Bureau des Poids et Mesures, in 1913. The precision of the comparison, which included 16 registrations between 19.54° and 20.23° was estimated to be consistently within ±0.001°, but was probably closer than this.[1]

In measurement, the corrections for stem exposure were very small, and their well known uncertainty consequently negligible; since the environmental temperature was always roughly constant and within 0.5° of the calorimetric. To maintain this constancy, however, it was found necessary to protect the entire stem of the calorimetric instrument by a mirror, which, in every measurement, was placed between it and the body of the operator.

In order that the calorimeter and bath thermometers should always register definitely comparable temperatures (a matter of the utmost consequence in the maintenance of adiabatic condition) the bath thermometer, which could not be immersed to the level of scale readings, was supported in such wise that the thick thread between scale and bulb was surrounded by a closely fitting cylinder of heavy copper plate, itself protected by a larger cylinder of silvered glass. Since both cylinders were half immersed in the bath, the lower thread of the thermometer was thus held at bath temperature. Both thermometers were further insulated above their points of support by silvered glass tubes packed with wool;

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[1] See the data of Table VI, p. 1938.

and this insulation extended to the same points on the two thermometric scales. By these devices (C and D in Fig. 1), the stem exposures of the two instruments were made identical, and thus negligible in a comparison of their registrations.

A source of thermometric error which seems not to have been observed or at any rate emphasized heretofore was noticed during the calorimetric measurements. At the end of each determination, the final condition, which should have been that of constant temperature, was tested by holding the whole system as closely as possible at equilibrium for an hour. In these tests, under the usual environmental conditions, a rise of 0.00005° per minute was always observed. This rise was very much greater than that due to the very slight stirring, and was the same whether the temperature of the room or that of the bath were above or below that of the calorimeter; but if, either before or after these tests were made, the incandescent tungsten filament lamps of the constant temperature closet were extinguished and the system still kept in equilibrium by flash-light observations and adjustments, there was, after the lapse of 15 minutes, no subsequent measurable temperature change whatever; that is, in the dark the system was constant to ±0.0005°. These observations, confirmed by the results of various modified procedures, seemed to indicate that the registration of encased mercury thermometers is sensibly affected by radiant heat from ordinary artificial illumination. The reason is not far to seek: it is without doubt what may be called, in a word, a "greenhouse" effect; and may be prevented or minimized not only by using light screens with all encased thermometers directly illuminated, but also by opening the shells of such instruments to permit free circulation of air around the thread tubes. The phenomenon is at present being quantitatively investigated.

Bath Adjustment and Control.—In the adiabatic calorimetry of swift reactions it is not impossible to control the bath by hand sufficiently well to reduce the error from thermal leakage to almost negligible magnitude.[1] If accessory devices for automatic regulation be employed, this error may be still further reduced, even beyond the limit of thermometric precision.[2] It is conceivable that similar regulation of the bath during the progress of slow reactions might be made likewise effective; but the precision of adjustment would have to be enormously increased to accomplish such result,[3] and any procedure seemingly adequate for the pur-

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[1] Richards and Barry, This Journal, 37, 1010, 1012ff (1915).

[2] Richards and Davis, *ibid.*, 39, 344ff (1917). Note especially the curves on p. 346. See also Richards and Osgood, *ibid.*, 37, 1918 (1915).

[3] The necessary thermal equilibrium could doubtless be indicated with sufficient precision and with least danger from direct conduction leakage, by a multiple thermo-element spanning the space between calorimeter and bath; and the regulation, to be comparably exact, would then have to be automatically controlled by the thermo-

pose would still be open to criticism unless simultaneously with regulation the maintenance of requisite precision were continuously and rigorously tested. For these reasons it was not attempted in this investigation to eliminate thermal leakage; but rather to control it within narrow limits, in such way that on the basis of accessory measurements which defined the relation between actual leakage and thermal head with the system employed, it could be safely corrected for.

The bath was a dilute solution of alkali, the temperature of which could be gradually raised or lowered with equal facility by drips of dil. sulfuric acid and of ice-water.[1] The ice-water was contained in a well insulated bucket high above the calorimeter, flowed through a double-walled tube of glass wrapped in thick felt, only a few centimeters of which, in the region of the attached stopcock, was left exposed, and dripped into the bath at a point diametrically opposite to the bath thermometer. It was determined by test that the insulations provided were sufficient to prevent any significant cooling of the air near the thermometers. The dil. sulfuric acid drip was similarly arranged. Both drips were under fairly constant pressure during any single determination, and their rates of flow were very precisely controlled by long-handled stopcocks lubricated with grease sufficiently viscous to prevent maladjustment from jarring. As essential accessories, and as provision against emergency or accident, an insulated beaker of broken ice and water, a stoppered Dewar cylinder of hot water, and a small buret of conc. sulfuric acid clamped securely above the bath were also kept in readiness.

With this apparatus the bath was controlled during the preperiod, and throughout the long period of slow temperature change which followed solution. Since the air of the closet-thermostat was held at the temperature of reaction, the bath was normally about 2° lower. It was, therefore, continuously heated by the dil. acid drip, so regulated that during 15 minutes its temperature relative to that of the calorimeter

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element itself. It is easy to imagine a workable mechanism of this character which would serve for the measurement of continuously exothermal processes; and its practical adaptation to the measurement of endothermal changes—as by combination with ice-water cooling in the bath, or by introduction of measured energy into the calorimeter—is likewise not inconceivable. Such devices have been more than once suggested, as separately applicable in special cases. But the complete machine constructed so as to follow both types of change in the course of one continuous process (which the present problem would require) seems, surely, a premature conception.

[1] Chemical, in comparison with electrical heating, is disadvantageous only with respect to the danger of possible leakage by corrosion, and of loss of control in long continued operations by accidental exhaustion of reacting material. By electrical heating, the lag in thermal distribution may be reduced, but at the cost of a lessened sensitivity in minute adjustment; and since the distribution lag is less than that of the thermometers, the advantage still remains with the chemical procedure. It is obvious that the ice-water drip is necessary in any case.

would gradually rise or fall to no more than 0.01° of thermal head. This condition was easily and quickly established; and during reaction could be maintained without difficulty by occasional readjustment of the rate of acid flow. When the bath had risen about 0.005° above or had fallen 0.005° below the point of equilibrium, its temperature was readjusted by adding ice-water or conc. acid in such determined quantity that the temperature difference 15 seconds later was the same but in the opposite sense. By this procedure the bath fluctuation, sufficiently defined by frequent thermometric readings, was made roughly periodic about the temperature of reaction, and the mean divergence from equilibrium correspondingly reduced.

In the 2- or 3-minute period which immediately succeeded the breaking of the bulb, the calorimetric temperature fell, and then rose too rapidly to be followed by the drips. By anticipating the first thermometric indication of temperature fall, its approximate rate and its magnitude, it was possible without difficulty to keep the bath during this time within 0.03° or 0.04° of the calorimetric temperature, and at the lowest temperatures reached (at which possible error from thermometric lag was greatest) more closely than this, by successive additions of ice-water and of acid from the accessory supplies. This manipulation, although sufficiently effective, was always hurried, and prevented careful thermometric reading during the first minutes of reaction. In the final determinations, therefore, the temperature fall was followed automatically by use of an ice-water buret. This was a straight glass tube about 3 cm. in diameter, jacketed by 2 larger, concentric glass tubes and thus insulated by 2 narrow dead-air spaces. It was provided with a glass stopcock of large orifice and a set of standardized tips, and was graduated in 0.01° intervals over the maximum range of temperature fall. By reference to the heat of solution measurements, the actual fall for any determination could be roughly estimated in advance from the sample weight; and the approximate lapse of time from initial to minimal temperature determined. In each measurement during the preperiod the buret was chilled by filtered ice-water from the accessory supplies, was then filled with the requisite quantity of the same material, previously held at 0.0° and poured through crushed ice in a Buechner filter; and was stoppered and fitted with a tip which would deliver its contents in the predetermined time. It was then fixed vertically near the drips and kept in readiness for not more than 30 minutes before the breaking of the bulb. It was shown by tests that during this time its contents were not warmed sufficiently either to alter its temperature significantly, or to affect the stem temperatures of the thermometers. A second before the bulb was broken the ice-water buret was opened. It naturally delivered its contents exponentially, so that, while it emptied, the falling temperature of the bath followed that of the calorimeter closely; and since during this time the thermometers could be read with ease at half-minute intervals, the temperature differences between calorimeter and bath were most precisely measured. The minimum bath temperature was never more than 0.02° higher or lower than that of the calorimeter, and was easily and rapidly adjusted to close equilibrium immediately afterward.

The effect of bath fluctuation on the calorimeter temperature was calculated from the results of a series of tests, in which, under different environmental conditions, definite differences of temperature between calorimeter and bath were maintained, with the smallest possible fluctuation, for times varying between 40 and 60 minutes. The results of these tests are tabulated in Table I, A (p. 1924). They show that for differences of less than 0.2° and greater than 0.05° the rate change of calorimeter temperature is proportional to the thermal head maintained, is of the same absolute value for the same thermal head whether the bath is higher than the calorimeter or lower[1] and is not influenced by environmental temperature when this is kept within one degree of the calorimetric. With reference to these data, on the basis of the legitimate assumption that the relations they exhibit will obtain for smaller thermal heads, correction was made in each determination for imperfect adiabaticity. The curve of temperature change within the calorimeter was plotted as a

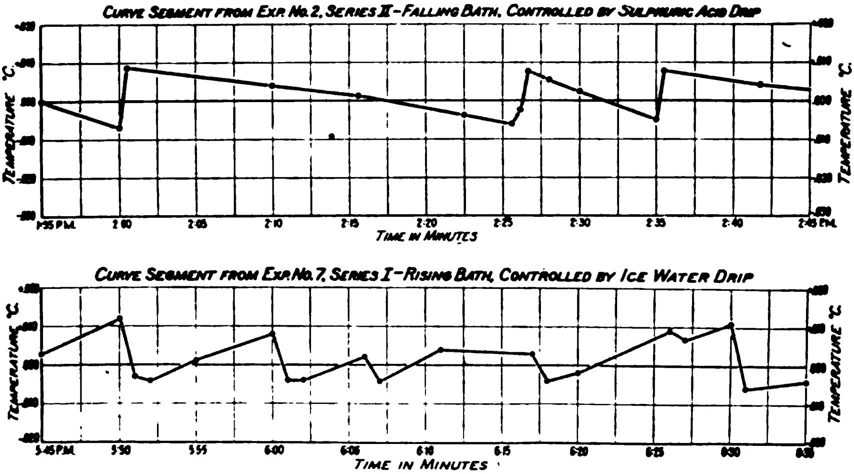

Fig. 2.—Bath temperature fluctuation.

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[1] These results, which, with reference to this calorimeter, appear to be unequivocal, are not in accord with certain observations of Richards and Burgess (This Journal, 32, 449 (1910)) who noticed a much greater rate of change when the bath was lower. This discrepancy is doubtless ascribable to differences in the conditions of experiment in the two cases.

straight line on heavy coördinate paper; and upon this line as axis of reference the curve of bath temperature fluctuation was plotted large by straight line interpolation. Segments of 2 such plots from the records of actual determinations, which show the determined points and very clearly exhibit the general character of the fluctuation, are here included (Fig. 2).[1]

TABLE I.

A.—Influence of Temperature Difference Between Bath and Calorimeter on Rate Change of Calorimetric Temperature.

Temp. of bath relative to temp. of calorimeter.	—0.20°.	—0.10°.	—0.05°.	+0.05°.	+0.10°.	+0.20°.	Environmental temps. °C.
Rates of	...	...	...	+0.00024	...	...	19.8
change in	...	—0.00050	—0.00025	...	+0.00050	...	20.0
calorimetric	...	—0.00050	...	...	+0.00042	...	20.2
temperature	...	...	...	...	...	...	20.4
(in degrees	...	...	...	...	...	...	20.6
per minute).	...	...	...	+0.00023	...	...	20.8
	...	...	...	...	+0.00047	...	21.0
	...	...	...	...	+0.00050	...	21.2
	—0.00100	—0.00050	...	...	...	+0.00097	21.4
	...	...	...	...	...	...	21.6
	...	...	...	...	...	...	21.8
	—0.00096	...	—0.00025	...	+0.00050	...	22.0

B.—Data on Maintenance of the Adiabatic Condition from Measurements of the Heat of Inversion of Sucrose.

	Expt. No.	Total time of maintenance (in minutes).	Heat interchange between calorimeter and bath (inflow + outflow) (in gram calories).		Heat gained by calorimetric system (inflow — outflow) (in gram calories).		Heat capacity of the system (in gram calorie units).	Temperature correction for imperfect adiabaticity. °C.
			Total.	Per 100 minutes.	Total.	Per 100 minutes.		
Series I.	1.......	161	4.5	2.8	—1.7	—1.1	1008°	+0.002
	2.......	234	6.7	2.8	—2.0	—0.9	1019	+0.002
	3.......	253	5.7	2.3	—1.0	—0.4	1 18	+0.001
	6.......	186	3.4	1.8	±0.0	±0.0	1006	±0.000
	7.......	232	4.2	2.0	+2.0	+0.9	1029	—0.002
Series II.	1.......	334	9.3	2.8	—1.0	—0.3	1007	+0.001
	2.......	375	12.3	3.3	+1.0	+0.3	1006	—0.001
	3.......	398	8.1	2.0	—0.5	—0.1	1007	+0.0005
	4.......	412	8.6	2.1	+0.9	+0.2	1147	—0.001

The branches of each curve thus drawn having been distinguished as upper or lower by proper designations, the areas between them and the line of reference were cut out as closely as possible, and the upper branch areas weighed against the lower ones. From the data so obtained, the weight of unit area of the paper being determined for each curve, the total temperature change within the calorimeter due to this fluctuation

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[1] The second curve illustrates the control of the bath when the environmental temperature is high, a condition unfavorable to measurement, but not impracticable.

could be readily calculated.[1] It was never greater than 0.002°, the anticipated maximum.

All significant data relative to the actual bath temperature fluctuation in the completed determinations of the heat of inversion of sucrose are collected in Table I, B (p. 1924). These data clearly show that in measurement, error in the correction for imperfect adiabaticity is wholly negligible.

Measurement of Heats of Solution. Accessory Data.

The first measurements carried out with the apparatus and according to the procedures described above were a series of determinations of the heat of solution of sucrose in water; and of anhydrous α-glucose in water, and in hydrochloric acid of the concentration used in the subsequent determinations of inversion heat. The collected results of these experiments served to test the adequacy of the means adopted for insuring quick and a complete solution, to determine the form of the solution curve in the inversion measurements, and to provide data for a comparison of solution heats in water and in acid.

The results of the first dependable measurements made with sucrose are summarized in Table II, A. The corresponding curves appear in Fig. 3 and the data derived from them in Table IV, A. Although these measurements were widely scattered in time, and were carried out under a variety of conditions and by varying procedure without the use of the ice-water buret, and with bulbs of various design only gently flattened, the calorimetric data they yield are fairly satisfactory. The results of the second series of like determinations, in which the ice-water buret was used, and the bulbs put under strain, are, however, more precise. These appear in Table II, B. The corresponding curves are plotted with those of the first series in Fig. 3, and the data derived from them are in Table IV, B. A comparison of corresponding values in the

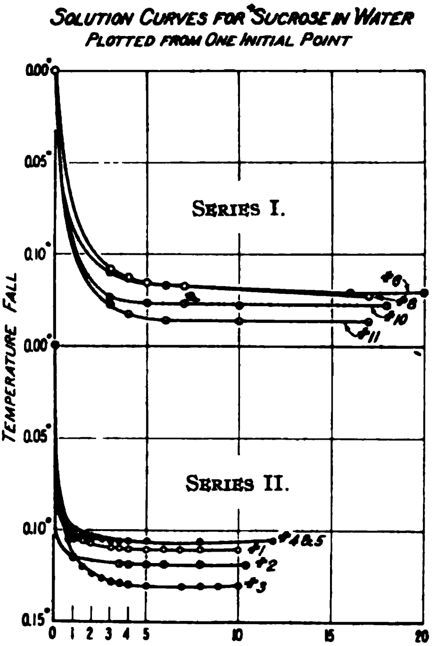

Fig. 3.—Sucrose solution curves.

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[1] The use of the planimeter for integrating curves of this character will have no advantage over the above procedure, a possible gain in time being more than compensated by a loss in precision.

2 series shows clearly the greater precision attained by the use of the ice-water buret, and the greater speed of solution made possible by the use of bulbs under strain.

Of greater present interest are the curves of solution. In Fig. 3, the sucrose curves of the first series have all been plotted through determined points without any smoothing out, and extrapolated to the origin in every case on the assumption that they are exponential; the constant for each curve $\left(p = \frac{1}{t} \log \frac{T_2 - T_1}{T - T_1}\right)$ having been determined from the entire temperature range $(T_0 - T_1)$ and the temperature at the first determined point, marked on the curve by an open circle. The exponential curve thus defined has been plotted across the time interval covered by the determined points and has been found to be very close to the experimental curve in every case, and actually coincident with it in the case of Curve 11. On account of the relatively large error in fixing the times at which solution began, and of the practical impossibility of making accurate readings during the initial period of rapid fall, the plotted initial slopes of these curves are certainly more widely varying, and these plotted curvatures, consequently, less closely exponential than the actual. It appears, therefore, from the general approach to coincidence between the actual and the derived curves that the process of solution is in this case very closely exponential in the sense $pt = \log \frac{T_2 - T_1}{T - T_1}$; and the data (Table IV, A) show that p is the same for all curves within a narrow margin of fluctuation.

In the second series of sucrose measurements, the automatic control of bath temperature by the ice-water buret made it possible to trace the actual curves of temperature fall to points much nearer the origin; so that from them the change in curvature could be determined directly. These curves were found to be of such character that if formulated as $p = \frac{1}{t} \log \frac{T_2 - T_1}{T - T_1}$, p was not a constant for any curve, but decreased with increase in t between similar limits in all cases. This variability is to be attributed for the most part to the greater speed of solution brought about by the use of bulbs under strain. In the first minute of fall, reading error and thermometric lag were on this account relatively large, and the dissolving process, in a mixture still inhomogeneous, was most rapid in the immediate vicinity of the thermometer bulb. All these conditions contributed to make p variable. After two minutes of fall, however, p became nearly constant and practically the same for all curves measured, as in the first series of measurements. Toward the end, p diminished slightly; but this effect was interpreted as due probably to the slow solu-

TABLE II.

Solution of Sucrose in Water: Calorimetric Data.

Expt. No.	Observed temperatures. Initial. (Thermometrically corrected.) T_1.	Minimal.	Selected final. T_2.	Observed temperature fall. T_1-T_2.	Calorimetric corrections: Corr. for stirring heat.	Corr. for imperfect adiabaticity.	Corrected temperature fall.	Weight of sucrose (grams *in vacuo*).	Temperature fall per gram sucrose.	Heat capacity of system (gram calorie units).	Heat of solution of sucrose in water (gm. cal. per gm.).
A—Series I.											
6	20.033	19.912	19.914	0.119	+0.004	+0.0001	0.123	41.435	0.00297	1152	3.42
8	20.011	19.8865	19.888	0.123	+0.006	+0.0002	0.129	42.531	0.00303	1150	3.49
10	20.149	20.023	20.024	0.125	+0.002	—0.0002	0.127	43.337	0.00293	1150	3.37
11	20.016	19.880	19.880	0.136	—0.001	+0.002	0.137	44.334	0.00309	1152	3.56
										Average,	3.46
							Extreme variation from the average,				2.9%
							Corresponding temperature error,				±0.004°
B—Series II.											
1	19.923	19.8165	19.818	0.105	+0.0049	+0.0006	0.1105	36.699	0.00301	1149	3.46
2	19.985	19.8685	19.8715	0.1135	+0.0041	+0.0002	0.1178	39.180	0.00301	1150	3.46
3	20.071	19.9425	19.945	0.126	+0.0074	+0.0005	0.1339	45.250	0.00296	1152	3.41
4	19.9855	19.882	19.883	0.1025	+0.0060	+0.0002	0.1087	36.565	0.00297	1149	3.41
5	20.0055	19.901	19.904	0.1015	+0.0045	+0.0002	0.1062	35.742	0.00297	1149	3.41
										Average,	3.43
							Extreme variation from the average,				0.87%
							Corresponding temperature error,				±0.001°

TABLE III.

Solution of Anhydrous α-Glucose in Water and in 1.64 Molar Hydrochloric Acid. Calorimetric Data.

	Observed temperatures.				Calorimetric corrections.						
Expt. No.	Initial. (Thermometrically corrected.) T_1	Minimal	Selected final. T_2.	Observed temperature fall. T_1-T_2	Corr. for stirring heat.	Corr. for imperfect adiabaticity.	Corrected temperature fall.	Weight of glucose (gms. *in vacuo*).	Temperature fall per gram glucose.	Heat capacity of the system (gm. cal. units).	Heat of solution (gm. cal. per gm.).
A—Solution in Water.											
1	19.599	19.217	19.226	0.373	+0.013	+0.0003	0.386	31.999	0.01206	1148	13.84
2	20.260	19.898	19.902	0.358	+0.010	—0.0007	0.368	29.854	0.01229	1147	14.11
3	20.120	19.760	19.763	0.357	+0.003	—0.0008	0.359	29.549	0.01215	1147	13.94
										Average,	13.96
								Extreme variation from the average,			1.1%
								Corresponding temperature error,			±0.004°
B—Solution in Acid.											
1	20.252	19.856	19.872	0.380	+0.023	—0.0023	0.401	29.347	0.01366	1005	13.72
3	20.078	19.682	19.687	0.391	+0.008	+0.0014	0.400	28.704	0.0139	1004	14.00
										Average,	13.86
								Extreme variation from the average,			1.0%
								Corresponding temperature error,			±0.004°

TABLE IV.

Data on Kinetics.

Solution of Sucrose in Water, and of Anhydrous α-Glucose in Water and in 1.6 Molar Hydrochloric Acid.

	Expt. No.	Constant of solution p. (in $\log_{10}$).	Time elapsed when solution was		Percentage dissolved		Mean constant of solution.	
			90% complete. (Minutes.)	99% complete.	in 5 minutes.	in 10 minutes.	(in $\log_{10}$). p_{10}.	(in $\log_e$). p_e.
A—Sucrose in water..................	6	0.17	2.9	13.0	95.4	97.5	..	..
Series I—Bulbs gently flattened........	8	0.16	3.1	14.0	94.7	97.0	..	..
	10	0.24	2.2	7.0	98.4	100	..	..
	11	0.19	2.7	5.0	98.9	100	0.19	0.44
B—Sucrose in water..................	1	0.65	0.7	2.5	100	...	..	..
Series II—Bulbs under strain...........	2	(0.7)	0.4[a]	1.0[a]	100	...	..	..
	3	0.56	1.2	6.0[b]	97.8[b]	100	..	..
	4	0.54	0.7	6.0[b]	98.2[b]	100	..	..
	5	(0.7)	0.5[a]	1.5[a]	100	...	0.6	1.4
C—Glucose in water..................	1	(0.4)	0.8	2.5	100	...	..	..
Bulbs under strain....................	2	(0.5)	1.2	3.5	99.0	100	..	..
	3	(0.6)	1.3	4.0	99.7	100	0.5	1.2
D—Glucose in water..................	1	(0.6)	1.1	2.6	100	...	..	..
Bulbs under strain....................	3	(0.4)	0.8	2.7	100	...	0.5	1.2

Values in parentheses are taken from extrapolated curves.

[a] Bulbs exploded.

[b] Sugar was trapped.

tion of trapped sugar as in Determinations 6 and 8 of the first series. The curves of the second series are doubtless typical; the irregularities they exhibit being common to all such curves, but relatively insignificant excepting when speed of solution is very rapid. The constant p is thus subject to greater variability the larger its value is. Since in the determination of concurrent effect in inversion determinations and the like, it is the ordinate $1/p$ which enters into the calculations,[1] the influence of such variability upon precision of measurement remains small, therefore; and as experiment shows, actually decreases with increase in the speed of solution, so that the maximum speed of solution remains the most advantageous speed, practically as well as theoretically. It is also clear from the theory already developed[2] that the error introduced into a measurement by uncertainty in the value of $1/p$ increases with the slope of the curve of inversion. It is, therefore, disadvantageous to increase the initial speed of reaction beyond a fairly well defined limit of the value k/p, where k is the constant of inversion. In the present measurements this limiting ratio was found to be about $\frac{0.0115}{0.44} = 0.026$. With this ratio, the error introduced by uncertainty in the value of p was $\pm 0.001°$; in the determinations actually carried out, with bulbs under strain in 1.64 molar hydrochloric acid to final concentration of 3.5 to 4% solution, the ratio was $\frac{0.0115}{1.4} = 0.008$, and the error negligible. The re-

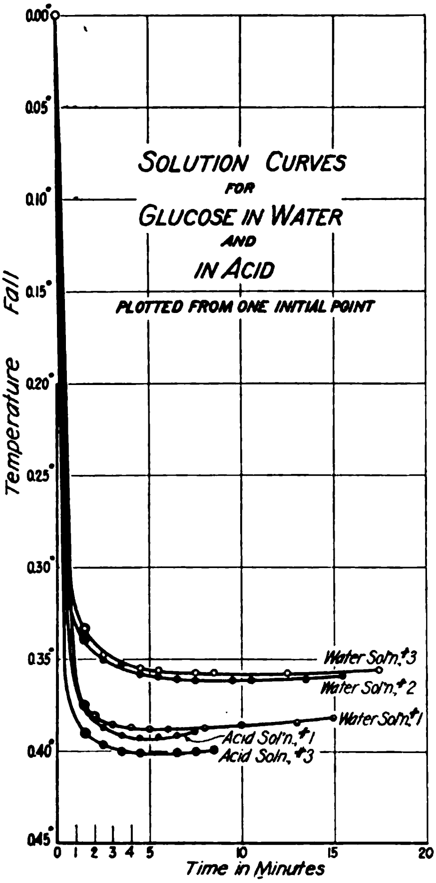

Fig. 4.—Glucose solution curves.

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[1] See THIS JOURNAL, 42, 1301ff (1920).

[2] For the purpose in view, invert sugar would have been the better substance to use. The measurements with α-glucose, however, were of greater interest; and when computed for different time intervals showed that within experimental error, varying speeds of mutarotation did not affect the form of the curve of solution heat.

sults of this series appear in Table II, B; the corresponding curves in Fig. 3, and the data derived from them in Table IV, B.

Three measurements were made of the heat of solution of anhydrous α-glucose in water, and 2 of its heat of solution in 1.6 molar acid. The results of this series are summarized in Table III; the corresponding curves appear in Fig. 4, and the data derived from these in Table IV, C and D. The curves of these measurements show that within the experimental error, no more significant in this case than in that of the sucrose measurements, the constant of solution is the same for water and acid. It follows, by analogy, that the value of p determined for the solution of sucrose in water by an established uniform procedure may be taken without significant error as equal to that for its solution in 1.6 molar acid. Thus the value of p for the inversion measurements was satisfactorily determined. That it may be still more precisely measured without altering in any way the mechanism for effecting solution is evident; but this would probably necessitate the employment of chronographic observations, which would be justifiable only if similar care in observation were justifiable in the inversion measurements; and such would hardly be the case so long as mercury instruments with considerable lag were employed.

For the temperature and acid concentration decided upon as best for the heat of inversion measurements, namely 20° and 1.6 molar concentration, the isothermal constant for the inversion of sucrose by acid $\left(k = \frac{1}{t} \log \frac{a}{a - x}\right)$ had never, apparently, been determined. It was necessary that the exact value of this constant and its isothermal variability under the adopted conditions of measurement be known. The determination of this constant was made at a thermostatic temperature of 20° ± 0.02°, according to established procedure and very carefully, by Dr. W. C. Vosburgh, to whom the writer desires to express in this place his great obligation. The data provided by these measurements appear in Table V, A and B. It is clear from this record that sucrose, while being inverted at this temperature by 1.6 molar hydrochloric acid, is not affected by any measureable side reaction; that under these conditions the inversion proceeds in the theoretical manner of monomolecular reaction within observable error; and that the constant of inversion is invariable for a range of sucrose concentration greater than that of the calorimetric work. In another set of measurements Dr. Vosburgh showed that under the same conditions the acid was without perceptible effect upon the products of hydrolysis within a full day after inversion began.[1]

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[1] Compare the experiments of M. M. Harrison (THIS JOURNAL, 36, 597 (1914)), which, as reported, are inconclusive with respect to the action of acids of greater concentration than 0.7 molar.

TABLE V.

Isothermal Inversion of Sucrose by 1.6 Molar Hydrochloric Acid at 20.0°.

	Time (in minutes). t.	Observed angular rotation (in degrees).	Per cent. inverted. x.	Isothermal constant $k_{10} = \frac{1}{t}\log_{10}\left(\frac{1}{1-x}\right)$.
A: Sucrose concentration = 3 g. in 100 g. of the mixture...............	0	(3.46)*	0	...
	1.5	3.34	...	...
	6.2	3.12	7.3	0.00531
	15.1	2.69	16.6	0.00522
	35.1	1.84	35.0	0.00533
	75.0	0.70	59.6	0.00525
	135.0	—0.30	81.2	0.00538
	∞	—1.17	100	...
				Average, 0.00530
B: Sucrose concentration = 5 g. in 100 g. of the mixture...............	0	(5.75)*	0	...
	1.3	5.57	...	...
	6.0	5.21	7.0	0.00525
	11.6	4.73	13.2	0.00532
	21.4	3.99	22.9	0.00528
	39.4	2.81	38.2	0.00530
	69.5	1.36	57.0	0.00528
	127.4	—0.33	79.0	0.00532
	∞	—1.95	100	...
				Average, 0.00529
C: Sucrose concentration = 5 g. in 100 g. of the mixture...............	0	(6.66)*	(0)	...
	1.6	6.29	4.1	...
	13.3	5.15	16.9	(0.00605)
	30.0	3.76	32.4	0.00567
	60.0	1.80	54.4	0.00568
	120.0	—0.42	79.2	0.00571
	180.0	—1.45	90.6	0.00570
	420	—2.24	99.6	...
	510	—2.28	(100.0)	...
	600	—2.28	...	...
	690	—2.26	...	...
	1410	—2.28	...	...
				Average, 0.00569

$$\text{From A and B: } \left.\begin{aligned} k_{10} &= 0.0053 \\ k_e &= 0.0122 \end{aligned}\right\} \text{ for both concentrations.}$$

* Extrapolated graphically.

A slight coloration appeared upon neutralization of the samples after 23.5 hours; but no change of rotation was then observable (see Table VI, C).[1]

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[1] The higher value of k in the last table is due to a slightly greater concentration of acid. The greater angular rotations are due to the fact that in the first measurements sodium light was used, and in the last, mercury vapor light.

Finally, from these data, the time necessary for measurably complete inversion under the given conditions is discovered to be closely 9 hours. From the data of Nelson and Beegle[1] it is known that long before this time has elapsed the mutarotation of the products of inversion will have been complete, so that the heat of inversion for the full period will include heat of mutarotation.

Measurement of the Heat Inversion.

Of the heat of inversion of sucrose by acid 2 series of determinations were made. The measurements of the first series, though consistent with those of the second, were relatively inexact, and need not be considered here. Those of the second series, more precise, were conducted in the following invariable manner. The calorimetric apparatus having been adjusted and tested, the closet thermostat was heated to 20.0°, and maintained at this temperature for an hour or so, while other preparation was in progress, all necessary precautions being taken against the possibility of excessive partial lag in coming to equilibrium. The bulb containing the sucrose sample, the partial weights of which were already known, having been tested for fracture by immersion in distilled water and dried, was adjusted to proper position in the calorimeter basket, and the whole inner calorimetric mechanism assembled, suspended from the jacket cover. The desired volume of constant boiling acid was then approximately measured out into a graduated cylinder, transferred into the clean calorimeter vessel, and balanced with its container against a fixed tare by pipetting to ±0.01 g., diluted with purest water while balanced against a second tare to within a gram or so of the desired total weight, and finally adjusted by pipetting in such a way as to avoid the removal of more than 2 or 3 drops of liquid to within about ±0.05 g. of equilibrium. The filled vessel, covered with a flat perforated glass plate, was then warmed to a temperature slightly higher than that desired on an electric stove—its temperature being taken by a thermometer previously wetted by acid of approximately the calorimeter acid concentration—readjusted without removal of liquid to within ±0.02 g. of equilibrium, and placed inside the calorimeter jacket. After the insulation had been electrically tested, the whole calorimetric apparatus was assembled and nicely adjusted with the basket immersed, the stirring begun, and the bath brought gradually to exact thermal equilibrium with the calorimeter. The dil. sulfuric acid drip was then adjusted so as to maintain this condition as closely as possible; and thereafter for 30 minutes or more, while the initial stirring correction was being taken and the system examined for possible irregularity of behavior, the bath was regulated in the manner already described.[2] When the stirring correc-

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[1] THIS JOURNAL, 41, 574 (1919).

[2] Page 1921.

tion was found to be constant for a sufficient time, the mirror protecting the calorimeter thermometer was removed, and then in quick succession the ice-water buret was opened, the bulb was broken, its fragments crushed and the contents of the basket rapidly stirred for 15 seconds by hand the inner stirrer, then, was attached to the mechanical stirring arrangement, the mirror replaced, and the fall of calorimetric temperature closely observed by half-minute readings. The whole time occupied by this manipulation was usually much less than a minute. Owing to the rigidity of the construction it was easily carried out in a routine manner, without causing any displacements, such as would involve scraping by the calorimeter stirrer, or any other irregularity of behavior. During the manipulation the temperature of the partially insulated calorimetric thermometer stem rose slightly; but it was shown by blank tests that a degree of warming greater than this did not affect its registration. The previous measurements on the heat of solution of sucrose in water had shown that in its final form the breaking apparatus was so effective that excepting in rare instances no significant amount of sugar was protected from solution by the accidental disposition of bulb fragments. Whenever this had occurred, or whenever any other accident had caused an irregular speed of solution, the thermometer always showed some recognizable indication of the fact. The form of the solution curve plotted at the conclusion of each determination was, therefore, taken as a criterion in judging the dependability of the measurement in this particular. It never showed significant irregularity. At the end of the temperature fall, the thermometer rose after very slight delay. This rise was followed for a few minutes by the addition of conc. sulfuric acid from the accessory buret, to the bath; after it had become uniform, the dilute acid drip was readjusted, and thereafter the bath was controlled as in the preperiod. Continuous stirring was maintained for 30 minutes or more, as a precautionary measure, although in all probability a shorter period would have been quite safe. Thereafter the system was stirred intermittently by a counted number of strokes in groups, immediately following and preceding the thermometric readings, which were taken in pairs. These pairs of readings were always identical within 0.0005°, and showed clearly that the intermittent stirring, although it was so slight as to cause a total rise of only 0.002° or 0.003° in the 6 or more hours during which it was applied, was quite sufficient to maintain a thermal homogeneity measurably constant.

Since for the purpose of estimating the heat of inversion alone by the process of extrapolation discussed in the first section of this paper,[1] it was necessary that the form of the reaction curve be known within the narrowest possible margin of observation error, the thermometric readings

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[1] THIS JOURNAL, 42, 1297ff (1920).

were taken at frequent intervals during the whole course of the change; in the preperiod at intervals of 5 minutes, in the period of rapid change at intervals of one-half and of one minute, and in the period of inversion at intervals of from 2 to 10 minutes. The bath temperatures were simultaneously read, and in the period of slower change more often, so as to ensure as nearly as possible a regularly periodic variation. The temperature change was never rapid enough, considering the thermometric error, to necessitate chronographic observations; the time for each thermometric reading was, therefore, taken with an ordinary but accurately regulated watch. The rate of stirring was taken at intervals of 30 minutes throughout the entire period of measurement, with an accuracy of 0.05%; and barometric observations were made at the beginning and at the end of each determination. The humidity, during the whole series of measurements, was found to be high and not significantly variable, by psychrometric measurements, interpreted by the results of previous observation upon the effects of widely changing humidity at higher temperatures upon the rates of thermal leakage between calorimeter and bath under conditions otherwise fixed. Finally, the illumination was the same at all times.

It was thought unnecessary and probably inadvisable to follow each reaction to full completion, and thus to magnify the possible error from thermal leakage for the sake of actually observing the final few thousandths of a degree of temperature rise. The reactions were, therefore, observed during times which ensured a close approach to completion, and the final temperature computed, by successive approximation from the known minimum temperature as a starting point, by the application of isothermal kinetic equations involving each the mean constant of inversion determined by the corrected curve of observed temperature change. This procedure was legitimate, since the heat of reaction, which was measurably the same for the isothermal and the adiabatic conditions,[1] alone was involved, and since for the minute range extrapolated the error of approximation in the inversion constant used was insignificant. It was determined by calculation that the largest possible error introduced in this process was quite negligible.

At the end of each such measurement the stirring was stopped, but the mechanism of the constant-temperature closet left in operation; and the calorimetric system was allowed to rest for 2 hours or more under the same external conditions. After this interval it was definitely known that the reaction of inversion would have come to an end, and that no consecutive reaction would have occurred (p.)1933. Thereupon, the system was again brought to precise apparent equilibrium, and this condition was maintained with very slight intermittent stirring for an hour or more.

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[1] THIS JOURNAL, 42, 1308 (1920).

The probable effect of radiation upon thermometric registration already described (pp. 1920–1) was thus detected. The calorimeter again under illumination was then continuously stirred for 40 minutes at an observed rate, while very precise adjustment of the bath was still maintained, and the final rate of temperature change due to this effect determined. This rate was always measurably constant, and excepting in the last determination, the same for all. Each complete measurement required from 12 to 14 hours of attention and about 7 + 3 hours of continuous observation.

After the completion of a measurement, the wholly corrected temperature readings were plotted against time observations on coördinate paper sufficiently large to permit the distinction of 0.0005° differences. The correction for imperfect adiabaticity was then determined and the data examined to discover whether or not irregularity in the fluctuation of bath temperature would have effected the form of the curve of observed temperatures (the Experimental Curve in Fig. 5). No such effect was ever discovered. Since it was already known[1] that changes in heat capacity as the reaction progressed would not affect the temperature readings beyond the thermometric error, it remained only to apply a correction for heat of stirring to obtain the true temperature curve of the change. This was done in the following way. The final stirring correction was taken as applicable to the whole period during which it was applied, from the end back to the time at which minimum temperature was reached; on the basis of the assumptions, first, that during this period the concentration was sufficiently constant, and, second, that the viscosities of the sucrose solution and that of the derived glucose solution were nearly enough the same. Accessory measurements of stirring heat in aqueous solutions of sucrose and glucose of corresponding but greater concentration showed that this last assumption, which alone needed confirmation, was justifiable. Significant variations in the stirring speed were corrected for upon the basis of the assumption that the rate change of temperature due to stirring was proportional to the square of the number of strokes the reciprocating stirrer made in unit time. This approximation, in view of the very slight variation of the observed stirring rate, was more than sufficiently close. Correction of this sort was always slight; it hardly affected the form of the derived curve, and introduced a correction never greater than 0.001° in the estimated total heat of stirring. The temperature change due to stirring, thus corrected, was calculated for each 10-minute interval of the reaction period, was graphically subtracted from the corresponding observed temperatures of the experimental curve, and through the new temperatures thus fixed a smooth curve of reaction was drawn. (See Fig. 5.) In every case this curve was very precisely defined by the determined points. In the process of

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[1] See THIS JOURNAL, 42, 1299.

"smoothing out" no such point fell more than 0.002° away from the probably correct position, and very few as far out as this. The magnitude of the combined effects of reading, thermometric correction and accidental experimental error on the form of the reaction curve was thus roughly indicated. The temperature toward the end of each measurement was always very nearly constant, although the actual reaction at this time was more than 2 hours short of measurable completion.

From this curve for any reaction it was possible to calculate the empirical constant of inversion for any small temperature range, by using the isothermal equation, which over short segments was strictly applicable. The curves for all determinations were examined in this way; the constant being calculated for 10-minute intervals measured from ordinates 5 minutes apart over 2 hours of the plotted range. The values thus obtained, which at 20.0° were measurably identical with the isothermal values otherwise determined by Dr. Vosburgh (Table V, A) showed with remarkable clearness a continuous increase in the value of the constant with rising temperature. The values shown in Table VI, taken from the curve apparently least affected by experimental error, show the manner and magnitude of this variation, the interpretation of which will be discussed later. At present it is relevant

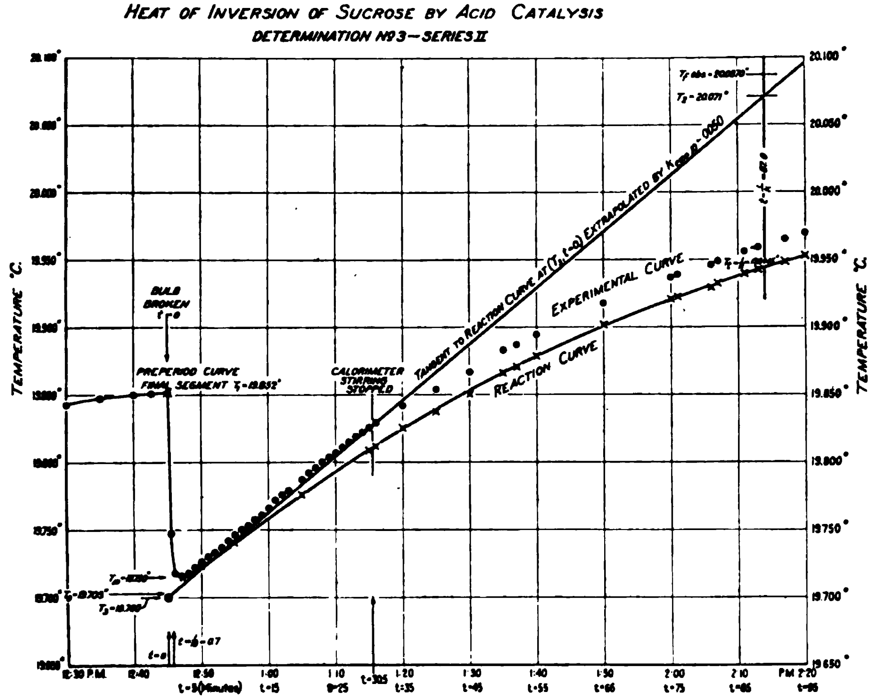

Fig. 5.—Curves of inversion.

TABLE VI.

A—Adiabatic Velocity Coefficients (from the Curve of Determination No. 3).

1. Time interval (t = reaction time elapsed, in minutes).	2. Corresponding observed temperature interval (in degrees).	3. k (in $\log_{10}$).	4. Observed differences between successive values of k.	5. Mean increments in k for 10-minute intervals. I. Taken from 25 m. intervals.	6. II. Taken from 30 m. intervals.	7. Mean increments in k per degree C. I. Taken from 30 m intervals.	8. II. Taken from 40 m. intervals.	9. Temperature coefficient of k Increment per degree C. Mean values.	10. Observed error in k caused by ±0.001° error in temperature observation.
t = 15 to t = 25	0.035	0.0049	±0.0000						±0.00014
20 to 30	0.033	0.0049	+0.0002	+0.00012		+0.0023		+0.0027	
25 to 35	0.032	0.0051	+0.0001		+0.00013		+0.0031		
30 to 40	0.031	0.0052	+0.0002					+0.0029	
35 to 45	0.030	0.0054	+0.0001	+0.00012		+0.0026			±0.00019
40 to 50	0.029	0.0055	±0.0000					+0.0024	
45 to 55	0.027	0.0055	+0.0001		+0.00010		+0.0022		
50 to 60	0.026	0.0056	+0.0001	+0.00008		+0.0020		+0.0021	
55 to 65	0.025	0.0057	±0.0000						±0.00025
60 to 70	0.023	0.0057	—0.0002						
65 to 75	0.021	0.0055	+0.0001	Calculations hereafter invalidated by experimental error					
70 to 80	0.020	0.0056	+0.0004	(see Column 10.)					
75 to 85	0.020	0.0060	—0.0006						±0.00032
80 to 90	0.017	0.0054	—0.0003						
85 to 95	0.015	0.0051	+0.0007						
90 to 100	0.016	0.0058	±0.0000						
95 to 105	0.015	0.0058	±0.0000						±0.00038
100 to 110	0.014	0.0058	—0.0001						
105 to 115	0.013	0.0057	—0.0001						
110 to 120	0.012	0.0056							

B—Temperature Coefficients of k (Calculated as Above).

Experiment number.	Mean increment in k per degree during first 70 minutes.
2	0.0021
3	0.0025
4	0.0026

to note only that the succession of differences between the constants of adjacent segments could be precisely extrapolated back, from times at which the system was surely homogeneous to the initial time, so that the curve itself could be similarly extended and completed. This was done in every case, and the temperature (T_3 in Fig. 5) at which the extrapolated curve cut the ordinate of initial time (t = 0) thus determined. It was then possible by a variety of graphical constructions described in the first section of this paper[1] to determine the temperature (T_0 in Fig. 5) at which the inversion would have begun had solution been instantaneous, and thus to separate the 2 thermal effects of solution and reaction. Among these, the best method was that called the Approximate Tangent Construction.[2] This in practise was found to be as exact as the theoretically preferable Exact Tangent Construction,[3] on account of its greater simplicity and precision. The two yielded in test constructions the same initial temperature. In the measurements of this, the second series, the Approximate Curve Construction[4] also gave identical results, as a consequence of the high speed of solution brought about by the use of bulbs under strain. The Minimum Construction,[5] however, yielded values which varied from the preceding by ±0.002°, as had been anticipated. In drawing the tangent of the accepted construction, advantage was always taken of the fact that, assuming the curve to be of the form $kt = \log \frac{T_2 - T_0}{T_2 - T}$, the tangent would intersect the abscissa of the final temperature (T_2) at $t = 1/k_e$, k_e being the isothermal inversion constant in Naperian logarithms. To eliminate error in the application of this relation to the adiabatic curve, the value k_e was taken as the mean of the corresponding initial and final empirical constants. That this procedure was sufficiently exact is apparent from an inspection of Table VI, which shows that over the interval $t = 0$ to $t = 1/k_e$ the determined temperature coefficient of k was constant within the probable error of measurement.

In this manner 4 consecutive determinations were carried out, the results of which are summarized in Table VII. This table illustrates in detail the preceding observations. The heat of inversion of sucrose is determined to be 10.4 gram calories per gram; and the heat of solution of sucrose in 1.64 molar hydrochloric acid, to 3.6% concentration of sucrose, 4.35 gram calories per gram.[6] The discrepancies between the

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[1] This Journal, 42, 1295 (1920).

[2] *Ibid.*, p. 1304.

[3] *Ibid.*, p. 1303.

[4] *Ibid.*, p. 1305.

[5] *Ibid.*, p. 1307.

[6] Among these measurements the first alone was affected by known accidental error. In this case it was found in the routine analysis of calorimeter liquid made after measure-

several results show a variation from the mean which corresponds to a thermometric variation of about ±0.003°, for both heats, and thus confirms the probability that the correction for imperfect adiabaticity involves slight variable error. It is noticeable that the heat of solution of sucrose in acid is distinctly different from its heat of solution in water.

Remarks on Error.

The following results were almost surely unaffected by uncertainty due to concomitant reactions or to change in concentration during measurement. The reacting materials were all of the purity demanded by the most exact procedures of quantitative analysis, and were neither visibly nor measurably affected by storage or manipulation. The various minute precautions taken to ensure this very necessary prerequisite of exact measurement will be discussed in a later communication, but may be omitted here; since the results submitted, though fairly precise, are illustrative rather than final.

In the measurements, the time-reading error was never greater than 10 seconds, and in the periods of rapid change no more than 3 seconds, as was shown by check readings. Error in the record of time intervals and of total time was shown, by standardization of the watch used, to be negligible. It is thus certain that no error in time measurement affected the final results, since thermometric readings taken during the period of rapid change were not used in extrapolation.

The thermometric reading error was ±0.0005°. The calibration error, well fixed not only by the manner of thermometric standardization but by the results obtained in evaluating the temperature coefficient of the constant of inversion (Compare Columns 3 and 10 in Table VI), was probably not greater than ±0.001°. Thermometric error caused by change in external pressure was known to be negligible; that due to possible change in ice point during a determination was assumed to be so, since the thermometers were never subjected to temperature changes exceeding 10° during a whole year. The correction for the effect of change in environmental temperature upon the exposed thermometer stems is negligible so far as the influence of conduction is concerned; but the effect of radiation from the sources of illumination—the possible

ment that copper had been dissolved both from the jacket cover by splashing and from the calorimeter stirrer through an abrasion of the gold plate. The result of this determination is known, therefore, to be too high, but the manner of the accident has prevented the application of a dependable correction. Because the data it provides have a certain value, the determination has been tabulated; but its final results are excluded from the averages.

The accident referred to was caused by the sudden explosion of the bulb, which having been put under too great a strain, was blown into minute fragments and in part pulverized. In the later determinations, the inner surface of the jacket, as well as the abraded area, was protected by paraffin, but no such explosion again occurred.

TABLE VII.
Heat of Inversion of Sucrose by Acid Catalysis.
Summary of Data.

	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.	13.
	Observed temperatures.						Calorimetric corrections (in degrees).				Kinetic data.		
		Calorimetric.										Empirical constant of inversion. k (in $\log_e$).	
Expt. No.	Environmental. Mean stem temperatures.	Initial, T_1.	Minimal, T_m.	Final, T_f.	Total reaction time observed (in minutes).	Observed final rate change of temperature due to stirring (degrees per min.).	Correction for incomplete reaction.	Correction for stirring heat.	Correction for incomplete adiabaticity.	Corrected final temperature, T_2.	Empirical constant of solution $_sp$ (in $\log_e$).	Initial.	Final.
1	20.0	19.9450	19.802	20.1855	334	+0.00055	+0.0045	—0.0202	+0.0008	20.1705	1.4	0.0120	0.0128
2	20.0	19.8520	19.716	20.0870	375	+0.00055	+0.0030	—0.0186	—0.0011	20.0705	1.4	0.0115	0.0134
3	20.1	19.8325	19.694	20.0825	398	+0.00055	+0.0020	—0.0272	+0.0005	20.0580	1.4	0.0115	0.0131
4	20.1	19.7805	19.641	20.0400	412	+0.00060	+0.0020	—0.0419	—0.0011	19.9990	1.4	0.0111	0.0124

	14.	15.	16	7	18	19.	20.	21.	22.	23.	24.
	Derived temperatures.										
Expt. No.	T_3.	T_0.	Observed temperatures at $t = 1/k$.	Value of $\frac{T - T_3}{T_2 - T_3}$ at $t = 1/k$.	Temperature rise caused by inversion, $T_2 - T_0$.	Weight of sucrose. (Grams *in vacuo*.)	Weight of acid. (Grams *in vacuo*.)	Heat capacity of system (gram calorie units).	Heat of inversion of sucrose (gram calories per gram).	Temperature fall caused by solution, $T_1 - T_0$.	Heat of solution of sucrose in acid (gram calories per gram).
1	19.7855	19.785	20.029	(0.631)	0.382	35.371	1095.2	1006.5	(10.87)	0.157	(4.45)
2	19.700	19.703	19.941	0.649	0.368	35.456	1095.2	1006.4	10.42	0.149	4.24
3	19.667	19.670	19.922	0.657	0.388	38.116	1095.2	1007.3	10.25	0.163	4.32
4	19.635	19.638	19.866	0.635	0.361	39.635	1255.4	1147.0	10.45	0.143	4.14
			Averages,		...	..			10.37	...	4.23
						Extreme variation from the average,			1.2%	...	2.1%
						Corresponding temperature error,			±0.004°	...	±0.003°

"greenhouse effect" already commented upon—is, unless all signs fail, far from insignificant. (See p. 1920.) Since throughout the series the illumination was practically invariable, however, this effect will have introduced a constant error, experimentally measurable. Subject to a correction so determined, the accumulated thermometric errors amount to no more than ±0.002° or 0.5%.

Error in the correction for thermal leakage, insofar as this is caused by radiation, or by air conduction and convection, is negligible, unless the results of the accessory measurements described on p. 1923 are called in question, since the comparative registrations of the calorimetric and bath thermometers, which were twin instruments of equal lag, equally exposed (pp. 1918, 1919) were precisely known, and since the curves of bath temperature fluctuation were rather minutely defined and interpreted with negligible error of approximation. The possible continuous thermal interchange between calorimeter and environment by direct conduction through thermometer and stirrer rods during the 7 or 8 hours of measurement seems also to be very small (p. 1920) but demands further investigation.

The final rate change in temperature due to stirring was subject to an uncertainty not greater than ±0.00003° per minute; and its correction for variation in stirring speeds during measurement (p. 1936) was negligible, since rates of stirring were frequently observed and were known to vary no more than 2%, and regularly. The maximum error in the stirring correction (that of Determination No. 4, in which stirring was unnecessarily continued for 65 minutes) was, therefore, ±0.002°, or 0.5%.

The correction for incomplete reaction, the maximum value of which was +0.0045° (in Determination No. 2) is doubtless unaffected by error in every case (p. 1935).

By a fairly complete examination of the geometrical constructions used in separating the concurrent effects of solution and inversion—an examination based upon estimates of the possible errors involved in the values of *p* and *k*, and extended by observations of divergence between the results yielded by different constructions on the same curve, each affected by such error—it has been discovered that the error involved in the practical application of the accepted methods of extrapolation is never necessarily greater than ±0.002°, or 0.5%.

The sum of these several possible errors approximates ±0.006°, or ±1.5%. This value defines the probable extreme discrepancy due to known causes, which is likely to be shown by the results of such a series of measurements. The actual variability for this series is ±1.2%, which indicates that the real precision of measurement was only slightly affected, if at all, by unsuspected factors of uncertainty.

Form of the Reaction Curve.

This inference is confirmed by the form of the determined curves of reaction. These were not only very smooth (see page 1930, and Table VI, A) but they yielded a temperature coefficient of the constant of inversion for the first hour of reaction which was, within thermometric reading error, the same for all dependable measurements (Table VI, B). This result implies directly that the divergence of these empirical curves from the isothermal form is due either to natural cause or to constant error. Since the adiabatic and isothermal heats of reaction are sensibly the same,[1] the only adequate natural cause would seem to be the effect of rising temperature on the value of the inversion constant. To this effect, the Marcelin equation $\frac{d \log k}{dt} = \frac{E}{RT^2}$[2] closely applies, when for this reaction E is taken as 25,000 calories; as Lamble and Lewis have shown.[3] It yields for the absolute temperature and range in these determinations the measurably invariable approximate value $dk/dt = 0.0001$, while the mean of the empirical values tested in Table VI, B is $dk/dt = 0.00025$. The values of $\frac{T_{t=1/k_e} - T_3}{T_2 - T_3}$ in Table VII provide further evidence of the same import. These are more widely variable than the empirical temperature coefficients, since unlike the latter they record direct observations of particular temperatures, and not averages. Their mean is 0.648. The corresponding value for the isothermal curve is 0.632, and that of the adiabatic curves calculated as above, 0.641. The rough agreement thus shown between the empirical results and those of theoretical calculation for the adiabatic condition is close enough to suggest that the original divergence of the exponential curves of reaction from isothermal form may have been due to natural cause alone; for it cannot be assumed that the present measurements embody all of the errors involved in these comparisons. It appears more probable, however, that constant errors, the aggregate effects of which upon reaction speed are of comparable magnitude, affect the present determinations.[4,5] It is the primary pur-

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[1] *Loc. cit.*, THIS JOURNAL, 42, 1308 (1920).

[2] Marcelin, *Compt. rend.*, 158, 116 (1914).

[3] *J. Chem. Soc.*, 107, 233 (1915).

[4] It is believed that the small discrepancies here recorded will soon be more definitely interpreted, in the course of current investigation. This result is desirable for other than calorimetric reasons. If constant error in measurements like those described can be demonstrably eliminated or accurately corrected for, it will become possible to determine any desired variety of adiabatic velocity coefficient and with greater precision their continuous variability over small selected temperature ranges by direct observation of energy changes alone, and thus without dependence on any specific properties of the reacting material. The precision, such measurement if re-

pose of investigations now in progress to trace the causes of such possible residual error. A considerably greater precision of measurement is still possible without abandoning the facile and dependable mercury thermometer. Within a narrower margin of variation, therefore, the known constant errors can be measured. Of these, the effect of radiation on thermometric registration and that of thermal leakage by direct conduction are now being examined; while a check upon the whole procedure, which incidentally provides a means for testing directly the validity of the correction for imperfect adiabaticity and the error of extrapolation, will be provided by the results of a series of measurements now in progress on the heat of hydrolysis of sucrose by invertase.

In conclusion, the writer desires to express his keen sense of personal obligation to the President of Columbia University, and to former colleagues of the Columbia Departments of Physics and Chemistry, by whose generous interest and hospitality the immediate completion of an interrupted work was made possible.

Summary.

1. A procedure is described, whereby the heat of inversion of sucrose by hydrochloric acid,—an exothermal reaction which involves a partially concurrent and endothermal heat of mixture, and which under favorable conditions continues for 9 hours,—is measured with a precision largely determined by the characteristic errors of precise mercury thermometry.

2. The adiabatic method, which alone is applicable in such determination, is thus shown to be generally adequate for the precise calorimetric measurement not only of swift reactions but of any reaction which at ordinary temperature requires less than a day for its completion.

3. A way is thus indicated whereby chemical kinetic and total energy data may in general be directly correlated. The procedure itself illustrates such correlation.

4. Incidently, the procedure suggests a general and uniform method for the precise determination of adiabatic velocity coefficients, and thus of the temperature coefficients of velocity constants, by energy measurement alone.

5. Various modifications of calorimetric practise, necessary for the measurement of slow reaction heats, but generally applicable, are described.

6. Attention is called to a probable source of error in mercury thermometry, due to the effect of radiation on encased thermometer threads.

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sistance thermometers were used, would be at least comparable with that of optical, or other customary procedure.

[5] Incidentally, the fixing of the value $(T_{t=1/k_0} - T_3) + (T_2 - T_3)$ would make possible the determination of T_2, T_3 having been found by direct extrapolation, without carrying the measurement beyond the time $t = 1/k_0$.

7. The following data are submitted.

Heat of inversion of sucrose by hydrochloric acid at 20° = 10.4 ± 0.06 gram calories per gram.

Heat of solution of sucrose in water at 20° to ca. 4% sucrose concentration = 3.43 ± 0.02 gram calories per gram.

Heat of solution of sucrose in 1.64 molar hydrochloric acid, at 20° to ca. 4% sucrose = 4.23 ± 0.05 gram calories per gram.

Heat of solution, anhydrous α-glucose in water and in 1.64 molar hydrochloric acid, at 20° to ca. 4% glucose = 13.9 ± 0.1 gram calories per gram.

NEW YORK CITY.

[CONTRIBUTION FROM THE POLYTECHNIC INSTITUTE OF WARSAW.]

ATOMIC REFRACTION.

BY W. SWIENTOSLAWSKI.

Received March 17, 1920.

In 1911, F. Eisenlohr[1] published new calculations of the refractivities of carbon, hydrogen, and other atoms in organic compounds. These calculations do not differ from those used by J. W. Brühl, because both authors assumed that the molecular refractions of the organic compounds are equal to the sums of the refractions of the separate atoms.

$$M_D = \Sigma A_D.$$

According to this supposition, the computation of atomic refraction depends on the average value of the refraction of the CH_2 group and those of certain atoms. If, however, the individual atomic refractions show even small deviations, this method cannot be used.

In order to determine the limits of variations in the refractions caused by carbon and hydrogen atoms in the compounds which contain only the linkings C–C and C–H, I have used the following method of calculation.

1. If we denote by r_C, r_H, and r_{CH_2} the refractions for the D lines of carbon, hydrogen, and the CH_2 group, the molecular refraction, M_D, of the hydrocarbon C_nH_m can be expressed by the following equation,

$$M_D = nr_{CH_2} + (m - 2n)r_H + \Sigma\Delta r_C + \Sigma\Delta r_H, \qquad (1)$$

or

$$M_D = nr_{CH_2} + (m - 2n)r_H + \Sigma\Delta r,$$

where

$$\Sigma\Delta r = \Sigma\Delta r_C + \Sigma\Delta r_H.$$

Equation 1 cannot be solved when the increments $\Sigma\Delta r$ are not known; therefore, we can compute the quantities r_C and r_H only by reference to several chosen compounds, thus obtaining the average values of r_C and r_H on the supposition that $\Sigma\Delta r = 0$.

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[1] *Z. physik. Chem.*, 75, 605 (1911).

2. In some cases it is more advantageous to use the quantities r_{C-C} and r_{C-H}, corresponding to refractions of the atomic linkings C–C and C–H, especially when it is desirable to compare these quantities with the thermochemical data. It is clear that the quantities r_{C-C} and r_{C-H} can be computed when r_C and r_H are known, for we have

$$r_{C-C} = 0.5 r_C$$
$$r_{C-H} = r_H + 0.25 r_C.$$

I have selected as the basis of calculation the following compounds, *n*-pentane, 2-methyl-butane, *n*-hexane, *n*-octane, di-isobutyl, di-isoamyl, cyclopentane, and cyclohexane.

Table I contains the values of the molecular refractions M_D and the equations connecting r_{CH_2}, r_H, and $\Sigma \Delta r$. These equations were solved by the method of least squares.

TABLE I.

	Name.	Formula.	M_D.	Equation.
1	*n*-Pentane	C_5H_{12}	25.23	$5r_{CH_2} + 2r_H + \Sigma\Delta r = 25.23$
2	*iso*-Pentane	C_5H_{12}	25.25	$5r_{CH_2} + 2r_H + \Sigma\Delta r = 25.25$
3	*n*-Hexane	C_6H_{14}	29.84	$6r_{CH_2} + 2r_H + \Sigma\Delta r = 29.84$
4	*n*-Octane	C_8H_{18}	39.16	$8r_{CH_2} + 2r_H + \Sigma\Delta r = 39.16$
5	Di-*iso*butyl	C_8H_{18}	39.11	$8r_{CH_2} + 2r_H + \Sigma\Delta r = 39.11$
6	Di-*iso*amyl	$C_{10}H_{22}$	48.33	$10r_{CH_2} + 2r_H + \Sigma\Delta r = 48.33$
7	Cyclopentane	C_5H_{10}	23.12	$5r_{CH_2} + \Sigma\Delta r = 23.12$
8	Cyclohexane	C_6H_{12}	27.72	$6r_{CH_2} + \Sigma\Delta r = 27.72$

Upon the assumption that $\Sigma\Delta r = 0$, we obtain the average values of $r_C = 2.490$, $r_H = 1.066$, and $r_{CH_2} = 4.622$, for our 8 selected hydrocarbons.

Table II contains a comparison of the observed and calculated values of M_D.

TABLE II.

Name.	Formula.	M_D (obs.).	(calc.).	Δr.	Δ%.
n-Pentane	C_5H_{12}	25.23	25.24	−0.01	−0.04
iso-Pentane	C_5H_{12}	25.25	25.24	+0.01	+0.04
n-Hexane	C_6H_{14}	29.84	29.86	−0.02	−0.07
n-Octane	C_8H_{18}	39.16	39.11	+0.05	+0.13
Di-*iso*butyl	C_8H_{18}	39.11	39.11	0.00	0.00
Di-*iso*amyl	$C_{10}H_{22}$	48.33	48.35	−0.02	−0.04
Cyclopentane	C_5H_{10}	23.12	23.11	+0.01	+0.04
Cyclohexane	C_6H_{12}	27.72	27.73	−0.01	−0.04
					Δ% = ±0.07

The small differences between the observed and calculated values show that Δr is very small, and that, therefore, it is very probable that the atomic refractions remain constant in the 8 compounds, at any rate within ±0.07%.

Comparing the values of r_C, r_H, and r_{CH_2} thus obtained with those of F. Eisenlohr

	r_C.	r_H.	r_{CH_2}.
F. Eisenlohr....................	2.418	1.100	4.618
W. Swientoslawski...............	2.490	1.066	4.622
	Deviation % = +3.0%	Deviation % = —3.1%	Deviation % = +0.09%

we see that his value for r_{CH_2} is in sufficient agreement with mine; those for r_C and r_H differ widely ($\pm 3.0\%$).

In order to explain why Eisenlohr's calculations of molecular refractions show a sufficient agreement with the direct measurements, it should be observed that the value of M_D for numerous organic substances arises from two terms

$$M_D = nr_{CH_2} + \Sigma r_X.$$

The first term nr_{CH_2}, is very large, while the second one, corresponding to the refraction of other atoms or groups in the molecule is always small. Therefore, small errors in the determination of the values of r_C and r_H, etc., do not exert any marked influence on the calculated values of M_D. Yet the determination of the real values of r_C and r_H is of great importance for our science.

As regards our computation, we can only maintain that the values found for r_C and r_H correspond to the average values of atomic refractions in the cases of the 8 compounds cited. By using a larger number of equations, for example,

$$\left.\begin{aligned}
M_D &= nr_{CH_2} + 2r_H + \Sigma\,\Delta r \text{ for hydrocarbons } C_nH_{2n+2}.\\
M'_D &= nr_{CH_2} + \Sigma\,\Delta r \text{ for hydrocarbons } C_nH_{2n}.\\
M''_D &= nr_{CH_2} - 2r_H + \Sigma\,\Delta r \text{ for hydrocarbons } C_nH_{2n-2}.\\
M'''_D &= nr_{CH_2} - 4r_H + \Sigma\,\Delta r \text{ for hydrocarbons } C_nH_{2n-4}.
\end{aligned}\right\}\begin{array}{l}\text{containing}\\ \text{only the link-}\\ \text{ings C–C and}\\ \text{C–H;}\end{array}$$

and by introducing new hydrocarbons C_nH_{2n-2}, C_nH_{2n-4}, etc., it is probable that we might obtain slightly different values for r_C, r_H, and r_{CH_2}. Therefore, this problem cannot be considered definitely solved.

In order to show that the refraction of carbon and hydrogen depends on the constitution of the hydrocarbons, in Table III are given the observed values of M_D for several compounds and those calculated from the formula, $M_D = \Sigma r_C + \Sigma r_H$, where r_C and r_H are the average values of atomic refraction obtained from the 8 hydrocarbons cited. For this purpose the methyl derivatives of polymethylene hydrocarbons have been chosen.

It is interesting to observe that all the deviations vary between 0.00 and +0.94%, excluding one case (1,1-dimethyl-cyclohexane, where $\Delta =$ —0.05% according to Lange's value). In some cases the deviations are very remarkable; for example, in the case of methyl-cyclohexane, which has been investigated so carefully by Kishner and Eisenlohr, the considerable deviation of between +0.34% and +0.37% is observed.

TABLE III.

Name.	Formula.	M_D.	Author.	nr_{CH_2}.	Δr.	$\Delta\%$.
Methyl-cyclohexane	C_7H_{14}	32.47	Kishner	32.35	+0.12	+0.37
Methyl-cyclohexane	C_7H_{14}	32.46	Eisenlohr	32.35	+0.11	+0.34
1,1-Dimethyl-cyclohexane	C_8H_{16}	37.12	Perkin	36.98	+0.14	+0.38
1,1-Dimethyl-cyclohexane	C_8H_{16}	36.96	Lange	36.98	—0.02	—0.05
1,2-Dimethyl-cyclohexane	C_8H_{16}	37.02	Eykmann	36.98	+0.04	+0.11
1,3-Dimethyl-cyclohexane	C_8H_{16}	37.26	Eykmann	36.98	+0.28	+0.76
1,4-Dimethyl-cyclohexane	C_8H_{16}	37.28	Eykmann	36.98	+0.30	+0.81
Dihydro-laurolene	C_8H_{16}	37.12	Perkin	36.98	+0.14	+0.38
Dihydro-*iso*-laurolene	C_8H_{16}	36.99	Perkin	36.98	+0.01	+0.03
1,2,4-Trimethyl-cyclohexane	C_9H_{18}	41.66	Eykmann	41.60	+0.06	+0.14
1,2,4-Trimethyl-cyclohexane	C_9H_{18}	41.75	Eykmann	41.60	+0.15	+0.36
1,3,5-Trimethyl-cyclohexane	C_9H_{18}	41.99	Eykmann	41.60	+0.39	+0.94
Pulegane	C_9H_{18}	41.74	Eykmann	41.60	+0.14	+0.34
Dihydro-campholene	C_9H_{18}	41.66	Eykmann	41.60	+0.06	+0.14

The only possible conclusion to be drawn from the data of Table III is, that *the refraction of carbon and hydrogen in the 8 selected compounds is not identical with that in the methylenic polymethylene hydrocarbons: the introduction of the CH_2 group* produces a small, but appreciable increase, Δr, in the molecular refraction.

In another paper it will be shown that the *methyl group exerts a similar effect upon the heat of formation of the atomic linkings C–C and C–H.*

In the case of compounds which contain other atoms in the molecule (for example, oxygen) the results obtained from F. Eisenlohr's values differ from those obtained by me, and the differences are found to be greater, the larger the value of Σr_X in the equation

$$M_D = nr_{CH_2} + \Sigma r_X,$$

where nr_{CH_2} corresponds to the refraction of the CH_2 group and Σr_X to that of the rest of the molecule.

For example, in the case of ketones and aldehydes, we have

$$\Sigma r_X = r_o + \Sigma \Delta r,$$

where r_o corresponds to the refraction of oxygen in the carbonyl group. In this case my calculations and those of Eisenlohr are in sufficient agreement because Σr_X is very small.

The calculations for ketones and aldehydes are given in Table IV.

Eisenlohr assumes $r_o = 2.211$, which value differs from mine ($r_o = 2.196$) by about +0.67%.

On comparing the various values of r_o in Table IV, considerable deviations from the average value, $r_o = 2.20$, are evident. These can be accounted for by supposing that the refraction of the carbonyl group, or of the oxygen, is variable and depends on the constitution of the molecule.

TABLE IV.

Name.	Formula.	M_D.	nr_{CH_2}.	$r_o + \Sigma\Delta r$.
Acetone	CH_3COCH_3	16.15	13.87	2.28
Methylethyl-ketone	$CH_3COC_2H_5$	20.67	18.49	2.18
Diethyl-ketone	$C_2H_5COC_2H_5$	25.18	23.11	2.07
Methylpropyl-ketone	$CH_3COC_3H_7$	25.20	23.11	2.09
Methyl-*iso*-propylketone	$CH_3COC_3H_7$	25.24	23.11	2.13
Ethylpropyl-ketone	$C_2H_5COC_3H_7$	29.71	27.73	1.98
Methyl-*iso*-butylketone	$CH_3COC_4H_9$	30.01	27.73	2.28
Oenanthol	$C_7H_{14}O$	34.79	32.35	2.44
Methylhexyl-ketone	$CH_3COC_6H_{13}$	39.28	36.98	2.30
Methylnonyl-ketone	$CH_3COC_9H_{19}$	53.00	50.84	2.16
n-Butyl-aldehyde	C_4H_9COH	20.64	18.49	2.15
iso-Butyl-aldehyde	C_4H_9COH	20.68	18.49	2.19

Average, $r_o + \Sigma\Delta r = 2.196$

This can be proved, for if we assume that $\Delta r = 0$, we may calculate the values of r_{CH_2} and r_o by the method of least squares from the series of equations

$$M_D = nr_{CH_2} + r_o + \Sigma\Delta r.$$

Thus, we obtain $r_{CH_2} = 4.631$ and $r_o = 2.137$.

The differences between M_D and the calculated values $(nr_{CH_2} + r_o)$ are given in Table V.

TABLE V.

Name.	M_D.	$nr_{CH_2} + r_o$.	Δr.	$\Delta\%$.
Acetone	16.15	16.03	+0.12	+0.74
Methylethyl-ketone	20.65	20.66	—0.01	—0.05
Diethyl-ketone	25.18	25.29	—0.11	—0.44
Methylpropyl-ketone	25.20	25.29	—0.09	—0.35
Methyl-*iso*-propylketone	25.24	25.29	—0.05	—0.20
Methyl-*iso*-butylketone	30.01	29.92	+0.09	+0.30
Ethylpropyl-ketone	29.71	29.92	—0.21	—0.70
Oenanthol	34.79	34.55	+0.24	+0.70
Methylhexyl-ketone	39.28	39.19	+0.09	+0.23
Methylnonyl-ketone	53.00	53.08	—0.08	—0.15
n-Butyl-aldehyde	20.64	20.66	—0.02	—0.10
iso-Butyl-aldehyde	20.68	20.66	+0.02	+0.10

Average, $\Delta\% = +0.34$

A comparison of the percentage deviations in Tables II and V shows that the refraction of the carbonyl group or of carbonyl oxygen varies within wide limits, and that the *deviations cannot be explained as being due to experimental errors.*

If we examine the following data

$$\begin{array}{llcllcllc}
CH_3CO.CH_3 & 2.28 & & C_2H_5CO.CH_3 & 2.18 & & i\text{-}C_4H_9CO.H & 2.19 & \\
 & & \}-0.09 & & & \}-0.11 & & & \}+0.09 \\
CH_3CO.C_2H_5 & 2.18 & & C_2H_5CO.C_2H_5 & 2.07 & & i\text{-}C_4H_9CO.CH_3 & 2.28 & \\
 & & \}-0.09 & & & \}-0.09 & & & \\
CH_3CO.C_3H_7 & 2.09 & & C_2H_5CO.C_3H_7 & 1.98 & & & &
\end{array}$$

we observe that the replacement of a methyl group by an ethyl or by a *n*-propyl group is accompanied by a considerable diminution in the value of r_o. These diminutions are almost identical in all cases and vary within narrow limits (—0.09 and —0.11). Likewise, we must note that the methyl group, when it is substituted for hydrogen in aldehydes, effects a very noticeable change equal to +0.09, when the rest of the molecule is *iso*-C_4H_9CO, for example.

The data of F. Eisenlohr which concern the atomic refractions of ether compounds, are not in agreement with those computed above. These variations pertain to the alcohols, ethers, and esters. This paper is not intended to give complete discussion of the question, but only to demonstrate by some example that the exact determination of the refractions r_C and r_H is indispensable in all calculations which deal with this problem.

If we calculate values for M_D for the alcohols and ethers by the formula

$$M_D = nr_{CH_2} + 2r_H + r_o + \Sigma \Delta r$$

it is clear that an error in the value assumed for r_H causes an error in the value of r_o. Table VI contains the calculated values of r_o assuming, as above, that $r_{CH_2} = 4.622$, $r_H = 1.066$, and that $\Sigma \Delta r = 0$.

TABLE VI.

Name, alcohol.	Formula.	M_D.	$nr_{CH_2} + 2r_H$.	$r_o + \Delta r$.
Methyl	CH_3OH	8.22	6.75	1.47
Ethyl	C_2H_5OH	12.74	11.38	1.36
n-Propyl	C_3H_7OH	17.52	16.00	1.52
iso-Propyl	C_3H_7OH	17.54	16.00	1.54
n-Butyl	C_4H_9OH	22.13	20.62	1.51
iso-Butyl	C_4H_9OH	22.16	20.62	1.54
Trimethyl-carbinol	C_4H_9OH	22.22	20.62	1.60
iso-Amyl	$C_5H_{11}OH$	26.74	25.24	1.50
iso-Amyl (ferm.)	$C_5H_{11}OH$	26.77	25.24	1.53
n-Heptyl	$C_7H_{15}OH$	36.05	34.49	1.56
Methylhexyl-carbinol	$C_8H_{17}OH$	40.56	39.11	1.35
			Average,	= 1.494

The average value, $r_o = 1.494$, differs from that of Eisenlohr ($r_o = 1.525$) by about +2.03%.

In Table VII, the data for the refractions of oxygen in the ethers are given.

TABLE VII.

Name.	Formula.	M_D.	$nr_{CH_2} + 2r_H$.	$r_o + \Sigma \Delta r$.
Methylal	$CH_3.O.CH_2.O.CH_3$	19.19	16.00	1.60
Acetal	$(CH_3.CH_2O)_2.CH.CH_3$	33.13	29.86	1.64
Ethylpropyl ether	$C_2H_5.O.C_3H_7$	26.95	25.24	1.71
Ethyl ether	$C_2H_5.O.C_2H_5$	22.43	20.62	1.81
			Average,	= 1.663

The value obtained by F. Eisenlohr is 1.643, which differs from 1.663 by about —1.2%.

It is to be noted that quite aside from this disagreement, the values of r_C, r_H, r_O, etc., are not constant. The calculation of average values of atomic refraction cannot be accepted as a satisfactory solution of the question before us.

In another paper I shall compare these results with the thermochemical data. In comparison I shall attempt to justify the selection of the 8 hydrocarbons as a basis for the calculation of the average values r_{CH_2}, r_C and r_H.

WARSAW, POLAND.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PRINCETON UNIVERSITY.]

THE EXPLANATION OF AN APPARENT ANOMALY OUTSTANDING IN THE RESULTS OF MEASUREMENT OF DISSOCIATION PRESSURES.

BY ALAN W. C. MENZIES.

Received March 29, 1920.

After brief reference to the nature of the anomaly in question and to the various explanations offered to account for it, it is proposed to adduce experimental results, supported by results of a parallel nature drawn from the work of others, to show that this apparent anomaly is disposed of by a knowledge of the real facts of the case.

The Nature of the Anomaly.—In 1888, Tammann,[1] applying a form of the gas-current saturation method to the measurement of the dissociation pressures of salt hydrates near 35°, obtained results which, while somewhat erratic,[2] were uniformly higher by from 2 to 5% than the results obtained by Frowein[3] with the tensimeter. This anomaly was confirmed by Schottky,[4] working under Nernst's guidance, who found that the initial dissociation pressures developed in tensimetric measurements were higher than the equilibrium values. In 1911, Partington[5] added further confirmation, again using the gas-current saturation method, although not in a form identical with Tammann's.

Explanation of the Anomaly.—Thoughtful elucidations and critical discussions have been offered by Tammann,[6] Nernst,[7] Partington,[6] Brereton Baker,[8] and Campbell,[9] those of Nernst and of Campbell being especially instructive. Lack of space forbids their outlining or consideration here.

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[1] Tammann, *Ann. Physik.*, 33, 322 (1888).

[2] Cf. Menzies, THIS JOURNAL, 42, 978 (1920).

[3] Frowein, *Z. physik. Chem.*, 1, 5 (1887).

[4] Schottky, *ibid.*, 64, 415 (1908).

[5] Partington, *J. Chem. Soc.*, 99, 466 (1911).

[6] *Loc. cit.*

[7] Nernst, *Z. physik. Chem.*, 64, 425 (1908).

[8] Baker, *Ann. Rep. Progress Chem.*, 8, 34 (1912).

[9] Campbell, *Trans. Faraday Soc.*, 10, 195 (1914).

Possible Sources of Experimental Error in Earlier Measurements.—Because it will be shown below that the real facts exhibit no anomaly, it seems desirable, for the sake of progress, to take space to indicate very briefly a few points at which error might have entered into the experimental work of the previous investigators. References to Tammann's work may be omitted[1] for brevity, because he himself was not satisfied with his results. With regard to Schottky's tensimetric results, it will be shown below that considerable pressures of permanent gas, which may be referred to as air, occasionally develop in Bremer-Frowein tensimeters after exhaustion. Schottky must have suspected this, for he allowed his tensimeters to lie in the horizontal position, with the opposite sides in free communication, for 12 hours prior to erection for observation. When, after erection, one bulb of the tensimeter is raised to the higher temperature, as was done in his work, not only will the dissociation pressure on that side increase but so also will the air pressure. But air is soluble in paraffin oil, which Schottky used, as well as in all common manometric liquids except mercury. One would, therefore, predict, in accordance with Henry's law, that Schottky should find, in the presence of air, exactly what he did find, an initial excess of pressure that slowly fell off to the true equilibrium value as the air pressures on opposite sides slowly became equalized by the mechanism of solution and diffusion of air in the oil. With regard to Partington's work, it is suggested that glasswool plugs[2] should not be used to filter rather small volumes of air of 100% humidity, if the humidity is later to be assumed as 100%. Partington does not state whether he corrected for the error that so long escaped the vigilance of Berkeley,[3] who pointed it out some years after Partington's work; nor even whether the more obvious correction for change of air pressure due to the head of water in his saturator was duly applied. Frowein assumed perhaps too lightly the absence of permanent gas from his tensimeters. Campbell points out that the observed static vapor pressure of water in air is less than in a vacuum; while this may be true, the difference in work like Tammann's is not such as to allow his results to be harmonized with Frowein's, as will appear from the evidence given below.

A Re-investigation of the Facts.—In view of notorious precedent in the case of Charles II and the Royal Society of London, it seemed worth while, despite the weight of triple authority cited above, to seek a still simpler explanation of the anomaly than those hitherto offered by once again critically examining the experimental facts. The dissociation pressure of the same sample of cupric sulfate pentahydrate was accord-

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[1] *Vide* ingenious criticism by Campbell, *loc. cit.*

[2] Cf. Menzies, *loc. cit.*

[3] *Nature*, **95**, 54 (1915).

ingly measured, near 25°, by both the gas-current saturation method and by the tensimetric method.

Experimental Procedure.—As comparative and not absolute measurements were contemplated, especial care was not taken to remove traces of impurity from the blue vitriol employed; this was, however, of the highest analytical quality, was free from chloride and contained less than 0.02% of iron. The absolute bath temperature was, however, known with needless accuracy, being measured by averaging the corrected readings of 2 mercurial thermometers graduated to 0.1°, each furnished with Reichsanstalt certificate of corrections rounded to fiftieths. The temperature of the experiments was actually near 24.70°, and the slope of Frowein's *p-t* curve was used in making the necessary small correction to reduce the values to 25.00°.

(*A*) *Gas-current Saturation Method.*—In order to test his results, a procedure like Partington's was followed. The water saturators were, however, of the Kahlenberg type,[1] 3 in series, each exposing a surface of about 5 × 25 cm. of water. A gentle agitation of the saturators was provided. Especial care was taken to minimize the surface condensation error.[2]

In view of the known phenomena of induction periods preceding the first loss of water from uneffloresced crystals,[3] the blue vitriol was converted to trihydrate to the extent of a few per cent. by gentle warming in air.[4] Even with crystals powdered so as to pass a 20-mesh sieve, a column 40 cm. long and of 1.1 cm. diameter was not sufficient to saturate at 25° air passing at 250 cc. per hour; while a column 35 cm. long and of 4.8 cm. diameter proved adequate even with somewhat faster air currents. The more important connections were furnished with ground-glass joints, whose lubricant was removed prior to weighing; other joints were of rubber, coated with paraffin wax, which is satisfactory if the weights of vapor transferred are not too small. The water-absorption tubes, containing calcium chloride and phosphorus pentoxide, were weighed against counterpoises of similar total displacement and external surface, containing air at barometric pressure. The complete apparatus was borne by a single ring-stand, and could be submerged beneath the water of a rapidly stirred water-thermostat kept constant to 0.01°. The air stream was not faster than 0.5 liter per hour, and no correction was required for pressure differences due to friction. The necessary correction, referred to above, for difference of volume of air emerging from water and blue vitriol saturator was, of course, applied. Each run occupied over 40 hours.

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[1] *Science*, July 21, 1905.

[2] Cf. Menzies, *loc. cit.*

[3] Cf. Rae, *J. Chem. Soc.*, 109, 1229 (1916).

[4] Cf. Guareschi, *Atti accad. sci. Torino*, 50, 765 (1915).

(*B*) *Tensimetric Method.*—Frowein's procedure was purposely followed rather closely. Instead of sulfuric acid, however, freshly fused potassium hydroxide, coarsely powdered while yet hot, was preferred.[1] A sample of cottonseed oil of density 0.9165 at 25° served as manometric liquid. Evacuation was effected, through a phosphorus pentoxide tube, by a mercury pump, and the pressures before sealing off, always less than 0.01 mm. of mercury, were read on a McLeod gage. A millimeter scale was transferred from a steel standard to the glass arms of the tensimeter by means of a beam compass. The instruments were immersed in the thermostat already referred to, which had 2 opposite sides of glass. Parallax was eliminated by the use of a scale of similar length to that of the tensimeter placed on the distant side of the tank. Equilibrium was reached within 24 hours in the cases reported below, although the tensimeters were allowed to remain in the bath for many days.

After equilibrium had been attained, the pressure of air in the apparatus was approximately determined, and so corrected for, by immersing the blue vitriol bulb in alcohol cooled below —50° by solid carbon dioxide. The value of this correction was as much as 0.3 mm. of mercury. To find whether, perhaps, this air was liberated only when the water of hydration left the blue vitriol in the process of efflorescence, an experiment was tried with but a small weight of slightly effloresced crystals in the tensimeter. This tensimeter showed much less air (0.06 mm. of mercury) after attaining equilibrium. This result points to the persistance of the air, during evacuation, as an adsorbed layer on the blue vitriol. The air liberated from the glass surface during the operation of sealing off is probably, in this case, a negligible factor.[2] Andreae,[3] in his careful comparative work, also encountered to a like extent difficulty with adsorbed air.

Experimental Results.—(A) The only 2 non-preliminary measurements by the gas-current saturation method gave 7.83 and 7.78 mm. of mercury at 0° as the dissociation pressure at 25.00° of the system $CuSO_4$-$(5-3)H_2O$ and vapor: average, 7.80 mm.

(*B*) The only 2 non-preliminary measurements by the tensimetric method gave 7.72 and 7.76 mm.; average, 7.74. Such results are over 5% higher than Frowein's values.

In spite of precautions to avoid condensation of saturated water vapor before reaching the absorption tubes, the results under (*A*) would be expected to turn out too high by a fraction of one per cent., in conformity with the consistent results of Berkeley and Hartley.[4] As the results

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[1] Cf. Baxter and Starkweather, THIS JOURNAL, **35**, 2038 (1916).

[2] Cf. Shrader, *Phys. Rev.*, **13**, 437 (1919).

[3] Andreae, *Z. physik. Chem.*, **7**, 241 (1891).

[4] Berkeley and Hartley, *Trans. Roy. Soc. London* (*A*), **209**, 177 (1909); cf. Menzies, *loc. cit.*

stand, therefore, it is obvious that the discrepancy is well within the experimental error of such measurements. And thus the anomaly disappears.

Comparison of the Results of Frowein with Those of Others.—As it would appear from the above that the results of Frowein, on which much reliance has been placed, are too low in this instance, it was thought well to compare his results for other salts with the available values obtained by later workers who have used the static method. This comparison is exhibited in Table I, in which the results of Andreae,[1] E. Cohen[2] Schottky, and Bolte[3] have been utilized. Frowein's values for barium chloride dihydrate and for strontium chloride hexahydrate were obtained by interpolation from the straight line obtained by plotting log *p* against $1/T$, using his mean experimental values.

TABLE I.

Comparison of Dissociation Pressure Results by Static Method.

A. Hydrate.	B. Temperature, ° C.	C. Press. in mm. Hg acc. to Frowein.	D. Andreae.	E. Excess of D over C. %.
$SrCl_2.6H_2O$	19.7	4.88	5.61	15
	25.6	7.77	8.72	12
	29.9	10.8	11.84	10
	34.1	14.7	15.83	8.0
	37.55	18.7	19.86	6.3
$MgSO_4.6H_2O$	...	...	Cohen	..
	30.75	18.35	18.96	3.4
$BaCl_2.2H_2O$	...	...	Schottky	..
	29.95	7.69	7.96	3.5
	34.95	11.38	11.62	2.2
	36.20	12.32	12.99	5.4
$MgSO_4.6H_2O$	...	...	Bolte	..
	30.75	18.35	18.92	3.1

The duplicate measurements of Cohen and of Bolte are very much more concordant than those of Frowein for the same salt; but this means little, for the latter obtains in other cases excellent concordance for duplicates each suffering severely from the same systematic error. It is evident from Table I that the results of Frowein are several per cent. too low for these salts also, and not alone for cupric sulfate.

Summary.

(1) The experimental results of Tammann, Schottky and Partington have been outlined so as to elucidate an anomaly that is outstanding at the present time, namely, that the dissociation pressures of salt hydrates appear higher as measured by the gas-current saturation method than

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[1] *Loc. cit.*

[2] Cohen, *Z. physik. Chem.*, 36, 517 (1901).

[3] Bolte, *ibid.*, 80, 338 (1912).

by the tensimetric method; and that early readings in a tensimetric measurement are higher than later ones.

(2) The suggested explanations of Tammann, Nernst, Campbell, Partington and Brereton Baker have been referred to.

(3) A number of criticisms, which it is hoped may be helpful to other workers, have been offered of the experimental work of users of both tensimetric and gas-current saturation methods.

(4) An experimental re-examination of the facts has been described.

(5) It has been shown that the real facts exhibit no anomaly.

(6) Reason has been given for accepting the tensimetric results of Frowein, often regarded as standard, only with caution.

PRINCETON, N. J.

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

THE STABILITY OF ATOMS AS RELATED TO THE POSITIVE AND NEGATIVE ELECTRONS IN THEIR NUCLEI, AND THE HYDROGEN, HELIUM, H_3, H_2 THEORY OF ATOMIC STRUCTURE.

BY WILLIAM D. HARKINS.

Received April 12, 1920.

The purpose of this article is to extend the theory presented in the earlier papers[1] of this series, the first of which were published in 1915. Using as a basis the evidence obtained from the electrolysis of solutions, from the positive ray work of Thomson,[2] and from the atomic weights of the elements and of the separate atomic species, insofar as the latter were then known, the writer presented the theory that the nuclei of all atoms are made up of positive and negative electrons, and evidence was presented which indicated that the nuclei of hydrogen atoms are positive electrons. It will be pointed out later in the present paper that in the light nuclei there are in general about half as many negative as positive electrons, and that in no known complex nucleus is the ratio of negative to positive less than one to two.

The theory indicated that the deviation of the atomic weight of helium (3.969 when calculated on the basis of hydrogen as 1) from a whole number, is due to a "packing effect" which amounts to a decrease of mass equal to 0.77%. This theory was based on the idea of Rutherford[3] that the nucleus of the atom is very minute. That there is a decrease of

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[1] THIS JOURNAL, 37, 1367–1421 (1915); 38, 186–214 (1916); 39, 856–879 (1917); 41, 970–992 (1919); *Phil. Mag.*, 30, 723–734 (1915); *Science, N. S.*, 46, 419–427, 443–448 (1917); 50, 577–82 (1919); *Proc. Nat. Acad. Sci.*, 1, 276 (1915); 2, 216–224 (1916); *Phys. Rev.*, 15, 73–94 (1920); *Z. anorg. Chem.*, 97, 175 (1916).

[2] Thomsen, "Rays of Positive Electricity," Longmans, Green and Co. (1913).

[3] Rutherford, *Phil. Mag.*, 21, 669 (1911); 26, 702 (1913); 27, 448 (1914).

mass when a positive and a negative electron approach each other is an essential postulate in the electromagnetic theory of Lorentz,[1] but he did not give the magnitude or even the sign of the effect. This was calculated for us by Professor A. C. Lunn, whose results showed that the packing effect found in the formation of helium from hydrogen, could be accounted for in the simplest system, consisting in one positive and one negative electron, by their approach until the distance between them is about 400 times the radius of the positive electron. In the first paper it was stated that Rutherford considers the hydrogen nucleus to be the positive electron, this information having been given to us in an oral report of one of his addresses. Reference was not made to an important specific part of one of Rutherford's papers which appeared while our papers were in process of preparation, though a general reference to the paper as a whole was given. This specific reference was of importance, and would have been given except for the fact that the writers, in looking over about 150 papers and books, failed to read these 2 pages near the end of a somewhat long paper. The content of these pages cannot be given in full, but it is desirable that the following 2 quotations be presented.[2]

"The exceedingly small dimensions found for the hydrogen nucleus add weight to the suggestion that the hydrogen nucleus is the positive electron, and that its mass is entirely electromagnetic in its origin."

"For the dimensions of the positive and negative electrons considered, the packing must be very close in order to produce an appreciable alteration in the mass due to this cause. This may, for example, be the explanation for the fact that the helium atom has not quite 4 times the mass of the hydrogen atom."

The first two papers of this series were written largely for the purpose of giving the evidence which existed in the atomic weights in favor of the above assumptions, and to indicate that where the atomic weights were not in their favor, the apparent discrepancy could be explained by the existence of isotopes. It was assumed in this connection that not only neon, as found by Thomson, but also chlorine, silicon, magnesium and nickel, copper, zinc, mercury, and nearly all other elements of atomic numbers 28 to 80, as well as the radioactive elements, are mixtures of isotopes. The ordinary atomic weights when considered in a systematic manner, give strong evidence in favor of this assumption.

Four Series of Atoms from the Standpoint of Composition are Now Known.[3]

Atoms belonging to at least 4 more or less independent series are now known, and a fifth, but dependent series also exists. These series are,

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[1] H. A. Lorentz, "The Theory of Electrons," 1909, pp. 47 and 48.

[2] Rutherford, *Phil. Mag.*, 27, 494–5 (1914).

[3] These series of atomic species have been classified according to the *composition*

1. Helium, or Helium-Thorium Series [(a) pure α-series (*b*), α-cementing electron series].
2. Meta-neon-Uranium Series (α, μ-series).
3. Lithium-Cobalt Series (α, ν-series).
4. Meta-chlorine series (α, ν, μ-series).

The dependent series is,

2*b*. Actinium series (Secondary α, μ-series), presumably one branch of the Uranium series.

While there are only 92 chemical elements in the series of elements now known, that is only 92 different kinds of atoms, if the arrangement of the outer or planetary electrons alone is considered, it is probable that at least three or four hundred elements exist if the viewpoint taken is that of atomic evolution and disintegration. However, since it is customary to class all elements which have the same planetary electron number and arrangement as one element, the different elements of this type will be considered as *different atomic species*, and the term element, which thus becomes entirely arbitrary, will be used to indicate a chemical element. Each of the 5 series of atoms, when considered in this sense, does not consist of a number of elements, but of a number of atomic species.

The 4 series of atoms are listed above in decreasing order of abundance. Thus *by far the greatest part of all known material belongs to the alpha or helium series.* The nuclei of all the more common atoms of this series may be assumed to consist of *α-particles alone*, or of *α-particles plus negative α-cementing electrons.* For convenience these will be referred to as Class 1 and Class 2 of this series. Most of the abundant atoms, as oxygen, α-magnesium, α-silicon, calcium and probably an α-nickel, belong to Class 1, though iron is very abundant and contains 2 cementing electrons in its nucleus. *No abundant species of atoms contains more than 2 such electrons.* The prefix α indicates a species of atoms whose nuclei consist of α-particles. Each α-particle is assumed to consist of 4 positive and 2 negative electrons (Fig. 1).

The atoms of the meta-neon-uranium series seem to have nuclei which consist of α-particles mostly, but which contain in addition one other group. Since the nature of this group has not been determined experimentally, its exact size is uncertain. However, the difference between a member

of their atoms, and from this standpoint they need not be considered as making up such series as are considered in the disintegration of the radioactive atoms, or even as series from the standpoint of atom building. However, since all of the descendents from uranium show the same type of composition, and since all of the known atoms of this type of composition among the radio elements, have also been proved to be descendents from uranium, it does not seem to be improbable that the series listed above are concerned in atomic aggregation and disintegration. This does not mean, of necessity, that in the building of atom nuclei there can be no passing over from one series into the other.

of the α- or helium series and a corresponding member of the meta-neon-uranium series consists in the presence in nuclei of the latter type of a group consisting of 2 positive and 2 negative electrons, of the formula $(\eta_2{}^+\beta_2{}^-)^\circ$, where η represents a positive and β a negative electron and $^\circ$ indicates that the net charge on the group is zero. *If this group exists by itself, it is a particle belonging to an element of zero atomic number.* It will be called the *mu* group, so the series is an α-μ-series. The lightest particle now known, which contains this group, is the nucleus of the meta-neon atom, which may be assumed to consist of 4 α-particles and one μ-group. It is possible that the primary group from the standpoint of structure may have the composition $(\eta_6{}^+\beta_4{}^-)^{++}$, in which case it would be the nucleus of a meta-helium atom, but the assumption of the presence of the μ-group leads to a simpler system, The atoms of this group, as a class, are not so abundant as those of the α-series, but they are probably more abundant than those of the third and fourth series, at least this will be found to be the case if the highest atomic weight isotopes of magnesium and silicon belong to this series, as is probable and if the present atomic weights[1] of these elements are correct within 0.1 unit. These isotopes have not been discovered, but they exist if the present atomic weights of magnesium and silicon are correct to within 0.2 unit in the case of magnesium and to 0.05 unit in the case of silicon.

Lithium-Cobalt Series.—This series as it is now known begins with lithium and ends with cobalt. It is practically certain, however, that cobalt is not the highest member of the series, and that it extends as high as *gold*, and possibly to bismuth. No members have been discovered among the radioactive elements of atomic number 84 or higher. The atoms of this series make up only about 1.3% of the material of the meteorites, while, so far as is known, about 98% or more belongs to the first 2 series, the helium and the uranium series. While the lithium nucleus is the lightest known particle belonging to this series, it is possible that a nucleus of mass 3 (or ν particle) exists, though it is probable that no appreciable amount of this element can be found on earth.

In the first paper of this series it was considered that the atoms of the lithium series contain a particle of mass 3, which was designated as the H_3 particle. If such a particle exists, though it contains 3 positive electrons or nuclei of hydrogen atoms, it does not contain 3 negative electrons, but less than 3. In the later papers the symbol ν has been used to indicate a *group* of 3 positive and 2 negative electrons $(\eta_3{}^+\beta_2{}^-)^+$, which is very evident in the *composition* of atoms of the lithium series. Whether this *group* contains the same number of negative electrons as the corresponding *particle* of weight 3, cannot be deduced from the general theory, though the only possibilities are that the 3 particles, if it exists, shall contain one

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[1] Mg = 24.32, and Si = 28.11.

or two negative electrons, though the indications are that it contains two.

This group is the first to be considered here which has an odd atomic weight, and as a *group* it has an odd positive charge. It will be shown later that it is probable that this *group* is responsible for the odd charge of most light atoms of odd atomic number.

Meta-chlorine Series.—Recent results obtained by Mr. C. E. Broeker and the writer in an investigation started early in 1916 seem to indicate that they have actually separated the element chlorine into isotopes, and the positive ray analysis of Aston indicates that the atomic weights of the isotopes are 35 and 37. Now Cl_{37}, or meta-chlorine, is a member of none of the 3 series already listed. While the nature of the groups present in its nucleus may seem somewhat in doubt, it is the first atom of odd nuclear charge whose atomic weight is 2 higher than the theoretical value, which is 35. Thus meta-chlorine differs from chlorine by the same amount as meta-neon differs from neon, and by the same amount as any member of the α,μ-series differs from the α-series. The simplest assumption is that the nuclei of Cl_{35} and Cl_{37} differ by one μ group, so if the chlorine nucleus is $(\alpha_8{}^{++}\nu^+)^{17+}$, the meta-chlorine nucleus would be $(\alpha_8{}^{++}\nu^+\mu)^{17+}$. While the form of the latter might be $(\alpha_9{}^{++}\eta^+\beta_2{}^-)^{17+}$ the former formula is in better accord with the general system of structure which is found. In either case, however, meta-chlorine belongs to a fourth series.

A study of the atomic weights of the 4 series indicates that in the *helium-thorium* or *α-series the atomic weights are divisible by 4, in the meta-neon-uranium or α-μ series they are divisible by 2 but not by 4,* or whenever divided by 4 a remainder equal to 2 is found. In the *lithium-cobalt series a remainder equal to 3* is left after a division by 4, *while in the meta-chlorine series*[1] *the remainder is equal to 1.*

While the above list may seem to exhaust the list of possible remainders, there are 2 types of atoms which have not been included in the 4 classes or series given above.

Groups which are Responsible for the Existence of Isotopes.
(Weights 4, 3, 2, and 1.)

Since the nuclei of isotopic atoms have the same net nuclear charge, their differences must be expressed by groups which have a zero net charge. The principal groups which are now evident are the μ or $(\eta_2{}^+\beta_2{}^-)^\circ$ group, and the $(\eta_4{}^+\beta_4{}^-)^\circ$ or $(\alpha^{++}\beta_2{}^-)^\circ$ group. The latter is an α-particle together with 2 negative *cementing* electrons, which serve the purpose of attaching an *extra* α-particle to a nucleus, that is an α-particle which is apparent in the mass, but is not apparent in the charge, of the nucleus.

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[1] While meta-chlorine was the only member of this series known when this paper was first written, Aston has just reported a xenon of atomic weight 133, which may be either of the type of beryllium, or of the type of meta-chlorine.

It is these cementing electrons which are given off in the β disintegrations of the radioactive atoms. The latter group has the same formula as a helium atom, but undoubtedly differs in that it has a much more compact structure. It will be called a helio group (or particle). All known differences between isotopes of *radioactive* atoms of high atomic weight seem to be caused by one μ group, one or 2 helio groups, or one μ and one helio group. Since members of the lithium series have not been discovered among such radioactive atoms, it is evident that *in this range* no isotopes which differ by a ν group plus a negative electron $(\nu^+\beta^-)^\circ$ or $(\eta_3{}^+\beta_3{}^-)$, are known. Isotopes which differ by a ν group plus one negative electron are to be expected in considerable numbers in the range between atomic numbers 29 to 79, and possibly higher. *Ordinary lead* may be either a mixture of uranium and thorium lead, or it may be an individual isotope, and in the latter case it *may* be a lithium derivative. However, it will be shown later that certain rules of structure which seem to hold generally, would indicate that a lithium derivative of even atomic number should have a relatively short life, which makes it seem probable that ordinary lead does not belong to the lithium series. It is not improbable that some isotopic atoms are formed by the addition of the group $(\eta^+\beta^-)^\circ$.

The Stability and Building of Atom Nuclei.

The large loss of mass (0.77%) in the formation of an α-particle from 4 positive and 2 negative electrons, indicates a probable structure for the α-particle, since to give this effect the positive and negative electrons should lie close together, while the positive electrons should be apart from each other, as should the negative electrons; since the closer the approach of the positive to the negative electrons, the greater the loss of mass, while the closer the approach of positive to positive or negative to negative, the greater the increase of mass. Fig. 1 presents a model for the α-particle in which the negative electrons, while represented as rings or discs, are not assumed to have any specific form, since the purpose of the figure is to give only a suggested relative position in space of the positive and negative electrons. If both the negative and the positive electrons are spherical, then the electro-

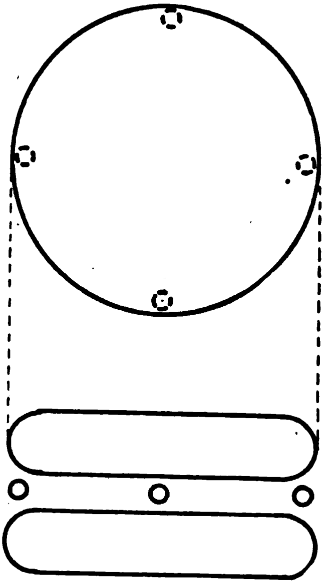

Fig. 1.—Model to illustrate suggested arrangement in the α-particle of positive electrons (small spheres), and negative electrons (large spheres or discs). The model is not intended to suggest any special form for the electrons themselves.

magnetic theory indicates, as has been pointed out by Rutherford, that the radius of the positive is only $^1/_{1835}$ that of the negative. Such questions as why the negative and positive electrons do not neutralize each other, why the apparent number of negative electrons is equal to the number of positive electrons, and why the charges are numerically equal, though of opposite sign, need not be considered here. The difference in size may have some bearing on the first of these questions.

The model suggested should represent an extremely stable system, provided the electrons of opposite sign do not coalesce. It has been suggested by Richardson and by G. N. Lewis that electrons have around them a field of force which alternates in sign as they are approached. On the basis of their theory each electron should consist of a series of concentric shells, decreasing in density with the distance from the center. Such a theory does not decrease the difficulties involved in explaining the stability relations, since it introduces a form of electron so complex that these difficulties are simply transferred to considerations concerning the electron structure itself. According to their theory there might well be a union and a consequent loss of mass with either positive electrons alone, as was assumed by Nicholson, or with negative electrons by themselves. It is of importance in this connection that in considering the composition of any group in which such a packing effect is found to exist we are forced to the conclusion that it consists of both positive and negative electrons, and usually contains more of the former, as in the case of the α or the ν group.

Having adopted a suggestive model for the α-particle based on the idea that electrons of unlike sign should lie close together, and those of like sign relatively far apart, in order to give the packing effect, let us consider the way in which α-particles unite with each other. The early papers of this series advanced the theory that from 3 to 8 and 10 α-particles unite with each other to form complex nuclei, without the inclusion of any other positive or negative electrons. It is probable that 9, and more than 10 α-particles, *probably as many as 14*, also unite, but in none of these cases, unless in nickel with 14, are there enough combinations of this kind to make these nuclei relatively abundant. All of these nuclei belong to the pure α-division of the helium series. Every α-particle carries a net positive charge of 2, so at all distances of ordinary magnitude α-particles would repel each other if at rest, according to the ordinary laws of electrostatics. However, since α-particles unite with each other to form complexes so stable as the nuclei of atoms of oxygen, magnesium, calcium, etc., it is evident that at the very minute distances between the α-particles in these nuclei they must attract each other in spite of their net positive charge. It is evident that this attraction might be considered on the basis of an alternating field around electrons according to the hypothesis of Richardson and Lewis, but it seems much more simple to treat it as due to the action of electrical couples, which might easily become more powerful at such short distances than the repulsion due to the net positive charge.

The fact that isotopic forms of ordinary elements are now being discovered, and the probability mentioned earlier in this paper that hundreds of such isotopes exist, make it unsafe to state that any special form of union is non-existent. For example, it is not certain that there is no lithium atom of atomic weight 5 though its existence is improbable. The nucleus of such an atom could consist of an α-particle plus one positive electron. An isotope of hydrogen might have a nucleus consisting on one α-particle plus a negative electron. However, it may be stated that if such nuclei exist at all, their quantity is so small that they are of little relative importance. So, when it is stated that neither a positive nor a negative electron make a stable union with an α-particle, the statement is made with reference to the above considerations. The model suggested for the α-particle, which may not be the only model which will meet the conditions, may be said to repel the positive electron on account of its net positive charge, and to repel the negative electron at very small distances, because the outer part of the model is largely negative. At considerable relative distances negative electrons would be attracted.

Since as many as 10, and probably even as many as 14, α-particles unite alone to form a stable intra-nuclear compound, the question may be raised as to why larger numbers of α-particles do not unite in the same way. The nuclei of carbon, oxygen, α-neon, α-magnesium, α-silicon, and sulfur, have, respectively, atomic weights of 12, 16, 20, 24, 28 and 32, and net positive charges 6, 8, 10, 12, 14 and 16. Their atomic weights and net charges are, therefore, 3, 4, 5, 6, 7 and 8 times the weight and charge of the α-particle, so these last numbers may be taken to indicate the number of α-particles in the respective nuclei. The ordinary argon nucleus, however, has a weight of 40, but its charge is only 18, so from its weight it should contain 10, while its charge indicates the presence of only 9, α-particles. The obvious explanation is that this nucleus contains one α-particle which is apparent in the weight, but is not apparent in the charge. That is, the argon nucleus contains enough extra or alpha *cementing* electrons to neutralize the positive charge of one α-particle. The number of α-cementing electrons rises as the atomic weight (number of positive electrons), or the number of α-particles increases, until in the thorium nucleus there are 26, and in lead from thorium, 22 such electrons. Argon is the element of lowest atomic number in whose normal atom these cementing electrons appear. *Thus, in the lightest atoms there are no α-cementing electrons, in the heavy atoms there are no nuclei without α-cementing elec-*

trons. The question which now arises relates to the necessity for the inclusion of these cementing electrons, together with the *extra* α-particles which always accompany them, in order to give stability to a heavy nucleus, while the stable nuclei which contain from 3 to 8, and even 10, α-particles, contain no such cementing electrons.

Suppose that several α-particles are approaching each other. Their mutual self-repulsion due to their net positive charges, tends to keep them apart unless they are driven together so strongly that they approach sufficiently close to enable the attractive effects of the mutual couples to become of significance. As the total net positive charge on the nucleus, once it is formed, increases, the repulsion due to this cause may be assumed to increase to such an extent that α-particles are no longer able to pass through the region of repulsion, and to attach themselves, though electrically neutral particles, such as the helio group $(\eta_4{}^+\beta_4{}^-)^\circ$ or $(\alpha^{++}\beta_2{}^-)^\circ$ group the mu group $(\eta_2{}^+\beta_2{}^-)^\circ$, the $(\eta_3{}^+\beta_3{}^-)^\circ$ or $(\nu^+\beta^-)^\circ$ group, and the $(\eta^+\beta^-)^\circ$ group could easily pass into and through this region.

The ratio of the number of negative to the number of positive electrons in the α-particle (helium nucleus) is one to two, or 0.5, and this may be said to be also the *normal* ratio in light atoms whose nuclei are made up from α-particles alone. This is the exact ratio in the nuclei of carbon, oxygen, α-neon, α-magnesium, α-silicon, sulfur and calcium; and also in α-argon (at. wt. = 36), if it exists. If this ratio were to be preserved the atomic weight of thorium (atomic number 90) would be 180, instead of 232, and the thorium nucleus would contain 45 instead of the actual 58 α-particles. However, as the repulsive effect of the net positive charge increases, this relative number of negative electrons becomes too small to overcome the repulsion, and extra groups containing 4 negative to 4 positive electrons, in which this ratio is 1 to 1, are taken up in order to increase the ratio in the nucleus as a whole. The ratio $\frac{\text{Total number of negative electrons}}{\text{Total number of positive electrons}}$ is of fundamental importance in determining in general the stability of complex nuclei,[1] since as the number of α-particles and the resultant positive charge on the nucleus, together with the accompanying repulsion increase, it is necessary to include negative cementing electrons in order to increase the percentage content of negative electricity. *The cementing electrons are thus included in the nuclei of high net positive charge in order to counteract the repulsive effect of the positive charges, by increasing the ratio of negative to positive charges in the nucleus as a whole.* These cementing electrons *add on in*

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[1] A recent paper by Kossel considers the ratio $\frac{\text{No. of formula electrons}}{\text{No. of formula } \alpha\text{-particles}}$ in this connection. *Physik. Z.*, 12, 265–9 (1919). This ratio will be considered in a later part of the present paper, under cementing electrons.

pairs, so for each addition the above ratio increases suddenly, and then, as more α-particles add on by themselves, the ratio decreases very slowly, until finally the net positive charge increases sufficiently to make another increment in the ratio essential for the maintenance of stability. According to this hypothesis, if the number of cementing electrons were to be plotted on the Y-axis, and the nuclear charge on the X-axis, a horizontal line coinciding with the X-axis would be obtained until atomic number 18 is reached, when the line would rise to 2 electrons. This is shown in Fig. 2. To the right of atomic number 18 the general form of the cementing electron plot should be given by a second horizontal line (indicated in the figure) extending toward the right, another sudden rise to 2 electrons, etc., that is by a series of horizontal steps of different width, but with a uniform vertical spacing (of 2 electrons). The lowest platform or step is the widest (in the horizontal or N or P direction), and in general the steps become somewhat narrower as the number of cementing electrons increases. The average width is about 2.7 α changes per step after the rise once begins.

The Ratio of Negative to Positive Electrons (N/P) in the Nucleus.

Fig. 3 gives the total number of negative nuclear electrons (N) on the Y-axis, and the number of positive electrons (P) on the X-axis. A slanting straight line drawn upward toward the right, starting at the origin, has a slope equal to $^1/_2$ or 0.5, *the normal slope for light atoms*. On this plot atoms of the helium-thorium series are represented by open circles, the meta-neon-uranium series by circles which are linked in, the lithium series by triangles, and meta-chlorine by a square. A cross indicates that the element weight (ordinary atomic weight) only, is known, and that the element is supposed to be a mixture of isotopes belonging to different series. It may be noted that up to about calcium the helium series atoms lie on this 0.5 line, those of the lithium series very slightly above it, and the meta-neon series still higher. Although meta-magnesium, and meta-silicon, have not been discovered, black circles which represent them, based on the hypothesis that they are members of the meta-neon series, are included in the plot in order to indicate what their relations would be. This is also true in all of the other figures of this general type. While there is little doubt that these meta elements exist, it is possible that they belong to another series. From calcium on, the slope of the plot is seen to be greater than 0.5. It may be seen that most of the elements are represented as, or assumed to be, mixtures. From nickel to uranium the whole plot will undoubtedly divide into a number of series similar to those represented on an enlarged scale at the top of the figure, where the radioactive atoms are plotted. However, between the radioactive atoms and the light atoms, other series than those thus far found among the heavy atoms, such as

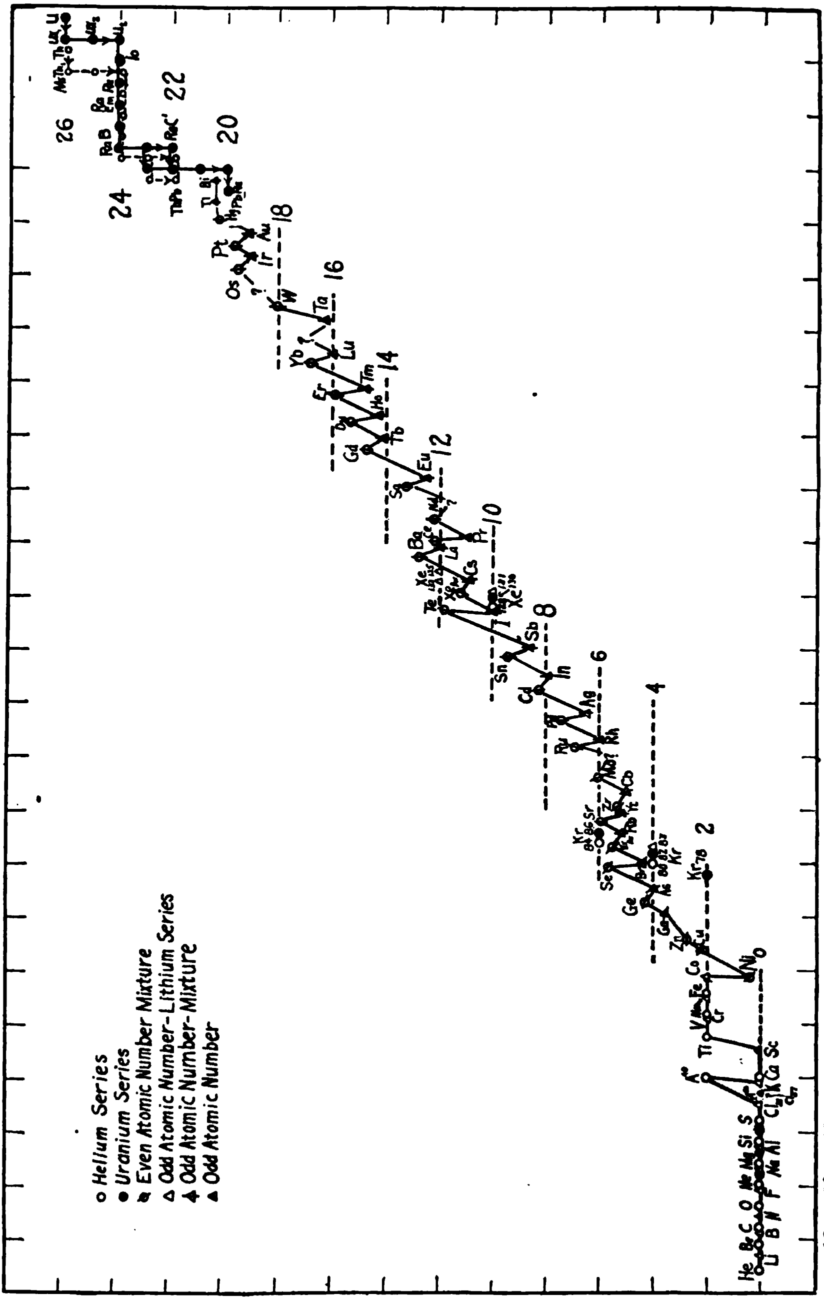

Fig. 2.—Cementing or β-Electrons in the Nuclei of Atoms.

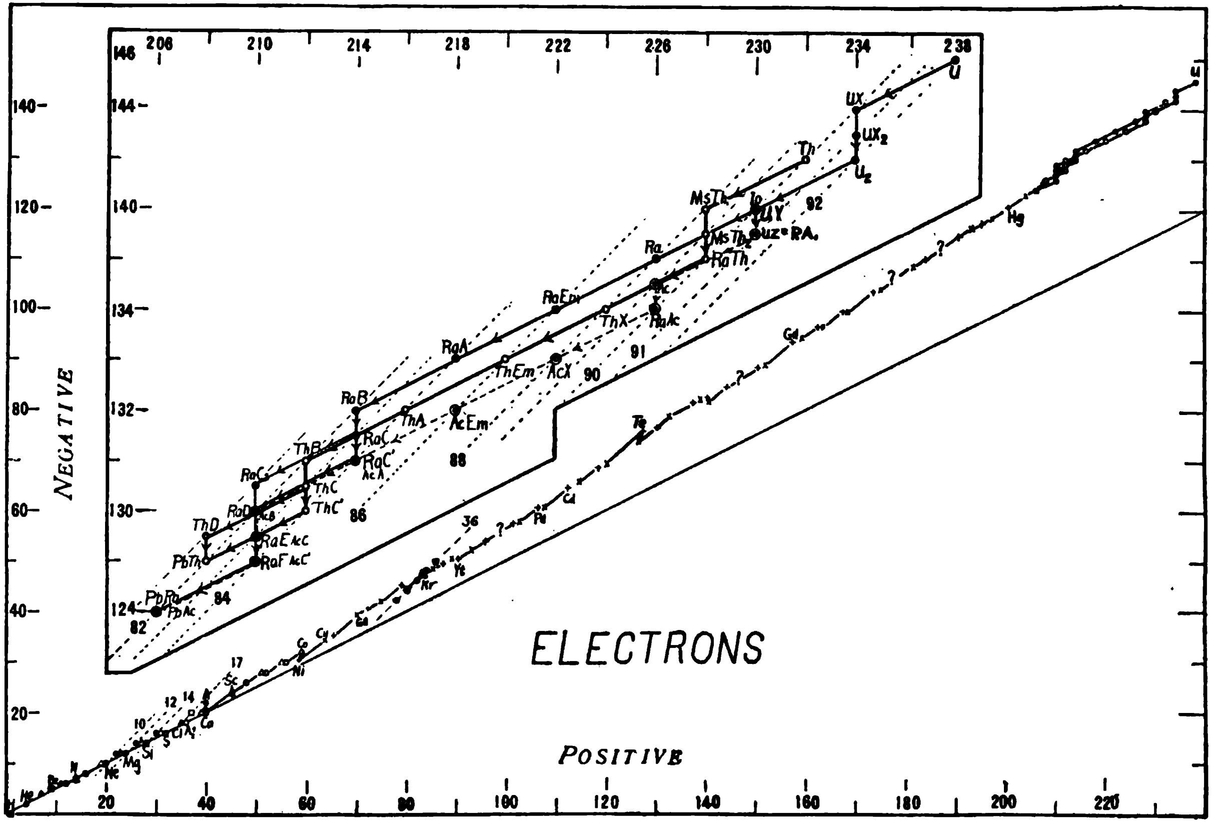

Fig. 3.—Positive and negative electrons in atom nuclei.

(Note: The position of the actinium series is still uncertain. Any later change will be to shift the whole series down or *much more probably up* along the isotopic lines.)

the lithium series, will be undoubtedly found; so from nickel to lead the final plot should be even more complicated than that given for the radio-elements. The dotted lines on the plot have a slope of 1 : 1, or of 45°. Thus they are lines along which the difference $P - N$ is constant, and since $P - N$ gives the nuclear charge or the atomic number, these are isotopic lines, or lines which give the same atomic number. The actinium series is assumed to be derived from uranium II. If it is derived from uranium itself the only change necessary in the diagram is to shift the whole actinium system two places upward along these isotopic lines.

Column r, or N/P, in Table I shows that the ratio of negatives to positive electrons for all of the light complex nuclei of even atomic number (sub-column *He*) with the exception of beryllium,[1] is exactly one to two, or 0.5. In the argon nucleus (of at. wt. 40) this ratio suddenly rises to 0.55, falls to 0.5 in calcium, rises suddenly again to 0.542 in titanium, after which it falls gradually to 0.536 in iron. *The subsequent fall to 0.522 in nickel probably indicates that one of the abundant isotopes in nickel has an atomic weight equal to 56*, and that this isotope belongs to the pure α division of the helium series. According to the theory advanced in this paper, the *sudden rise* in the ratio, and its subsequent *gradual fall*, should be characteristic of each series of atoms through its entire course after the first rise takes place, the rise with increasing atomic number being coincident with the addition of *two* cementing electrons, while the gradual fall is due to the addition of α-particles in which this ratio is 0.5, which, it is apparent, has the effect of reducing any ratio higher than itself. Table I (Sections C, D and E) shows that this is exactly what happens in each radio series. Consider, for example, in inverse order of the disintegrations which occur, the primary branch of the uranium series, beginning with radium G, the lightest atomic species. The ratio starts at 0.602, falls to 0.600 (α-addition), rises (β-additions) quickly to 0.605 and 0.610, then falls again by 0.002 to 0.608, rises abruptly to 0.612 and 0.617, and then falls by 4 steps of 0.002 to 0.607, rises to 0.612 and 0.616, and finally ends in 0.614 in uranium. The ratios in the thorium and actinium series follow a similar set of changes, with very nearly the same values.

These relations may be made more prominent by considering not these ratios themselves, but the excess of the ratio over the lowest constant value (0.5), that is $N/P - 0.5$. In the table these numbers have been multiplied by 4 and are given in the Col. 4 ($N/P - 0.5$).

In the lithium series the N/P values start at higher values for the light atoms than in the helium series. Thus it is about 0.52 for fluorine, sodium, and aluminum, rises to about 0.55 for vanadium, manganese and

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[1] Leaving out of consideration the less abundant isotopic series of atoms (Sub-Column *U*).

cobalt, which is not much higher than in the helium series. Finally, after nickel is passed, and the mean number of cementing electrons begins to rise steadily, the ratio falls to practically the same values as, and even below those for the helium series, but shows the same gradual rise, reaching the value 0.602 in iridium. The ratio is specially high in both of the isotopic (meta-neon and meta-chlorine) series, being about 0.54 for meta-neon (meta-magnesium, meta-silicon) and meta-chlorine. This particularly high ratio is due to the presence of the μ group, so it is found on comparing members of the uranium and thorium series containing the same number of α-particles, that the ratio is always higher in the uranium derivative. The ratio is specially high (0.572) in lithium, and also high in beryllium (0.556), and boron (0.545).

The Abundance of Atomic Species as Related to the Ratio (N/P) of Negative to Positive Electrons in the Nucleus.

The details of the abundance relations of the elements in the crust of the earth and the meteorites have been treated in an earlier paper of this series.[1] While the ratio N/P is not the only factor upon which the stability of an atom depends, it is evidently of primary importance. *Thus lithium, beryllium, and boron, with the relatively high values of the ratio given in the preceding paragraph, are rare both in the metorites and on earth.* Carbon, the first atom in the system in which the ratio falls to the normal value 0.5, is the lightest complex atom found in any considerable quantity in the meteorites, and is about 26 times more abundant in the lithosphere than any of the three atomic species just mentioned. Nitrogen, which also has a ratio of 0.5, is, however, not abundant, indicating that other factors are of importance.[2] However, among the elements of atomic number less than 18, all of the abundant atomic species, oxygen, magnesium, silicon, and sulfur, have just this value of the ratio. Iron, in whose nuclei this ratio has a value 0.536, is, nevertheless, a very abundant element, but its nuclear charge is somewhat high (26) which would increase the value of N/P essential for stability, according to the theory presented earlier in this paper.

Both from the known data on the abundance of the elements in the meteorites, and from Clarke's estimate of the composition of the crust of the earth, *it is evident that no atomic species which has a ratio of N/P greater than 0.54 (or a net positive nuclear charge higher than 29) occurs in an atomic percentage greater than 0.01.* In other words, all such elements and atomic species are relatively very rare.

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[1] "The Evolution of the Elements and the Stability of Complex Atoms," This Journal, 39, 856–79 (1917).

[2] The nitrogen nucleus contains an *odd number of negative electrons*. In an earlier paper it has been pointed out that the presence of an odd number of negative electrons is always accompanied by a low stability for a radioactive atom, and a low abundance for other atoms, which also indicates a low stability.

Cementing and Excess Electrons in Atom Nuclei.

The early papers of this series gave 2 equations[1] for the atomic weights of the various atomic species, and from them calculated the number of cementing electrons (c) in the light[2] and also in the heavy[3] atoms. If W is taken to represent the atomic weight, then

$$W = P \tag{1}$$

where P is the number of positive electrons in the nucleus of each atom if the weight is that for a pure species of atoms, but is merely an average value if the elements is a mixture and the element weight is used. Now for atoms of the *helium-thorium series:*

$$P = 2(n + c) = W \tag{2}$$

where n is defined by the equation

$$n = P - N \tag{3}$$

in which N represents the total number of negative electrons in the nucleus. Thus n is the net positive charge on the nucleus, which is equal to the atomic number, and also to the number of non-nuclear or planetary electrons. It is evident that for the calculation of the number of α-cementing electrons, Equation 2 may be put in the following form,

$$c = W/2 - n = P/2 - n = \frac{P - 2n}{2} \tag{4}$$

That is, the number of cementing electrons is equal to the excess of half the number of positive electrons over the net positive nuclear charge. The latter is sometimes called the number of "free" positive electrons in the nucleus, but there is considerable danger that this term may be interpreted in a false sense, since all of the positive electrons in the α-particles present are bound with exceeding firmness.

The above formulas are valid for *only* the members of the *helium-thorium series*, but they may be used for the *lithium series also, provided* an extra term is added. This addition gives

$$P = W = 2(n + c) + 1/2 + 1/2(-1)^{n-1} \tag{5}$$

$$c = W/2 - n - 1/4 - 1/4\,(-1)^{n-1}. \tag{6}$$

While Equations 5 and 6 hold for both the helium and lithium series, they are not valid for *metaneon-uranium series*. For this last series the following relation is true

$$c = W/2 - n - 1 = P/2 - n - 1. \tag{7}$$

While it might be possible to combine Equation 7 with Equation 6 in such a way as to give one equation for the number of cementing electrons

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[1] This Journal, 37, 1380, 1385, 1386, 1395 (1915).

[2] *Ibid.*, 39, 857–9 (1917).

[3] *Phys. Rev.*, 15, 78–79, 77, 85–94 (1920).

in all 3 series, the resulting formula would be so complicated that it is more convenient to use the equations separately.

In 1917 Durrant[1] made a study of our Equations 2 to 5, and in agreement with the structural formulas for the atoms published one month later by the writer, showed that c remains zero up to argon, then suddenly increases by 2, decreases to 0 in potassium, calcium, and scandium, increases again by 2, and remains at that value up to atomic number 27 (cobalt). Durrant plotted c and showed that at atomic number 29 its value begins to increase with an almost constant slope equal to $^1/_2$, but that this slope increases slightly when the radioactive elements are reached. He supported the idea presented in the first paper of this series, according to which this is a region of numerous isotopes and possibly consists partly of the remnants of radioactive series, which may still be disintegrating with extreme slowness, and may extend downward as far or farther than iron.

Whenever Equations 2 and 4 are used for members of the uranium or lithium series, they should be represented in a slightly different way in order to prevent confusion.

$$W = 2\,(n + f) = P \tag{8}$$

or

$$f = W/2 - n \tag{9}$$

where f is a function whose values are equal to the number of cementing electrons whenever the atomic species is a member of the helium-thorium series, but *does not represent any specific electrons when it is applied to any other series, since it indicates the presence of an odd number of cementing electrons in atoms of the uranium series when an even number are present, and the presence of half of a cementing electron in many of the atoms of the lithium series.* In spite of this fact Kossel,[2] in 1919, plotted the values of f as obtained from our Equation 9, and considered the equation to give the number of cementing, or of what he calls beta (β) electrons, in the uranium as well as in the thorium series. The plot which he obtained is practically the same as that obtained several years earlier by Durrant.

A Theoretical Basis for the Rule of Fajans.

The rule of Fajans states that when isotopes alone are considered it is found that the β-disintegrations *increase* in velocity and the α disintegrations *decrease* in velocity, as the atomic weight rises. In order to give this rule greater theoretical significance Kossel puts it is essentially the following form: The greater the ratio of the number of β (cementing) electrons (β) to the number of α-particles (α) in the nucleus, that is the

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[1] Durrant, THIS JOURNAL, 39, 621–7 (1917).

[2] Kossel, *Physik. Z.*, 20, 2659 (1919). The papers of Durrant and of Kossel should be consulted in the original, together with the earlier papers by the writer, if a proper view of their interrelations is to be obtained.

greater β/α, the more rapid is the β disintegration which lowers the ratio, and the less rapid is the α disintegration which raises it. Unfortunately, this formulation of the rule, while extremely suggestive, is nevertheless incorrect. However, Kossel also states the rule in another form, in which he replaces the ratio β/α as given above, by the ratio f/W. In this second form the rule is found to hold as well as the Fajans rule from which it is derived, though it will be shown later that it is not entirely exact, since when the differences in the values of the ratio f/W are too small, certain specific factors sometimes obscure the relationship.

The explanation of the above discrepancy lies in the fact that Kossel considers that the ratios β/α and f/W are proportional to each other, which is not the case, as may be easily seen. Thus since

$$P = W \quad f/W = f/P. \tag{10}$$

From (3), (8) and (10)

$$f/P = P/2P - N/P = 1/2 - \frac{P-N}{P} = N/P - 1/2. \tag{11}$$

Now $P/4$ is *approximately* equal to the number of α-particles in the nucleus, and f is *approximately* equal to the number of cementing electrons, so

$$4f/P = 4(N/P - 1/2) \tag{12}$$

is approximately equal to the ratio β/α, but the approximation is not close enough to make the Kossel relation valid when expressed in terms of the latter ratio.

The equations given above indicate that the real theoretical basis of the rule of Fajans does not lie in the ratio β/α, but in the term $N/P - 0.5$, which is the excess of the ratio of total nuclear negative to positive electrons, over the normal value (0.5) of N/P in helium itself, and in the light atoms of the helium series. Since the relation holds for $N/P - 0.5$, it must also hold for the values of N/P, which is the important factor, and not the values of β/α.

The rule of Fajans may now be stated in the following new form. *The greater the ratio* $\dfrac{\text{Total number of negative electrons}}{\text{Total number of positive electrons}}$ *in the nucleus the more rapid is a β-disintegration which lowers the ratio, and the less rapid is an α-disintegration which raises it, provided the net positive charge on all of the nuclei considered is the same*, that is, when isotopes alone are considered.[1] In Fig. 3 the ratio N/P increases with the height along an isotopic

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[1] *Note on a Reversal of the Above Relationship.* The general idea on which the above relationship is based, is that as it becomes more negative in the sense that N/P increases, the nucleus binds positively charged particles more firmly, and negatively charged particles less firmly. While if isotopic atoms alone are considered, that is nuclei of constant net charge, there are only two complete exceptions to the relationship in about 37 disintegrations, there is an apparent reversal of the rule when the

line, and, therefore, the period of β disintegrations decreases, and of the α disintegration increases, with the height along these lines. This figure gives a plot which may be considered to present the normal or equilibrium values of N and P for the more stable types of atoms. It will be seen that while *the isotopes of krypton*[1] *differ in atomic weight by 8, a considerable difference, none of these isotopes lies very far away from the line representing the mean values of N and P for the adjacent elements.* Aston's work indicates that Kr_{78}, the isotope which lies farthest away from the line of mean values, is present in krypton in only very small quantities. Figs. 4 and 5 give the values of the function f, that is of $N/P - 1/2$, so they represent the rise of the N, P plot in Fig. 3 above the straight line which has the normal slope equal to $^1/_2$. The *heavy* line in Fig. 5 represents the number of *cementing electrons*, given separately in Fig. 2, while the lighter lines plot the values of the function f. It will be noted that both Fig. 4 and Fig. 5 have the same general form, and that the former appears very much as if it were the latter plot, the peaks of which have all been pushed over toward the right. This is due to the fact that the higher the f values in isotopic species of atoms ($P - N$ = const.), the higher is the total number of negative electrons, and therefore the greater is the value of P, which is plotted on the X-axis in Fig. 4.

In the principal plots of these figures an open circle represents a member of the helium-thorium series of atoms between atomic numbers 2

nuclear charge varies. There are also 3 partial exceptions to the rule, in that members of the radium and actinium series of the same N/P ratio, have different periods, but this is to be expected as the result of more specific influences. These statements are based on the idea that the actinium series springs from U_{II}. Thus the reversal occurs in successive α disintegrations, since as is well known, the period and, therefore, the stability of the nucleus, with reference to the giving off of α-particles, decreases rapidly as the disintegration proceeds. That is, as it becomes *less* positive, both with respect to its net charge and with reference to the ratio N/P, the nucleus holds each succeeding positive particle *less* firmly, so as the relative negative electron content increases, the stability with reference to the retention of positive α-particles decreases. In the radium series there are 5, and in both the actinium and the thorium series as now known, 4 such successive α-disintegrations. There is also a reversal with respect to the loss of negative electrons, since the second β-disintegration is always more rapid than the first in the case of 2 successive changes of this nature, even though the nucleus is becoming more positive by the loss of its β-particles. There is thus an irregular, but periodic variation in the stability of nuclei in any one series. As an hypothesis to account for this fact it has been suggested in an earlier paper that the negative cementing electrons are grouped in pairs, and that in the nucleus the α-particles are grouped in aggregates containing 4 or 5 (and probably other numbers, as low as one) such particles in each group, and that each aggregate becomes less stable as it decreases in size. (*Phys. Rev.*, **15**, 88 (1920)).

[1] When this paper was sent to THIS JOURNAL Aston's note in *Nature*, giving news of his work on the isotopes of krypton, xenon, etc., had not been received. The discussion presented here, and the values representing the isotopes of silicon as presented in Table I and Fig. 4, were inserted later by permission of the editor.

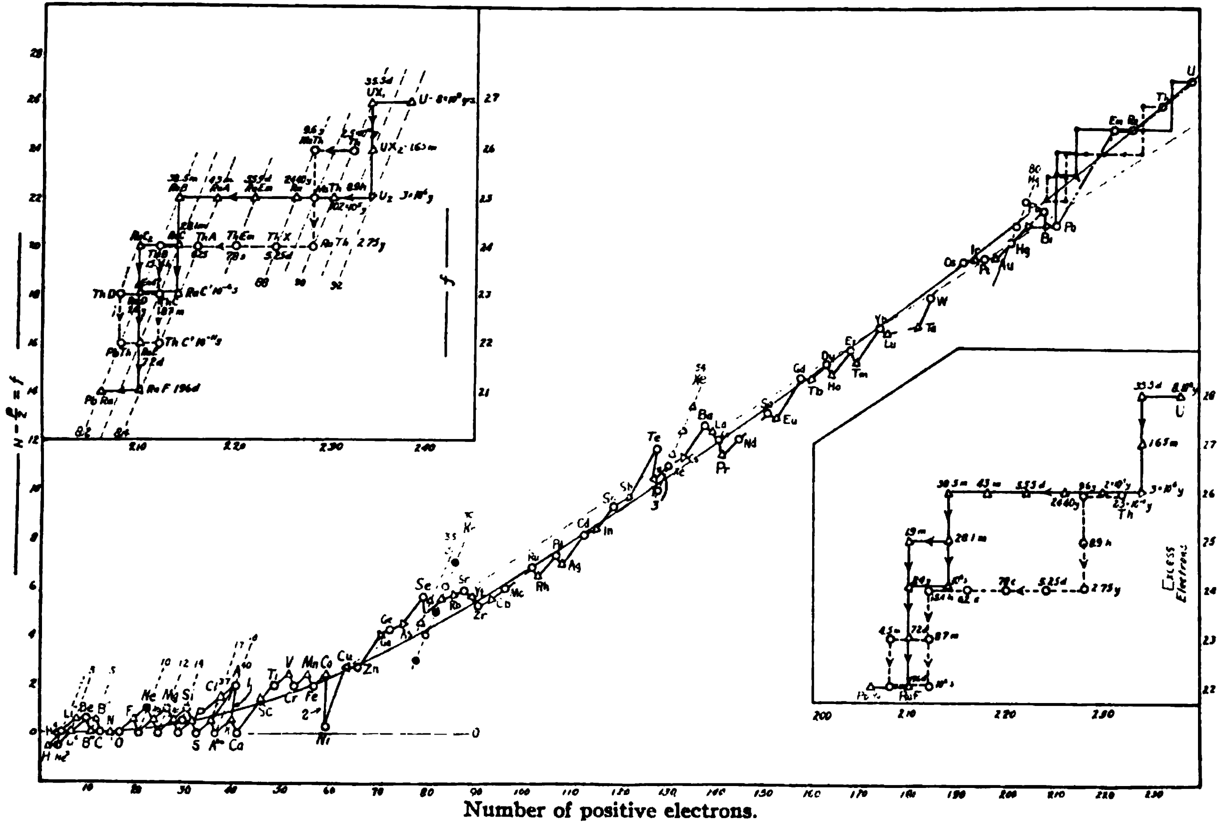

Fig. 4.—(Note: This figure was revised after the completion of the paper in order to include new works by Rutherford and by Aston.)

(The ordinates represent $f = N - P/2$. The small letter n given above should be replaced by N.)

and 27, but from 28 to 80 they represent only that the atomic number is even, except where more than one isotope is given. With the same conventions, an open triangle represents either a lithium series atom, or an element of odd atomic number, while an inked in circle indicates a number of the metaneon-uranium series, and a similar triangle, of the metachlorine series.

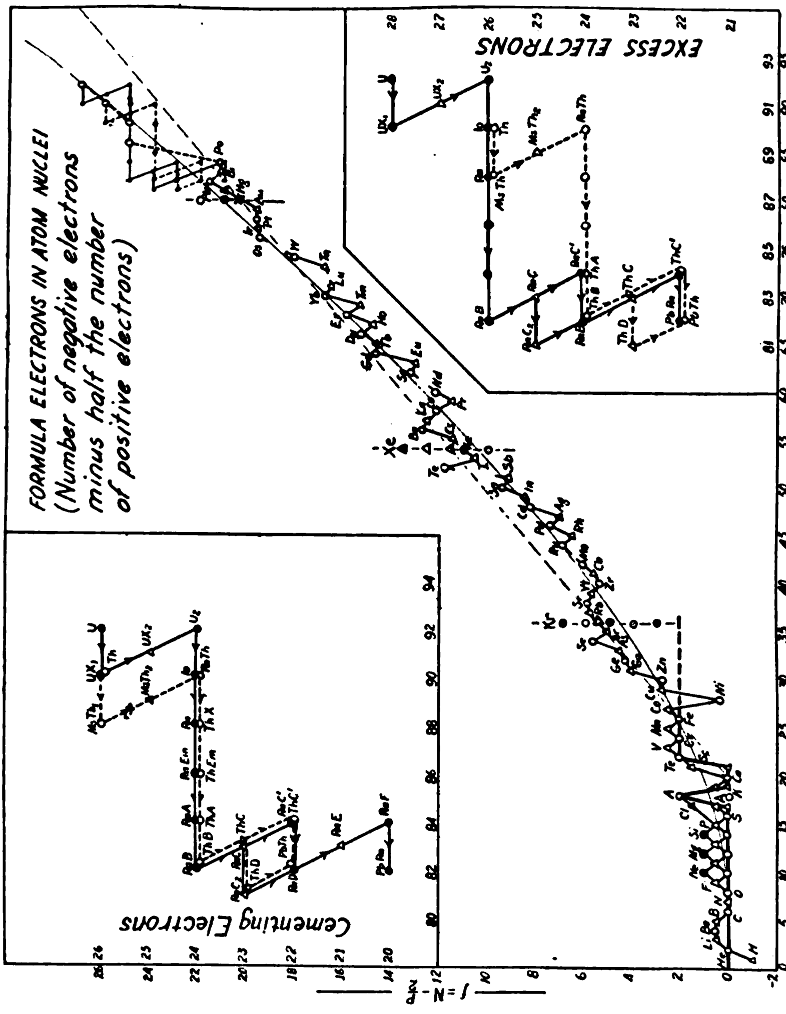

Fig. 5.—(Fig. 4 is more accurate with respect to details.)

It will be seen that Kr_{80} in Fig. 3 is almost coincident with $Br_{av.}$ and Kr_{86} is not far from $Sr_{av.}$. The number of formula electrons in krypton is 3, 4, 5, $5^1/_2$, 6 and 7 for the atomic weights 78, 80, 82, 83, 84 and 86. Aston finds the atomic weights of xenon to be 128, 130, 131, 133 and 135, and this indicates formula electron contents 10, 11, $11^1/_2$, $12^1/_2$, and $13^1/_2$.

TABLE I.—POSITIVE AND NEGATIVE ELECTRONS IN THE NUCLEI OF ATOMS.

n. Net positive charge.	*b.* Element or atomic species.	*P.* Positive electrons.	α-Particles.	*N.* Negative electrons.	*r.* Ratio *N/P.*			*C.* Cementing electrons.	*E.* Excess electrons.			*f.* Formula electrons.			4(*N/P* — 1/2).		
					He.	U.	*o.*		He.	U.	*o.*	He.	U.	*o.*	He.	U.	*o.*
1	Hydrogen	1		0										0.5			
2	Helium	4	1	2	0.5							0.0			0.0		
3	Lithium	6		3			(0.5)										
3	Lithium	7	1	4			0.572	0			2			0.5			0.288
4	Beryllium	9	2	5	0.555			0	(1)			(0.5)			(0.22)		
5	Boron	10	2	5			(0.5)	0									
5	Boron	11	2	6			0.545	0			2			0.5			0.180
6	Carbon	12	3	6	0.5			0	0			0.0			0.0		
7	Nitrogen	14	3	7			0.5	0			1			0.0			0.0
8	Oxygen	16	4	8	0.5			0	0			0.0			0.0		
9	Fluorine	19	4	10			0.526	0			2			0.5			0.104
10	Neon	20	5	10	0.5			0	0			0.0			0.0		
	Meta-neon	22	5	12		0.545		0		2			1.0			0.180	
11	Sodium	23	5	12			0.522	0			2			0.5			0.088
12	Magnesium	24	6	12	0.5			0	0			0.0			0.0		
	Meta-magnesium	26	6	14		0.538_5		0		2			1.0			0.144	
13	Aluminum	27	6	14			0.518_6	0			2			0.5			0.074

14	Silicon	28	7	14	0.5			0	0			0.0			0.0		
	Silicon 29	29	7	15	(0.517)			0									
	Meta-silicon	30	7	16		0.533_8		0		2			1.0			0.133	
15	Phosphorus	31	7	16			0.516	0			2			0.5			0.064
16	Sulfur	32	8	16	0.5			0	0			0.0			0.0		
17	Chlorine	35	8	18			0.514_6	0			2			0.5			0.058
	Meta-chlorine	37	8	20		0.541		0			4			1.5		0.164	
	Chlorine 39	39	9	22			0.564	2									
18	Argon 36	36	9	18	0.5			0									
18	Argon	40	10	22	0.550			2	2			2.0			0.200		
19	Potassium	39	9	20			0.513	0			2			0.5			0.052
20	Calcium	40	10	20	0.5			0	0			0.0			0.0		
21	Scandium	45	11	24			0.533_6	0			2			1.5			0.134
22	Titanium	48	12	26	0.542			2	2			2.0			0.168		
23	Vanadium	51	12	28			0.549	2			4			2.5			0.196
24	Chromium	52	13	28	0.539			2	2			2.0			0.156		
25	Manganese	55	13	30			0.546	2			4			2.5			0.184
26	Iron 52	52	13	26	0.5			0	0			0			0		
26	Iron	56	14	30	0.536			2	2			2.0			0.144		
27	Cobalt	59	14	32			0.543	2			4			2.5			0.172

TABLE I, B.—HEAVY ATOMS (AVERAGE VALUES FOR MIXTURES OF ISOTOPES).

n. Net positive charge.	*b.* Element or atomic species.	*P.* Positive electrons.	α-Particles.	*N.* Negative electrons.	*r.* Ratio *N/P.*			*f.* Formula electrons.			4(*N/P* — 1/2).		
					e.	*n.*	*o.*	*e.*	*n.*	*o.*	He.	*n.*	*o.*
28	Nickel..................	58.68	14	30.68	0.522_5			1.34			0.090		
29	Copper..................	63.57	15	34.57			0.544			2.78			0.176
30	Zinc....................	65.37	16	35.37	0.541			2.68			0.164		
31	Gallium.................	70.1	17	39.1			0.558			4.05			0.232
32	Germanium...............	72.5	18	40.5	0.555			4.25			0.220		
33	Arsenic.................	75	18	42			0.560			4.48			0.240
34	Selenium................	79.2	19	45.2	0.570_5			5.6			0.282		
35	Bromine.................	79.92	20	44.92			0.562			4.96			0.248
36	Krypton.................	82.92	20	46.92	0.566			5.46			0.264		
37	Rubidium................	85.45	21	48.45			0.567			5.72			0.268
38	Strontium...............	87.63	21	49.63	0.566_5			5.81			0.266		
39	Yttrium.................	89.33	22	50.33			0.563_5			5.66			0.254
40	Zirconium...............	90.6	22	50.6	0.558_5			5.3			0.234		
41	Columbium...............	93.1	23	52.1			0.559_5			5.55			0.238
42	Molybdenum..............	96.0	24	54	0.562_5			6.0			0.250		
43	Eka-manganese..........												
44	Ruthenium...............	101.7	25	57.7	0.577_5			6.85			0.310		
45	Rhodium.................	102.9	25	57.9			0.562_5			6.45			0.250
46	Palladium...............	106.7	26	60.7	0.569			7.35			0.2756		
47	Silver..................	107.88	26	60.88			0.564_5			6.94			0.2576
48	Cadmium.................	112.40	28	64.40	0.573			8.2			0.2920		
49	Indium..................	114.8	28	65.8			0.573			8.4			0.2928
50	Tin.....................	118.7	29	68.7	0.578			9.35			0.3150		
51	Antimony................	120.2	30	69.2			0.576			9.1			0.30218
52	Tellurium...............	127.5	31	75.5	0.592			11.75			0.36817		
53	Iodine..................	126.92	31	73.92			0.582			10.46			0.32918
54	Xenon...................	130.2	32	76.2	0.585			11.1			0.341		
55	Cesium..................	132.81	33	78.81			0.594			11.40			0.344
56	Barium..................	137.37	34	81.37	0.592			12.68			0.369		
57	Lanthanum...............	139.0	34	82.0			0.590			12.5			0.360

n.		P.	a.	N.	e.	o.			o. ½(N/P—n).
58	Cerium	140.25	35	82.25	0.586		12.12		0.346
59	Praseodymium	140.9	35	81.9		0.581		11.45	0.325
60	Neodymium	144.3	36	84.3	0.584		12.15		0.337
61	Eka-neodymium								
62	Samarium	150.4	37	88.4	0.588		13.2		0.351
63	Europium	152.0	38	89.0		0.586		13.00	0.342
64	Gadolinium	157.3	39	93.3	0.593		14.63		0.372
65	Terbium	159.2	39	94.2		0.592		14.6	0.367
66	Dysprosium	162.5	40	96.5	0.594		15.25		0.375
67	Holmium	163.5	40	96.5		0.590		14.75	0.361
68	Erbium	167.7	41	99.7	0.594		15.85		0.378
69	Thulium	168.5	42	99.5		0.590		15.25	0.362
70	Ytterbium	173.5	43	103.5	0.596_5		16.75		0.386
71	Lutecium	175.0	43	104.0		0.594_5		16.50	0.377
72	Eka-lutecium								
73	Tantalum	181.5	45	108.5		0.598		16.75	0.369
74	Tungsten	184.0	46	110.0	0.598		18.0		0.391
75	Eka-manganese II								
76	Osmium	190.9	47	114.9	0.602		19.45		0.407_5
77	Iridium	193.1	48	116.1		0.602—		19.55	0.405
78	Platinum	195.2	48	117.2	0.601—		19.6		0.401
79	Gold	197.2	49	118.2		0.600		19.6	0.397
80	Mercury	200.6	50	120.6	0.602		20.3		0.405_5
81	Thallium	204.0	51	123.0		0.603		21.0	0.412—
82	Lead	207.2	51	125.2	0.604		21.6		0.416_5
83	Bismuth	208.0	52	125.0		0.601		21.0	0.404
84	Polonium	210.0	52	126.0	0.600		21.0		0.400
85	Eka-iodine		55						
86	Radium emanation	222.0		136.0	0.613		25.0		0.450
87	Eka-cesium								
88	Radium	226.0	56	138.0	0.611		27.0		0.478
89	Actinium								
90	Thorium	232.15	58	142.15	0.612		26.0		0.448
91	Protoactinium	234		143		0.612—		26.0	0.445—
92	Uranium	238.16	59	146.16	0.614		27.0		3_5 50.4

Table I, C.

Uranium Series in Order of Disintegration.

							Electrons.			
Element.	Net positive charge.	Atom.	Positive electrons.	Negative electrons.	α-Particles.	*N/P*.	Cementing.	Excess.	Formula.	4(*N/P* —0.5).
U	92	U	238	146	59	0.614	26	28	27	0.4538
Th	90	UX_1	234	*144*	*58*	*0.616*	*26*	*28*	*27*	*0.4615*
Bv	91	UX_2	234	*143*	*58*	*0.612*—	*25*	*27*	*26*	*0.4446*
U	92	U_2	234	142	58	0.607	24	26	25	0.4273
Th	90	Io	230	140	57	0.609	24	26	25	0.4350
Ra	88	Ra	226	138	56	0.611	24	26	25	0.4425
Nt	86	RaEm	222	136	55	0.613	24	26	25	0.4505
Po	84	RaA	218	134	54	0.615	24	26	25	0.4587
Pb	82	RaB	214	*132*	*53*	*0.617*	*24*	*26*	*25*	*0.4672*
Bi	83	RaC	214	*131*	*53*	*0.612*	*23*	*25*	*24*	*0.4482*
Po	84	RaC′	214	130	53	0.608	22	24	23	0.4300
Pb	82	RaD	210	*128*	*52*	*0.610*	*22*	*24*	*23*	*0.4380*
Bi	83	RaE	210	*127*	*52*	*0.605*	*21*	*23*	*22*	*0.4190*
Po	84	RaF	210	126	52	0.600	20	22	21	0.4000
Pb	82	RaG	206	124	51	0.602	20	22	21	0.4078

Secondary Branch of Uranium Series.

Pb	82	RaB	214	*132*	*53*	*0.617*	*24*	*26*	*25*	*0.4672*
Bi	83	RaC	214	131	53	0.612	23	25	24	0.4482
Tl	81	RaC_2	210	*129*	*52*	0.614_3	*23*	*25*	*24*	*0.4570*
Pb	82	End	210	128	52	0.609_5	22	24	23	0.4380

Table I, D.

Thorium Series in Order of Disintegration.

Th	90	Th	232	142	58	0.612	26	26	26	0.4485
Ra	88	$MsTh_1$	228	*140*	*57*	*0.614*	*26*	*26*	*26*	*0.4562*
Ac	89	$MsTh_2$	228	*139*	*57*	*0.610*	*25*	*25*	*25*	*0.4387*
Th	90	RaTh	228	138	57	0.605	24	24	24	0.4210
Ra	88	ThX	224	136	56	0.607_1	24	24	24	0.4285
Nt	86	ThEm	220	134	55	0.609_1	24	24	24	0.4363
Po	84	ThA	216	132	54	0.611_1	24	24	24	0.4445
Pb	82	ThB	212	*130*	*53*	0.613_2	*24*	*24*	*24*	*0.4527*
Bi	83	ThC	212	*129*	*53*	0.608_6	*23*	*23*	*23*	*0.4343*
Po	84	ThC′	212	128	53	0.603_8	22	22	22	0.4150
Pb	82	PbTh	208	126	52	0.606	22	22	22	0.4230

Secondary Branch of Thorium Series.

Pb	82	ThB	212	*130*	*53*	0.613_2	*24*	*24*	*24*	*0.4527*
Bi	83	ThC	212	129	53	0.608_6	23	23	23	0.4343
Tl	81	ThD′	208	*127*	*52*	0.610_5	*23*	*23*	*23*	*0.4421*
Pb	82	End?	208	126	52	0.606—	22	22	22	0.4230

TABLE I, E.

Actinium Series (Assumed to be Derived from U^2).[a]

											$4(N/P—1/2)$ if from U.
Th	90	UY	230	140	57	0.608_8	24	26	25	0.4350	0.4615
Pa	91	Eka-Ta	230	139	57	0.604_3	23	25	24	0.4172	0.4446
Ac	89	Ac	*226*	*137*	*56*	0.606_2	*23*	*25*	*24*	*0.4248*	*0.4523*
Th	90	RaAc	226	136	56	0.602—	22	24	23	0.4070	0.4350
Ra	88	AcX	222	134	55	0.603_6	22	24	23	0.4144	0.4425
Nt	86	AcEm	218	132	54	0.605^4	22	24	23	0.4220	0.4505
Po	84	AcA	214	130	53	0.607_5	22	24	23	0.4298	0.4587
Pb	82	AcB	*210*	*128*	*52*	0.609_5	*22*	*24*	*23*	*0.4380*	*0.4672*
Bi	83	AcC	210	127	52	0.605	21	23	22	0.4192	0.4482
Po	84	AcC′	210	126	52	0.600	20	22	21	0.4400	0.4300
PbAc	82	AcE	206	124	51	0.602	20	22	21	0.4078	0.4380
Pb′	82	AcD	206	124	51	0.602	20	22	21	0.4078	..

P = no. of positive electrons, N = no. of negative electrons.

[a] E. Q. Adams considers that the atomic weight of lead derived from actinium is 207. If this is the case all of the values for the actinium series should be recalculated.

The cementing electron content is of much more interest (Fig. 2). For the lowest krypton it is 2, for the next 3 higher it is 4, and for the 2 highest it is 6, so if the heavy cementing electron line were to be extended toward the right in Fig. 5, there would be 3 horizontal steps at 2, 4 and 6. This indicates, too, that the step for 2 cementing electrons, extends from argon to krypton, or from atomic number 18 to 36 at least, which is almost equal to the range of the 0 step from helium to calcium. However, as has already been stated, it is extremely likely that one of the isotopes of nickel (No. 28) has a zero cementing electron content, so the extent of the zero step is considerable (equal to about 26). The number of cementing electrons in the lowest 3 xenons is 10, in the next higher is 12, and in the highest it is uncertain. If this xenon 135 is a member of the meta-chlorine series, it contains 12 such electrons and there are only 2 such steps. Here the cementing electrons are only those concerned in cementing on extra α-particles. Whether electrons may be given off from ν or μ groups has not been determined, if not, such electrons should be classed as binding electrons.

Col. E, in Table I, gives the number of *excess* electrons e where this term indicates all of the nuclear negative electrons which are not contained in the α-particles themselves, or

$$e = N - N_{ab} \qquad (13)$$

where N_{ab} is the number of *binding* electrons in the α-particles.

In the helium-thorium series

$$e = c \qquad (14)$$

in the metaneon-uranium series

$$e = W/2 - n + 1 = P/2 - n + 1 \qquad (15)$$

and in the lithium series

$$e = c + 2 = P/2 - n + 3/2. \qquad (16)$$

In Table I the sub-columns marked He include members of the helium-thorium series, those marked U include members of the metaneon-uranium series, *o* indicates that the sub-column relates to atoms of odd, and *e* that it relates to atoms of even atomic number.

Suggested Formulas for the More Abundant Light Atoms.

Formulas for the light atoms which are in agreement with the data of Table I, are given in Table II. These formulas were given in part in an earlier paper in THIS JOURNAL, but it is desirable to reproduce them to indicate minor changes and to correct errors in typesetting.

TABLE II.

Hypothetical Composition of Light Atoms and their Nuclei.

	Formula of nucleus.						Non-nuclear electrons.		
			Lithium series.		Metachlorine series.				
Symbol.	Helium series.	Metaneon series.	*a.*	*b.*	*a.*	*b.*	Inner.	Middle.	Valence or outer.
He.......	α	..	...	...	...	...	e_2	...	..
Li........	..	..	λ	$\alpha\nu$	...	...	e_2	...	e
Be........	$(\alpha_2\eta\beta)$ or $(\eta_2\beta)_2\beta_2$	..	...	...	...	...	e_2	...	e_2
B........	..	..	$\lambda\alpha$	$\alpha_2\nu$	...	...	e_2	...	e_3
C........	α_3	..	...	...	...	...	e_2	...	e_4
N........	..	..	...	$(\alpha_3\mu_2\beta)$	...	...	e_2	...	e_5
O........	α_4	..		...	...	...	e_2	...	e_6
E.........	..	..	$\lambda\alpha_3$	$\alpha_4\nu$	...	...	e_2	...	e_7
Ne_{20}......	α_5	..	...	...	...	...	e_2	e_8	..
Ne_{22}......	..	$\alpha_5\mu$	...	...	...	...	e_2	e_8	..
Na........	..	..	$\lambda\alpha_4$	$\alpha_5\nu$	...	...	e_2	e_8	e
Mg_{24}......	α^6	..	...	...	...	...	e_2	e_8	e_2
Mg_{26}......	..	$(\alpha_6\mu)$	...	...	...	...	e_2	e_8	e_2
Al.........	..	..	$\lambda\alpha_5$	$\alpha_6\nu$	...	...	e_2	e_8	e_3
Si_{28}.......	α_7	..	...	...	...	...	e_2	e_8	e_4
Si_{30}.......	..	$(\alpha_7\mu)$	...	...	...	...	e_2	e_8	e_4
P.........	..	..	$\lambda\alpha_6$	$\alpha_7\nu$	...	...	e_2	e_8	e_5
S.........	α_8	..	...	...	...	...	e_2	e_8	e_6
Cl_{35}.......	..	..	$\lambda\alpha_7$	$\alpha_8\nu$	...	...	e_2	e_8	e_7
Cl_{37}.......	..	..	...	...	$\lambda\alpha_7\mu$	$\alpha_8\nu\mu$	e_2	e_8	e_7
A_{36}.......	α_9	..	...	...	...	...	e_2	$e_8 + e_8$	..
A_{40}.......	$\alpha_{10}\beta_2$	..	...	...	...	...	e_2	$e_8 + e_8$	..
K........	..	..	$\lambda\alpha_8$	$\alpha_9\nu$	...	...	e_2	$e_8 + e_8$	e
Ca.......	α_{10}	..	...	...	...	...	e_2	$e_8 + e_8$	e_2
Sc........	..	..	...	$(\alpha_{11}\eta_2\beta)$	...	...	e_2	$e_8 + e_8$	e_3
Ti........	$\alpha_{12}\beta_2$	..	...	...	...	...	e_2	$e_8 + e_8$	e_4
V........	..	..	$\lambda\alpha_{11}\beta_2$	$\alpha_{12}\nu\beta_2$	...	...	e_2	$e_8 + e_8$	e_5
Cr........	$\alpha_{13}\beta_2$	..	...	...	...	...	e_2	$e_8 + e_8$	e_6
Mn.......	..	..	$\lambda\alpha_{12}\beta_2$	$\alpha_{13}\nu\beta_2$	...	...	e_2	$e_8 + e_8$	e_7
Fe........	$\alpha_{14}\beta_2$	..	...	...	...	...	e_2	$e_8 + e_8$	e_8
Co.......	..	..	$\lambda\alpha_{13}\beta_2$	$\alpha_{14}\nu\beta_2$	...	...	e_2	$e_8 + e_8$	e_9

Columns *a* and *b* give alternative formulas for the respective nuclei, the formulas in Col. *b* being based on the hypothesis that the nucleus of the lithium atom contains one α-particle.

The parentheses around the nuclear formulas for nitrogen and scandium indicate that these nuclei do not belong to the series under which they are placed, while those around the formulas for metamagnesium and metasilicon indicate that these species have not been discovered.

Formulas for the heavy atoms will be found in an earlier paper [1] It should be noted that the formulas given above for A_{40} and Ca, indicate that their atoms are *isomeric*.

The New Periodic System and the Values of $N - \frac{P}{2}$, (equal to $\frac{P}{2} - n$) or the Number of Formula Electrons.

The writer has already presented evidence that there is a periodic variation in the abundance of the elements as a function of the atomic number, and N. F. Hall[2] has shown the same periodicity in the properties of the radioactive elements. Figs. 4 and 5 indicate that there is also a periodic variation of the same general nature, in the values of f, that is in $N - P/2$. Leaving the isotopic atoms out of account, it is apparent that the values of f for the atoms of odd nuclear charge are higher than for those of even number among the atoms from atomic number 8 to 28, that is the peaks occur on the odd numbers. Strangely enough, this relationship is reversed in the average values plotted for elements 31 to 82, for in this range practically all of the peaks occur on the even numbers, and practically all of the troughs on the odd numbers.

The seeming reversal of this relationship seems to be complete in certain ranges. Thus from atomic numbers 44 to 51, and from 59 to 71 (with the possible exception of 61, which has not been discovered) each even number is represented by a peak and each odd number by a trough. If the diagram is examined between atomic numbers 9 and 15 it will be seen that this is, however, just the relationship which also holds in this range if the thorium series atoms are left out of account, and if the uranium or isotopic species of atoms are the only ones considered for the even numbers. Thus the general relations between atomic numbers 44 and 51, and 59 and 71, is just what would be expected if most of the even atomic species in these ranges belong to the uranium, and not to the thorium series, that is if the most abundant isotopes are members of the former series. It is apparent from the large scale plot that in the ranges above specified the mean elevation of the points which represent even, above those which represent the adjacent odd atomic numbers is of about the same magnitude as is found between the uranium and lithium series

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[1] *Phys. Rev.*, 15, 86–89 (1920).

[2] N. F. Hall, THIS JOURNAL, 39, 1616–9 (1917).

among the light atoms. However, that this apparent explanation may not be correct, is indicated by the fact that the same relation is found between thallium (odd), ordinary lead (even), and bismuth. Now it seems probable that ordinary lead is a mixture in almost equal percentages of lead from uranium, so it is possible that the explanation may be found in the electron content of the atoms of odd number.

It is evident that all of the atoms of extremely high relative negative electron content, have even atomic numbers. For example, tellurium (52) particularly, and barium (56), and selenium (34), lie on especially high peaks. The atoms from 31 to 34, and much more markedly the radioactive atoms from radium to uranium, exhibit abnormally large values of f. In fact the f values for all of the radio atoms are high when compared with the rest of the plot, with the exception of radium F, radium-lead, thorium C′, lead from thorium, and uranium.

The electron content is relatively low in elements 39 to 51, and 59 to 63, the latter elements being praseodymium, neodymium, eka-neodymium, samarium, and europium, the former yttrium to antimony. From 34 to 42 the formula electron content is almost constant at about 12, as has been pointed out by Kossel. The slope of the plot from atomic number 29 to 84 is approximately 0.335 electrons per atomic number, or $^1/_3$, or on the average one *pair* of cementing electrons is added for each 3 α additions, while among the radioactive atoms this occurs on the average for 1.66 α changes.

Fig. 5 shows that whenever the atomic weight decreases with increasing atomic number, this is due to a sudden drop in the number of formula electrons, accompanied by a corresponding decrease in the cementing electrons in the nucleus.

An important deduction may be drawn from the cementing electron plot (Fig. 2) which gives the number of cementing electrons between atomic numbers 2 and 27 and between 82 and 92, as calculated from Equations 6 and 7, while from 28 to 81 only Equation 6 is used. *It will be noted that in the range between numbers 32 and 79 every even numbered element is represented by a peak in the curve, while every odd numbered element is represented by a trough,* though between atomic numbers 2 and 27 both the even and the odd numbered elements lie together on 2 horizontal lines, that is 2 lines which indicate a cementing electron content of 0 and 2, respectively. This suggests that while the atomic species represented between numbers 2 and 27 are largely pure, between numbers 32 and 79 either each even or each odd numbered element, or both, ceases to be a single pure species. An inspection of Equation 6 indicates that if an odd numbered element should happen to contain a considerable proportion of helium series atoms, Equation 6 would give too *low* a content of cementing electrons, as the equation is developed on the basis that odd numbered elements consist entirely of members of the lithium series. If the *odd numbered element* should belong entirely to the helium series, then a result too low by 0.5 of a cementing electron would be obtained. On the other hand, the inclusion of either lithium or uranium series atoms in elements of even atomic number increases the result calculated from Equation 6 above the proper value (by 1.5 if the element contains only lithium series, or by 1.0 if it contains only uranium series atoms). It is of interest to note that in the range given the mean elevation of the even over the odd numbered points is 1.1 cementing electrons.

On the Existence of Alpha Particles in Complex Nuclei.

Two recent papers[1] have treated the structure of complex nuclei as if they are aggregates of positive and negative electrons which are not grouped into α-particles or μ or mass 3 particles, but are arranged in what seems to the writer of the paper, the most stable general arrangement for the number of positive and of negative electrons concerned. There are a number of facts and well grounded theories which seem to indicate that the α-particles largely preserve their identity in complex nuclei. Thus (1) α-particles are shot out from such nuclei, (2) the atomic weights and nuclear charges of pure species indicate that complex nuclei are largely built from groups with a weight of 4 and a charge of 2, and (3) while there is a change of weight and presumably of mass equal to 0.77% in the formation of one α-particle from 4 positive and 2 negative electrons, *the change of weight and mass when 3 or more α-particles unite to form a more complex nucleus, is so small that it has not been detected. Thus the α-complexes are extremely less stable than the α-particles itself.* It should be kept in mind, however, that there may be some loss of identity in the union into a complex nucleus, since there may be a partial redistribution of linkages with little change in the total energy, and, therefore, very little packing effect, that is loss or gain of mass.

The Search for Eka-Cesium and Eka-Iodine, and the Question as to the Existence of Elements of Higher Atomic Number than Uranium.

Serious attempts to separate eka-cesium have been made by Richards and Archibald,[2] by Baxter,[3] and by Dennis and Wyckoff.[4] So far as is known to the writer no extensive investigation has been carried out for the purpose of dicovering an element of higher atomic number than uranium. The positive charge on the nucleus of uranium has already a high value (92) and the resultant self-repulsion *may* be so high that if any atoms of higher atomic number have existed on earth at any time, they have already disintegrated so completely that they exist in such small

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[1] Haas, *Physik. Z.*, **18**, 400–2 (1917); Schmidt, *ibid.*, **20**, 448–50 (1919).

[2] *Proc. Am. Acad.*, **38**, 443 (1903).

[3] THIS JOURNAL, **37**, 286 (1915).

[4] *Ibid.*, **42**, 985 (1920).

amounts that they cannot be detected by any ordinary means. That serious endeavors to discover such elements have not been made is probably due to a widespread, but unexpressed idea that such elements, if they exist, would be extremely radioactive, and so would have been detected in radioactive measurements on known materials. It seems worth while, in this connection, to consider certain facts in regard to the atoms of high atomic number.

Ordinary bismuth, which is probably a mixture of isotopes, though it may or may not consist largely of one atomic species, has a nuclear charge equal to 83. Above this there is no very stable species of atoms up to thorium, (90) the most stable isotope of which has an average life of 2.5×10^{10} years. It is also a fact that the most stable isotope of elements of even atomic number, has in general a greater stability than when the atomic number is odd. It would seem that if any such elements exist at all, they would be more likely to belong in the osmium, platinum, mercury, lead, or polonium groups, with possible atomic numbers 94, 96, 98, 100, and 102. Which of these would be the most stable is not indicated by the theory in its present state, though 98 or 100 would be indicated if the series above uranium should be similar to that below it.

With respect to eka-cesium and eka-iodine it should be noted that bismuth (83) has the highest atomic number which is odd with the exception of those atomic species which are descendents of the uranium or of thorium, and that both of the uranium series (radium and actinium series), and the thorium series as well, as now known, omit the atomic numbers 85 (eka-iodine) and 87 (eka-cesium), while both the uranium-actinium and the thorium series include every other atomic number from 82 to 92, inclusive. From this standpoint the discovery of either of these elements involves either the discovery of new branches of these radio series or of a new radio series, or else it involves the pushing upward of the odd numbered series from a nuclear charge of 83 (bismuth) to 85 and 87. The odd numbered descendents of uranium and thorium owe their odd nuclear charge to an odd number of negative nuclear electrons, which, it has been seen, leads to instability. That eka-cesium and eka-iodine are indicated by the Mendeleef periodic system does not show that they exist any more than it shows the existence of atoms with a nuclear charge higher than 92. On the other hand, eka-manganese, dwi-manganese, eka-neodymium, and eka-lutecium have atomic numbers which are small enough to give little reason to suspect their non-existence.

Mutual Electromagnetic Mass, the Relativity Effect, and the Question of a High Frequency Radiation Taken up or Given Off by Atom Nuclei.

According to one of the older theories the disintegration of radio atoms is due to energy absorbed in the form of radiation; in later years the energy utilized has been supposed to be that stored up in the nucleus. The older theory has recently been revived by Perrin. If the atomic weights of the radio elements were known with sufficient accuracy, it should be possible to make a decision between these 2 theories, provided only one of these effects is operative. If the latter theory is considered, it is found that when interpreted in accord with the idea that energy has mass, it indicates that the change of mass, and presumably of atomic weight between uranium and lead, should be greater than the sum of the masses of the α-particles shot off, when the mass of the latter is taken when they are at rest. According to the relativity theory it should be 0.05 g. per gram atom greater in the specific case cited. According to the idea that the energy is absorbed from a penetrating radiation, the difference in the atomic weights need be no more, and from the point of view taken by Perrin, that the reaction is highly endothermal, would be less than the sum of the masses of the α-particles. The present atomic weights indicate a difference greater than that required by the energy storage theory, but this fact does not decide the question, since the accuracy of the atomic weights is at present too low for a definite decision. According to the radiation theory the different atoms of a pure atomic species would differ in mass slightly, according to their energy content, and would have a specially high mass just before they disintegrate. In later paragraphs the data will be discussed from the standpoint of the storage-relativity theory, though the writer is favorably inclined toward the idea that energy may enter and leave the nuclei by the action of some form of radiation.

The decrease in mass in the formation of one gram atom of helium nucleus is equivalent to 6.71×10^{11} calories according to the relativity theory. Earlier papers of the series show that the change of mass which occurs is 0.77%, and that when these α-particles combine with each other there is practically no change of mass. The question which now arises concerns the packing effect in other primary electron groups, such as the ν group (or lithium nucleus), and the μ group. If the atomic weights of lithium, determined by Richards and Willard, and of boron, determined by Smith, are considered as exact, then it is found that the packing effect in both would be abnormally high, amounting to a decrease of mass of 1.62% in the former case, and 1.69% in the latter if isotopes were absent which is improbable. If it is now considered that the lithium nucleus is the primary group of the odd numbered series, and that boron consists of one lithium plus one helium group, and that the packing effect in the latter has its normal value, that is that its weight is 4.00, then it is found that the lithium group in the boron nucleus has been subjected to the extremely large packing effect of 2.18%, while if it is assumed that the boron atom consists of two α-particles and one ν group, the packing effect in the latter, calculated on a similar basis, amounts to 4.11%. The decrease of mass calculated for the apparent ν particle in the *lithium* nucleus is 2.75%. While packing effects of these magnitudes are not at all impossible, they do not seem very probable, when compared with those calculated in cases where the atomic weights are known with more certainty. Unfortunately, for this special problem, the nitrogen nucleus may or may not contain particles of mass 3, though it may be noted that it has the weight of 2 lithium nuclei, and the atomic weight of fluorine is not known with sufficient accuracy for our purpose though it is probably close to 19.00. The atomic weight of sodium is already so large that a small difference in the packing effect in the ν group (or lithium nucleus) contained in it, would not be noticed. However, the atomic weight of the ν group calculated from sodium comes close to 3.00. On the whole it seems probable that the packing effect in the ν group is of about the magnitude as in the α-particle. If the atomic weights 6.94 and 10.9 for these elements are sufficiently exact, which is almost certain it seems very much more reasonable to suppose that both lithium and boron contains small amounts of lighter isotopes, than to assume that such abnormally large packing effects as those cited above are real. According to the general theory presented in this paper, the value of N/P for the less abundant and lighter isotopes of lithium and boron should be 0.5, so the atomic weight of the lighter isotope of lithium should be 6, and that of the lighter isotope of boron should be 10.

If there were no packing effect in the μ group, its atomic weight would be 2.0156, while if this effect is equal to that in the α-particle, it would be 2.00. Since only one μ group occurs in any single atom, so far as can now be determined, and since the atomic weights have been determined accurately only for the heavier members of the μ or uranium series, no error of importance will be made by the use of the latter value.

TABLE III.—ATOMIC WEIGHT OF INTRA-ATOMICALLY COMBINED HELIUM.

In atom of even atomic No.	No. of α-particles.	At. wt.	Atom of odd No.	No. of α-particles.	At. wt.
Carbon	3	4.001	Sodium	5	4.000
Oxygen	4	4.0000	Aluminum	6	4.017
Sulfur	8	4.008	Phosphorus	7	4.003
(Argon)[a]	10	(3.99)	Vanadium	12	4.000
Calcium	10	4.007	Manganese	13	3.995
Titanium	12	4.008	Cobalt	14	3.998
Chromium	13	4.000			
(Iron)[a]	14	3.989			
Thorium	58	4.0026			
Uranium	59	4.0030			
Radium	56	3.9983			
Radio-lead (RaG)	51	4.0014			

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[a] Probably argon contains an isotope of atomic weight 36, and iron of atomic weight 52.

As nearly as is now known, the atomic weight of helium itself is 4.000 (oxygen = 16). The weight of intra-atomically combined helium may be obtained by dividing the atomic weight of any pure atomic species by the number of α-particles contained in its nucleus. In cases where ν or μ groups are also present the weight 3.00 or 2.00 will first be subtracted. The preceding table contains values calculated in this way from the element weights (so-called atomic weights) which have been determined with considerable accuracy for elements which seem to consists mostly of a pure atomic species.

The average of the above results is 4.0013, for the 8 light atoms of even number it is 4.0008, for the 6 light atoms of even number 4.0022, and for the 4 heavy radio atoms 4.0013. Thus the average for the heavy atoms is very close to that for the light atoms.

Discussion of the Atomic Weights on the Basis of the Energy Storage Theory.

The mass equivalent of the heat given off in the disintegration of the radio atoms was calculated by R. Swinne[1] in 1913. Two years later an independent calculation of these values was made for me by W. D. Turner, and his values, which are practically the same as those of Swinne, will be used here. According to these calculations 8 α-changes in the uranium series give an energy change equivalent to 0.0519 g., or 0.0065 g. per α-change. In the thorium series 7 α-changes are equivalent to 0.0534 g. (0.0076 g. per α-change), and 5 disintegrations of the same type in the actinium series, to 0.0401 g. (0.0080 g. per α-change), all calculations being made for a gram molecule. Thus the mass effect per α-disintegration is greatest in the actinium, and least in the uranium series.

If the atomic weight of helium is taken as 4.000, and if it is assumed that all of the α-particles in the uranium nucleus give the same average energy of disintegration as in the radioactive series, then the loss of mass should be 4.000 plus 0.0065 or 4.0065 instead of the 4.0009 g. calculated from the atomic weights of uranium, radium, and radio-lead. In the thorium series the corresponding values are 4.0076 and 4.0023. Thus, on the average, there seems to be a smaller mass effect in the atoms as a whole than that calculated from the radioactive atoms alone.

The atomic weight assigned to thorium by the International Committee is 232.15. The weight of thorium lead should be this value minus 6 × 4.000 and also minus the relativity effect of approximately 0.05 g., or 208.10. That of radium-lead should be 238.175 minus 8 times 4 and also minus approximately 0.05, or 206.12. The lowest determination of the atomic weight of this lead obtained by Hönigschmidt is 206.06, and by Richards, 206.08, an average of 206.07, or a difference of 0.05

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[1] Swinne, *Physik. Z.*, 14, 145 (1913).

from the value calculated above. Hönigschmidt obtained 225.97 for the atomic weight of radium, and after making an allowance for the relativity effect, it is found that the determined difference in the atomic weights of uranium and radium is 0.19 units greater than the calculated deviation. It is, however, possible, as suggested by Piccard, that uranium contains an isotope of higher atomic weight.

It is quite evident from the above calculations that if the radioactive elements were to disintegrate completely into helium, the amount of heat given off per alpha disintegration could not, on the basis of the energy storage theory, continue to be as great as that which is liberated in the different radioactive series. This is just what would be expected, since the heat of disintegration becomes smaller as the period lengthens, that is as the atoms become more stable. It is of importance in this connection that the atomic weights of helium, and of the radioactive elements, should be determined with a considerably greater accuracy, since it is evident that the present atomic weights are not sufficiently accurate to indicate whether the disintegration of the radioactive elements is highly endothermal, as is claimed by Perrin in his radiation theory, or is highly exothermal, as indicated by the ordinary, or energy storage theory,[1] though the discussion given above shows that the most recent atomic weights of thorium and uranium indicate even a greater difference than that calculated by the storage theory, which, insofar as it has any value, is unfavorable to the theory of Perrin, though, on the other hand, the present atomic weights of radium and lead from radium are quite in accord with his theory.

The most important experiment which could be carried out in connection with the relation between the loss of mass and the relativity theory would be to weigh at intervals over a period of many years a carefully sealed and protected sample tube, containing an amount of mesothorium or radium equivalent in activity to possibly 10 g. of radium (or less with a delicate microbalance), so sealed that no α-particles and few β-particles could escape. The amount to be used could be calculated when the sensitivity of the balance and its accuracy have been determined. In this way energy could be allowed to escape in such amounts, that it should be

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[1] Even on the basis of the theory of Perrin it is necessary to assume that the radioactive species of atoms are more unstable than the ordinary atoms, or else that their nuclei absorb more of the penetrating radiation. The relations between the periods of the radioactive elements have been shown in this paper to depend upon the relations between the number of positive and negative electrons in the nucleus, and upon other factors of a similar nature, which seem to indicate that the disintegration is related to the instability of the nucleus, rather than to the amount of energy picked up in the form of radiation. I would like to suggest that it is quite likely that a combination of the 2 theories may be found more in accord with the facts when they are sufficiently determined, than either Perrin's or the ordinary theory alone.

possible to determine its weight by difference. It is probable that this experiment has suggested itself to a number of workers, but the difficulty in the way of its execution is the great initial expense.

The Atomic Weights of Pure Atomic Species are Very Nearly Whole Numbers on the Basis of Oxygen as 16.

It is probable that the atomic weights of the light atoms which consist of only one species would be made more accurate by changing them to whole numbers. The atomic weights of nearly all of the light *elements*, with the exception of those where it is now almost certain that stable isotopes exist, are whole numbers, while from atomic number 28 to 80 they are no closer to whole numbers than they should be by the laws of chance, that is, this is the region of isotopes which are stable. The atomic weights now used for uranium and thorium are closer to a whole number than corresponds to chance, even though both of these elements contain isotopes. However, in this region the stability of one isotope is so much greater than that of the others as to make it so predominant in abundance that both of these elements occur as nearly pure species.

Nickel.

From the standpoint of atom-building nickel is one of the most interesting of all elements with the exception of hydrogen, helium, lithium, and the radioactive elements. Nickel, as is seen in Figs. 2, 3, 4 and 5, has an abnormally low negative-electron content, exceedingly low for its position in the system, and lies just at the beginning of the rapid increase in electron content. It is the first element in which the divisibility of the atomic weight by both 1 and 4 suddenly stops. It is the last of the abundant elements as the atomic number or weight increases, and it undoubtedly is a mixture of isotopes, as are most of the elements of higher atomic number. It should be possible to show the presence of the isotopes, most quickly by the positive ray method, and with much difficulty by diffusion. We are preparing to study the problem and especially the *isotopes of lithium* in this laboratory. Evidently no species of atoms in which the number of cementing electrons per atom is greater than 2 occurs abundantly either in the meteorites or on earth.

Summary.

1. The negative electrons in the nuclei of atoms are largely associated in *pairs*, either as *binding* or *cementing* electrons. The pairs of binding electrons serve to bind together a number of positive electrons into a primary group or particle. The *most abundant by far of all of these is the α-particle*, which consists of 2 negative and 4 positive electrons, and, therefore, has a net positive charge of 2. Its formula is $(\eta_4{}^+\beta_2{}^-)^{++}$, where η^+ is the positive and β^- the negative electron. This α-particle probably makes up about 90 or more % of all known material in the meteorites. A second less

abundant group is the $(\eta_2{}^+\beta_2{}^-)^\circ$ or μ group, which has a zero net charge, and probably makes up more than half of the rest of known material. It is, of course, possible that this may occur only in union with the constituents of an α-particle as $(\eta_6{}^+\beta_4{}^-)^{++}$, or meta-helium, but the former hypothesis has the advantage of greater simplicity, with no loss of usefulness. Thus nearly all of the material which consists of complex nuclei, exists in the form of groups made up of pairs of negative binding electrons, *together with an even number of positive electrons.* Isotopes of higher, differ from those of lower atomic weight by the presence of a single μ group, or of one or two helio groups, or of both a helio and μ group. The term helio group is used to designate an α-particle together with two negative electrons, which may be said to "cement" it to the nucleus of the atom. The above discussion of the abundance relations of the primary electron groups is based on data obtained from the composition of the meteorites and of the earth. Some of the stars and nebulas probably contain large amounts of hydrogen, and in such a case the relations of abundance given could be expected to hold only for the complex nuclei, and not for the positive electron (hydrogen nucleus). Atoms of odd net nuclear charge are relatively rare. They, also, consist mostly of α-particles, but the odd value of the net charge is caused by the presence of one odd numbered ν group $(\eta_3{}^+\beta_2{}^-)^+$ in the nucleus of each atom of odd atomic number. Of the light atoms only beryllium and nitrogen seem to contain an odd number of negative nuclear electrons, and these elements are not abundant. Even among the radioactive nuclei there are only a few which contain an odd number of negative electrons, and they are very unstable.

2. The α-particle may be assumed to be electrically negative in most of its exterior, but to have a net positive charge of 2. Such particles would repel each other at all ordinary and small distances, and would only attract when brought extremely close together in such a way that electrical couples are able to produce a greater attraction than the repulsion due to the net charge. Neither a single positive or a single negative electron can attach itself to such a particle, nor does it seem that 2 such particles will unite, but from 3 to 8, and also 10, but not more than 10 α-particles unite to form a complex nucleus in which the mass is twice the charge, and the ratio of negative to positive electrons is 1 to 2, or 0.5. *This ratio is of great importance in relation to the stability of nuclei.* Eleven positively charged α-particles will not alone unite[1] to form a complex nucleus, since their positive charge, 22, is so large that the attractive action of the α-particles is not able to overcome the repulsive effect of this posi-

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[1] It is likely that this is not strictly true, since it is probable that as many as 14 α-particles unite to form the nucleus of the lightest nickel atom without the inclusion of any negative α-cementing electrons. However, the above statement is true if only the most abundant isotope of each element is considered.

tive charge. *However, more positive α-particles will add on if at the same time the ratio of negative to positive electrons is increased. The ratio is increased by the addition of an α-particle together with 2 cementing electrons,* or what has been called a helio group. This helio group increases the ratio of negative to positive electrons by a sudden jump from 0.5 to 0.55 (approximately). The increased ratio makes it possible for an extra positive α-particle to attach itself, so two α-particles add on in this one step, and in addition 2 cementing electrons. *Thus the function of cementing electrons is to keep the nucleus stable as its self-repulsion, due to its increasing positive charge, increases, by also increasing the relative negative electron content. This causes 2 α-particles to add on, so the atomic weight increases by 8, instead of the normal 4.* More α-particles then add on, decreasing slightly the N/P ratio, until the repulsion of the positive charges again becomes so high that a second increase in the ratio becomes necessary, when a second pair of negative cementing electrons adds on, and the atomic weight again rises with abnormal rapidity. Thus if the atomic number is plotted on the X-axis, and the number of cementing electrons on the Y-axis, the plot consists of a series of horizontal lines, each of which has at its right a vertical rise of 2-cementing electrons, followed by another horizontal line; that is, a series of steps with equal vertical spacing. The N/P ratio plot is somewhat similar, but the steps all slant downward slightly toward the right.

3. The writer shows that 4 series of atoms are now known; the *helium-thorium* series, the *meta-neon-uranium* series, the *lithium-cobalt* series, and the *meta-chlorine* series. The relation of these 4 series to his periodic system is briefly discussed.

4. *The atomic weights of all pure species of atoms are very close to whole numbers when calculated on the basis of oxygen as 16.* This is practically the statement made by Harkins and Wilson in 1915. At that time it was plainly seen that this rule holds for all light atoms, and for the heavy atoms far up in the series, but there was some doubt as to the magnitude of the relativity effect, that is the change of mass due to packing. The atomic weight determinations of Richards and Hönigschmidt show that these atomic weights are either whole numbers, or else very slightly above whole numbers. If the energy given off on disintegration comes from potential energy which remains stored in the nucleus as long as it exists, then it is probable that there is a slight drift away from whole numbers in some parts of the series on account of the mass associated with the energy changes involved, which amounts to about 0.05 g. per gram atom in each radio series, involving 6 or 8 α-changes. If the energy comes from without, as is assumed in the recent theory of Perrin, the loss of mass of the complex atom might be equal to or more probably less than the sum of

the masses of the α-particles ejected, the masses being taken when the α-particles are at rest.

5. Tables are given for the total positive, total negative, α-cementing, excess, and formula, electron content of the nuclei of all known atoms, and the more important relations which are apparent, are pointed out.

6. When the net positive charge on the nucleus of an atom rises higher than 28 it seems probable that the resultant self-repulsion due to the unneutralized positive charge becomes so great that relatively few atoms of this class can be formed. Such atoms are relatively rare and probably do not make up more than one-thousandth of the total material of the earth and the meteorites, though they constitute more than $^2/_3$ of all of the elements, and probably more than $^3/_4$ of the atomic species. In all abundant atoms the ratio $\frac{\text{Total number of negative electrons}}{\text{Total number of positive electrons}}$ is 0.5 or only very slightly above that value. Thus it is 0.5 in oxygen, 0.5 in Si_{28}, 0.536 in Fe_{56}, 0.5 in Mg_{24}, 0.5 in sulfur, 0.5 in Ca_{40}, and 0.522 in $Ni_{m58.68}$, the 7 most abundant atomic species. Here m58.68 indicates that all of the isotopes of nickel, with a mean atomic weight of 58.68, are included. The atoms become rare as soon as the cementing electron content of the nucleus rises above 2, that is it seems probable that no number of cementing electrons is able to impart stability of a high order to a nucleus whose positive charge is greater than 28.

7. In general nuclei which contain an odd number of positive electrons are rare, and those which contain an odd number of negative electrons are much rarer still. This means that atoms of odd nuclear charge are rare, and when they exist the odd number of the charge is almost always due to an odd number of positive, not of negative, electrons.

8. The peculiar relations of nickel are pointed out. It is undoubtedly a mixture of isotopes. Nickel has an extremely low mean negative electron content in its nucleus, and, therefore, has a low atomic weight for its position in the system.

9. Nitrogen, and also scandium if its most recent atomic weight determination is correct, are not members of any of the 4 ordinary series of atoms listed above.

10. Nickel, potassium, calcium and iodine, have an abnormally low nuclear content of negative electrons, while the number of such electrons in argon, tellurium, barium, and to some extent in selenium, is relatively very high. It will be noted that most of these abnormally high and low values lie in close proximity to the 3 reversals in the atomic weight increase with increasing atomic number.

11. While there are only 92 elements, in the limited sense in which the term is now used, in the ordinary system, there are probably 300 or more different species of atoms, which, in a broader sense of the term, are truly

elements. It is obvious that the word element is now used in a very arbitrary sense to denote all atoms in whose nuclei the difference $P - N$ (where P stands for the number of positive, and N, the number of negative electrons) has the same value.

12. The plot of the cementing electron content of atom nuclei, indicates that nearly all of the elements from atomic number 32 (Ge) up to 79 (Au), are mixtures of isotopes, and that in general there are probably several isotopes present in considerable percentages in each element. Other facts indicate strongly that the region in which isotopes become extremely prominent begins with atomic number 28 (nickel).

13. The atomic weights of the light elements are mostly whole numbers on the oxygen basis, and in the case of the elements of even number are divisible by 4. This indicates, according to the theory of the earlier papers of this series, that isotopes do not occur in *high percentages* in any of these elements, with the exception of neon, chlorine, magnesium and silicon (possibly in aluminum). From atomic numbers 28 to 80 the atomic numbers are no closer to whole numbers, and the atomic weights of the even numbered elements are no more nearly divisible by 4 than corresponds to the laws of chance. Among the radioactive elements, however, both the approximation to whole numbers, and divisibility by 4 in the case of the thorium series, again become prominent.[1] In other words, the general relations found earlier by the writer hold both for the light and for the very heavy atoms, but not for those in the intermediate range. This is easy to understand from the viewpoint taken in the earlier papers. The light atoms are made up from relatively few α- and other particles, and not many stable arrangements could be expected under these conditions. As the number of particles in the nucleus increases, the number of possible arrangements increases, and in the region of stable atoms the number of stable arrangements increases and becomes large between atomic numbers 28 and 84. However, in the region of the very heavy atoms, while there are many possible arrangements, even the most stable of these is already unstable, so it could not be expected that the less stable atoms would have such long period of existence as to give them prominence by their abundance. Thus, among the radioactive atoms, in spite of the presence of numerous isotopes, there is seldom more than one species of atoms in an element which has sufficient stability to be largely represented in the atomic weight.

14. The atomic weights of lithium and boron indicate the existence of lighter isotopes, and the theory indicates that in them the ratio N/P should be 0.5, so the atomic weight of the lighter lithium (present probably to the extent of about 6% in lithium) should be 6, while that of boron should be 10. Also an isotope of iron, presumably of atomic weight 52;

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[1] A table illustrating these facts is presented in the *Phys. Rev.*, **15**, 81 (1920).

a higher isotope of calcium, possibly atomic weight 44; and a higher isotope of potassium, are all indicated, in addition to several isotopes of nickel as mentioned above, *presumably* with atomic weights 56, 60, and *possibly* other values including 58.

15. Attention is called to the suggestion made in an earlier paper in the *Physical Review* that atoms of zero atomic number may exist and be of importance in atom building. Such atoms might have masses 4, 3, 2, and 1, and possibly other values, and they would contain no non-nuclear electrons, so they would have no chemical, and almost none of the ordinary physical properties, aside from mass.

16. The general theory of nuclear structure presented in the earlier papers of this series indicates, as has been pointed out by N. F. Hall,[1] that *in general the number of isotopes present in elements of even atomic number should be considerably greater than in elements of odd atomic number.* According to the theory presented in the present paper it is probable that this relation may not hold true for atoms of low atomic number, but it may be expected to be valid beyond atomic number 26 and possibly beginning with still lower atomic numbers. It is of interest to note in this connection that, *since this paper was submitted* Aston has found 6 isotopes of krypton and 5 of xenon, elements of even number, but only 2 for bromine (79 and. 81) and only one atomic species for arsenic, both elements of odd atomic number.

17. It is of interest to note that the formula for the atomic weights presented 5 years ago does not give the atomic weights of all of the isotopes of an element, but it picks out that of the most abundant isotope. It does this in the range of the light atoms (atomic numbers up to 27) at least. Thus for neon, with atomic weights 20, 22, and probably 21, it designates the species of atomic weight 20, which makes up about 90% of the element neon. The formula is

$$W = 2(n + c) + {}^{1}/_{2} + {}^{1}/_{2}(-1)^{n-1}.$$

18. The paper states that the *element chlorine has been separated into isotopes of separate atomic species* by Mr. C. E. Broeker and the writer. We suggested in *Nature* that in addition to Cl_{35} and Cl_{37}, there seemed to be some indication of another chlorine of higher atomic weight. The atomic weight of this last chlorine was later found by Aston to be 39, but the percentage in ordinary chlorine is very small. In the experimental investigation Dr. W. D. Turner did most of the early, and Mr. T. H. Liggett some of the later work. The separate publication of this work has been delayed by the death of Mr. Broeker.

19. The whole number relation of the atomic weights when oxygen as 16 is taken as a basis, may be stated in the form that in all known complex nuclei the positive electron has the weight 1.000 ± 0.001, while the free positive

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[1] *Loc. cit.*

electron has the mass 1.007, very nearly. This might be stated more accurately by giving the weight of the average electron pair, positive plus negative electron, as 1.000 ± 0.001 in any complex atom, but as 1.0077 in hydrogen itself where the positive electron is *free* and not bound. The constancy in the packing effect may be a characteristic of the positive and negative electrons themselves.

20. In considering the foregoing paper it should be realized that it develops some *very general relations*, such as those involving the ratio of negative to positive electrons in the nucleus (N/P), which are very likely to prove entirely valid, and that it gives very *special details*. such as formulas for nuclei, etc., which are not expected to fit the facts in every special case, but are only intended to illustrate the general relations and to give a specific theory to which the facts as they are discovered may be related. The nucleus is so complex that it is possible that nuclei of atoms of the same element may have a different composition with reference to the particles of masses 4, 3, 2, and 1, even when their atomic weights are the same. It is quite likely that the relations concerning the ratio N/P are much more general than those relating to the specific formulas. Thus the important feature about the oxygen nucleus *may* be that in it the ratio N/P is 0.5, and not so much that it consists of 4 α- particles.

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[CONTRIBUTION FROM THE HENRY PHIPPS INSTITUTE, UNIVERSITY OF PENNSYLVANIA.]

THE X-RAY FLUORESCENCE OF CERTAIN ORGANIC COMPOUNDS.

BY H. S. NEWCOMER.

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In a previous[1] paper I pointed out that it might in the future become possible to make use, biologically, of a localized transformation of penetrative radiant energy with very feeble abiotic properties (X-ray), into a much more active, although less penetrative type of ray (ultra-violet) through fluorescent substances as intermediaries. It was shown, in fact, that fluorite under the influence of the X-ray emitted bactericidal rays. Progress from this point demanding that we have for use in place of the insoluble fluorite a similarly active soluble substance, a survey was made of a large number of substances, for the most part organic chemicals, to see which of them might fluoresce under the influence of the X-ray.

Kunz and Baskerville[2] have examined the action of radiation on 13,000 minerals in the collection of the American Museum of Natural History. Their most noteworthy observations were the variability in like minerals

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[1] H. S. Newcomer, *J. Exp. Med.*, **26**, 675 (1917).

[2] G. F. Kunz and Chas. Baskerville, *Science*, **18**, 769 (1903).

from the same source. There would seem to be 2 types of fluorescence, a specific type characteristic of the substance such as is found in the case of fluorite and a nonspecific type variably associated with the substance as in the case of willemite, hyalite, gypsum, etc. Others publishing literature on X-ray fluorescence are Edison,[1] Burbank,[2] Arnold,[3] and Precht,[4] Wiedemann and Schmidt.[5]

Pohl[6] has determined the amount of energy transformed into fluorescent light by barium platinocyanide and by calcium wolframite and finds it to be 3.7%. McIlkney[7] states that calcium tungstate crystals emit light whose wave length is further toward the ultra-violet the smaller are the crystals. The range is given as from the yellow to the ultra-violet border.

Our examination included both visual and photographic observations. The purpose of the latter was to detect any invisible ultra-violet radiation which might be developed, the ordinary photographic plate being uniformly sensitive from about 5000 Ångstrom units (blue-green), down to 2200 Ångstrom units, quite far out into the ultra-violet. The X-rays fell horizontally on the compounds arranged 6 at a time in separate black pasteboard compartments directly beneath a Graflex plate; the plate being protected from the action of the X-rays by a $^1/_2$-inch block of lead in its plane. The exposures were for 2 minutes. The solid compounds were placed in black paper containers, the liquids in 30 cc. "Nonsol" beakers, the photographic effect of whose fluorescence was practically nil.

In order to determine the presence of visible fluorescence the eyes were first thoroughly dark-accommodated and kept so, assistants doing all the handling of the materials. The solids were placed on black sheets of paper, the liquids in paraffined paper cups, the fluorescence of which was barely within the limits of visibility.

The X-ray tube was entirely enclosed. The rays passed through, besides the glass of the tube itself, a layer of black paper. All of the compounds were also examined with the additional interposition of a one mm. aluminum screen. The effect of the screen was to reduce slightly the intensity of the fluorescence observed.

The machine was a Victor fluoroscopic outfit of 1500 watts capacity, having a Coolidge fine focus tube. The distance of the compound from the anticathode was 22 cm. The machine was run at about a maximum

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[1] Thos. Edison, *Elec. Rev.*, 165, 53 (1896).

[2] J. J. Burbank, *Amer. J. Sci.*, 155, 53 (1898).

[3] W. Arnold, *Ann. physik. Chem.* n. f., 61, 313 (1897).

[4] J. Precht, *ibid.*, 61, 330 (1897).

[5] E. Wiedemann and G. C. Schmidt, *ibid.*, 56, 201 (1895).

[6] R. Pohl, "Die Physik der Röntgenstrahlen," Braunschweig, 1912, 147.

[7] P. C. McIlkney, *Elec. World*, 28, 664 (1896).

continuous load, the energy delivered varying slightly from time to time, but being maintained so as to give a maximum illumination of the fluorescing screen of the outfit, the existence of such a maximum being frequently checked. As the machine did not have good meters the exact conditions were not known, but the current across the tube was about 15 milliamperes and the potential about 55,000 volts, these figures being checked by later measurements in which the conditions of the experiment were reproduced.

There is good reason for believing that maximum fluorescence is produced by a maximum delivery of X-ray energy, or that within a considerable range the fluorescence is independent of the quality of the X-rays and proportional to the energy alone. Several experiments were set up, using a much larger machine and a new Coolidge tube in which a fluorescent screen, indeed several screens, were radiated without the interposition of anything between the screen surface and the X-ray tube except black paper, selective absorption of the softer rays, especially by aluminum, being avoided. Using various potentials across the tube the current was so adjusted as to produce a certain definite faint fluorescence in the screen, the intensity of the fluorescence being taken such as to make variations most perceptible. The current was read on a milliammeter and the voltage computed from the alternative spark gap between 1.9 mm. polished steel balls.[1,2] It was found that with the intensity of the fluorescence judged constant the product of the milliamperage and the square of the potential was approximately constant, that is, the energy was constant. The potential range was from about 10,000 to 70,000 volts. Within some such range the fluorescence is thus independent of the X-ray wave length and dependent on the energy alone. So far as I can determine the quality of the fluorescence, its color, is dependent on the substance alone and not on the quality of the X-rays.

The compounds used were not specially purified. The larger number of the organic compounds were imported commercial samples. Some were prepared in the laboratory in the course of the synthesis of dyes. The dyes were mostly of German origin.

It is well known that slight impurities may determine the character of fluorescence. Fluorescence is, however, not necessarily associated with the presence of impurities. Of the compounds listed in Table II only the fluorescence of the amino acids seems to have been due to the presence of impurities. In general, compounds of different origin and occasionally even of different appearance behaved alike under the X-rays. Occasionally small particles of presumably foreign material were observed as brightly shining specks in an inert material.

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[1] F. E. Fowle, *Smithsonian Inst. Pub.*, 63, 2269 (1918), No. 6.

[2] G. W. C. Kaye and T. H. Laby, "Tables of Physical and Chemical Constants and some Mathematical Functions," London, 1916.

In recording the visual effect produced by the fluorescence it was convenient to take 1+ as the minimum of light that could be seen with certainty and 8+, corresponding to the luminosity of the several diamonds which were tried, as the maximum luminosity observed. It was found possible to recognize differences repeatedly in this scale. It was, of course, necessary to consider only the surface brightness of the substance and not the total quantity of light which a large body might emit. The recording of visual intensity is somewhat unsatisfactory because its apparent amount is so closely connected with its color. The dark-accommodated eye is most sensitive to light of wave length about 5400 Ångstrom units (green). Its sensitivity varies much with the color and in its region of maximum sensitivity it can detect light many times fainter than that in any region necessary to affect the photographic plate.

All of the compounds which affected the photographic plate were studied spectrographically. They were placed in paste-board containers before a 3 mm. slit of a quartz spectrograph (size C, Adam Hilger), and X-rayed for 2 hours. Eastman Graflex plates were used. Allowing for the distortion due to the wide slit, Table I gives the wave lengths and general characteristics of the fluorescent light so analyzed.

The result of the survey is to show that many organic compounds, whether solid or liquid, fluoresce under the X-ray. This fluorescence lies more commonly in the violet, blue and green parts of the spectrum. It is rarely sufficiently strong to affect a photographic plate. It is often at the violet-ultra-violet border. It seems probable that in approaching the far ultra-violet fluorescence becomes less common. A set up to determine the existence of a fluorescence of wave length appreciably less than 2000 Ångstrom units would be extraordinarily difficult and tedious to execute. Fluorescence is again common in the region of the X-ray spectrum.

As a rule liquids, amorphous colored substances (dyes) and substances in solution, when they are fluorescent, are feebly so and the conditions as to the observation must be rigid, particularly in respect to darkness and accommodation. Solutions in water of fluorescing solids have in some instances been tried. These solutions have been faintly fluorescent. The faintness is in part accounted for by the dilution of the material. It does not seem to be proportional to the dilution, but no extended study has been made of this question. Amorphous colored compounds seem to be distinctly less fluorescent than closely related but distinctly crystalline substances. There are, however, many colorless amorphous substances which fluoresce brightly. Most of them are inorganic compounds, in fact the most brightly fluorescing compounds are inorganic Many of those substances which give off bright and often distinctly colored light when subjected to ultra-violet radiation give off light just as strongly under the influence of X-rays. The ordinary luminous watch is a good example. It is interesting that the air is very faintly fluorescent under the action of X-rays. Certain compounds were found to be distinctly phosphorescent.

The results of this work when assembled are apparently not susceptible of rational classification based on chemical relationships. They are, therefore, arranged in two tables, II and III, giving the visible fluorescence observed.

Sodium bromide is the only substance found which emits rays of wave lengths which we know to be bactericidally active (below 2800 Ångstrom units). Of organic compounds certain phenols and other benzene derivatives approach this most closely. Visible fluorescence of considerable intensity without effect on the photographic plate was found quite commonly among derivatives of benzol, particularly benzoic acid and its relatives and among the naphthalene derivatives.

TABLE I.

Substances Affecting the Photographic Plate.

Compound.	Wave length of the fluorescence in Ångstrom units.	Visible fluorescence.	Intensity and the position of the maxima and minima.
Potassium iodide	4400–4750	Moderate	Peak at 4550, very faint.
Potassium bromide	4200–4900	Bright	Peak at 4650, faint.
Sodium bromide	2400–5000	Bright	Strong, extends beyond these limits in both directions. Broad region of slightly diminished intensity at 4000.
Strontium salicylate	3950–4900	Bright	Symmetrical, fairly strong
Benzoic acid	2950–5000	Moderate	Not strong, region of diminished intensity at 3900.
p-Sulfone-amine-benzoic acid	2950–3500	Bright	Peak at 3200, faint.
Phenol	2960–5000	Moderate	Strong, peaks at 3080 and at 4850. Broad region of diminised intensity at 3500.
p-Amidophenol hydrochloride	2950–3350	Moderate	Not strong, peak at 3050.
Diphenyl	3450–4500	Bright	Flat even distribution, fairly strong.
Naphthalene	3300–4500	Moderate	Strong, peak at 3460.
β-Naphthalene sodium sulfonate	3300–4900	Bright	Broad peak at 3900, fairly strong.
β-Naphthalene sodium sulfonate, purified crystals	3300–5000	Bright	Peak at 3500 sloping gradually to the visible, fairly strong.
Naphthalene calcium disulfonate	3700–4500	Moderate	Faint.
Sodium naphthionate	4100–4700	Bright	Faint.
2,6-β-Naphthol ammonium sulfonate	3700–5000	Bright	Not strong, even.

NOTE.—It is possible that of the other substances listed in Table II there is also a photographic effect from *o*-hydroxybenzoic acid; sodium *o*-hydroxybenzoate; *o*-aminobenzoic acid; benzidine and hexamethylene tetramine triguaiacol.

TABLE II.[1]

The Visible Fluorescence of Organic Compounds.

Substance.	Visibility.
acetamide	0
acetanilide	3
methyl-acetanilide	2
acetone*	3
acridine	4
phenyl-acridine	7
alanine	0
phenyl-alanine	2
phenyl-alanine (from casein)	3
phenyl-alanine hydrochloride	2
sodium alizarin sulfonate	0
aminoid peptone (amino acid N = 60%) beef	0
aminoid peptone (amino acid N = 50%) casein	2
aminoids (biuret free) casein	0
aminoids (biuret free) beef	0
amino acid still-residue	1
diamino-stibene	0
amyl alcohol*	1
iso-amyl iodide*	0
aniline*	0
diethyl-aniline*	2
dimethyl-aniline*	6
iodo-aniline	0
m-iodo-aniline*	0
p-iodo-aniline*	0
m-nitro-aniline	0
p-nitro-aniline*	1
p-nitroso-dimethyl-aniline	0
anthracene	8
dibromo-anthracene	7
anthraquinone	2
anthraquinone sodium sulfonate	4
anthraquinone monosodium sulfonate	1
asparagine	0
benzene*	3
p-amino-azobenzene	0
amino-azobenzene hydrochloride	0
diamino-azobenzene hydrochloride	0
dimethyl-amino-azobenzene*	0
p-dimethyl-amino-azobenzene *o*-carboxylic acid (methyl red)	0
amino-azobenzene disulfonic acid	0
hydrazo-benzene	0
diazo-aminobenzene	0
bromobenzene*	2
o-bromo-nitrobenzene	2
ethyl benzene	0
iodobenzene*	2
iodosobenzene-*p*-sulfonic acid	4
benzene ethylsulfonate	0
benzene-*m*-sodium disulfonate	8 P
benzophenone	7
benzil	6
benzyl alcohol*	0
benzyl aniline	2
benzyl chloride*	1
benzyl cyanide*	3
benzyl ethyl ether*	2
benzoyl acetone	2
benzonitrile*	3
benzoyl thymol*	1
benzidine	6
benzidine C	1
benzidine 2 H acid	0
benzidine poly-iodo-acetate	0
benzidine sulfone	1
benzidine sulfone 2 R salt	0
benzidine sulfone mono-sulfonic acid	0
benzidine sulfone disulfonic acid	0
benzidine mono-sulfonic acid 2 H salt	0
benzidine mono-sulfonic acid 2 R salt	0
benzidine mono-sulfonic acid NH_2R salt	0
benzidine trisulfonic acid	3
diaceto-benzidine	0
m-diamino-benzidine hydrochloride	1
1-iodobenzidine hydrochloride	2
2-iodobenzidine hydrochloride	2
4-iodobenzidine hydrochloride	0
benzamidine hydrochloride	7 P
hydrobenzoin	4 P
benzoic acid	5 P
o-aminobenzoic acid	5 P

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[1] The figures 0 to 8 under visibility indicate the intensity of the fluorescence. P stands for distinct phosphorescence. Liquids are indicated by an asterisk *.

TABLE II (*continued*).

Substance.	Visibility.
m-aminobenzoic acid	0
p-aminobenzoic acid	0
o-chlorobenzoic acid	5 P
o-hydroxybenzoic acid (salicylic acid)	8
m-hydroxybenzoic acid	1
p-hydroxybenzoic acid	5 P
1,2,5-homohydroxybenzoic acid	0
1,2,4-dihydroxybenzoic acid (β-resorcylic acid)	6
iodo-hydroxybenzoic acid	0
methyl-*o*-hydroxybenzoic acid ester	8
phenyl-*o*-hydroxybenzoic acid ester	6
sodium-*o*-hydroxybenzoate	3
o-iodobenzoic acid	4
o- and *p*-iodobenzoic acid	3
iodosobenzoic acid	0
o-nitrobenzoic acid	0
p-nitrobenzoic acid	0
1,3,5-dinitrobenzoic acid	2
p-sulfone amine benzoic acid	6
sodium benzoate	5
benzaldehyde*	0
p-amino-benzaldehyde	0
hydroxy-benzaldehyde	0
1,2,4-dihydroxy-benzaldehyde (β-resorcyl-aldehyde)	2
1,2-hydroxy-5-bromo-benzaldehyde	8
bromal hydrate	0
bromobutyril bromide*	1
camphor	4
calcium camphor sulfonate	2
carbon tetrachloride*	3
chloroform*	2
cholesterol	0
cinchonidine	4
isocinnoline*	3
creosol*	2
o-cresol*	0
m-cresol*	0
p-cresol	2
tricresol *	1
cumene	0
cyanacetic acid	0
elaidic acid	0
ethyl alcohol*	0
ethylamine hydro-iodide	0
ethylene bromide*	2
ethylene chloride*	1
glutamic acid	7
glutamic acid	2
glutamic acid	0
glutamic acid hydrochloride	0
glycerol*	0
glycine anhydride	3
glycine anhydride	0
glycylglicine hydrochloride	0
glycylglicine	5
glycine ester hydrochloride	1
glycine ester hydrochloride	0
glycine ethyl ester hydrochloride	0
phenyl-glycine	0
dibromo-guaiacol	5
dibromo-*o*-guaiacol potassium sulfonate	0
iodoguaiacol sodium sulfonate	0
hexamethylene-etramine triguaiacol	5 P
H acid	1
dichlorohydrin*	1
hydroquinone	4
hydroxy-hydroquinone	0
dibromo-thymoquinone	0
iodoform	0
leucine	0
leucine 60–100	0
leucine 100–130	0
leucine 130–150	0
residue from leucine purification	1
mercury ethyl	0
methyl alcohol*	0
naphthalene	4
naphthylene-1,2-diamine	1
naphthylene-1,2-diamine hydrochloride	0
naphthylene-1,5-diamine	0
naphthalene boric acid	0
bromo-naphthalene*	5
α-methyl-naphthalene*	7
β-methyl-naphthalene*	5
1,5-dinitro-naphthalene	0
1,8-dinitro-naphthalene	0
α-naphthalene sulfochloride	2
β-naphthalene sulfochloride	1
α-naphthalene sulfonic acid	5
β-naphthalene sulfonic acid	6
β-naphthalene sodium sulfonate	6

TABLE II (*continued*).

Substance.	Visibility.
β-naphthylene sodium sulfonate (Witt method)	7
naphthalene disulfonic acid	5
naphthalene calcium disulfonate	5
1,8,3,6-dihydroxy-naphthalene sodium disulfonate (chromotropic acid chromogen-1)	3
naphthalene sodium trisulfonate (crude)	4
α-naphthol	4
β-naphthol	2
β-naphthol	0
1,4-α-naphthol monosulfonic acid (crude) (Neville and Winther's acid)	2
1,5-α-naphthol monosulfonic acid (crude)	1
2,6-β-naphthol ammonium sulfonate	6
1,4,8-α-naphthol disulfonic acid (crude) (Schollkopf's acid)	0
1,3,8-α-naphthol disulfonic acid (crude)	4
β-naphthol disulfonic acid	1
2,6,8-β-naphthol disulfonic acid, G acid (crude)	6
2,3,6-β-naphthol disulfonic acid, R acid	6
2,6,8-β-amino-naphthol sulfonic acid (crude)	4
1,8,3,6-amino-naphthol sodium disulfonate H (crude)	0
1,8,4,6-amino-naphthol sodium disulfonate K (crude)	1
α-naphtho-cinnoline	5
α-naphthonitrile*	4
β-naphthonitrile	6
β-naphthoquinone monosulfonic acid	0
naphtho-resorcinol	0
α-naphthyl salicylic acid	5
α-naphthylamine	4
α-naphthylamine hydrochloride	4
β-naphthylamine	2
β-naphthylamine chloride	3
dimethyl-α-naphthylamine*	6
phenyl-α-naphthylamine	7
phenyl-β-naphthylamine	7
2,7-naphthylamine sulfonic acid (crude) (Delta acid) (F acid)	4
1,5-α-naphthylamine sulfonic acid (crude) (Laurent's acid)	0
2,6-β-naphthylamine sulfonic acid (crude) (Bronner's acid)	4
2,8-β-naphthylamine sulfonic acid (crude)	6
2,3,6-β-naphthylamine disulfonic acid (crude) (amino R acid)	4
2,6,8-β-naphthylamine disulfonic acid (crude) (amino G acid)	6
naphthionic acid	1
hydroxy-naphthionic acid	4
sodium naphthionate	8
α-aceto-naphthalide	4
β-aceto-naphthalide	6
benzoyl-α-naphthalide	4
acenaphthene	6
p-nitro-anisole	0
phenacetine	4
phenacetolin	0
phenanthraquinone	1
phenanthrene	7
phenetole*	1
p-phenetole sulfonate	5 P
dibromo-phenetole-4-sulfonic acid	0
p-isobutyro-phenetidine	0
phenol	4
phenol (in water 72%)*	3
phenol (in water 8%)*	1
m-aminophenol	0
p-aminophenol hydrochloride	4
p-bromophenol sulfonic acid	1
p-dibromophenol sulfonic acid	0
tribromophenol	5
o-chlorophenol sulfonic acid	3
chloro-nitrophenol	0
2,6-dichloro-phenol-4-sulfonic acid	5
p-iodophenol	0
di-iodophenol-4-sulfonic acid	0
di-iodophenol iodide	0
o-nitrophenol	0
p-nitrophenol	0
o-nitrophenol, condensed with HgO	0
o-nitro-chlorophenol condensed with HgO	0
phenolphthalein	0
diphenyl	6
di-iodo-diphenyl	0
diphenyl-iodo-iodide	0

TABLE II (*continued*).

Substance.	Visibility.
diphenyl carbonate	4 P
diphenylamine	5 P
diphenylamine hydrochloride	1
methyl-diphenylamine* (crude)	7
1-phenyl-3-methyl-5-pyrazolone	0
3-phenyl-5-chloropyrazole	4
hydroxyphenyl mercury acetate	0
diamino-diphenyl-thio-urea	0
p-phenylene-diamine	5
p-aceto-phenylene-diamine	2
phenylene - diamino - azo - *o* - toluidine	0
p-phenylhydrazine sulfonic acid	0
p-amino-acetophenone	1
cinnamylidene-acetophenone	3
pinene*	0
α-bromo-propionic acid*	0
iodo-propionic acid	1
bromo-propionyl chloride*	0
pyridine*	0
pyridine hydrochloride*	1
pyrogallol-dimethyl ether barium sulfonate	3
pyrogallol-trimethyl ether barium sulfonate	3
bromo-pyrogallol-dimethyl ether	6
bromo-pyrogallol-trimethyl ether	6
bromo-pyrogallol-dimethyl sulfonic acid	3
quinine hydrochloride	3
quinine sulfate	2
quinoline*	0
o-hydroxy-quinoline	0
resorcinol	4 P
resorcinol dimethyl ether*	0
tribromo-resorcinol	0
di-iodo-resorcinol	0
tri-iodo-resorcinol	0
terpine hydrate	0
theobromine	6 P
thymol	0
toluene*	3
p-bromotoluene*	2
dinitrotoluene*	0
o-nitro-toluene sodium sulfonate	1
tyrosine	1
tyrosine	0
tyrosine and cystine	0
xylene*	4
o-xylene*	3
m-xylene*	2
1,3-xylenol-4*	4

TABLE III.[1]

The Visible Fluorescence of Dyes.

Substance.	Visibility.
acridine	3
acridine orange	0
phenyl acridine	6
ethyl red	0
alizarine dry	0
aniline blue	1
anthracene blue	0
acid anthracene brown R	0
anthracene red	1
anthracene yellow G	2
auramine	5
aurantia	0
azo blue	3
azo-eosin	0
benzo-azurine	5
benzo-azurine G	1
benzo-azurine 3 G	2
benzo black blue 5 G	1
benzo blue 3 B	0
4 benzo blue	0
benzo brown G	0
benzo fast blue R	0
benzo fast pink 2 BL	4
benzo fast scarlet 4 BS	0
benzo fast yellow 5 GL	0
benzo olive	4
benzo purpurin	0
benzo purpurin 4 B	0
benzo purpurin 6 B	0
benzo purpurin 10 B	0
benzo sky blue	5
bismarck brown	0
bitter almond oil green	0
bordeaux G	0
brazilin	0
brilliant cresyl blue	0

[1] The figures 0 to 8 under visibility indicate the intensity of the fluorescence. No dye fluoresced brightly and none was noticeably phosphorescent.

Table III (*continued*).

Substance.	Visibility.	Substance.	Visibility.
carminic acid	0	naphthamine blue BXG	0
quinoline yellow	3	naphthamine blue BXR	0
quinoline yellow spirit	1	naphthamine blue JE	0
quinoline red	0	naphthamine blue 3 R	0
chloro-fuchsin	0	naphthamine blue 3 RE	0
chromogen	4	naphthamine brilliant blue B	0
chrysamine G	0	naphthamine brilliant blue BW	0
chrysoidine	0	naphthamine brilliant blue BWO	0
congo red	0	naphthamine brilliant blue G	0
coralline	0	naphthamine brown 8 B	0
coralline alcohol soluble	0	naphthamine brown GX	0
coralline water soluble	0	naphthamine brown 4 G extra	0
crocein	1	naphthamine brown H	0
crystal violet	0	naphthamine brown RB	0
cyanine	0	naphthamine deep black HW	0
diamond black	1	naphthamine direct black C	0
eosin w.	1	naphthamine direct black EK	0
erythrosine	0	naphthamine direct black O	0
fluorescein	0	naphthamine direct black RWK	0
fuchsin f. bac.	0	naphthamine direct brown 2 R	0
gentian violet BP	0	naphthamine fast black KS	0
hematoxylin	0	naphthamine fast black SDE	0
hemalaun dry	0	naphthamine fast black SE	0
hematein	0	naphthamine fast black VE	0
indigo carmine	0	naphthamine fast bordeaux BG	0
iodo-methylene blue	0	naphthamine fast scarlet B	0
iodo-eosine	0	naphthamine fast scarlet R	0
iodine green	0	naphthamine green A	0
malachite green	0	naphthamine green AB	0
methylene blue	0	naphthamine green AG	0
methylene blue 2 B extra	0	naphthamine green B	0
methyl eosine	0	naphthamine green TE	0
methyl orange	0	naphthamine orange 2 R	0
methyl violet	0	naphthamine red H	0
naphthalene red	0	naphthamine scarlet B	0
naphthamine black BN	0	naphthamine violet BE	0
naphthamine black BNN	0	naphthamine violet N	0
naphthamine black GE	0		
naphthamine black H	3	1,2-naphthoquinone-4,6-sodium disulfonate	0
naphthamine black HRE	3		
naphthamine black 2 RE	0	1,2-naphthoquinone-4-sodium sulfonate	0
naphthamine black 3 RE	0	naphthol yellow S	0
naphthamine black 4 RE	0	naphthol green	0
naphthamine black RGE	3	naphthol orange	0
naphthamine blue	0	naphthylamine black 10 B	0
naphthamine blue 7 B	0	naphthylamine black BOO	0
naphthamine blue 12 B	0	naphthylamine black NR	1
naphthamine blue BE	0	neutral red	0
naphthamine blue 2 BL	0	nigrosine base	0
naphthamine blue 2 BX	0	nile blue sulfate	0

TABLE III (*continued*).

Substance.	Visibility.	Substance.	Visibility
orange G	0	rubin	0
orcein	0	safranine (alcohol)	0
phloxin red	0	scarlet red	0
phosphin 3 R	0	solid green	0
ponceau PR	0	sudan III	0
pyronine	0	tropaeolin	0
rapid filter yellow	0	tropaeolin-*o*-resorcine yellow	0
rapid filter green I	0	trypan blue	2
resorcine fuchsine	0	trypan red	1
rosanilin acetate	0	uranin (fluorescent)	2
rose bengale	0		

Summary.

An extended search for a substance which might be available for application in animal experiment (relatively soluble), and at the same time capable of emitting fluorescent rays in the mid-ultra-violet region of the spectrum under the influence of the X-ray, has revealed only sodium bromide as possessing these qualities. Many organic chemical compounds fluoresce brightly in the visible region of the spectrum and a moderate number of them give fluorescence which is capable of blackening the photographic plate.

It has been shown that there are solids, liquids, gases and certain solutions which fluoresce. The phenomenon is not limited to any physical state. The nature of the fluorescence excited in any material, both as to intensity and quality is independent of the quality of the exciting X-rays and dependent on their energy alone.

I wish to express my appreciation to Dr. Paul Lewis for the very considerable interest which he has taken in this problem.

PHILADELPHIA, PENNA.

[CONTRIBUTION FROM THE PHYSICAL CHEMISTRY LABORATORIES OF THE UNIVERSITY OF CAPE TOWN.]

HYDROGEN OVERVOLTAGE.

Criticism of the Papers by MacInnes, Adler and Contieri.[1]

BY EDGAR NEWBERY.

Received June 1, 1920.

In these papers the authors appear dissatisfied with the explanations so far proposed for the influence of the physical condition of the electrode surface on hydrogen overvoltage, and they have carried out certain experiments and restated in a modified form the theory of Möller to account for these changes. Unfortunately, their method of experiment and also certain vital parts of their reasoning are open to most serious objections. It is to be feared that these objections are of such a nature

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[1] THIS JOURNAL, 41, 194 and 2013 (1919).

as to invalidate completely the whole work so far as its original purpose is concerned. A few of these objections will be pointed out in the present criticism, but many others could be given if needed.

1. The definition of overvoltage given at the commencement of the first paper is quite incorrect. The potential of an electrode at which molecular hydrogen is being formed from hydrogen ions depends not only upon the overvoltage but also upon the applied E. M. F., the resistance of the electrolyte, and especially upon the transfer resistance.

Overvoltage is of necessity an *active* voltage or electromotive force, capable of doing work after all external sources of E. M. F. have been removed. Transfer resistance is a purely *passive* or frictional force which entirely ceases when the external E. M. F. is interrupted. These 2 forces work in the same direction during the passage of the current; but directly this current is interrupted, overvoltage alone exists and may then be measured. Although overvoltage and transfer resistance occur together in this way, they are mutually independent and frequently vary in opposite directions.

A fairly full account of the behavior of transfer resistance is given in the *Transactions of the Faraday Society*, 15, Part I, 1919, under the title "The Resistance of an Electrolytic Cell." It will there be seen that when hydrogen is being liberated, transfer resistance is greatest at low current-densities. In the work under discussion, extremely low current-densities were employed, but these current-densities were just sufficient to liberate visible bubbles of gas. The electrodes must, therefore, have been saturated with gas; and the authors, apparently without knowing it, have chosen ideal conditions for obtaining the highest possible transfer resistances. Since the surface area of the electrode used was very small (no definite data are given), the transfer resistance at the electrode must have amounted to at least 1000 ohms, and may have been 100,000 ohms. Under these conditions, therefore, the effect of overvoltage is negligible and the whole work of the authors has consisted in measuring, not overvoltage, but the excess potential required to overcome transfer resistance.

(2) The authors are under some misapprehension as to the true overvoltage of platinum. They state (p. 194) that "a polished platinum electrode may show an overvoltage as high as 0.1 volt, whereas for platinized platinum it is nearly zero." This statement is incorrect. Platinum has 4 overvoltages corresponding to 4 states of valence, 0, 8, 4 and 2. These overvoltages are approximately 0.0, 0.18, 0.45 and 0.65 volt respectively, and are shown by both polished and platinized platinum, the only difference between the two being the greater care and time required to make the latter show the higher overvoltages. The "raison d'etre" of their work (*viz.*, the difficulty of explaining the supposed in-

fluence of physical condition of the electrode upon overvoltage) appears, therefore, to be non-existent.

(3) In evolving their theory, the authors appear to look upon the electrode as something in the nature of a spongy mass exuding gas through its pores, and lose sight of the fact that this gas has first to penetrate through the layer of adhering molecules before it can give up its electric charge to the electrode. The fact that this molecular layer cannot be seen with the microscope is, of course, no evidence whatever against its existence, and the well known sudden rush of current rapidly falling to nearly zero when an E. M. F. is first applied to a fresh electrode should have led the authors to suspect the presence of such a gas film. The formation of bubbles is then due to the gradual creeping together of this surface gas, and this process in certainly affected by surface conditions but has nothing to do with overvoltage.

(4) The proposed theory is quite unable to account for the dependence of overvoltage upon valence; the sudden rapid changes shown by a metal such as iridium from one definite and constant overvoltage to another equally definite and constant; the remarkably constant overvoltage shown by a metal such as thallium under the greatest variations of current density and time; the high "metal overvoltages" shown by iron, nickel and cobalt during electrolytic deposition from solutions of their salts; passivity, permanent and periodic; valve action; and many other electrode phenomena, all of which are readily accounted for by the hydride and higher oxide theory.

(5) The effect of external pressure upon true overvoltage is almost zero, no appreciable change being produced by pressures of 100 atmospheres or more of hydrogen or oxygen.[1] The effects observed by the authors are, therefore, due to changes of transfer resistance and as such are of considerable interest.

Many more objections could be stated, but sufficient has been said to show that this theory as it stands is quite untenable. If it is borne in mind that overvoltage in their experimental work is a negligible quantity and that transfer resistance is the main quantity which is being measured, many interesting points may be observed. The fluctuations of potential due to escape of bubbles are among these, and are evidently due to changes in the state of strain and tenuity of the molecular gas film which is the prime cause of transfer resistance. It is, however, unnecessary to use such small electrodes and sensitive galvanometers to observe these phenomena, since they are easily studied with electrodes of one sq. cm. area and a milliammeter. Polished surfaces show the phenomena best and also show a different effect when placed horizontally from that observed when held vertically. Mercury in particular shows

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[1] *J. Chem. Soc.*, 105, 2428 (1914).

the effect in a very marked manner even when fairly high current densities are used, and if the authors have access to an oscillograph (which the present writer has not), it is hoped they will utilize it in further experiments on this subject. These effects were observed by the present writer in 1914, when engaged on the preliminary work on overvoltage, but were then considered (perhaps wrongly) to be of insufficient importance for discussion. They may be explained as follows.

The gas bubbles grow in size by continually attracting smaller bubbles, dragging them against considerable frictional forces over the surface of the electrode. These large bubbles, therefore, produce a condition of lateral strain in the gas film on the surface, increasing its tenuity and hence diminishing its opposition to the entrance of new ions from the solution, in other words, lowering the transfer resistance. The attractive power of the bubble, and hence the diminution of transfer resistance, will therefore vary with the radius of the bubble. Directly the bubble breaks away, this surface strain is released, the surface film rapidly thickens and thus increases the transfer resistance until a new bubble forms, when the process is repeated. The gas nucleus left behind is probably attached to some projecting point on the electrode surface, and the absence of such points accounts for the intensification of the phenomena in the case of mercury.

The equation which the authors deduce

$$FE = \frac{3RT}{2pr}\gamma,$$

showing the relation between transfer resistance, bubble-radius, and external pressure, is very interesting, and when rightly applied may perhaps afford a mathematical basis for explaining the behavior of transfer resistance. The reason why its application is less successful with metals other than platinum is evidently due to the disturbing effect of true overvoltage which will be quite appreciable with most other metals. This can fortunately be eliminated by determining the overvoltage directly with the aid of a rotating commutator, and this commutator may be short-circuited by means of a plug key when the excess potential due to overvoltage plus transfer resistance is to be measured. If this is done, the equation will probably represent the facts with very fair accuracy in all cases, even where high current densities and high-overvoltage metals are used.

The effect of change of pressure on transfer resistance described by the authors is also a matter of considerable interest. The assumption that p is accurately represented by the external atmospheric pressure is, however, somewhat doubtful. In the case of very small bubbles, it may be far from true, since the electrostatic and surface tension forces present may greatly increase the actual value of p. At the same time, since the radii only of the larger bubbles just on the point of escaping were measured, the value of p for these is probably not far removed from that for the external pressure. It is quite possible that the observations on the increase of efficiency of metal deposition at low pressures may find important technical applications.

It is hoped that the authors will continue their investigations along these lines, taking the precaution to eliminate overvoltage effects by the introduction of a rotating commutator as already suggested.

CAPE TOWN, SOUTH AFRICA.

[CONTRIBUTION FROM THE GAYLEY CHEMICAL AND METALLURGICAL LABORATORY OF LAFAYETTE COLLEGE.]

FLUIDITIES AND SPECIFIC VOLUMES OF MIXTURES OF BENZYL BENZOATE AND BENZENE. XXIX.

BY EUGENE C. BINGHAM AND LANDON A. SARVER.

Received July 15, 1919.

Introduction.

Evidence has been accumulating to prove that the old hypothesis that viscosities are additive is quite untenable. At the same time there is both theoretical and experimental proof that fluidities are additive. The decision as to whether one or the other or neither of these properties is additive is of course absolutely imperative before fluidity can come into use for solving physical chemical problems. Since fluidity is very well suited to solve many such problems, it seems strange to the uninitiated that the fundamental decision has been arrived at so late. The reason, however, is not far to seek. To test the hypothesis that fluidities are additive, it would be most natural and easy to measure the fluidities of mixtures of 2 pure inert liquids. The difficulty comes in finding liquids which are "inert," *i. e.*, individually non-associated as well as without tendency to combine with each other.

We have more or less satisfactory methods for determining when a given liquid is non-associated, but we are unable to predict with certainty when loose combinations may be formed; much less are we able to explain the nature of the "molecular compounds."

It is this complication of "variables" which has hitherto rendered the problem of their separation insoluble. One procedure is that advocated by Bingham of seeking evidence outside of mixtures of liquids in suspensions and pure liquids, which seems to speak more unequivocally in favor of the view that fluidities are additive. If this course is pursued and we boldly maintain that fluidities are additive the number of variables is at once reduced and it becomes possible to calculate the association of liquids and in simple cases the combination in mixtures. It is generally true that combination produces effects on other physical properties which can be used to the greatest advantage in testing out the inherent probability of each of our conclusions. Hence it becomes possible to build up a considerable structure of truth resting upon a foundation which is tested out at every point, in order to determine its stability or instability. This can be well illustrated as follows.

Thorpe and Rodger measured the viscosities of mixtures of chloroform and ether. When the curve was plotted it showed a point of inflection, to explain which made it necessary to assume that (1) in certain mixtures combination took place, whereas (2) in other mixtures the opposite effect was shown, such as might be produced by breaking down of association. When it is noted that in *every* mixture there is contraction in volume and heat evolution, these 2 hypotheses become improbable. However, when we plot the fluidities of chloroform and ether against the volume concentration, the point of inflection disappears and the curve shows positive curvature throughout. This is explained by the *single* hypothesis that chloroform and ether form a loose combination, a conclusion supported by all of the other evidence which we have had at hand.

Kendall,[1] in 1912, examined a considerable portion of the available viscosity data and came to the conclusion that a formula

$$\log \eta = a \log \eta_1 + b \log \eta_2$$

gives better average agreement than any hitherto proposed. It hardly seems likely, however, that the logarithms of the viscosities should be additive. Certainly no physical meaning for such an awkward conception has been put forth. But as one of us has pointed out,[2] if it happens that on mixing combination takes place more frequently than dissociation, it might well be that some purely empirical formula such as the above would show better statistical agreement than the true formula, which we believe to be the additive fluidity-volume concentration formula, $\varphi = a\varphi_1 + b\varphi_2$. But it is important to note that on account of the disturbing factors of association and combination, no single formula, either empirical or otherwise, can apply to all mixtures.

Kendall and Monroe[3] have attempted to settle the question finally by studying "inert" liquids of widely differing fluidities,[4] namely, mixtures of (1) benzene and benzyl benzoate, (2) benzene and ethyl benzoate, (3) toluene and ethyl benzoate, and (4) toluene and benzyl benzoate. In speaking of the mixtures of benzene and benzyl benzoate they say[5] "so far

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[1] Kendall, *Meddel. K. Vetenskapsakad. Nobelinst.*, 2, No. 25 (1913).

[2] *J. Phys. Chem.*, 18, 157 (1913).

[3] Kendall and Monroe, THIS JOURNAL, 39, 1787 (1917).

[4] *Am. Chem. J.*, 35, 199 (1906).

[5] THIS JOURNAL, 39, 1796 (1917).

as can be judged, this system is ideal. Careful calorimetric measurements failed to indicate any heat evolution or absorption on admixture of equal volumes of the two liquids. Density determinations showed that no volume change occurred." The other mixtures appeared to the authors to be equally inert. However, none of the mixtures gave results which would be predicted by any hypothesis given above. As a matter of fact, no empirical formula was found which would fit *all* of the data, although the first 3 mixtures are represented by a formula

$$\eta^{1/3} = a\eta_1^{1/3} + b\eta_2^{1/3},$$

where the concentrations are molecular. That they have found an empirical formula which will reproduce the viscosities of mixtures of benzene and benzyl benzoate with a divergence of only 3.8% is not remarkable. But it is remarkable that there should be a larger deviation from the fluidity-volume concentration curve, provided that these liquids are inert as they maintain and fluidities are truly additive. This apparent exception, therefore, demanded investigation.

Since Kendall and Monroe have not given their data in regard to the densities of their solutions and only mention the subject in the somewhat vague way quoted above, it seemed best to repeat a portion of their work, as there might have been at least slight changes in volume and in temperature which might have been ascribed to experimental error. If benzene and benzyl benzoate form an ideal mixture as Kendall and Monroe think they do at 25°, then they certainly should also do so at other temperatures. On the other hand, if fluidities are additive and there were combinations taking place, causing the sag from the linear fluidity curve, then it is probable that the amount of combination will be less at the higher temperatures and greater at the lower temperatures, hence there will not be the concordance found by Kendall and Munroe except at the one temperature investigated.

Preparation of Materials.

Benzene.—Pure commercial benzene was shaken repeatedly with sulfuric acid until the latter showed no coloration. It was washed with distilled water, and *N* sodium hydroxide solution, to remove the last traces of acid; and finally 5 times with water to remove the alkali. After drying it was recrystallized 6 times by freezing it in a round-bottomed flask, shaking occasionally with a circular motion and pouring off the last portion each time; in this way the liquid forms a solid cake around the walls of the flasks, freezing at constant temperature until only a few cc. remain. This liquid is poured off, the solid melted and the process repeated. At the end no change of freezing-point temperature could be observed while the last portion was freezing. The benzene, thus purified was dried over freshly cut sodium which had been carefully washed with pure benzene; and it was then fractionated between 80.2° and 80.3° into a carefully cleaned, dust-free bottle.

Benzyl Benzoate.—One mole of pure benzyl alcohol was added drop by drop to one and one-half moles of benzoyl chloride heated to 140° in an oil-bath. Hydrogen chloride was freely evolved, and the reaction was complete in 2 hours. The oil was fractionated to remove the excess of benzoyl chloride, giving a yield of over 90% of nearly pure ester. It could not be dried with phosphoric anhydride, since under the influence of the latter substance the ester passed over almost quantitatively into benzoic acid and benzyl phosphate. To free it from benzoic acid the oil was titrated with 0.05 N sodium hydroxide, using one milligram of phenolphthalein dissolved in a known quantity of alkali for an indicator, until the aqueous solution was colored permanently red; the solid phenolphthalein was soluble chiefly in the oil, while the sodium salt was soluble only in the alkaline aqueous solution. The ester was washed many times with water to remove last traces of alkali, and dried by heating for several hours on a water-bath, *in vacuo*, while a current of dry air was being drawn through it. The substance was now recrystallized 3 times to free it from benzyl alcohol; the ester was mixed with $^1/_{10}$ of its volume of ether, frozen, filtered on a platinum cone, melted, and the process repeated. The material, thus purified, was again subjected to the treatment with dry air, *in vacuo*, to remove last traces of ether and water, and finally fractionated 3 times, *in vacuo*, into dust-free apparatus. A large sample of the pure ester was melted, showing a slight softening at 17.55°, and melting at 18.2°. It was absolutely colorless and had a faint odor. The substance decomposed slightly when distilled at atmospheric pressure, giving a pale yellow color and a faint odor; hence it was necessary to conduct all distillations under reduced pressure.

Standardization of Apparatus.

The viscometer used had previously been carefully calibrated;[1] several observations on dust-free water showed the values given there to be correct. In the formula $\eta = Cpt - C'\rho/t$, $\log C = 3.15555 - 10$ and $\log C' = 8.37598 - 10$.

Experimental.

Observations were made upon the 2 pure substances and 3 mixtures over a range of temperature from 5° to 75°. The mixtures were made by first weighing out the benzyl benzoate in a glass-stoppered bottle, then adding the benzene from a capillary pipet; the 2 liquids were then mixed with a circular motion, care being taken not to wet the stopper, lest differential evaporation should change the concentration. Great care was taken at all times to protect reagents and apparatus from dust. A summary of results follows.

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[1] See Bingham and Jackson, Bur. Standards, *Bull.* 298.

TABLE I.—BENZYL BENZOATE.

Temp. bath °C.	Time Sec.	p_0.	P.	η in cp.	φ.	v.	ρ.
5	2359.0	401.3	401.3	19.280	5.185	0.8818	1.1134
15	2111.5	401.3	401.3	12.120	8.249	0.8890	1.1249
25	1438.5	403.0	402.9	8.292	12.06	0.8958	1.1163
40	909.6	403.0	402.9	5.243	19.07	0.9058	1.0780
60	566.6	402.6	402.0	3.259	30.68	0.9200	1.0870
80	390.7	402.6	401.5	2.245	44.56	0.9330	1.0546
90	333.4	402.4	400.8	1.912	52.30	0.9430	1.0604
100	289.0	402.4	400.3	1.655	60.42	0.9460	1.0571

TABLE II.—BENZENE.

5	564.1	103.2	102.7	0.8293	120.5	1.1187	0.8939
15	477.5	103.2	102.6	0.7012	142.5	1.1323	0.8832
25	410.1	103.4	102.5	0.6018	166.1	1.1461	0.8725
40	336.9	103.5	102.2	0.4912	203.5	1.1675	0.8565
60	266.9	103.5	101.6	0.3877	257.9	1.1980	0.8347
75	331.6	71.08	69.86	0.3314	301.8	1.2371	0.8083

TABLE III.

Benzyl Benzoate 75%; Benzene, 25% by Weight.

Temp. bath °C.	Time Sec.	p_0.	P.	η in cp.	φ.	v.	ρ.
5	905.8	410.2	410.0	5.313	18.86	0.9402	1.0640
15	683.0	410.3	409.7	4.004	24.99	0.9483	1.0550
25	524.2	410.3	409.7	3.073	32.54	0.9565	1.0454
40	372.1	410.5	409.4	2.180	45.88	0.9685	1.0325
60	256.7	410.4	407.7	1.556	64.27	0.9854	1.0148
75	209.7	410.4	406.5	1.220	82.00	0.9985	1.0015

TABLE IV.

Benzyl Benzoate, 50%; Benzene, 50% by Weight.

5	534.8	308.4	308.3	2.356	42.44	0.998	1.0016
10	474.0	307.7	307.4	2.084	47.97	1.002	0.9980
15	424.1	307.7	306.7	1.861	53.73	1.008	0.9925
25	345.6	307.7	306.3	1.514	66.04	1.018	0.9825
40	410.4	198.9	197.8	1.161	86.13	1.032	0.9687
60	306.6	198.9	197.2	0.865	115.6	1.053	0.9560
75	255.2	199.0	196.6	0.718	139.3	1.069	0.9359

TABLE V.

Benzyl Benzoate, 25%; Benzene, 75% by Weight.

5	461.1	199.0	198.2	1.308	76.4	1.056	0.9468
15	380.0	199.0	198.0	1.076	92.8	1.068	0.9363
25	320.6	199.0	197.5	0.9057	110.3	1.080	0.9263
40	257.0	199.0	196.7	0.7205	138.8	1.098	0.9106
60	314.2	125.4	123.9	0.5578	179.3	1.123	0.8904
75	266.3	125.5	123.4	0.4702	212.7	1.143	0.8750

TABLE VI.

Molecular and Volume Percentages of Mixtures.

Temperature. ° C.	25% benzene.		50%.		75%.	
	Molecular.	Volume.	Molecular.	Volume.	Molecular.	Volume.
5	47.50	29.72	73.10	55.92	89.04	79.19
15	...	29.80	...	56.02	...	79.29
25	...	29.89	...	56.12	...	79.32
40	...	30.06	...	56.31	...	79.45
60	...	30.27	...	56.56	...	79.62
75	...	30.47	...	56.80	...	79.78

The tables are self-explanatory except that the manometer pressure p_0 is the corrected average pressure in grams per square centimeter used in producing the flow, whereas P is the pressure used purely in overcoming viscous resistance. The viscosity[1] is therefore, $\eta = CPt$. The specific volumes are represented by v, the densities by ρ.

The viscosities are given in centipoises,[2] *i. e.*, absolute c. g. s. units $\times 10^{-2}$. The fluidities φ of benzene are practically identical with the values obtained by Thorpe and Rodger[3] except at the 2 highest temperatures where our fluidities are about 1% higher; thus at 25° our value is 166.2, that of Thorpe and Rodger is 166.1, that of Kendall and Monroe is 165.4. For benzyl benzoate our value is 12.06 as com-

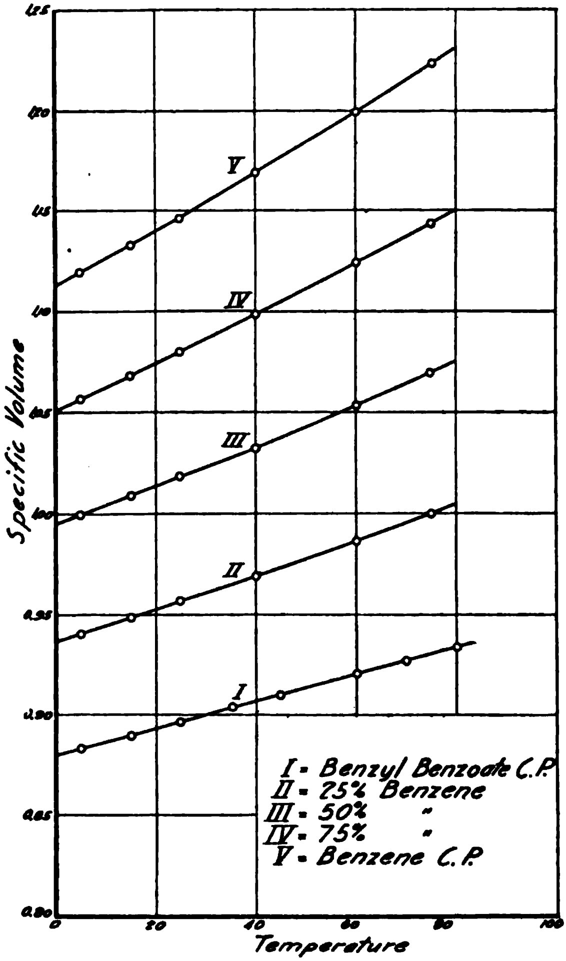

Fig. 1.—The specific volume-temperature curves of mixtures of benzene and benzyl benzoate.

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[1] Bur. Standards, *Bull.* 14, No. 298, 70 (1917).

[2] *Ibid.*, p. 72.

[3] Thorpe and Rodger, *Phil. Trans.* (*London*), 185A, 521 (1894).

pared with 11.83 found by Kendall and Monroe. We have not used the same mixtures that were employed by Kendall and Monroe, but their values plot on a smooth curve with ours, a fact which is significant, because in using a volatile component like benzene there is need for care in manipulating the mixtures to prevent the composition of the mixture changing subsequent to preparation. It is, however, regarded as impossible that the effects with which we are here concerned can be due to this cause; and it is almost certain that if an error has been inadvertently introduced it would not be proportionately the same for all of the mixtures and for different observers, using presumably different methods of manipulation.

The densities ρ were determined in a special pycnometer devised by Bingham and Van Klooster[1] to be described in another communication. The densities are all corrected for buoyancy of the air and are based on water at 4° as standard. The densities of benzene were not determined by us, the values giving being those of Kopp.

Discussion.

The specific volume-temperature, the fluidity-temperature, and fluidity-specific volume curves are given in Figs. 1, 2 and 3, respectively. The fluidity-temperature curves, Fig. 2, are approximately linear but, never-

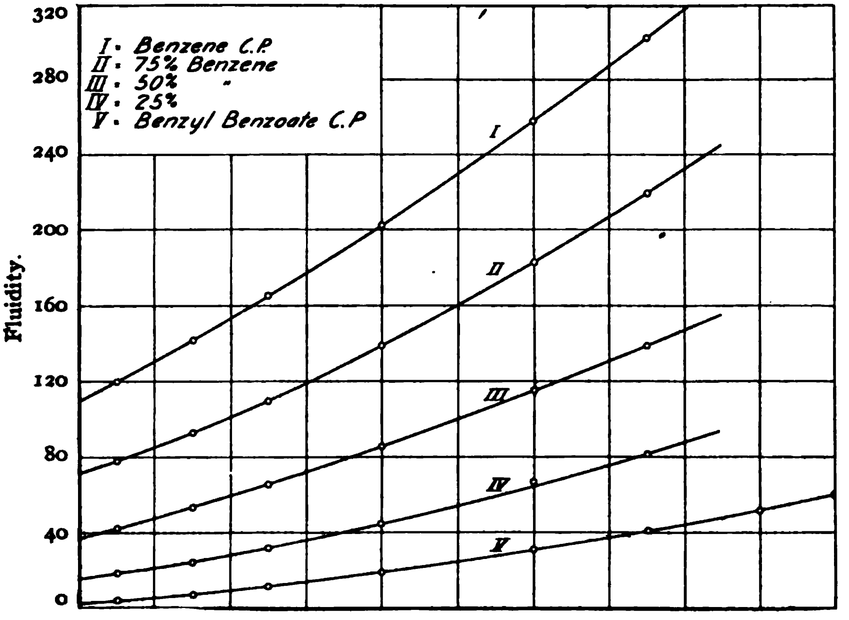

Fig. 2.—The fluidity-temperature curves of mixtures of benzene and benzyl benzoate.

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[1] Bingham and Van Klooster, *J. Phys. Chem.*, 24, 6 (1920)

theless, definitely and distinctly sagged. The volume-temperature curves, Fig. 1, are still more nearly linear, the curve for benzoyl benzoate not departing noticeably from a straight line. The law of Batschinski, which says that the fluidity of a liquid is directly proportional to its free volume,[1] is fairly well substantiated by Curves I, II, III, IV and V of Fig. 3, representing the fluidities of a given liquid over the range of temperature from 5° to 75°; but when this law is applied to the various mixtures at a given temperature (Curves VI, VII, VIII, IX, X, and XI) it breaks down badly, although Batschinski in a private communication reports that the law holds in certain cases tried by him.

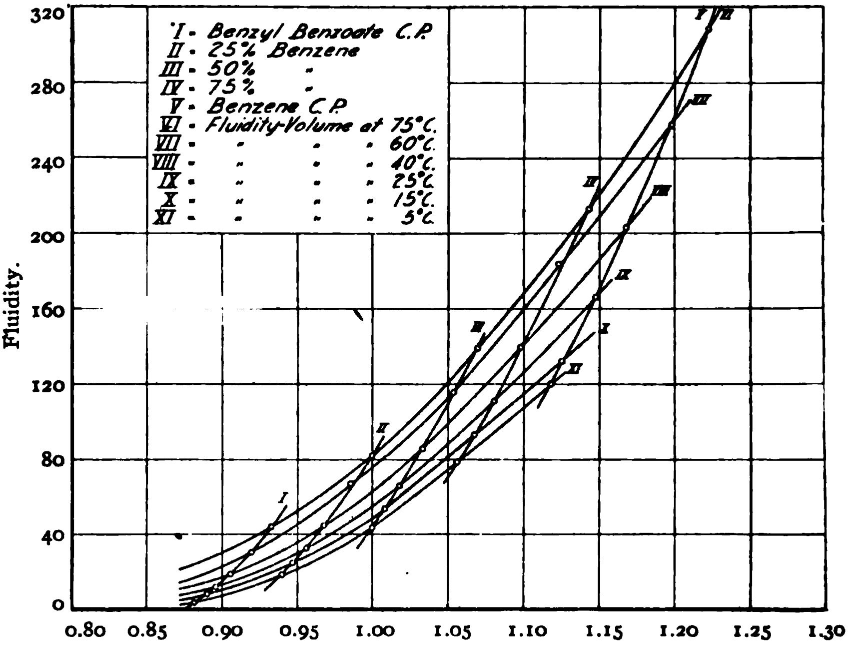

Fig. 3.—The fluidity-specific volume curves of mixtures of benzene and benzyl benzoate at different temperatures.

The specific volume-volume concentration curves, Fig. 4, show that contraction in volume has taken place on mixing at every temperature. Therefore, we are justified in the conclusion that combination has certainly taken place; hence the fluidity-volume concentration curves should deviate from a straight line according to the hypothesis that fluidities are additive, and in Fig. 5 this is observed to be the case. The sag in the specific volume-volume concentration curves is least at the lowest temperature, and it would seem that the sag in the fluidity-volume con-

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[1] This Journal, 39, 1787 (1917).

centration curves would also be likely to be least at the lowest temperature, as Fig. 5 shows to be true.

We have plotted the observed and calculated curves of fluidity against molecular concentration. Whereas there is good agreement between the two at 25°, as Kendall and Monroe have pointed out, there is no such agreement at other temperatures, the observed values being too high at low temperatures and too low at high temperatures, the deviation of the calculated values from the observed in the 50% mixture by weight being 34% at 25°, 15.6% at 5°, and —6.0% at 60°.

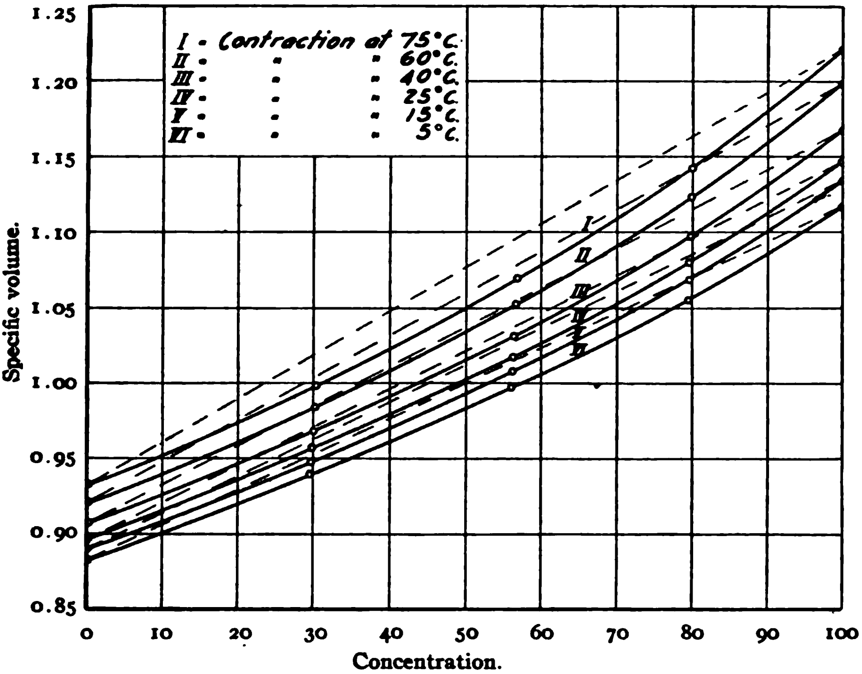

Fig. 4.—The specific volume-volume concentration curves of mixtures of benzene and benzyl benzoate for different temperatures. The sagging of the curves shows that benzene and benzyl benzoate unite with contraction in volume, solvation probably taking place.

If benzene and benzyl benzoate form an ideal pair of liquids, as Kendall and Monroe maintain, and the cube roots of viscosities are truly additive, then it is hard to explain why mixtures demonstrate it at one temperature only. We, therefore, return with renewed confidence to the hypothesis that fluidities are normally additive. When fluidities are not a linear function of the volume concentration we may safely predict that evidence of abnormality may also be found in the other physical properties.

The assumption that the fluidity-volume concentration curve is linear is represented by Curve I in Fig. 6. The assumption that the logarithmic-molecular concentration curve should be linear is represented by Curve II. The assumption that the cube roots of the viscosities should be a linear function of the molecular composition is represented by Curve III. There are, of course, an indefinite number of other curves depending upon the function of the fluidity which is arbitrarily selected and also dependent upon whether we choose the volume, weight, molecular, or some other concentration as the second variable. For example, the viscosity-molecular concentration would be much lower than any of those shown.

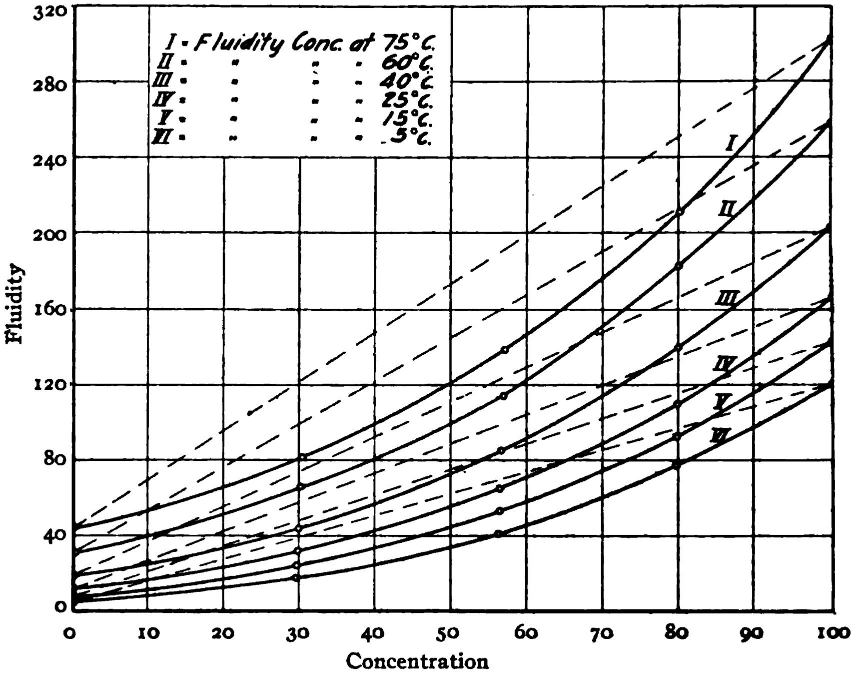

Fig. 5.—The fluidity-volume concentration curves of mixtures of benzene and benzyl benzoate. According to the hypothesis that fluidities are additive, the sagging of these curves is a confirmation of the solvation which was indicated by the sagging of the specific volume-volume concentration curves, Fig. 4.

The observed fluidities are plotted in full lines instead of dashes, Curves IV, V and VI, according to weight, volume, and molecular concentrations, respectively. Curve VI lies close to Curve III, for this particular pair of liquids at 25°, but this fact certainly does not warrant the conclusion that the normal fluidity-volume concentration curve is not linear. A study of the nature of viscous flow[1] which can only be referred to here

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[1] Bur. Standards, *Bull.* 13, 321 *et seq.* (1916).

shows that we must employ volume concentrations. On the other hand, being convinced that fluidities and volume concentrations are related to each other in a linear manner, the divergence between Curves I and V can be used to calculate the degree of solvation, and this result can be compared with the solvation as calculated by other methods.

In this particular case, one must be cautious in interpreting results due to the fact that benzene and benzyl benzoate are probably both associated[1] to some extent, which complicates the problem. However, we note that all temperatures the greatest deviation of the fluidity-volume concentration curve from the linear curve is in a mixture which contains about 58% of benzene which corresponds to a molecular compound of the formula $C_6H_5.COO.CH_2.C_6H_5.3C_6H_6$. The fact that the maximum deviation does not shift at the different temperatures is also taken as strong evidence of the correctness of the hypothesis that fluidities are

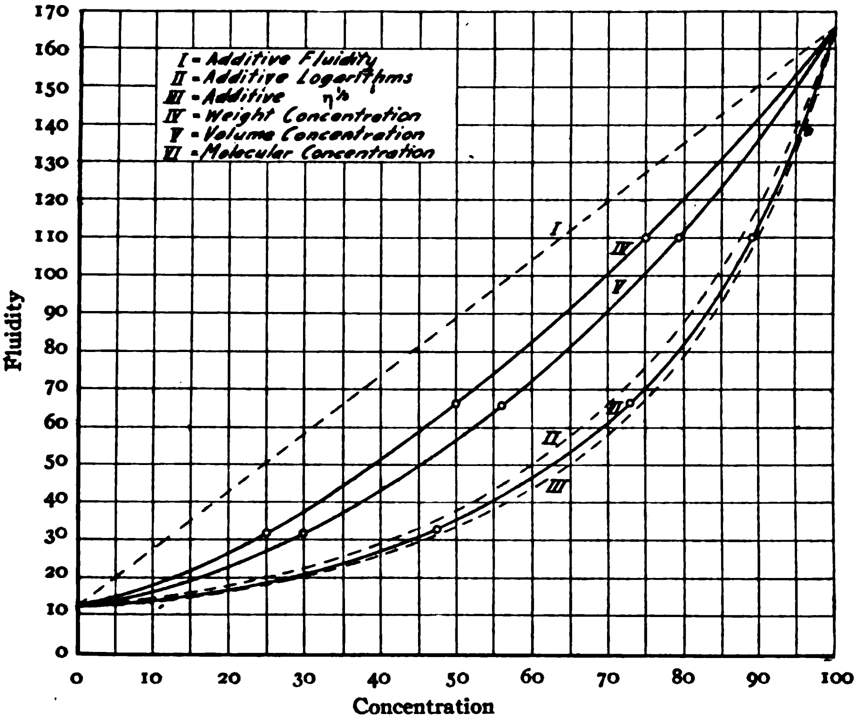

Fig. 6.—A few of the indefinite number of empirical curves are shown by dashes, and observed fluidities, as plotted against weight, volume, and molecular concentrations, are shown by full lines. To base any fundamental conclusion upon the accidental proximity of two of these curves, would be manifestly unwarranted, unless it was supported by other proof of a very strong character.

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[1] Benzene and many esters are associated (*Z. physik. Chem.*, 66, 28 (1909)).

additive. It would be rather embarassing to have to explain a pronounced shift of the maximum deviation.

Summary.

When inert liquids are mixed it is assumed that the fluidity is a linear function of the volume composition. It had been reported that benzene and benzyl benzoate are inert as indicated by absence of contraction or heat evolution on mixing, yet at 25° their fluidity-volume concentration curve is not linear, and the cube roots of the viscosities are a linear function of the molecular concentrations.

This paper proves that benzene and benzyl benzoate show quite perceptible concentration on mixing, which is proof of aggregation which we would expect from the fluidity-volume concentration curve.

Furthermore, the cube root equation applies at only the one temperature used in the earlier work, but it does not apply at either higher or lower temperatures. This example is, therefore, not only not evidence against the fundamental hypothesis that fluidities are additive, but it is strong evidence in its favor.

EASTON, PA.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NEW HAMPSHIRE COLLEGE.]

A DETERMINATION OF THE ATOMIC WEIGHT OF THULIUM.

BY C. JAMES AND O. J. STEWART.

Received August 6, 1920.

The material used in this work was obtained and purified as described under Thulium.[1] Owing to the fact that the fractions were very small, several of them were united. All the purest material was combined to form oxalate A, while B and C were two other sets containing small amounts of neoytterbium.

These oxalates A, B and C were converted to the hydrated chloride in a manner identical with that used for samarium. Since a detailed description of this process has already been given in a paper from this laboratory,[2] it need not be repeated here.

Dehydration of the hydrated chloride then followed, using the same method that was employed for samarium. The fused chloride dissolved quickly and completely in pure water.

The ratio, $TmCl_3 : 3Ag$, was then calculated from results obtained from the chloride analyses which were in every respect similar to those mentioned for samarium, silver and other reagents of equal purity being used.

Since each fraction contained only enough material for one analysis, Fractions A and B, after being analyzed once, were again purified as chloride for the second analysis.

[1] THIS JOURNAL, 33, 1332 (1911).

[2] *Ibid.*, 39, 2605 (1917).

The determination of the specific gravity of anhydrous thulium chloride was not undertaken. In lieu of this experimentally determined constant, the approximate density figure (3.000) was used in the atomic weight calculations. This figure was obtained by extending the curve which results from plotting density against atomic weight for those rare earths for which these constants are known.[1] Since a change in density of 0.50 causes a change in atomic weight of only 0.01, this correction is of little significance in the present work.

TABLE I.—ANALYSES.

Series $TmCl_3:3Ag$.

Ag = 107.880. Cl = 35.457.

No. of analysis.	Fraction.	$TmCl_3$ in vacuum. G.	Ag in vacuum. G.	Ag added. G.	Corrected wt. of Ag in vacuum.	Ratio $\frac{TmCl_3}{3Ag}$	At. wt. of thulium.
1.........	A	2.17052	2.54519	0.00152	2.54671	0.85228	169.46
2.........	A	4.01446	4.71437	−0.00346	4.71091	0.85216	169.42
					Av.	0.85222	169.44
3.........	B	2.03868	2.39185	−0.00125	2.39060	0.85279	169.63
4.........	B	1.53851	1.80439	−0.00071	1.80368	0.85299	169.69
					Av.	0.85289	169.66
5.........	C	2.35242	2.76209	−0.00636	2.75573	0.85365	169.90

The results obtained from the purest material gave an average atomic weight of 169.44. This figure is a little higher than the usually accepted value, 168.5, which was considered by Urbain[2] to be the maximum after he had examined some fractions obtained during the separation of lutecium. The amount of ytterbium (neoytterbium) required to raise the atomic weight from 168.5 to 169.44 would be considerable. It would seem that the material used by the writers was of too high a purity for such a consideration.

Very much larger amounts of thulium oxide are being collected in this laboratory, and it is hoped that before long a much more decisive result will be obtained.

DURHAM, N. H.

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[1] *Ann. chim. phys.*, **20**, 547 (1910); *ibid.*, **21**, 49 (1911); *Compt. rend.*, **140**, 1340 (1905); *Chem. News*, **91**, 280 (1905).

[2] Urbain, *Compt. rend.*, **145**, 759 (1907).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

THE STABILITY OF THE COBALTAMMINES.

BY ARTHUR B. LAMB AND ALFRED T. LARSON.

Received August 6, 1920.

The marked tendency of the cobaltic ion to combine with ammonia and similar unsaturated molecules is evidently responsible for the existence of the numerous, variegated and frequently very stable cobaltammines. It appeared to us of interest to determine the actual magnitude of this tendency toward complex formation and to examine how it varies among the different ammines.

A direct and elegant method of accomplishing this purpose, since we can be sure that the concentration of the simple cobaltic ions is minute under any experimental conditions, is to determine the ratio of the cobaltic and cobaltous ion concentrations by measurements of the oxidation potentials of solutions containing known concentrations of cobaltous ions and of the cobaltammines. From these ratios we at once know the actual cobaltic ion concentrations, and these in turn are an inverse measure of the stabilities, since evidently the more stable the complex ion the less the equilibrium concentration of the cobaltic ion in its solutions.

This method has entailed certain subsidiary determinations. Thus, it has been necessary to determine the cobaltous ion concentrations in ammoniacal solutions of cobalt salts; also since the existing data on the normal oxidation potential of the cobaltic-cobaltous electrode are very meager, additional determinations of this potential in solutions containing known concentrations of the respective ions have been required.

Attempts were first made to measure the oxidation potential in neutral and slightly acid solutions of the ammines, but definite and reproducible results could not be obtained under these conditions. Satisfactory results were, however, obtained in concentrated ammoniacal solutions, the observed potentials varying normally with changes in the cobaltic-cobaltous ion concentrations. Nevertheless, the use of such solutions involved much inconvenience since they had to be scrupulously protected from contact with the air.

Preparation of Ammines.

The 6 ammines studied were prepared and carefully purified by the most recent methods of Jörgensen,[1] and were in general used promptly after preparation. These precautions as to purity and freshness are necessary, since it was found that with certain ammines small amounts of impurities have a noticeable effect on the potential, while with other ammines, and in particular the aquo-tetrammine chloride, changes occur on standing even in the dry state which produce marked effects on the potential.

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[1] Jörgensen, *Z. anorg. Chem.*, 17, 455 (1898).

Certain modifications were made in the method of preparing hexammine chloride which greatly facilitated its preparation in large amounts and in a high degree of purity. Instead of digesting small quantities of chloropentammine chloride with ammonia in glass pressure bottles, a large, loosely covered glass jar, placed in a strong autoclave, was used as a container; also the slightly soluble chloro-pentammine chloride was converted, by warming with a little ammonia, into the easily soluble aquopentammine salt before putting it into the autoclave, thus obviating any need for stirring or shaking, and securing a much more rapid action.

A typical procedure was as follows. 50 g. of chloro-pentammine cobalt chloride was added to 300 cc. of water and warmed on a steam-bath. Small quantities of concd. ammonium hydroxide were added from time to time and the heating continued until the chloro-pentammine had been transformed into the aquo-pentammine chloride. The solution was then filtered to remove oxide, and while still hot was poured into the glass jar within the autoclave. 10 g. of ammonium chloride was added and 200 cc. of concentrated ammonia. The autoclave was then closed and the whole heated in a water-bath for from 3 to 4 hours. The autoclave was then allowed to cool and the contents poured into an evaporating dish. The ammonia was at once neutralized with hydrochloric acid to prevent a reversion of the hexammine to pentammine,[1] and was heated on the water-bath for about one hour to convert any unchanged aquo-pentammine into the difficultly soluble chloro-pentammine. If a residue separated out it was filtered off and solid ammonium chloride was added to precipitate the hexammine. This was filtered off, redissolved and a saturated solution of ammonium oxalate added to complete the precipitation of the hexammine as oxalate. The combined precipitate was filtered and redissolved in dil. nitric acid. The ammine was reprecipitated as oxalate, filtered and redissolved and reprecipitated with hydrochloric acid as chloride. This gave a good yield of very pure hexammine cobaltic chloride.

Apparatus.

The ease with which cobaltous ammine is oxidized to the cobaltic state made it necessary to construct a cell into which the solutions could be introduced and their potential measured out of contact with oxygen. The apparatus employed for this purpose, shown diagrammatically in Fig. 1, consisted essentially of the Cell A, containing the oxidation-reduction electrodes, and the Cell G, containing the reference electrode, electrically connected by siphon tubes dipping into the Beaker F. The two cells were immersed in a water thermostat regulating at 25° ±0.05°. The glass Tube B, provided at its lower end with a sealed-in propeller blade of platinum, served as a stirrer, rotating in the brass bearing C, guided by a glass tube in the Stopper D. It was filled with mercury, and contact was established by a wire dipping into this at the upper end. The Stopper D also carried 2 additional electrodes, one of bright and the other of platinized platinum. The siphon Tube E was filled with agar-agar made up with normal potassium chloride solution. Under ordinary

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[1] In Jörgensen's method the hexammine solution is allowed to stand in a draft until all the ammonia is volatilized. We find that considerable reversion to pentammine chloride occurs under these conditions.

circumstances this type of junction would not have been adopted, for it does not give the utmost accuracy, but its use here was necessitated by the fact that the entire cobaltic-cobaltous mixture had to be hermetically sealed within the Cell A; moreover, a low resistance was desirable.

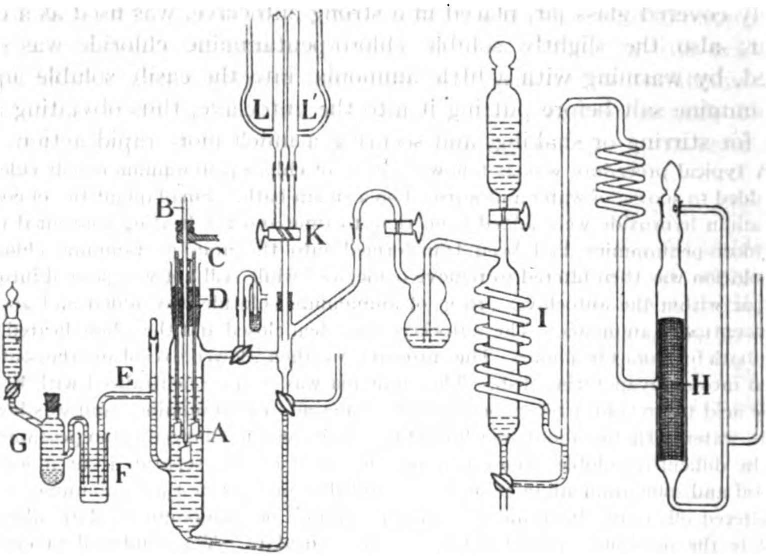

Fig. 1.—Apparatus.

For sweeping out the cell nitrogen free from oxygen was prepared by passing air, or better still commercial nitrogen from cylinders, over copper gauze (H), washed by a solution containing equal parts of 0.93 sp. gr. ammonium hydroxide solution and saturated commercial ammonium carbonate solution. The effluent gas was freed from ammonia by passing it through a spiral wash-bottle (T) containing sulfuric acid, and an indicator to show when the acid was spent. The flow of gas was regulated by means of a capillary stopcock.

The solutions of ammonia and of cobaltous chloride were kept in stoppered bottles, on a shelf above the main apparatus, connected by means of siphon tubes to 2 burets, L and L′, connected to the 3-way cock, K, by means of which either solution could be introduced into the Cell A. In all the experiments, the results of which are given below, the same stock solutions of ammonium hydroxide and cobaltous chloride were used.

Effect of Stirring.

We early noticed that stirring had a marked influence on the potential of the platinum electrodes. Measurements were, therefore, carried out to determine the magnitude of this effect. A bright platinum and a platinized-platinum electrode were attached to the same shaft and rotated at different rates in a solution one day old of hexammine chloride in 6.0 *M* ammonium hydroxide solution, and their potential against a *M* NaOH | HgO | Hg electrode observed. The cell had previously been carefully swept out with a current of oxygen-free nitrogen, which was, however, discontinued during the observation. The results are collected in the following table. The observed potentials are given in Cols. 2 and 4. There is, evidently, a steady trend of both electrodes towards a more negative potential independent of stirring, the bright electrode changing more rapidly than the platinized one and thus becoming more nearly identical with it. These slow changes are observed in all of the ammoniacal cobaltammine solutions which we have studied, but prolonged measurements have shown that ultimately the electrodes do become identical. The observed potentials at different rates of stirring have been corrected for this slow change and the average corrected results for each rate of stirring are given in Cols. 5 and 6. In Cols. 7 and 8 are given the total changes in potential, expressed in millivolts, produced by the stirring.

TABLE I.
Effect of Stirring.

0.0010 *M* $CoCl_2$.
0.00075 *M* $Co(NH_3)_6Cl_3$.
6.0 *M* NH_4OH.
Temp. 25.0°.

Time min.	Speed R.P.M.	Obs. potential. Volt.		Corrected potential. Volt.		Total change. Mv.		Change per revolution. Mv.	
		Platinized.	Bright.	Platinized.	Bright.	Platinized.	Bright.	Platinized.	Bright.
0	750	−0.360	−0.170	−0.360	0.170	52	20	0.02	0.01
10	400	−0.370	−0.174	...	...	..	..	..	...
30	400	−0.372	−0.176	−0.371	0.173	41	17	0.05	0.02
45	400	−0.372	−0.179	...	...	..	..	..	..
55	250	−0.380	−0.180	...	...	..	..	..	..
75	250	−0.382	−0.184	−0.379	0.176	33	14	0.07	0.03
90	250	−0.382	−0.184	...	...	..	..	..	..
95	120	−0.392	−0.188	...	...	..	..	..	..
105	120	−0.392	−0.188	−0.389	0.181	23	9	0.12	0.05
115	120	−0.392	−0.198	...	...	..	..	..	..
120	0	−0.412	−0.202	...	...	..	..	..	..
135	0	−0.420	−0.204	−0.412	0.190	0	0	0.20	0.10
150	0	−0.424	−0.204	...	...	..	..	..	..
155	750	−0.370	−0.186	...	...	..	..	..	..
165	750	−0.366	−0.188	−0.360	0.172	53	18	0.02	0.01
170	750	−0.366	−0.192	...	...	..	..	..	..

It can be seen that both electrodes are very considerably affected by the stirring, the platinized being about 50 and the bright electrode about 20 mv. more positive when at rest than when rotated at the rate of 750 revolutions per minute. Stirring, therefore, tends to make the electrodes change in the direction *opposite* to that toward which they are slowly changing while at rest or standing, and this effect is more pronounced on the platinized than on the bright platinum.

These effects can be in part explained if we assume that the slow change which the solutions evidently undergo even on standing is catalyzed by the electrodes, and also that as would be expected, this effect is greater on the platinized than on the bright platinum. The electrodes would then register a potential corresponding to a solution more nearly converted to the equilibrium condition than is the bulk of the solution, the platinized electrode registering a more altered potential than the bright electrode. Stirring will, of course, tend to render the electrolyte in contact with the electrodes more nearly identical with the bulk of the solution, and would, therefore, cause both electrodes to become less negative; the bright electrode, being nearest to the potential characteristic of the whole solution, of course, exhibiting the lesser change.

In order to estimate what the potential of the electrodes would be at very high rates of stirring and so to infer what the potential of the solution would be in the absence of the catalytic influence of the electrode, the total changes in potential produced by different rates of stirring (Cols. 7 and 8) were plotted against revolutions per minute. Curves were obtained which were evidently approaching a limit asymptotically, that for the bright electrode being approximately 22 mv., and that for, the platinized electrode about 66 mv.

This explanation is not, however, wholly satisfactory, for these differences do not by any means account for the whole discrepancy between the potentials of the platinized and the bright electrodes.

By taking the slope of these curves at different rates of stirring an estimate can be made of the effect upon the potential of variations in the number of revolutions per minute. The results of this estimation are given in Cols. 9 and 10. The absolute change is very small for high rates of stirring, but for the same percentage variation in the rate of stirring there is very little to choose between the different rates. At 400 revolutions per minute a variation of 5% in the rate of stirring would cause an uncertainty of one mv. on the platinized platinum and 0.4 mv. on the bright platinum electrode. This degree of regularity could easily be obtained.

Since it was in general desirable to have the electrodes record as nearly as possible the characteristic potential of the solution as a whole, 400 revolutions per minute was selected as the rate of stirring for the actual measurement, as this was the highest speed which could be maintained with satisfactory constancy by our apparatus.

Execution of the Measurements.

In general all experiments were conducted as follows. A weighed quantity of the solid cobaltic ammine was placed in A, a measured volume of cobaltous chloride solution was then added by proper manipulation of the cock K. The 3-way cock H was set so that the main body of the cell A communicated with the mercury trap N. The cock I was placed in a vertical position, the cobaltous chloride solution running through it and into the cell body A. Nitrogen was then admitted, the gas pressure forcing the liquid over into the cell body, and was bubbled through the solution for at least 6 hours to remove oxygen. The ammonia water was then introduced through cock K, and forced into the main body of the cell by means of the gas pressure, first precipitating cobaltous hydroxide which redissolved in the excess. As soon as solution was complete the potential measurements were made, the first setting of the potentiometer being made with a Lippmann electrometer and the final adjustment by means of a galvanometer.

As a rule the cell as described above was set up late in the afternoon, and oxygen-free air passed through the apparatus until the following morning. The required amount of ammonia was then introduced and potential measurements were made as soon as the cobaltous hydroxide had dissolved. Except in duplicate experiments on the same ammine a freshly prepared agar-agar salt bridge was made.

The Measurements. Their Concordance and Reproducibility.

Measurements were always made on all 3 electrodes, rotating platinized, stationary platinized and stationary bright platinum. The platinized electrodes, except in the case of the aquo-pentammine chloride, always agreed within 10 minutes to less than 2 or 3 millivolts. The bright electrode at the start frequently differed from the other 2 by many millivolts, but all 3 electrodes came to within a few tenths of a millivolt of the same potential after about 3 hours. To illustrate this, the observations made on the 3 electrodes in aquo-pentammine chloride solution, where

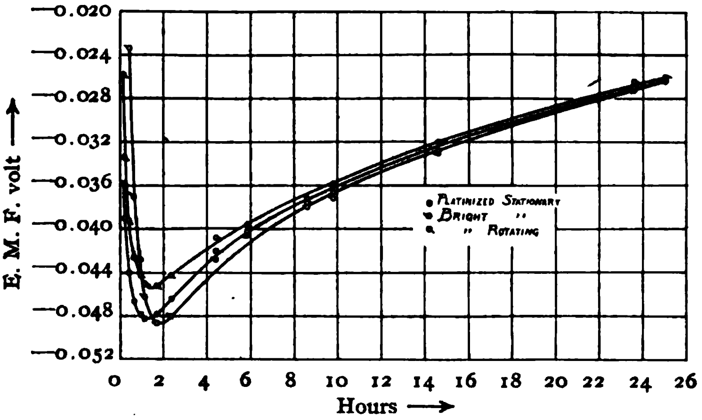

Fig. 2.—Comparison of different electrodes.

they differed more than in any other case, are given in Table II and are shown in Fig. 2.

Duplicate runs were made on separate solutions of each ammine. Except for a few of the earlier runs, where the purification was found to be inadequate and which were, therefore, discarded, the agreement was excellent, the differences never exceeding 2 or 3 millivolts. To show this concordance the duplicate runs made on diaquo-pentammine chloride solution are shown graphically in Fig 3.

The measurements made on all the ammines are collected in Tables III and IV and in Figs. 4 and 5, but in each case, to save space, only the measurements made on the stationary platinized electrode and in one of the 2 duplicate runs are given.[1]

TABLE II.

Comparison of the Three Electrodes.

Change of the Oxidation Potential of Aquo-pentammine Cobaltic Chloride with the Time.

3.256 NH_4OH.		0.077 *M* $[Co(NH_3)_5H_2O]Cl_3$.		0.019 *M* $CoCl_2$.
Time.		E. M. F.		
Hours.	Min.	Plat. stat.	Plat. rotat.	Bright stat.
0 :	08	−0.0358	−0.0258	+0.0062
0 :	14	−0.0390	−0.0334	−0.0064
0 :	26	−0.0440	−0.0392	−0.0234
0 :	40	−0.0466	−0.0426	−0.0370
0 :	55	−0.0478	−0.0442	−0.0428
1 :	09	−0.0482	−0.0450	−0.0462
1 :	42	−0.0478	−0.0452	−0.0486
2 :	20	−0.0464	−0.0442	−0.0480
4 :	25	−0.0420	−0.0408	−0.0428
5 :	52	−0.0402	−0.0396	−0.0406
8 :	35	−0.0372	−0.0376	−0.0380
9 :	49	−0.0366	−0.0358	−0.0372
14 :	33	−0.0328	−0.0320	−0.0330
23 :	37	−0.0270	−0.0264	−0.0272
25 :	04	−0.0264	−0.0260	−0.0262

The reproducibility and reality of the oxidation potentials is further shown by a series of experiments made with hexammine cobaltic chloride, in which the order of mixing the solutions was varied. Our regular procedure in this particular, as outlined above, was to mix the cobaltic ammine with a cobaltous salt solution in the cell, sweep this out thoroughly with oxygen-free nitrogen and finally add to it ammonium hydroxide solution.

We modified this procedure in 2 directions in 2 separate experiments. In one an aqueous solution of the hexammine was prepared in the cell, swept free from oxygen, its potential observed, and finally an ammoniacal

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[1] All the measurements are given in full in a dissertation entitled, "Cobalt Ammine Potentials," by A. T. Larson, Harvard University, Cambridge, 1917.

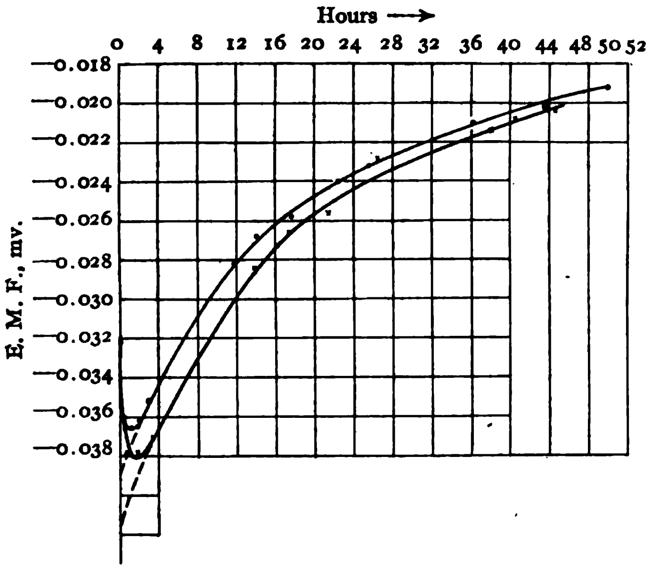

Fig. 3.—Agreement of duplicate runs.

solution of cobaltous chloride was added. In the other, an ammoniacal solution of the cobaltous chloride was prepared in the cell, its potential was observed and the hexammine solution was finally added to it. The

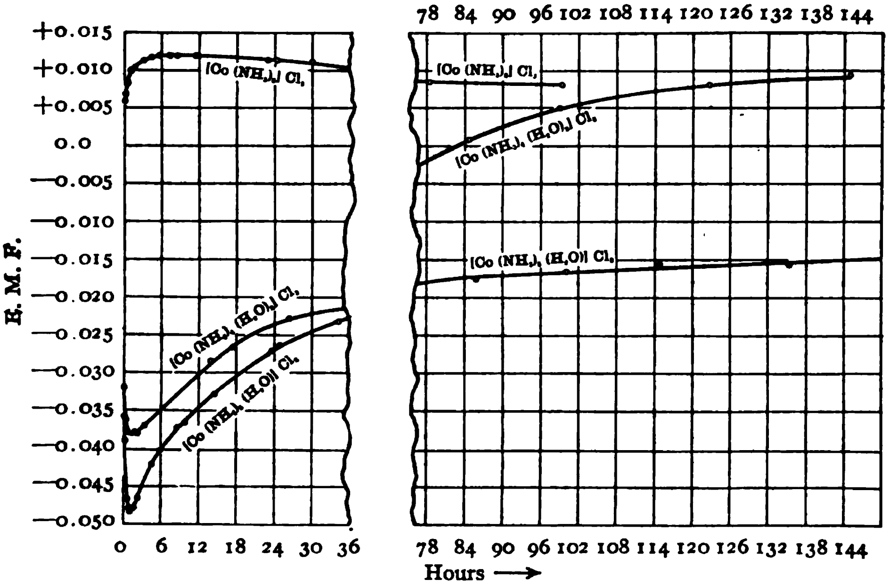

Fig. 4.—Oxidation potentials of hexammine, aquo-pentammine and diaquo-tetrammine chlorides.

TABLE III.

Oxidation Potentials.

3.256 *M* NH_4OH. 0.077 *M* Cobaltic Ammine. 0.019 *M* $CoCl_2$.

Hexammine. Cobalt chloride.		Aquo-pentammine. Cobalt chloride.		Diaquo-tertrammine. Cobalt chloride.	
Time, hours : min.	Pt. black. Volt.	Time, hours : min.	Pt. black. Volt.	Time, hours : min.	Pt. black. Volt.
0 : 06	—0.0060	0 : 08	—0.0358	0 : 05	—0.0320
0 : 14	—0.0070	0 : 14	—0.0390	0 : 20	—0.0362
0 : 32	—0.0084	0 : 26	—0.0440	0 : 40	—0.0378
1 : 09	—0.0100	0 : 40	—0.0466	1 : 50	—0.0378
2 : 18	—0.0104	0 : 55	—0.0478	2 : 15	—0.0380
3 : 07	—0.0114	1 : 09	—0.0482	3 : 25	—0.0370
4 : 22	—0.0118	1 : 42	—0.0478	13 : 55	—0.0284
5 : 37	—0.0120	2 : 20	—0.0464	17 : 25	—0.0266
7 : 19	—0.0120	4 : 25	—0.0420	26 : 25	—0.0228
8 : 32	—0.0120	5 : 52	—0.0402	37 : 55	—0.0214
11 : 22	—0.0120	8 : 35	—0.0372	50 : 20	—0.0200
22 : 52	—0.0114	9 : 49	—0.0366	62 : 00	—0.0196
24 : 22	—0.0114	14 : 33	—0.0328	74 : 40	—0.0180
27 : 32	—0.0112	23 : 37	—0.0270	85 : 50	—0.0176
30 : 07	—0.0112	25 : 04	—0.0264	100 : 20	—0.0166
36 : 44	—0.0102	34 : 17	—0.0232	114 : 55	—0.0156
46 : 12	—0.0088	39 : 07	—0.0208	135 : 20	—0.0156
47 : 52	—0.0094	51 : 37	—0.0176	158 : 00	—0.0146
49 : 08	—0.0092	61 : 07	—0.0126	182 : 00	—0.0124
72 : 22	—0.0088	72 : 22	—0.0048		
78 : 22	—0.0086	84 : 45	+0.0008		
99 : 22	—0.0082	99 : 07	+0.0050		
		122 : 42	+0.0082		
		144 : 47	+0.0096		

TABLE IV.

Oxidation Potentials.

3.256 *M* NH_4OH. 0.015 *M* Cobaltic Ammine. 0.019 *M* $CoCl_2$.

Nitro-pentammine. Cobalt chloride.		1-6 Dinitro-tetrammine. Cobalt chloride.		1-2 Dinitro-tertrammine. Cobalt chloride.	
Time, hours : min.	Pt. black. Volt.	Time, hours : min.	Pt. black. Volt.	Time, hours : min.	Pt. black. Volt.
0 : 05	—0.0450	0 : 08	—0.0734	0 : 10	—0.028
0 : 15	—0.0480	0 : 23	—0.0728	0 : 18	—0.0272
0 : 25	—0.0482	0 : 38	—0.0716	0 : 30	—0.0272
0 : 35	—0.0484	1 : 08	—0.0700	1 : 20	—0.0266
0 : 53	—0.0482	2 : 23	—0.0666	2 : 50	—0.0278
1 : 10	—0.0479	2 : 38	—0.0640	4 : 30	—0.0290
1 : 35	—0.0478	4 : 38	—0.0604	12 : 40	—0.0346
2 : 30	—0.0476	14 : 38	—0.0484	17 : 35	—0.0368
12 : 35	—0.0448	16 : 38	—0.0470	21 : 00	—0.0378
16 : 30	—0.0444	21 : 53	—0.0456	26 : 45	—0.0398
19 : 05	—0.0446	28 : 08	—0.0438	36 : 40	—0.0416
23 : 05	—0.0446	39 : 23	—0.0420	40 : 40	—0.0420
		42 : 58	—0.0418	46 : 45	—0.0436
		52 : 53	—0.0418		
		64 : 33	—0.0418		

final solutions had the same composition in all 3 experiments, but in each of them the electrodes were exposed to different solutions previous to the final mixing.

Before adding the third ingredient, the cobaltous ammine solution showed a constant potential of —0.2436 ±0.0004 volt; the ammoniacal hexammine solution showed a potential rising in 4 hours from +0.0634 to +0.0766, while solutions of hexammine and cobalt chloride showed a potential varying by several millivolts around +0.340; that is, in the different solutions before mixing, the electrodes showed potentials differing by over half a volt. Within a few minutes after mixing the potentials all became identical to 2 or 3 mv. This marked concordance of the potentials, irrespective of the previous history of the electrodes and the order of mixing, is strong evidence for the conclusion that the final potential is indeed an equilibrium one. These results are shown graphically in Fig. 6.

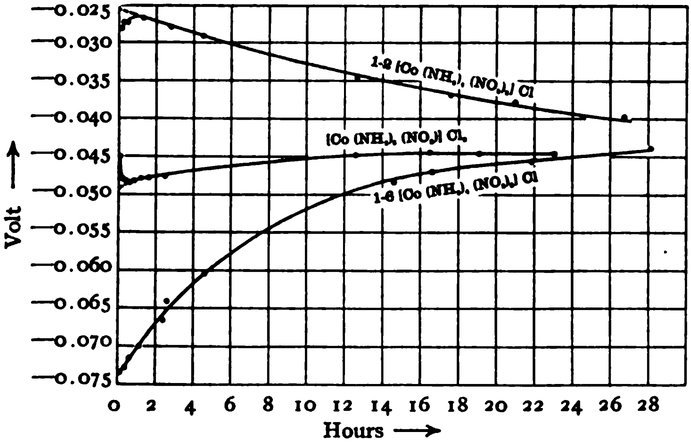

Fig. 5.—Oxidation potentials of nitro-pentammine, 1,6-dinitro- and 1,2-dinitro-tetrammine chloride.

The Change of the Potential with the Time.

It is evident from the tabulated results, and even more patently from the curves (Figs. 2, 4 and 5) that the potentials of all the ammines change with the time. Those of the hexammine and the nitro-pentammine change but slowly, while those of others, particularly of the aquo-pentammine, change quite rapidly.

The most striking feature in connection with this phenomenon is that after some weeks at this temperature the hexa-, aquo- and diaquo-ammines apparently reach the same potential (about +0.007). This is shown particularly by Fig. 4. The potentials of the 2 isomeric dinitro-tetrammines (Fig. 5) become identical within about 30 hours, as might have been expected, the equilibrium potential lying a little toward the side of the 1–2 modification, in spite of the fact that the 1–6 modification is supposed to be the more stable. This equilibrium potential (0.042) is very nearly the same as that of the other ammines when a correction for the difference in concentration is applied, $(\log \frac{0.077}{0.015} \times 0.259) = +0.042$. The potential of the nitro-pentammine chloride changes very slightly with the time, and its final equilibrium value is not very different from that of the other ammines when a correction for difference in concentration is made.

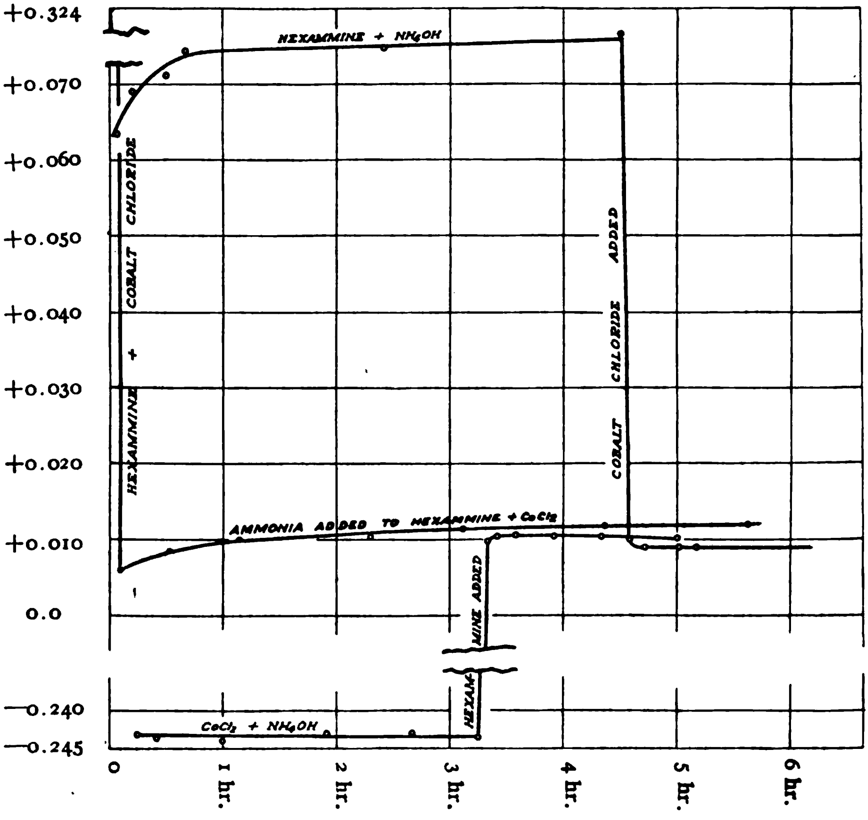

Fig. 6.—Effect of different orders of mixing on the hexammine potential.

These observations indicate that the hexa-, aquo- and diaquo-ammine chlorides all react with ammonia or water, as the case may be, to form the same equilibrium mixture of ammines in which all are present, the hexammine strongly predominating at this concentration of ammonia. The isomeric dinitro-tetrammines also each react to form another identical mixture with the 1–2 variety predominating. From this point of view the hexammine, the nitro-pentammine and the 1,2-dinitro-tetrammine are the most stable of these ammines, since they undergo the least change.

Another striking characteristic of the change of the potential of these ammines with the time is that each curve shows a more or less pronounced maximum (or minimum) within 3 to 4 hours after the start, sloping gradually from that point to its final equilibrium value; in other words, there is a short initial portion of each curve in which the potential is invariably changing *away* from its final equilibrium value. The curve is, therefore, the result of at least 2 superposed reactions, an initial, fairly rapid one, and a later slow change which results in the formation of an equilibrium mixture containing all the possible ammines.

At first glance it would appear as though these initial portions of the curves merely represented the slow charging of the electrodes, but from independent observations we know that all these ammines when mixed with cobaltous chloride in faintly acid solution give strongly positive potentials (+0.8 to +1.1 v.). The direction of the initial portion of the curves ought then always to be same, while inspection shows that the direction is upward for the hexa- and nitro-pentammine chloride and downward for the other ammines. This shows, then, that the initial change is not connected with the original condition of the electrode.

This phenomenon can perhaps be explained on the basis of the conclusions drawn from the experiments on the effect of stirring. Assuming as we did then that the electrical adjustment is rapid on the electrode and that the chemical rearrangement of the ammines also takes place more rapidly there than in the body of the solution, the electrode would evidently assume almost immediately a potential identical, or nearly identical, with that of the equilibrium mixture. Diffusion would then occur and the potential would tend to approach a value more characteristic of the solution as a whole; that is, the potential would move away from its equilibrium value.

It is not clear, however, from this explanation why it takes so long (3 to 4 hours) for the diffusion to attain its full effect. It is possible that the surface of the electrode slowly loses its catalytic effect on this reaction, so that after a few hours the potential recorded is substantially that of the solution. This is, however, so far as we know, a strictly *ad hoc* assumption.

Another and perhaps more reasonable explanation would be that the initial portions of the curves represent the quite rapid formation of a relatively unstable substance which in turn reacts to form a stable mixture of ammines. The initial portions of the curves then extrapolated to zero time would give the potentials of the unchanged ammines; the main portions of the curves extrapolated to zero time and neglecting the initial portions of the curves would give the potentials of the unstable products first formed from the original ammines.

On either of the above explanations the extrapolation of the main portions of the curves back to zero time should give the more significant results. On the basis of the diffusion explanation the resulting potential would be that of the solution of the unchanged ammine. On the basis of the second explanation, where the primary formation of an unstable ammine is assumed, the extrapolated value would represent a potential characteristic of a solution of this primary product. It is this method of extrapolation which we have adopted, and the characteristic potential of the various ammines are collected in Table VI.

TABLE VI.

Ammine solution.	Obs. extrapolated. E. M. F. Volt.	Liquid junction potential. Volt.	Corr. E. M. F. Volt.	Single oxidation potential. Volt.
0.077 *M* Hexammine cobaltic chloride	+0.0124	—0.0013	+0.0137	+0.1558
0.077 *M* Aquo-pentammine cobaltic chloride	—0.0550	—0.0013	—0.0537	—0.0884
0.077 *M* Diaquo-pentammine cobaltic chloride	—0.0400	—0.0013	—0.0387	0.1034
0.015 *M* Nitro-pentammine cobaltic chloride	—0.0488	+0.0004	—0.0492	0.0929
0.015 *M* 1,6-Dinitro-tetrammine cobaltic chloride	—0.0286	+0.0009	—0.0265	0.1156
0.015 *M* 1,2-Dinitro-tetrammine cobaltic chloride	—0.0738	+0.0009	—0.0747	0.0674

Single Potentials.

In order to compute the single oxidation potentials of the cobaltic ammines from the extrapolated values for the above cells,

$$\mathrm{Hg} \mid \mathrm{HgO} \mid M\ \mathrm{NaOH} \mid M\ \mathrm{KCl} \mid \left\{\begin{array}{l}\text{Cobaltic ammine}\\ \text{Cobaltous ammine}\\ \text{Ammonium hydroxide}\end{array}\right\} \text{Sol.} \mid \mathrm{Pt}.$$

it is necessary to know the potential of the mercuric oxide electrode, and the liquid junction potentials between the sodium hydroxide and the potassium chloride on the one hand, and the potassium chloride and the ammine solutions on the other.

The first 2 of these data were obtained by a direct measurement of the cell:

$$\mathrm{Hg} \mid \mathrm{HgO} \mid M\ \mathrm{NaOH} \mid M\ \mathrm{KCl} \mid \mathrm{HgCl} \mid \mathrm{Hg}$$

which gave definite and concordant values, averaging 0.1429 volt at 25° (the mercuric oxide electrode being negative). It follows, since the potential of the normal calomel electrode is +0.2850 with respect to the normal hydrogen electrode, that the potential of the normal mercuric oxide electrode inclusive of the NaOH | KCl potential is +0.1421 on this same basis.

The liquid junction potentials between the potassium chloride and the ammine solutions were computed by means of the Henderson[1] formula. In these computations the mobilities of the tri-, di- and monovalent complex ions were obtained from the measurements of Harkins[2] on hexa-, nitro-penta-, and dinitro-tetrammine cobaltic chloride. We applied the Storch-Bancroft equation to these measurements and obtained a satisfactory concordance using the following constants.

TABLE V.

	n.	K.	Λ.
Hexammine..........	1.5	0.00120	181.8
Pentammine..........	1.6	0.00084	140.0
Tetrammine..........	1.5	0.00087	110.4

The mobility of 75.5 ¹/ohm given by Johnston[3] for the chloride ion was adopted.

The degrees of ionization were computed on the assumptions (*a*) that the divalent cobaltous ammine ions have the same equivalent mobility as the divalent cobaltic ammine ions (nitro-pentammine); (*b*) that the ionization of each salt in a mixture is equal to that which it has when present alone in a solution of the same total equivalent ion concentration.[4]

In this way the ionization of the 0.019 *M* cobaltous ammine was found to be 57% in the presence of the 0.077 *M* hexammine, aquo-pentammine and diaquo-tetrammine cobaltic chloride; 72% in the presence of 0.015 *M* nitro-pentammine, and 75% in the presence of 0.015 *M* dinitro-tetrammine chloride. Similarly, the ionizations in these solutions of the hexammine, aquo-pentammine and diaquo-tetrammine were found to be 48%, that of the nitro-pentammine 72% and that of the dinitro-tetrammine 83% in the presence of the cobaltic ammine.

The liquid junction potentials computed from these values are given in Col. 3 of Table VI; the sign of the potentials is that of the ammine solution.

In order to express the single oxidation potentials of these ammines on the basis of the normal hydrogen electrode at 0°, it is necessary only to subtract the above liquid junction potentials from the observed extrapolated e. m. f. of the above cells. The results thus obtained are given in the last column of Table VI.

In order to compute the concentration of the cobaltic ion in these solutions it remains to determine the concentration of the cobaltous ions in the same solutions and to ascertain the normal oxidation potential of the cobaltic-cobaltous electrode.

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[1] Henderson, *Z. physik. Chem.*, 59, 118 (1907); 63, 325 (1908).

[2] Harkins, THIS JOURNAL, 38, 2656 (1916).

[3] Johnston, *ibid.*, 31, 1010 (1909).

[4] See Bray and Hunt, *ibid.*, 33, 794 (1911).

Concentration of Cobaltous Ion in the Cobaltammine Solution. The Cobalt-Cobaltous Electrode.

(*a*) **In Cobalt Chloride Solution.**—The method employed to determine the cobaltous ion concentration was to measure the potential of a metallic cobalt electrode, first, in a cobaltous chloride solution of known ion concentration and then in cobaltous ammine solutions whose cobaltous ion concentrations were desired.

The cobalt-cobaltous potential has been studied by Neuman,[1] Labendzinski,[2] Cofetti and Foerster,[3] and particularly by Schildbach.[4]

To compare the results of these investigators we have computed them to equivalent normal cobaltous chloride at 25°, taking the normal hydrogen electrode as zero. The liquid junction potential between normal cobaltous chloride and normal potassium chloride has been computed as above and found to be 0.002 volts. The resulting cobaltous potentials are as follows.

	Volts.
Neuman, cobalt plated on platinum	—0.262
Labendzinski, cobalt plated on platinum	—0.307
Schildbach, finely divided cobalt	—0.292
Schildbach, cobalt plated on platinum	(—0.268)

Unfortunately Schildbach did not measure the potential of electrolytic cobalt in cobalt chloride, but in cobalt sulfate he found that it gave a potential 24 millivolts less negative than that of finely divided cobalt. Applying this correction to his result for finely divided cobalt in cobaltous chloride, the value given in brackets is obtained. This brings his value in close accord with that of Neuman. Schildbach also observed that cobalt which had been cathodically polarized for sometime gave at first a decidedly more negative potential than the above equilibrium value, but on prolonged standing readjustment to this value occurred. This perhaps explains the relatively high negative potential obtained by Labendzinski.

We prepared a number of cobalt electrodes by electroplating from solutions of cobalt chloride in water, in boric acid solutions and in ammoniacal solutions, on platinum and on carbon. These electrodes, measured in cobalt chloride solutions of different concentrations at 25° and against a normal calomel electrode, gave potentials constant to within a millivolt over many hours, and even days, although the electrodes usually exhibited individual variations. These measurements, made over a period of nearly 2 years, are summarized in the following table.

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[1] Neuman, *Z. physik. Chem.*, 14, 215 (1894).

[2] Labendzinski, *Z. Elektrochem.*, 10, 77 (1904).

[3] Cofetti and Foerster, *Ber.*, 38, 2936 (1905).

[4] Schildbach, *Z. Electrochem.*, 16, 967 (1910).

TABLE VII.

Potential Measurement on Cell:

Co]$CoCl_2$ Sol. | *M* KCl | HgCl | Hg.

Electrode No.	Co Plated.		Conc. $CoCl_2$. *M*.	Dissoc. %.	E. M. F. of cell.		π Co-Co.$^{++}$
	From.	On.			Obs.	Corrected Eq. *N*. $CoCl_2$.	Corrected H_2/elect = 0.
1.......	$CoCl_2$	Platinum	0.01	83.6	0.583	0.539	0.257
2.......	$CoCl_2$	Platinum	0.01	83.6	0.588	0.544	0.262
3.......	$CoCl_2$	Platinum	0.01	83.6	0.579	0.535	0.253
4.......	$CoCl_2$	Platinum	0.01	83.6	0.578	0.534	0.252
3.......	$CoCl_2$	Platinum	0.02	78.6	0.570	0.534	0.252
4.......	$CoCl_2$	Platinum	0.02	78.6	0.570	0.534	0.252
3.......	$CoCl_2$	Platinum	0.05	70.8	0.556	0.530	0.248
4.......	$CoCl_2$	Platinum	0.05	70.8	0.556	0.530	0.248
5.......	$CoCl_2$	Platinum	1.00	40.4	0.539	0.544	0.262
6.......	$CoCl_2$	Platinum	1.00	40.4	0.540	0.545	0.263
7.......	$CoCl_4$ + boric acid	Platinum	2.00	34.2	0.524	0.536	0.254
8.......	$CoCl_2$ + boric acid	Carbon	2.00	34.2	0.526	0.538	0.256
						Average,	0.255
							±0.004
9.......	$CoCl_2$ + NH_4OH	Platinum	2.00	34.2	0.559	0.571	0.289
10.......		Massive Co	1.00	40.4	0.423	0.428	0.146
11.......		Massive Co	1.00	40.4	0.424	0.429	0.147

From the above observed values of the E. M. F. the potential of the cobalt electrode in equivalent normal cobalt chloride solution has been computed, by means of the Nernst concentration formula, using degrees of dissociation derived from Kohlrausch's conductivity data by means of the Storch-Bancroft formula. The values $n = 1.52$ and $K = 0.00098$ in this formula were found to give satisfactory concordance. These corrected values are given in the seventh column of the above table.

The corrected potentials of all the electrodes prepared from cobalt chloride or boric acid solutions show slight individual variations, but the average deviation from the mean (—0.255) is after all only ±4 millivolts. The mean value agrees reasonably well with those of Neuman (0.262) and Schildbach (0.268).

The normal potential of the cobalt electrode in molar solution of cobalt *ions* would be on the basis of this value —0.255 + 0.018 = —0.237 volt.

(*b*) **In Ammoniacal Solutions of Cobalt Chloride.**—In measuring the potential of cobalt electrodes in ammoniacal solutions the same precautions were taken as in the measurements made in ammoniacal solutions of the cobaltic ammines, and a similar mercuric oxide electrode and normal potassium chloride agar-agar salt bridge were employed. In addition any exposed platinum or carbon of the electrodes was coated with paraffin. It was found that the potentials adjusted themselves quite rapidly and definitely. The measurements made in 6 molar ammonium hydroxide are summarized in the following table.

TABLE VIII.

Cobalt-cobaltous Potential in Ammoniacal Solution.

Cell Co | 6 *M* $NH_4OH + x$ *M* $CoCl_2$ | *M* KCl | *M* NaOH | HgO | Hg at 25°.

Conc. $CoCl_2$. *M*.	% Dissoc.	Observed E. M. F. Cell Electrode No. 1.	2.	3.	4.	Single Potential Co | *M* $CoCl_2$. Electrode No. 1.	2.	3.	4.
0.00047	95.9	0.794	(0.766)	0.800	0.802	0.565	...	0.572	0.573
0.00095	94.1	0.784	0.771	0.792	0.798	0.563	0.550	0.571	0.577
0.00475	87.9	0.764	0.754	...	...	0.563	0.553	...	...
0.0052	87.3	...	...	0.760	0.756	...	...	0.560	0.556
0.0095	83.9	0.748	0.742	0.753	0.750	0.556	0.550	0.561	0.558
0.0190	79.0	0.740	0.727	...	...	0.556	0.542	...	...
0.0380	73.4	0.735	0.724	...	...	0.559	0.546	...	...
0.057	69.6	0.731	0.724	...	...	0.560	0.553	...	...
0.076	66.8	0.728	0.720	...	...	0.560	0.552	...	...
0.095	64.4	0.723	0.718	...	...	0.557	0.552	...	...
					Average,	0.558	0.550	0.561	0.557
	(Omitting first 2 values),					±0.002	±0.003	±0.001	±0.001
					Final average,		—0.556		±0.003 volts

From the observed potentials the single potential of the cobalt electrode in an equivalent normal solution of cobaltous ammine has been computed. In making this computation the cobaltous ammine was assumed to follow the same dilution formula as aqueous cobalt chloride solutions. The liquid junction potentials between the ammoniacal and the potassium chloride solutions were computed on similar assumptions and were found in general to be only a few tenths of a millivolt. The resulting values are given in the last four columns of Table VIII. It can be seen that there is a close agreement (±0.003 v.) between the values computed from the different concentrations of cobaltous ammine solution. This indicates that the potential is a reversible one and that the cobaltous ammine ion is divalent. The average value (0.556) corresponds to a concentration of about 1×10^{-11} *M* simple cobaltous ions and shows that the cobaltous ammine complex is decidedly stable under these conditions.

Formula of the Cobaltous Ammine Ion in Solution.—While the above measurements at different total cobalt concentrations show clearly that the potential registered by the cobalt electrode is definite and reproducible, that the cobaltous ammine ion is divalent, and that the concentration of the simple cobaltous ions is extremely minute, they do not give any information as to the number of ammonia molecules associated with the cobalt atom in the cobaltous ammine ion. To secure this information it was necessary to study the effect on the potential of the ammine of various concentrations of the ammonia. Measurements were, therefore, carried out in which the total concentration of cobalt was maintained constant while the ammonia concentration was varied from 2 to 6 molar. The results are collected in the following Table IX.

TABLE IX.

Cell Co | 0.05 *M* $CoCl_2$ + *x* *M* NH_4OH | *M* NaOH | HgO | Hg at 25°.

Empirical Formula: $\log C_{Co^{++}} = +0.46 - n \log P_{NH_3}$.

Conc. NH_4OH	Volts.						Log conc. *M* Co^{++}.		
M.	Electrode 1.	Electrode 2.	Ave.	E. M. F. Co/Co^{++}.	E. M. F. Differ.	P_{NH_3}. Mm.	Obs.	Comp. $n = 6$.	*n*.
6	0.716	0.714	0.715	0.574[*]	0.337	107.7	11.42	11.71	5.86
4	0.694	0.692	0.693	0.551	0.314	63.4	10.64	10.35	6.16
3	0.660	0.658	0.659	0.517	0.280	44.7	9.49	9.44	6.03
2	0.622	0.618	0.620	0.478	0.241	27.8	8.17	8.20	5.98
								±0.16	±0.09

[*] A correction of +0.001 volt has been applied to this value, since computations show that the higher concentrations of the ammonia will result in a change in the liquid junction potential of this amount.

By subtracting the E. M. F. of the combination Hg | HgO | NaOH | KCl (p. 2039) from the observed E. M. F. of the cell the single potentials of the cobalt electrodes in the different concentrations of ammonia are obtained; these values for the average of 2 different electrodes are given in the fifth column of the table. Finally, subtracting the potential of the cobalt electrode in molar cobaltous ions (—0.237 volt) and substituting in the Nernst formula gives the desired concentration of the cobaltous ions. The logarithms of these values, given in Col. 8, show an enormous change, in the concentration of the cobalt ion 1800 times, for a threefold change in the total concentration of ammonia.

The reaction for the formation of the cobaltous ammine ion would be represented by the equation

$$Co^{++} + n\,NH_3 \rightleftharpoons Co(NH_3)_n{}^{++}.$$

From this it follows that $\dfrac{C_{Co^{++}} \times C_{NH_3}{}^n}{C_{Co(NH_3)_n{}^{++}}} = K$, and since the relative concentration of the simple cobaltous ion is negligible in comparison with that of the cobaltous ammine ion, the latter is substantially equal to the total cobalt concentration, which is in turn a constant; that is

$$C_{Co^{++}} \times C_{NH_3}{}^n = K_1,$$

and, therefore,

$$\log C_{Co^{++}} = \log K_1 - n \log C_{NH_3}.$$

The concentration of free ammonia in the ammoniacal solution is not identical with the total concentration, and indeed is not definitely known,[1] but it is certainly always proportional to the partial pressures of the ammonia from these solutions, and accurate measurements of these pres-

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[1] See Abegg's "Handbuch der Anorg. Chemie," III, 3, 71, Leipzig (1907).

sures have been made by Perman.[1] Plotting his data, and interpolating, the values given in the seventh column of Table IX are obtained. When the logarithms of these values in turn are plotted against the logarithms of the corresponding concentrations of the cobalt ions the points are found to lie very nearly on a straight line represented by the equation

$$\log C_{\mathrm{Co}}{}^{++} = 0.46 - n \log P_{\mathrm{NH_3}}.$$

The values of $\log C_{\mathrm{Co}}{}^{++}$ computed from this equation are given in the ninth column. They are seen to agree excellently (±0.16 or ±0.005 volt) with the observed values. Conversely, when the value of the coefficient n is computed from the observed values of $P_{\mathrm{NH_3}}$ and $C_{\mathrm{Co}}{}^{++}$, taking $\log K_1 = 0.46$, the values given in the tenth column are obtained. They show an average deviation of only 1.5% from the mean value of 6. There is some uncertainty in these results in that, unfortunately, the absolute ammonia concentration was determined only by means of hydrometer measurements, although the dilution was made with burets. In spite of this the evidence appears to be very strongly in favor of the conclusion that the coefficient n does have the value 6, and that the formula of the ammine, therefore, is $\mathrm{Co(NH_3)_6}{}^{++}$ in the presence of an excess of ammonia.

Concentration of Cobaltous Ion in the Cobaltic-Cobaltous Ammine Solution.—The equilibrium constant for the dissociation of the cobaltous ammine ion into ammonia and the simple cobaltous ion is, therefore, in accordance with the above

$$K = \frac{K_1}{C_{\mathrm{Co(NH_3)_6}}} = \frac{10^{0.46}}{0.05} = 57.7$$

and, therefore,

$$\frac{C_{\mathrm{Co}}{}^{++} \times P_{\mathrm{NH_3}}{}^{6}}{C_{\mathrm{Co(NH_3)_6}}{}^{++}} = 57.7 \text{ at } 25°.$$

The total concentrations of the ammonia and the cobaltous chloride in all the solutions used for the measurements of the oxidation potentials of the cobaltic ammine were 3.265 and 0.019 M respectively. Using the above empirical equation for the effect of ammonia, the concentration of the cobaltous ion in this solution is readily found to be

$$C_{\mathrm{Co}}{}^{++} = 0.74 \times 10^{-10}\, M.$$

It is interesting to compare the stability of this ammine with that of the few other ammines which have been studied.[2] All of these have been collected in the following Table X, where

$$K_c = \frac{(C_{\mathrm{Me}})(C_{\mathrm{NH_3}})^n}{C_{\mathrm{Me(NH_3)}_n}} \text{ at } 25°,$$

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[1] Perman, *J. Chem. Soc.*, 83, 1171 (1903).

[2] Abegg's "Handbuch der anorg. Chem.." III, 3, 69, Leipzig (1907); Bodlander, *Z. physik. Chem.*, 39, 597 (1901); Abegg, *ibid.*, 40, 84 (1902); 45, 461 (1903); Euler, *Ber.*, 36, 1854, 2878, 3400 (1903).

C_{Me} representing the concentration of the metallic ion and n the number of molecules of ammonia in the ammine. To facilitate comparison, we have converted our value of K for cobaltous ammine, expressed in mm. of Hg, to this same basis of molar concentrations, by dividing by 12.9, a proportionality factor applying approximately over these ranges of ammonia concentrations.

TABLE X.

Stability Constants of Metallic Ammines.

Ammine.	K_c.
$Ag(NH_3)_2$	6.8×10^{-8}
$Cu(NH_3)_2$	1.5×10^{-9}
$Cd(NH_3)_4$	1.0×10^{-7}
$Zn(NH_3)_4$	2.6×10^{-10}
$Co(NH_3)_6$	1.25×10^{-6}

On the basis of these values of K_c the cobaltous ammine is evidently less stable than the other ammines in a molar solution of ammonia. Because of the relatively high value of n (6), it is relatively even less stable at lower ammonia concentrations but is more stable at higher ammonia concentrations.

The Cobaltic-Cobaltous Potential.

The cobaltic-cobaltous potential has been measured by Stephen Jahn[1] and by Oberer[2] at 0°, but unfortunately for our purposes at no other temperature. We have therefore repeated their measurements at 0° and have also made measurements at 16°, the highest temperature to which one can go without excessive decomposition of the cobaltic salt. By extrapolating we have found the cobaltic-cobaltous potential at 25°.

Our procedure was substantially that of the above-mentioned investigators. Cobaltic sulfate was prepared by the electrolytic oxidation of cobaltous sulfate in 8 *M* sulfuric acid. The dried crystalline product and crystalline cobaltous sulfate were dissolved in 2 *M* sulfuric acid and the potential measured on both gold and platinum electrodes against a hydrogen electrode immersed in sulfuric acid of the same concentration. A rotating platinum stirrer and 2 stationary electrodes were inserted through the stopper. Holes were also provided in the stopper for a thermometer and a calibrated pipet. Following a suggestion of Jahn, one platinum electrode was coated with a thin layer of cobalt oxide formed by the evaporation and subsequent ignition of a film of cobalt nitrate solution upon it.

When the potential had become constant, samples of the electrolyte were transferred by means of an ice-jacketed pipet into a solution of potassium iodide, and the liberated iodine was tirated by means of thio-

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[1] Jahn, *Z. anorg. Chem.*, 60, 292 (1908).

[2] Oberer, Dissertation, Foerster's Laboratory, Zurich, 1903.

sulfate solution. A slow decomposition of the cobaltic salt occurred, so that successively lower ratios of cobaltic cobaltous concentrations could be measured simply by stirring the cell for a few hours and again observing the potential and analyzing for cobaltic cobalt.

When the run had been completed the remaining electrolyte was analyzed for total cobalt by electrolysis. From these data the cobaltic-cobaltous ratio could be computed for each of the potential measurements. The results are collected in Table XI.

TABLE XI.

E. M. F.—Cell Pt(Au) | $(Co)(SO_4)_3 + CoSO_4 + 8\ M\ H_2SO_4$ | $M\ H_2SO_4$ | PtH_2.

		Obs. E. M. F. Cell.		Normal potential Co^{+++}/Co^{++}	
Temp. °C.	Ratio. Co^{+++}/Co^{++}	Platinum. Volts.	Gold	Platinum. Volts.	Gold.
0	0.58	1.7246	1.7562	1.7385	1.7718
0	0.46	1.7536	1.7568	1.7748	1.7780
16	0.44	1.7692	1.7736	1.7953	1.7997
16	0.34	1.7662	1.7690	1.7986	1.8014

The gold electrodes gave higher potentials than the platinum, an observation wholly in accord with the experiments of Jahn[1] and since slow spontaneous decomposition of the cobaltic salt is continually taking place in the solutions it doubtless records more nearly the true cobaltic-cobaltous potential; indeed, we consider the higher values in general as the more probable.

This formula is in agreement with what would be expected from the known solid compounds of ammonia and cobaltous chloride. While a cobaltous diammine had been prepared in the dry state[2] the hexammine is the stable compound obtained by precipitation from strongly ammoniacal solutions or by treatment of the dry chloride with an excess of ammonia.[3]

To obtain the single cobaltic-cobaltous potential from these measurements we must eliminate the potential of the hydrogen electrode in 2 *M* sulfuric acid at the temperatures of the observations. This we have done by measuring the E. M. F. of the cell,

$$Hg \mid Hg_2Cl_2 \mid M\ KCl \mid Sat.\ NH_4NO_3 \mid 2\ M\ H_2SO_4 \mid H_2,$$

obtaining +0.2878 volt at 0° and +0.2816 volt at 16°. Auerbach gives for the potential of the normal calomel electrode against the normal hydrogen electrode +0.289 at 0° and +0.286 at 18°, or +0.2863 at 16°. Assuming with Auerbach[4] and others that the normal hydrogen electrode

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[1] *Loc. cit.*

[2] F. Rose, Unters. über Ammoniak-Kobaltverbindung, Heidelburg, 1871, p. 26; Naumann, *Ber.*, 37, 4334 (1904).

[3] Frémy, *Ann. chim. phys.*, [3] 35, 257; Rose, *loc. cit.*; Naumann, *loc. cit.*; Ephraim, *Ber.*, 45, 1323 (1912); 51, 130 (1918).

[4] Auerbach, *Z. Elektrochem.*, 18, 136 (1812).

has a zero temperature coefficient over this range, this gives for the single potential of the $H_2 \mid 2M\ H_2SO_4$ electrode +0.0012 at 0° and +0.0047 at 16°. Subtracting these values we obtain the single cobaltic-cobaltous potentials given in the last 2 columns of Table XI.

Our value at 0° (1.775) agrees reasonably well with Jahn's average value of 1.774, measured against a hydrogen electrode in 1.5 *M* sulfuric acid. No accurate data are available regarding this latter electrode, but assuming that the concentration of the hydrogen ion in this acid is 1.2 *M* the normal potential would be 1.779 volts.

From the average of the values at 0° and at 16° a temperature coefficient of +0.00169 volt is obtained, giving a normal cobaltic-cobaltous potential at 25° of +1.817 volts.

Concentration of Cobaltic Ion in the Cobaltic Ammine Solutions.—The concentration of the cobaltic ion in the various cobaltic ammine solutions can now be easily computed from the equation

$$E = E_n + 0.059 \log \frac{C_{Co}{}^{+++}}{C_{Co}{}^{++}} = 1.817 + 0.059 \log \frac{C_{Co}{}^{+++}}{0.74 \times 10^{-10}}$$

$$\text{or } \log C_{Co}{}^{+++} = E - \frac{2.415}{0.059}.$$

TABLE XII.

Conc. *M*.	Ammine.	Oxidation. Potent.	$C_{Co}{}^{+++}$ Obs. $\times 10^{-40}$.	$C_{Co}{}^{+++}$ In *M* Ammine. $\times 10^{-38}$.
0.077	Hexammine cobaltic chloride..........	0.1558	52.	6.8
0.077	Aquo-pentammine cobaltic chloride....	0.0884	3.7	0.48
0.077	Diaquo-pentammine cobaltic chloride..	0.1034	6.8	0.87
0.015	Nitro-pentammine cobaltic chloride....	0.0929	4.4	2.9
0.015	1,6-Dinitro-tetrammine cobaltic chloride	0.1156	10.7	7.1
0.015	1,2-Dinitro-tetrammine cobaltic chloride	0.0674	1.7	1.1

The resulting values are given in the fourth column of Table XII. Corrected to a molecular normal concentration of the cobaltic ammine the values given in the last column of Table XII are obtained. It is evident from these values that all the cobaltic ammines are extremely stable, yielding exceedingly small cobaltic ion concentrations. Relatively the stability increases downward in the order: 1,6-dinitro-tetrammine, hexammine, nitro-pentammine, 1,2-dinitro-tetrammine, diaquo-pentammine, aquo-pentammine.

Expressing these results, taking the hexammine for illustration, in the same form as was employed with the cobaltous ammines (see above).

$$K = \frac{(C_{Co}{}^{+++})(P_{NH_3})^6}{C_{Co(NH_3)_6}{}^{+++}} = \frac{(6.8 \times 10^{-38})(49.5)^6}{1} = 1.0 \times 10^{-27}$$

or

$$K_c = 2.2 \times 10^{-34}.$$

This shows that compared with cobaltous hexammine and with the other metal ammines, cobaltic hexammine (and similarly the other cobaltic ammines) are extremely stable.

Summary.

1. The oxidation potentials of aqueous solutions of 6 representative cobaltic ammines have been measured in 3.265 *M* ammonium hydroxide solution. From these potentials the concentrations of simple cobaltic ions in these solutions have been computed and the relative stabilities of the ammines thus ascertained. Their stability is very great as compared with other metal ammines. The 6 ammines, arranged in the order of stability, are as follows: Aquo-pentammine cobaltic chloride, diaquo-tetrammine cobaltic chloride, 1,2-dinitro-tetrammine cobaltic chloride, nitro-pentammine cobaltic chloride, hexammine cobaltic chloride, 1,6-dinitro-tetrammine cobaltic chloride.

2. Incidentally:

(*a*) The potentials of the cobalt-cobaltous electrode in cobaltic chloride solution and in ammoniacal cobaltic chloride solutions have been measured. From them the formula of the cobaltous ammine ion in the presence of excess ammonia has been shown to be $Co^{++}(NH_3)_6$ and the equilibrium constant for its dissociation into ammonia and simple cobaltous ions has been computed.

(*b*) The cobaltous-cobaltic potential has been determined at 16° and redetermined at 0°. From them the potential at 25° has been obtained by interpolation.

(*c*) The potential of the hydrogen electrode in 2 *M* sulfuric acid has been measured at 0° and at 16° C. against a calomel electrode.

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[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR. CHEMICAL LABORATORY OF HARVARD COLLEGE.]

THE DETERMINATION OF POTASSIUM AS PERCHLORATE. III.

BY GREGORY P. BAXTER AND FRANK E. RUPERT.

Received August 7, 1920.

In recent papers Baxter and Kobayashi[1] have proposed certain modifications in the procedure for the determination of potassium as perchlorate and have supported the use of absolute ethyl alcohol containing perchloric acid and saturated with potassium perchlorate as the washing liquid, after the initial extraction of sodium perchlorate has been carried out with alcohol containing perchloric acid only. They have also advocated working at freezing temperature and found that at least one solution of the precipitate in water and evaporation to dryness with a slight

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[1] Baxter and Kobayashi, THIS JOURNAL, 39, 249 (1917); 42, 735 (1920).

excess of perchloric acid is necessary to eliminate inclusion of sodium salt by the potassium salt.

As substitutes for ethyl alcohol we have investigated in a similar fashion methyl alcohol, and ethyl alcohol denatured with 5% of methyl alcohol.

Potassium perchlorate was purified for the experimental work by 2 crystallizations from water. Fairly pure *perchloric acid* was twice distilled under reduced pressure in an all-glass apparatus. By determining the specific gravity of the distillate it was found to contain 56.3% of acid. After evaporation in a weighed platinum crucible 30 cc. left a residue of 0.5 mg. wholly soluble in a few cc. of alcohol. *Sodium perchlorate* was made from the distilled perchloric acid and twice crystallized sodium carbonate. After the solution had been evaporated to dryness, the residue was dissolved in absolute ethyl alcohol containing 0.1% of perchloric acid, and the solution was filtered through a platinum sponge crucible. The operations of evaporation to dryness, solution in alcohol and filtration were then repeated. This last solution was evaporated to dryness and the residue was dissolved in water to make a 10% solution, from which suitable quantities could be measured out for separate experiments. *Ethyl* and *methyl alcohols* were dehydrated over lime and distilled through a Hempel column.

First, approximate determinations of the solubility of potassium perchlorate were made in methyl alcohol, and in ethyl alcohol denatured with 5% of methyl alcohol, both with and without the addition of perchloric acid. A large excess of finely powdered potassium perchlorate was placed in 100-cc. flasks, which were filled with the alcoholic solution and frequently shaken by hand while kept at the temperature in question by immersion in an ice-bath or in a thermostat maintained at 20°. The solutions were filtered through platinum sponge crucibles into weighed platinum dishes in which they were evaporated to dryness over an electric stove. The residues were heated to about 200° before being weighed.

Since the solubility in methyl alcohol was found to be many times that in the denatured alcohol, while the latter differs very little from pure ethyl alcohol in its effect, no further experiments with methyl alcohol were made.

TABLE I.

Grams of $KClO_4$ in 100 cc. of Methyl Alcohol.

$HClO_4$ %.	0°.	20°.
0.0	0.0497	0.0745
0.0	0.0492	0.0749
0.4	..	0.0216
0.4	..	0.0216
0.8	0.0090	0.0176
0.8	0.0096	0.0178
2.4	..	0.0120
2.4	..	0.0123

TABLE II.

Grams of $KClO_4$ in 100 cc. of Denatured Alcohol.

$HClO_4$. %.	0°.	20°.
0.0	0.0086	0.0120
0.0	0.0086	0.0114
0.1	0.0022	0.0033
0.1	0.0021	0.0032
0.2	0.0022	0.0030
0.2	0.0021	0.0029
0.4	0.0018	0.0028
0.4	0.0019	0.0028
0.8	..	0.0025
0.8	..	0.0026

Blank experiments for the recovery of potassium perchlorate in the presence of sodium perchlorate were carried out as in the work by Baxter and Kobayashi, except that denatured alcohol was substituted for ethyl alcohol. The procedure was as follows.

An exactly weighed quantity of dry potassium perchlorate together with an approximately weighed portion of sodium perchlorate was dissolved in water in a platinum dish, and the solution was evaporated to dryness with a small quantity of perchloric acid. The residue was extracted with 20 cc. of denatured alcohol containing 0.2% of perchloric acid and was washed with two 5 cc. portions of the same solution, which is designated "A" in the tables. The first extract and rinsings were poured through a weighed platinum-sponge crucible. Next the potassium perchlorate was dissolved in water and the solution was evaporated to dryness with a small quantity of perchloric acid and the residue was extracted, washed by decantation and transferred to the original platinum-sponge crucible with denatured alcohol containing 0.2% perchloric acid and saturated with potassium perchlorate.[1] This solution is designated "W" in the tables. In the experiments recorded in Table III the operations were performed at 0°, while the experiments recorded in Table IV were performed at about 20°.

Since Expts. 3 to 9 and 14 to 19 show positive errors in nearly every case, in Expts. 10 to 13 and 20 to 23, in order to eliminate residual inclusion of sodium salt, the second precipitate of potassium perchlorate, after being rinsed, was dissolved in dil. perchloric acid and the solution evaporated to dryness still again before the final extraction and transfer to the crucible. The later modification had little if any effect.

The following experiments indicate that ethyl alcohol denatured with 5% of methyl alcohol may safely be substituted for ethyl alcohol in the washing of potassium perchlorate.

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[1] Made by dissolving the necessary quantity of potassium perchlorate in warm conc. perchloric acid and adding the solution to the alcohol.

TABLE III.

Expt.	First extract. Cc.	Washings. Cc.	At 0° NaClO$_4$ taken. G.	KClO$_4$ taken. G.	KClO$_4$ found. G.	Error. G.
1.....	A 20 + 5 + 5	W 90	0.0	0.3013	0.3011	—0.0002
2.....	A 20 + 5 + 5	W 90	0.0	0.3451	0.3449	—0.0002
3.....	A 20 + 5 + 5	W 75	0.5	0.3021	0.3027	+0.0006
4.....	A 20 + 5 + 5	W 75	0.5	0.3446	0.3450	+0.0004
5.....	A 20 + 5 + 5	W 75	0.1	0.3002	0.3005	+0.0003
6.....	A 20 + 5 + 5	W 75	0.1	0.3326	0.3329	+0.0003
7.....	A 20 + 5 + 5	W 75	0.3	0.2999	0.3002	+0.0003
8.....	A 20 + 5 + 5	W 75	1.0	0.3029	0.3033	+0.0004
9.....	A 20 + 5 + 5	W 75	1.0	0.3164	0.3168	+0.0004
10.....	A 20 + 5 + 5	W 90	0.5	0.3018	0.3019	+0.0001
11.....	A 20 + 5 + 5	W 90	0.5	0.3183	0.3183	+0.0000
12.....	A 20 + 5 + 5	W 90	1.0	0.3002	0.3004	+0.0002
13.....	A 20 + 5 + 5	W 90	1.0	0.3188	0.3189	+0.0001

TABLE IV.

At 20°.

Expt.	First extract. Cc.	Washings. Cc.	NaClO$_4$ taken. G.	KClO$_4$ taken. G.	KClO$_4$ found. G.	Error. G.
14.....	A 20 + 5 + 5	W 75	0.5	0.3003	0.3007	+0.0004
15.....	A 20 + 5 + 5	W 75	0.5	0.3083	0.3084	+0.0001
16.....	A 20 + 5 + 5	W 75	0.1	0.2984	0.2983	—0.0001
17.....	A 20 + 5 + 5	W 75	0.1	0.3052	0.3053	+0.0001
18.....	A 20 + 5 + 5	W 75	1.0	0.3008	0.3010	+0.0002
19.....	A 20 + 5 + 5	W 80	1.0	0.3056	0.3059	+0.0003
20.....	A 20 + 5 + 5	W 95	0.5	0.3017	0.3019	+0.0002
21.....	A 20 + 5 + 5	W 100	0.5	0.3091	0.3093	+0.0002
22.....	A 20 + 5 + 5	W 100	1.0	0.3020	0.3022	+0.0002
23.....	A 20 + 5 + 5	W 100	1.0	0.3096	0.3099	+0.0003

It also is evident that in the procedure described the temperature is unimportant, if the washing liquid employed after the initial extraction is previously saturated with the precipitate.

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GELATIN AS AN EMULSIFYING AGENT.

BY HARRY N. HOLMES AND WM. C. CHILD.

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Various theories of the action of emulsifying agents have been offered. Plateau[1] and Quincke[2] considered the lowering of surface tension of one of the 2 liquids as the most important factor, with viscosity next. Pickering[3] believed that a droplet covering of small insoluble solid particles was a vital factor. He demonstrated his theory by the use of basic ferrous and cupric sulfates. Martin Fischer[4] states that solvated sub-

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[1] Plateau, *Ann. Physik.*, **141**, 44 (1870).

[2] Quincke, *ibid.*, **271**, 580 (1888).

[3] Pickering, *J. Chem. Soc.*, **91**, 2001 (1907).

[4] Fischer, *Science*, **43**, 468 (1916); "Fats and Fatty Degeneration," Wiley and Sons (1917).

stances are the best emulsifying agents. Bancroft[1] thinks that each droplet must be covered with an adsorption layer of colloid particles in the form of a coherent film.

The object of this research was to use gelatin as a typical hydrated colloid in aiding the emulsification of oil in water and to observe the order of importance of the factors mentioned above. With kerosene-water emulsions we made a study of 2 factors usually considered as influencing stability of emulsions. (1) A study of the surface tension of the gel-oil interface; (2) a determination of whether or not gelatin is adsorbed to form a concentration layer around the oil droplets; (3) a study of the viscosity of the gelatin solutions used.

Experimental Methods.

After trying several of the best available gelatins, such as ossein stock and calf stock direct from a manufacturer, Nelson's photographic gelatins and others, we selected "Difco"[2] as the best brand for our purpose. It had an ash content of 1.1% and a water content of 13.6%. A 1.1% solution in water was so stiff that it would not flow from a 35 mm. tube when inverted. We might have lowered the ash content still further by repeated precipitation in alcohol and washing with water.

The emulsions studied were made up as follows. The gelatin was weighed into an emulsion bottle (125 cc. bottles, 35 mm. in diameter) and 10 cc. of water or the solution of some electrolyte added from a pipet. The bottle was then placed in a water-bath at 45–50° and kept there until all the gelatin was in solution, or peptized. Kerosene was then added in 5 cc. portions and the bottle placed in a shaking machine and given 1232 double strokes after each addition. The machine handled 9 bottles at a time, giving them about 4.5 complete 10-cm. strokes per second. An automatic shut-off was used to stop the shaking on the 1232nd stroke. After the last addition of oil, 3693 shakes were given the emulsion. Unless otherwise stated, all the emulsions contained 30 cc., or 75% of oil.

The emulsions were all of the oil-in-water type. They were allowed to stand for about 3 months and their conditions noted at the end of that time. Unlike soap emulsions, most gelatin emulsions are slow to cream, that is, to separate a rich emulsion layer above a very dilute emulsion layer. Those that cream first are, as a general rule, the first to show a general breakdown. We, therefore, considered the poor emulsions the ones, that creamed the fastest and separated the most oil. It was not often that the emulsion separated a uniform layer of oil on top but instead showed a general breakdown all the way through. Eight or nine bottles were grouped in a series and shaken at the same time.

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[1] Bancroft, *J. Phys. Chem.*, 17, 501 (1913).

[2] Digestive Ferments Co., Detroit.

Experimental Results.

Since the alkaline iodides and thiocyanates have a liquefying action on gelatin in water, it was assumed that this might be due to peptization, a subdivision of the particles. With smaller particles of gelatin colloidally dispersed, it seemed possible that a more coherent layer could form around the oil droplets and thus lend confirmation to Bancroft's theory.

Accordingly, 8 different concentrations of gelatin were made, varying from 0.3 g. to 1.0 g. per 100 cc. of solution, and these were all made 0.5 *M* with sodium iodide, sodium chloride and sodium nitrate as liquefying salts and 0.5 *M* with the tartrate, citrate and sulfate of sodium as solidifying salts.

It was found that with the liquefying salts more than 0.8 g. of gelatin per 100 cc. did not serve as well in stabilizing the emulsions as did lower concentrations. But with solidifying salts, which of course increase the viscosity of the liquid, the greatest permissible concentration of the gelatin was much lower, not above 0.6 g. per 100 cc. This seemed to point towards a favorable viscosity, no matter how secured, as important.

In Table I, the most generally suitable concentration of gelatin, 0.75 g. per 100 cc., was used, and the influence of liquefying salts, solidifying salts, acids and bases studied in concentrations ranging from *M*/256 to molar.

TABLE I.

Condition of emulsion in three or four months.

Gelatin per 100 cc. solution. G.	Electrolyte.	Moles of electrolyte per liter.					
		None.	$^1/_{256}$, $^1/_{128}$.	$^1/_{64}$, $^1/_{32}$.	$^1/_{16}$, $^1/_8$.	$^1/_4$, $^1/_2$.	1.
0.40	NaI	good	good	good	fair	fair	poor
0.75	NaI	good	good	good	fine	good	poor
1.00	NaI	fair	fair	fair	fair	fair	fair
0.40	Na_2SO_4	good	good	good	fine	good	fair
0.75	Na_2SO_4	good	good	fair	fair	poor	bad
1.00	Na_2SO_4	fair	fair	fair	poor	bad	bad
0.75	NaI	good	good	good	fine	good	poor
0.75	NaBr	good	good	good	fine	good	poor
0.75	NaCl	good	good	good	fine	good	poor
0.75	$NaNO_3$	good	good	good	fine	good	poor
0.75	NaCNS	good	good	good	fine	good	poor
0.75	Na_2SO_4	good	good	fair	fair	poor	bad
0.75	Na acetate	good	good	good	fair	fair	poor
0.75	Na tartrate	good	good	fair	fair	poor	bad
0.75	Na citrate	good	good	fair	fair	poor	bad
0.75	HCl	good	good	good	poor	bad	none
0.75	HNO_3	good	good	good	poor	bad	none
0.75	H acetate	good	good	good	good	fair	fair
0.75	Cl_3CCOOH	good	good	good	poor	bad	none
0.75	NaOH	good	good	good	fair	bad	none
0.75	LiOH	good	good	good	fair	bad	none

This table makes plain the fact that liquefying salts in 0.5 M concentration permit the formation of good emulsions with gelatin as the agent but solidifying salts in the same concentrations cause the formation of poor emulsions. An excess of any acid and especially strong acids and bases makes the emulsions very poor.

Surface Tension.—To study the surface tension at the gel-oil interface, the cold gels, made up as for emulsions, but allowed to cool without the addition of oil, were put into the shaking machine and shaken for about 5 minutes, which was enough to break completely the structure of the gels and make them about as mobile as water. The gel was then poured into a test-tube and drop numbers taken by passing oil through the gel from a Donnan pipet. The drop numbers obtained are found in Table II. Since duplicate drop numbers sometimes varied as much as 2, we made no attempt to carry our density determinations or the surface tension calculations beyond 2 figures.

Harkins[1] determines surface tension by means of the formula

$$T = (M - m)g/2\pi r f(r/V^{1/3}),$$

where m is the weight of a drop of oil, M is the weight of an equal volume of the water phase, g is the gravitational factor, 4 is the radius of the pipet tip, $f(r/V^{1/3})$ is a small function of the radius of the tip with the cube root of the volume of the drop. With the same tip used throughout we can, for comparison, reduce the equation to

$$T = \frac{k\ (\text{density water phase}) - (\text{density oil})}{\text{drop number}}.$$

This introduces an error less than 0.5% between our extreme values. This is much less than our experimental errors, and so is the formula adopted in calculating relative surface tensions for gels made up with half molar salts.

Under no conditions does gelatin compare with soap in ability to lower the surface tension of water.

When an electrolyte was present no change in surface tension was observed unless the concentration of electrolyte was at least eighth molar.

Acids, bases and liquefying salts slightly lowered surface tension at the gel-oil interface while solidifying salts raised it slightly.

As we increased gelatin from 0 g. to one g. per 100 cc. of water, the surface tension rapidly fell until the 0.30 g. content was reached and then remained constant from 0.30 g. to 1.0 g. On the other hand, a series of oil-water emulsions containing respectively, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 and 1.0 g. of gelatin per 100 cc. of water increased in stability rapidly up to the 0.3 g. content, but at 0.6 g. or 0.7 g. began to fall off again.

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[1] Harkins, This Journal, 41, 520 (1919).

TABLE II.

Gelatin per 100 cc. G.	Electrolyte.	Drop number of half molar solution.	Density.	Relative surface tension.
None	Water	20 (for pure water)	1.00	100
0.75	Water	27	1.00	73
0.40	NaI	35	1.06	74
0.75	NaI	39	1.06	67
1.00	NaI	40	1.06	65
0.40	Na_2SO_4	35	1.06	74
0.75	Na_2SO_4	32	1.06	81
0.75	NaI	39	1.06	67
0.75	$NaNO_3$	34	1.03	68
0.75	NaCl	31	1.02	71
0.75	NaCNS	34	1.02	65
0.75	Na_2SO_4	32	1.06	81
0.75	NaAc	28	1.03	82
0.75	NaTart	32	1.06	81
0.75	HNO_3	34	1.02	65
0.75	HAc	32	1.01	66
0.75	NaOH	35	1.03	64

We must conclude from these results that the ability of gelatin to lower the surface tension of water from a relative 100 to 73 is not a negligible factor in emulsification.

Adsorption Films.—We found no evidence that as the oil content increased the gelatin content also had to be increased to secure an equally good emulsion. Pickering, on the other hand, found that increasing proportions of oil demanded increasing proportions of soap. In our work it appears that a definite gelatin content can be selected that makes the best emulsion for any oil content.

Thus 10 cc. of a 0.6 g. gelatin per 100 cc. $M/2$ sodium iodide gave us fine emulsions with 20, 30, 40, 60, and even 90 cc. of oil. The last emulsion was 90% of oil, very rich. The use of 0.8 g. of gelatin per 100 cc. resulted in poorer emulsions for all oil mixtures and emulsions using 1.2 g. gelatin per 100 cc. were worse yet.

Had there been any concentration by adsorption around the oil droplets the liquid below the cream should have been poorer in gelatin than the original solution. To test this we withdrew 5 cc. from the lower layer and analyzed for nitrogen by the Kjeldahl method. Even with the most dilute gelatins analysis showed a loss of only 0.0008 g., which meant nothing, since in making emulsions we did not attempt accuracy beyond one part in a thousand.

Viscosity.—We had some difficulty in measuring the viscosity of gelatin-water. It was impossible to draw up the gels in a pipet and measure time of outflow with accuracy for the structure of the gel was so altered in drawing it up that successive determinations varied by 100%. The following was the method finally adopted. Although not extremely accurate, it served very well for comparative results.

We made up the gel as for the emulsion but placed in in the shaking machine without the addition of oil and gave it 30 minutes shaking. This shaking was necessary as without it the gel was not homogeneous on cooling, and gave discordant results or at times clogged the pipets. The gels were then placed in a thermostat at 21.5°. ± 0.02° and kept there for 28 hours. The tip of a short pipet was then carefully lowered into the gel and the time it took to fill the pipet under a suction of 245 mm. of water was measured by means of a stop-watch. The pipet was of 5 cc. capacity with the stem cut off short and the tip drawn down to a 0.35 mm. opening.

TABLE III.

Effect of Electrolytes on the Viscosity of Gelatin.

Molar strength.

Gelatin per 100 cc. G.	Electrolyte.	Seconds, time of flow into pipet.									
		None.	1/256.	1/128.	1/64.	1/32.	1/16.	1/8.	1/4.	1/2.	1.
0.00	H_2O	19.5	.....	....	.....	..	.....	.....	.....	......	.....
0.40	NaI	19.0	19.6	19.2	19.6	19.4	19.2	19.5	.....	20.0	20.9
0.75	NaI	68.1	.....	74.0	68.9	54.4	33.5	20.2	.....	20.2	21.4
1.00	NaI	1039.0	912.4	695.7	640.9	385.1	108.4	23.6	.....	20.3	21.4
0.40	Na_2SO_4	20.3	19.9	19.4	19.5	19.7	19.6	20.2	.....	21.8	21.0
0.75	Na_2SO_4	66.3	69.2	82.9	82.8	87.4	90.4	126.8	.....	312.2	20.9
1.00	Na_2SO_4	1000.0	(approx.)								20.8
0.75	NaCl	60.1	55.0	81.2	76.6	81.8	65.0	51.3	.....	26.8	20.2
0.75	$NaNO_3$	75.8	84.3	75.7	70.8	64.8	48.6	30.8	.....	19.6	20.0
0.75	NaCNS	......	79.8	76.9	63.1	52.6	29.6	20.0	.....	19.4	19.8
0.75	NaAc	77.3	71.6	76.7	85.8	89.4	91.9	.....	180.5	297.0	527.0
0.75	NaTart	58.1	69.8	....	90.2	91.9	104.9	.....	335.0	1042.3	21.5
0.75	NaCit	......	47.8	52.9	61.1	71.1	88.4	124.7	.....	692.3	32.9
0.75	HCl	57.2	19.6	19.7	19.2	19.5	19.4	19.5	.....	19.3	19.3
0.75	HNO_3	......	19.6	19.7	19.2	19.5	19.4	19.5	.....	19.3	19.3
0.75	HAc	79.2	45.0	22.0	19.6	19.4	19.5	19.6	.....	20.0	19.6
0.75	Cl_3CCOOH	......	19.5	19.5	....	.....	.....	.....	.....	......	.....
0.75	NaOH	......	21.3	19.0	19.4	19.3	19.1	19.0	.....	19.4	19.7
0.75	LiOH	72.0	19.5	....	....	.....	.....	.....	.....	......	.....

Sodium tartrate, citrate, and sulfate in molar concentration precipitate the gelatin, leaving a liquid as fluid as water. Pure water ran into the pipet in 19.5 seconds and molar sodium iodide (no gelatin) ran through in about one second more. Half molar liquefiers or strong acids of any concentration reduce the viscosity of the gelatin solution nearly to that of water.

Although the viscosity measurements are rather rough, still it is noticeable that all salts when present in less than $M/32$ concentration tend to stiffen the gelatin slightly. Loeb[1] calls attention to the fact that if only

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[1] Loeb, *J. Biol. Chem.*, 33, 531 (1918).

dilute salts are used or if the excess is washed out, sodium chloride, bromide, iodide,. nitrate, sulfate, acetate, tartrate and citrate all increase the swelling of his gelatin. That is, if the excess of salt is washed out, the salts do not follow the Hofmeister order which rules that the first salts mentioned cause more swelling than pure water and that the latter cause less, but they all have the same effect. Where we are using 0.75 g. of gelatin per 100 cc. we also notice that all salts when dilute have a similar effect. However this stiffening produced by the dilute liquefying salts is very slight.

By comparing Tables I and II and III with the other data, we see that the ability of gelatin to make a good emulsion can be summed up in the statement that provided that at least 0.3 g. of gelatin per 100 cc. of solution is used, any gel of less than 40 seconds flow will make an excellent emulsion, any gel of less than 100 seconds flow will make a good emulsion. The farther above this value we go the poorer the emulsion. On the other hand, we cannot use strong acids above *M*/16 or strong bases above *M*/8, or salts above 0.75 *M*. In other words, the liquefying must not be carried too far. Whether the gel is made too stiff by an excess of gelatin or by the presence of much solidifying salt the emulsion is much poorer. Since this is true no matter how surface tension varies we believe that viscosity plays the dominant part in the stability of gelatin emulsions.

All these stability tests required long standing. For a final test we added oil in small portions, shaking intermittently until another addition of oil broke the emulsion. Table IV gives the results.

TABLE IV.

Order of Breaking of Emulsions on Overloading with Oil.

Grams of Gelatin Per 100 cc. of Solution.

	0.1.	0.2 and 0.3.	0.4, 0.6 and 0.8.	1.2.	1.6.	2.4.
NaI	1st	2nd	3d	4th	5th	last
H_2O	1st	2nd	3d	last	2d	1st
Na_2SO_4	1st	2nd	last	3d	2d	1st

When a gel was highly liquefied by sodium iodide the most concentrated gelatin, 2.4 g. per 100 cc., was the last to break, that is, we were able to add more oil to it than to any other before breaking. With no salt present the same gelatin content of 2.4 g. per 100 cc. was one of the first of the whole series to break. In the absence of any salt a gelatin content of 1.2 g. per 100 cc. was loaded with oil as heavily as any. With sodium sulfate the higher gelatin content took up the least oil before breaking. It is to be noted that the solutions withstanding the greatest overloading with oil are not those giving the stablest emulsions as measured by long standing. It is clear that too great viscosity is just as prejudicial to emulsion stability as too little. The viscosity and hydration of gelatin are closely related. Salts and acids compete with gelatin for the water present but they also peptize gelatin. It must be that both degree of hydration and size of peptized particles are important only insofar as they secure favorable viscosity.

Summary.

When kerosene was emulsified in water by the aid of gelatin it was found that:

1. The maximum lowering of surface tension should be secured. This is obtained just as well by 0.3 g. or 0.4 g. of gelatin per 100 cc. of water as by 1.0 g. Acids, bases and liquefying salts also lower it a little while solidifying salts raise it.

2. Viscosity must not be increased more than a little beyond that of water. This means either (1) that only a small amount of gelatin can be used or (2) that the gelatin must be liquefied by the proper electrolytes. The latter method yields the better emulsion.

3. An excess of acid, base or liquefying salt should not be used. This probably means that the structure of the gelatin must not be entirely destroyed or that it must not be reduced to near molecular sizes.

4. There is no convincing evidence that gelatin particles are withdrawn from the solution to form adhesion layers about the oil droplets.

5. There is no evidence that as the oil content is increased the gelatin content must also be increased in order to produce as good an emulsion. This would surely be the case were adhesion layers formed around the oil droplets. One gelatin content in a given volume of water can be selected that will make the best emulsion for all oil contents.

6. The leading factor in oil-water emulsification with the aid of gelatin is viscosity, not the maximum but the most favorable viscosity. These conclusions refer only to gelatin, but investigation may show that they apply to all highly hydrated compounds.

OBERLIN, OHIO.

NOTE.

The Separation of Iron from Aluminum by Precipitation as Prussian Blue.—In Dr. Ddgar F. Smith's "Chemistry in Old Philadelphia," it was suggested[1] that a study should be made of the possibility of a quantitative separation of iron from aluminum by precipitation as prussian blue. The work of Robinson[2] showed that double and triple ferrocyanides of magnesium, aluminum and cerium are formed when solutions of the chlorides of these metals are mixed with potassium ferrocyanide. He tried only 0.5, 0.25 and 0.125 *N* solutions.

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[1] P. 47.

[2] Robinson, *J. Chem. Soc.*, 95, 1356 (1909).

Acting on this suggestion, we have repeated Robinson's experiments and have attempted to prevent the formation of the jelly usually obtained. Solutions were tried ranging in concentration from 0.25 to 0.025 *N*. Hydrochloric acid was added in concentrations ranging from *N* to 0.01 *N*. It was found that the acid retarded the formation of the jelly increasingly as the concentration was increased. However, there is no permanent preventative effect; the jelly only required a longer time for settling.

After the addition of an equimolecular amount of potassium ferrocyanide to acid solutions of aluminum chloride of 0.5, 0.05, and 0.025 *M* concentration, aluminum hydroxide was precipitated with ammonium hydroxide; but instead of the usual flocculent precipitate, the mass set to a jelly. Boiling had no noticeable effect.

The composition of the jelly from aqueous solutions is represented by the formula $KAlFe(CN)_6.6H_2O$; that of the jelly from ammoniacal solutions, by $NH_4AlFe(CN)_6.6H_2O$.[1]

The precipitation of prussian blue from a ferric solution took place immediately in the presence of only a little free hydrochloric acid, but a larger amount greatly retarded, or even prevented, the formation of the precipitate. This is in accordance with the results obtained by Vordlander.[2]

Means of coagulating and filtering the prussian blue thus obtained were then tried. The work of Pappada[3] and that of Ishizaka[4] show that according to the theory of Freundlich, the coagulating effect of the electrolytes depends upon the atomic weights and the valences of the active ions. In order to study this a precipitate of prussian blue was prepared by adding an excess of ferric chloride to an aqueous solution of potassium ferrocyanide; this was considered the best method of obtaining true insoluble prussian blue of the composition $Fe_4Fe(CN)_6.\ 9H_2O$.[5] This prussian blue was a negative colloid in aqueous solution. Solutions of the following salts were added as coagulators: sodium chloride, barium chloride, aluminum chloride, potassium sulfate, and potassium acetate. With very concentrated solutions of these substances perfect coagulation took place and the precipitates settled rapidly. With very dilute solutions, however, a distinct difference in the times of coagulation was detected. The best results were obtained with aluminum chloride. However, free hydrochloric acid greatly retarded coagulation and prevented it from being complete. After coagulation it was found that quantitative filtration was impossible, although centrifuging gave good results.

[1] Robinson, *loc. cit.*

[2] Vordlander, *Ber.*, 46, 181 (1913); *C. A.*, 7, 1337 (1913); 13, 1274 (1919).

[3] Pappada, *Z. Chem. Ind. Koll.*, 6, 83 (1910); *C. A.*, 4, 1706 (1910).

[4] Ishizaka, *Z. physik. Chem.*, 83, 97 (1913); *C. A.*, 7, 2878 (1913).

[5] Roscoe and Schorlemmer, "A Treatise on Chemistry," 4th ed, 2, 1235–8.

Conclusions.

The quantitative separation of iron from aluminum as prussian blue cannot be effected because the aluminum interacts with the excess ferrocyanide, forming a jelly which cannot be handled.

The precipitate of prussian blue cannot be successfully filtered even after apparently perfect coagulation.

HARRISON HALE AND G. O. BURR.

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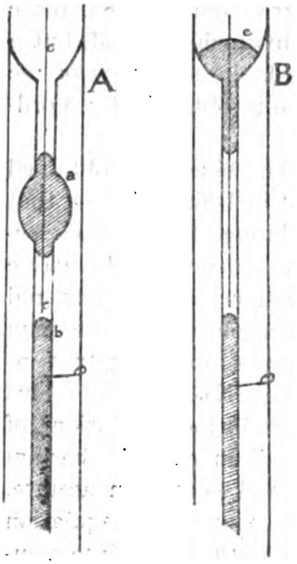
A Thermo-regulator.—The purest mercury, when used for thermoregulators, becomes dirty in the capillary tube due to oxidation by the small arc formed when the contact is broken between the mercury column and the adjustable wire contact. Devices are used for passing a stream of inert or reducing gas over the top of the mercury so that the arc will be formed in the presence of the gas. This method of oxide prevention requires a side tube on the regulator and an apparatus for generating a continuous flow of gas. I have found a much simpler device to be quite as effective and one which can be used on old regulators. New regulators can be better fitted by a slight modification in design.



In the drawing A shows the capillary of a regulator with a small bulb blown at *a*. The wire *c c* makes a contact at *b*. A small capillary pipet is slipped down to *b* and a stream of some inert gas is passed in to displace the air in the capillary. Then the capillary is sealed with a few drops of mercury in *a*. This mercury rises and falls with the rise and fall of *b* but never slips down to connect with *b*. Any arc formed between the wire and the mercury column at *b* is in the presence of the inert gas.

In the capillary of an ordinary regulator, B, a drop of mercury at *e* seals the capillary. I have also found it perfectly satisfactory to insert a drop of mercury in the capillary tube without first displacing the air. In this case, the oxygen soon combines with the mercury, forming a small amount of oxide. Then the regulator can be permanently set and the arc is formed in an atmosphere of the nitrogen which remains.

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THE PREPARATION OF BENZYL ESTERS AND OTHER BENZYL-DERIVATIVES FROM BENZYL CHLORIDE.

BY M. GOMBERG AND C. C. BUCHLER.

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The facility with which carbon tetrachloride, benzotrichloride and benzophenone chloride can be made to condense with various derivatives of the aromatic series, with the aid of catalysts and often without them, suggested the idea that benzyl chloride also might be brought into a wider number of direct combinations than has been done hitherto, diverse as the reactivity of benzyl chloride is already known to be. The susceptibility of benzyl chloride to various metals has been observed before. Marussia Bakunin succeeded in inducing condensation of benzyl chloride with phenol,[1] and with α- and β-naphthol[2] by the use of zinc as catalyst. Onufrowicz[3] observed that benzyl chloride, heated with a considerable amount of copper at 110–140°, gave dibenzyl; but, as hydrochloric acid is produced, the reaction must be more complicated than the author judged. In technical works it has been found necessary to employ distilling vessels with the interior glass-enameled, in order to avoid the catalytic influence of iron which may otherwise lead to explosive decomposition of the chloride.

A trial with phenol showed us that benzyl chloride begins to react with it at 160–80°, with evolution of hydrogen chloride. The addition, however, of a minute quantity of copper bronze was found to accelerate the reaction greatly, and a temperature of 115–20° sufficed. The influence of copper was next tested in the preparation of benzyl esters. Benzyl chloride was heated with dry sodium benzoate under a reflux condenser for from 6 to 10 hours, but even in the most successful experiments the yield of the ester was only 10 to 18%. However, on the addition of a small amount of copper powder, the yield rose to 50 or 60%. This is probably the highest yield that may be expected in this reaction, for the reason that while copper undoubtedly accelerates the reaction between benzyl chloride and sodium benzoate, at the same time it accelerates the decomposition of the benzyl chloride itself. As a matter of fact, there was produced invariably a certain amount of a high-boiling viscous brown mass. A blank experiment with benzyl chloride and a very small amount of copper powder proved definitely that the above mentioned by-product results from the decomposition of some benzyl chloride.

Thus, the dry method, while fairly satisfactory, was found to have its

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[1] Bakunin *Gazz. chim. ital.*, [2] 33, 454 (1903).

[2] Bakunin and Barberio, *ibid.*, 33, 457 (1903); Bakunin and Altieri, *ibid.*, 33, 487 (1903).

[3] Onufrowicz, *Ber.*, 17, 833 (1884).

limitations as regards the yield of ester. The addition to the mixture of benzyl benzoate as a solvent was without noticeable effect, since the amount of viscous by-product was about the same as before. Alcohol as a medium for this sort of reaction has been extensively used in the past. Obviously, for large scale production, water, if it could serve the purpose, would be preferable. Benzyl chloride, while generally quite reactive, is nonetheless remarkably stable towards water for such an active substance, and can even be distilled with steam. It owes its protection against rapid hydrolysis to the fact that it is only slightly soluble in water; this, at the same time, favors the reversibility of the reaction (I). Since this is the case, it seemed probable that benzyl chloride would give esters when it reacted with the salts of organic acids in aqueous solution, because the benzyl esters, as a rule, are even less soluble in water than is the chloride, and, consequently, would suffer hydrolysis at a rate even slower than the chloride. Evidently the successful preparation of esters by this procedure is contingent upon the relative velocities of the 3 principal reactions.

$$C_6H_5CH_2Cl + H_2O = C_6H_5CH_2OH + HCl \qquad (I)$$

$$C_6H_5CH_2Cl + NaOCOR = C_6H_5CH_2OCOR + NaCl \qquad (II)$$

$$C_6H_5CH_2OCOR + H_2O = C_6H_5CH_2OH + HOCOR \qquad (III)$$

It should be feasible to determine by experiment in the case of each individual acid just what are the most favorable conditions as regards time and temperature of reaction in order to get the highest yield of ester according to this procedure.

Trials with sodium benzoate gave quite satisfactory results. Yields of the ester up to 70 or 80% of the calculated amount were readily obtained, and the only by-product found was benzyl alcohol. Catalysts were found to be without effect. By the same procedure good results were obtained with acetic, propionic, butyric, lactic, phenylacetic and cinnamic acids; fair results with salicylic and succinic acids; no ester, or but a small amount, was obtained with formic, oxalic and *o*-phthalic acids. We have not attempted at this time to determine the most favorable conditions for the preparation of each ester; our main aim has been to find out how generally applicable this method is. In view of its apparent simplicity, it is strange that the procedure here described should have failed of application in the past. We have found only one instance where it has been employed. Paal and Bodewig[1] found that *o*-nitrobenzyl chloride, when heated with sodium acetate or benzoate in alcohol, gave only relatively small amounts of the ester, but in water good yields of the esters were obtained, and in each case the product was free from unchanged benzyl chloride.

Some additional experiments were made to determine to what extent

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[1] Paal and Bodewig, *Ber.*, 25, 2962 (1892).

it may prove possible to employ aqueous solutions in the coupling of benzyl chloride with phenols, with ammonia or with amines, and in the preparation of benzyl cyanide and of benzyl alcohol. The results obtained indicate that such a procedure is quite feasible.

Esters.

Benzyl Benzoate.—Claisen's[1] method, an extension of the Cannizzaro reaction, has been the standard for the preparation of this ester. Benzaldehyde, heated at 100° with a small amount of sodium benzylate, suffers intermolecular condensation, and yields benzyl benzoate as the principal product.

$$2C_6H_5CHO \longrightarrow C_6H_5COOCH_2C_6H_5.$$

The substitution of aluminum alcoholate[2] for sodium benzylate can hardly be considered as an essential modification. Other reactions recorded to give more or less ester are interesting from the theoretical point of view only.

The advantage of the Claisen method is that benzaldehyde, almost entirely free from chlorine in the nucleus, can be obtained on a technical scale fairly readily, certainly more readily than benzyl chloride; and such aldehyde, of course, would yield benzyl benzoate practically free from chlorine. The complaint that a great deal of the ester lately on the market contained considerable amounts of chlorine, suggests either that the ester has been made by the Claisen method from benzaldehyde not sufficiently free from chlorine-substituted aldehydes, or that, perhaps, it has been made through the interaction of benzyl chloride with sodium benzoate. If the latter surmise be correct, then the chlorine in the ester may have come either from an admixture in the reacting mass of some chloro-substituted benzyl chloride, or of some chloro-benzoic acid. If this, however, were the only source of chlorine in the reaction product, then there should be no great difficulty in separating benzyl benzoate from these higher boiling chloro-substituted esters through fractional distillation *in vacuo*. But the separation of benzyl benzoate from the last traces of benzyl chloride is not readily accomplished merely by distillation. There is good reason to believe that commercial benzyl benzoate, if it contains chlorine, owes its content of the latter not so much to the presence of chloro-substituted esters as to the presence of some benzyl chloride, assuming that the ester was made directly from benzyl chloride. A similar conclusion has been reached by Braisaz[3] concerning the source of chlorine in benzyl acetate and other benzyl derivatives which are made directly from benzyl chloride.

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[1] Claisen, *Ber.*, 20, 646 (1887); Comp. Earl of Berkeley, *J. Chem. Soc.*, 109, 522 (1910).

[2] Tischtschenko, *J. Russ. Phys. Chem. Soc.*, 38, 355 (1906).

[3] Braisaz, *Mon. sci.*, 24, 384 (1911).

We do not know whether benzyl benzoate actually has been made on a technical scale by the action of benzyl chloride on sodium benzoate. In our own laboratory experiments, the following procedure was adopted. Benzyl chloride was placed in a flask and 2 g. in excess of the required amount of thoroughly dried sodium benzoate was added. Then the mixture, with or without the addition of the catalyst, was heated under a reflux condenser in a metal bath until no appreciable amounts of benzyl chloride reached the condenser. At this stage, water was added to the solid mass, the solution was made alkaline, and the ester was extracted with benzene. After the solution was dried the solvent was distilled and the residue fractionated. At first some unchanged benzyl chloride usually came over, then the temperature rose rapidly, and the fraction between 320–330° was collected separately and was considered as practically pure ester, its boiling-point being 323°. Some dark-colored, heavy oil was always left in the distillation flask. This product resulted from the catalytic decomposition of benzyl chloride itself. The catalysts tried were copper bronze, of which in each experiment only a few mg. was used, and nickel, employed as nickel chloride. In each run 32 g. of benzyl chloride was used, which required for complete reaction 36 g. of sodium benzoate, while the amount actually employed was 38 g. The acid which did not enter into the reaction was always recovered and its quantity determined; this served as a check upon the yields of the ester as actually found by distillation. The yield calculated as that theoretically possible was based upon the amount of the benzyl chloride employed. Table I gives a summary of the experiments. In Run No. 8, 30 g. of benzyl benzoate was added to the reaction mixture at the beginning of the experiment, and this amount was subtracted from the ester recovered at the end of the experiment.

TABLE I.

38 G. of Sodium Benzoate and 32 G. of Benzyl Chloride Used in Each Experiment.

Run No.	Temp. of metal bath. ° C.	Time of run. Hrs.	Catalyst.	Yield of ester. G.	Yield of ester. %.
1	200–205	6	....	7.0	13.2
2	200–230	6	....	10.0	18.8
3	Refluxed	1.5	Cu	8.0	11.3
4	190–205	3.5	Cu	29.5	55.6
5	190–205	6	Cu	24.0	45.2
6	200–240	6	Cu	28.0	52.8
7	235–260	6	Cu	28.0	52.8
8[a]	250–260	6	Cu	30.0	56.6
9	190–300	3.5	Cu	32.0	60.3
10	200–300	6	Cu	32.0	60.0
11	200–210	5	$NiCl_2$	14.0	26.4

[a] Benzyl benzoate used as solvent.

Thus, with the aid of copper as catalyst, yields of 50 to 60% of the ester may be obtained by this procedure. The ester, however, contains some benzyl chloride, which can be removed only by subsequent treatment of the ester with dil. alkali. Also, it contains a small amount of the high-boiling product which results from the decomposition of benzyl chloride, which accounts for the fact that, in distilling the ester, the boiling-point always rose a little above that for the pure ester.

The esterification experiments, wherein water was employed as a solvent for the sodium salt of the acid, were carried out as follows. The desired amount of sodium benzoate was dissolved in 150 to 200 cc. of water, all the benzyl chloride was added and the mixture was heated in an oil-bath at 110–115°. The flask was connected with a reflux condenser and carried an efficient stirrer. The reaction was allowed to proceed for 4 or 5 hours, although it seems certain that a shorter time would have sufficed. Then the ester was extracted with benzene, the solution was dried and fractionated. After the solvent was removed, the temperature rose rapidly and remained stationary for a short time in the neighborhood of the boiling-point of benzyl alcohol; then it rose again and remained at 310–15° until practically all of the substance had distilled. Hardly any residue remained in the distilling flask. The ester was free from benzyl chloride, and one redistillation under reduced pressure, with hardly any loss of material, gave a product which was water-white, free from unpleasant or pungent odor, and gave no test for chlorine. Table II gives a summary of these results. It will be noticed that in Runs 1 to 6 the amount of sodium benzoate used was 50% in excess of that calculated; in Runs 7 and 8, 200% in excess; in Run 9, the benzyl chloride was 200% in excess. The benzoic acid which remains unacted upon by the benzyl chloride is readily recovered from the aqueous solution.

TABLE II.

Run No.	Sodium benzoate. G.	Benzyl chloride. G.	Temperature of oil-bath. ° C.	Benzoic acid recovered. G.	Yield of ester. G.	%
1	27	16.5	110–115	13	11	40
2	36	21	100	17	22	63
3[a]	55	32	50	41	3	6
4	55	32	115–120	20	37	70
5	55	32	115	21	37	70
6	55	32	115	22	37	70
7	110	32	115	70	42	79
8	220	64	118	143	84	79
9	29	75	110	14	17	40

[a] Much sodium benzoate remained undissolved.

Benzyl Acetate.—Conrad and Hodgkinson[1] gave explicit directions for the preparation of benzyl acetate. They advise heating anhydrous potassium acetate instead of sodium acetate with benzyl chloride in al-

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[1] Conrad and Hodgkinson, *Ann.*, 193, 299 (1878).

cohol as a solvent. Seelig[1] substituted glacial acetic acid for alcohol and thereby was able to use sodium instead of potassium acetate with equally good results. Still, to convert 150 g. benzyl chloride required 200 cc. of acetic acid and 25 to 30 hours boiling. Bodroux[2] reduced the time of reaction by employing lead instead of sodium acetate. He thus converted 80 g. of benzyl chloride into the acetate in one hour with a yield of 60% of the pure product. Quite recently, Klever[3] took out a patent, which suggested the use of glacial acetic acid and sodium acetate, but in much smaller proportion than Seelig used, namely, 1.1 to 1.2 mol. of acid to 1 mol. of benzyl chloride.

We found that benzyl chloride and anhydrous sodium acetate, with copper as catalyst, and without the use of a solvent, gave from 30–40% ester after several hours of heating. But when the salt is dissolved in water and the mixture, thoroughly stirred, is heated as described for the benzoate, a yield of 80% of pure acetate, b. p. 205–210°, is readily secured. The results are summarized in Table III. The amount of sodium acetate which is required for a run with 32 g. of benzyl chloride is 20.5 g. when an anhydrous salt is taken; the amount actually used is given in Col. 3.

TABLE III.

32 G. of Benzyl Chloride Used in Each Experiment.

Run No.	Sodium acetate. G.	Excess salt used. G.	Temp. of oil-bath. ° C.	Time of run. Hrs.	Catalyst or solvent.	Yield of ester. G.	Yield of ester. %.
1........	36	16	200	6	Cu	13	34.6
2........	36	16	180–200	5	$HgCl_2$	14	37.3
3........	36	16	150	3	$HgCl_2$	19	50.6
4........	36	16	140–145	3	Cu_2Cl_2	0	0
5........	30	10	110	7.5	H_2O	25	66.6
6........	53	33	115	8	H_2O	30	80.0
7........	53	33	115	8	H_2O	31	82.6
8[a]........	105	85	115	8	H_2O	8	21.5

[a] Not enough water added to dissolve all of sodium acetate used.

Benzyl Propionate.—Conrad and Hodgkinson[4] prepared this ester from potassium propionate and benzyl chloride in alcohol. The mixture was boiled from 30 to 40 hours. It can be prepared much more readily if an aqueous solution of the salt is used. Thus, 64 g. of the acid was dissolved in about 100 cc. of water, neutralized with sodium carbonate. 32 g. of benzyl chloride was added, and the mixture was heated as described for the other acids. The ester possessed a most agreeable odor, and boiled at 220–230°. The yield was 85%.

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[1] Seelig, *J. prakt. Chem.*, [2] 39, 164 (1889).

[2] Bodroux, *Bull. soc. chim.*, [3] 21, 288 (1899).

[3] Klever, *C. A.*, 9, 694 (1915); Brit. pat. 20,504.

[4] Conrad and Hodgkinson, *Ann.*, 193, 311 (1878).

Benzyl Butyrate.[1]—This ester also was prepared in aqueous solution, using 66 g. of acid, neutralizing and adding 32 g. of benzyl chloride, 37 g. of the ester was obtained, *i. e.*, 83% yield. The ester boiled at 235–242°. The butyrate, similar to the acetate and propionate, possesses a pleasant aromatic odor.

Benzyl Lactate.—This ester was made similarly to the others. An aqueous solution of the sodium salt containing 67 g. of lactic acid and 32 g. benzyl chloride gave 25 g., 55% yield, of ester which boiled between 150 and 156° under 205 mm. pressure. It is practically devoid of odor.

Benzyl Phenyl Acetate.—This ester was first prepared by Slawick[2] and later Hodgkinson[3] made it by digesting benzyl chloride for a week with an alcoholic solution of phenyl acetate. By the method here described 49 g. treated with 12.6 g. benzyl chloride gave 17 g. of ester, b. p. 204–210° under 20.5 mm., which is a 75% yield. 23 g. of phenylacetic acid out of the 26 g. excess employed was recovered from the aqueous solution.

Benzyl Cinnamate.—Grimaux's[4] procedure for the preparation of this ester in which sodium cinnamate is treated with benzyl chloride in alcohol, gave a yield of only 40% of a product contaminated with ethyl cinnamate. According to a procedure patented by Kalle and Co.,[5] solid sodium cinnamate heated with benzyl chloride at 140–170° gives good yields of the ester. In our method, 40 g. of the acid dissolved in 100 cc. water was neutralized with sodium hydroxide and treated in the usual manner for 4 hours with 13 g. of benzyl chloride. At the end of the experiment 34 g. of cinnamic acid was recovered, and 20 g. of the pure ester, boiling between 240 and 244° under 25 mm. pressure, was obtained, which is 83% of the amount theoretically possible, calculated on the quantity of the benzyl chloride employed.

Benzyl Salicylate.—This ester, patented by the Aktien Gesellschaft[6] for use as a *fixateur* in perfumery, was prepared by them by heating dry sodium salicylate with benzyl chloride at 130–140°; at higher temperatures, the phenolic hydroxyl group also reacts. We obtained the same ester by the use of aqueous solutions. Our yields varied from 40 to 45%, the ester boiled between 211 and 214° under 22.5 mm. The use of acetyl salicylic acid instead of salicylic acid gave no better yield. In fact, the acetyl group was removed by hydrolysis during the process of esterification.

Dibenzyl Succinate.—This ester received considerable attention in

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[1] Conrad and Hodgkinson, *Ann.*, 193, 317 (1878).

[2] Slawick, *Ber.*, 7, 1056 (1874).

[3] Hodgkinson, *J. chim. Soc.*, 37, 485 (1880).

[4] Grimaux, *Z. Chem.*, 5, 157 (1869).

[5] *Friedlaender*, 6, 1234; D. R. P. 127,649.

[6] *Friedlaender*, 6, 1108; D. R. P. 119,463.

view of the possible existence of 2 isomeric esters corresponding to the 2 probable tautomeric modifications of the chloride of succinic anhydride. In the past this ester has been prepared by a variety of methods, from benzyl bromide and the silver salt of succinic acid;[1] from benzyl alcohol and succinyl chloride at high temperatures, or from benzyl alcohol and succinic acid at 180°.[2] from benzyl iodide and silver succinate.[3] By all these methods the identical ester, m. p. 49–50°, was obtained. By our method, in aqueous solution, with an excess of sodium succinate and 25 g. of benzyl chloride, boiled for 7 hours, we obtained 13 g. of dibenzyl ester, which is 43% of the theoretical amount. At the same time 9 g. of benzyl alcohol was formed. The ester was distilled under highly reduced pressure. It melted without further purification at 47–48°.

Several other acids, with which only one or two runs were made, gave the following results. *Oleic acid*, about a 45% yield of ester, distilled under highly reduced pressure. *Formic*, *oxalic* and *phthalic* acids gave no ester

Condensation with Phenols.

The condensation of benzyl chloride with phenols has been the subject of numerous investigations. Lauth and Grimaux,[4] Sintenis,[5] have shown for phenols, and Staedel,[6] more fully, for phenol, α- and β-naphthols and for other phenols, that benzyl chloride and alkali salts of phenols when boiled in alcohol react and give the corresponding benzyl ethers of the phenols as expected. On the other hand, when benzyl chloride acts upon phenol, or upon α-naphthol or β-naphthol in presence of small amounts of zinc dust,[7] or in presence of zinc chloride,[8] then the condensation occurs in a different sense, since benzyl phenols, $C_6H_5CH_2C_6H_4OH(p)$, or the corresponding benzyl naphthols, $C_6H_5CH_2C_{10}H_6(OH)$ result.

We have performed some experiments in aqueous solution which bear upon the condensation of benzyl chloride with phenols; also some in the absence of solvents, and some with and without catalysts. As regards the experiments with alkaline solutions of phenols, one would have expected scarcely any other result than the formation of benzyl alcohol, if the weak acid character of the phenols and the consequent hydrolysis of their salts is taken into consideration. This, however, is far from being the case. In each experiment, the 32 g. of benzyl chloride used, required, theoretically, 23 g. of phenol or 38 g. of naphthol, respectively, while the alkali employed was exactly equivalent to the amount of phenol. Other-

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[1] Del Zanna and Guareschi, *Gazz. chim. ital.*, 11, 256 (1881).

[2] C. A. Bischoff and A. von Hedenström, *Ber.*, 35, 4078 (1902).

[3] R. Meyer and K. Marx, *ibid.*, 41, 2460 (1908).

[4] Lauth and Grimaux, *Ann.*, 143, 81 (1867).

[5] Sintenis, *ibid.*, 161, 337 (1872).

[6] Staedel, *ibid.*, 217, 43 (1883).

[7] H. Schiff, *Ber.*, 5, 288, 435 (1872).

[8] Ad. Liebmann, *ibid.*, 15, 152 (1882).

wise, the procedure was similar to that employed in the esterification experiment. The phenol, whenever it was possible, was separated by means of water, otherwise a mixture of the phenol and benzyl phenol was separated from benzyl ether by means of alkali, in which the benzyl ethers are insoluble. The final separation and purification was accomplished by, distillation under reduced pressure and by subsequent crystallization of solid products. The results are summarized in Table IV.

TABLE IV.

Run No.	Phenols.	G.	Temperature of oil-bath. 0° C.	Time of run. Hrs.	Catalyst or solvent.	Yield of.	
						Ethers, %.	Benzyl-phenols, %.
1	C_6H_5OH	25	100–105	3	...	..	24
2	C_6H_5OH	25	150–180	3	...	..	30
3	C_6H_5OH	25	115–120	3	Cu	..	40
4	C_6H_5OH	25	140–145	3	Cu	..	35
5	C_6H_5OH	35	105	1	H_2O	60	..
6	C_6H_5OH	40	110	2	H_2O	61	..
7	C_6H_5OH	26	120–125	8	Acetone	..	..
8	C_6H_5OH	25	230	5	Toluene	..	13
9	α-$C_{10}H_7OH$	40	105	2	H_2O	8.5	20
10	β-$C_{10}H_7OH$	54	110	2	H_2O	5	50

So far as they go, these results indicate, (1) that in the absence of solvents benzyl chloride acts upon phenol at 150–180° and gives benzyl phenol. In presence of copper, the yields are much better and the reaction temperature need not exceed 115–120°; with zinc as a catalyst, even room temperature suffices;[1] (2) that in aqueous solution quite satisfactory yields of benzyl-phenyl ether are obtained, almost as good as those with alcohol as a solvent, or as those secured by the electrolytic reduction of phenyl benzoate;[2] (3) that the naphthols in aqueous solution also give some of the corresponding ethers, but a great portion is converted into the corresponding benzyl naphthols—a behavior wholly unanticipated. If these results can be verified by further experiments it would seem that β-naphthol is considerably more reactive toward benzyl chloride than α-naphthol is. This unanticipated behavior of the naphthols is somewhat akin to the behavior of phenols toward carbon tetrachloride and chloroform in presence of concentrated alkalies, the Reimer-Tiemann reaction.

Benzyl Chloride and Amines.

Leaving entirely out of consideration the many various indirect methods which lead to the formation of either the mono-, the di-, or the tri-benzylamines exclusively, we have the method, usual in reactions of this nature, which consists in heating alcoholic ammonia and benzyl chloride in a

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[1] Marussia and Bakunin, *Gazz. chim. ital.*, [2] 33, 454 (1903).

[2] C. Mettler, *Ber.*, 38, 1752 (1905).

sealed tube.[1] Under these circumstances a mixture of the 3 amines results. The tertiary amine constitutes by far the greatest portion of the reaction products. Mason[2] showed that benzyl chloride is attacked by a cold alcoholic solution of ammonia. He employed a 15% alcoholic ammonia solution. When he allowed a large excess of ammonia, 20 mol. to 1 mol. of benzyl chloride, to stand for 5 days and subsequently heated it for a short time, he obtained a combined yield of the 3 amines equal to 75%, distributed thus, 29% to the mono-, 38% to the di-, and 8% to the tribenzylamine. With 2 mol. of ammonia to 1 mol. benzyl chloride, under the same conditions, practically all of the latter was converted into tribenzylamine. Trials with an aqueous solution of ammonium hydroxide gave us indications of favorable reaction, and the substitution of ammonium carbonate for ammonia gave results which leave no doubt of the advantages of this procedure. When only 5 mol. of ammonium carbonate and 1 mol. of benzyl chloride were heated for 5 to 6 hours, a combined yield of 80% of the amines was obtained, distributed thus, 16% to pure mono-, 20% to di-, and 44% to tribenzylamine. The separation was made according to Mason's method, by fractional distillation under reduced pressure and by crystallization of the tribenzylamine from alcohol. It seems quite probably, that, with a larger excess of ammonium carbonate, with lower temperature and longer time, the relative proportion of the primary amine may become larger.

In the preparation of benzyl derivatives of aniline and its homologues in aqueous solution, we had better results than in the case of benzylamine, and, by varying the relative proportion of aniline and benzyl chloride, we could get either mono- or dibenzyl aniline, respectively, as the principal product of the reaction. In the past it has been the custom to use the anhydrous ingredients, often with the addition of solid alkalies and to heat these under pressure, or for a longer period in open flasks at lower temperatures.

Except for the patented method of making dibenzyl-*m*-toluidine,[3] we are not aware that, prior to this, aqueous solutions of the aromatic amines have been employed for the preparation or benzyl anilines. In Table V is given a summary of the results we obtained. Theoretically, 1 mol. of benzyl chloride requires either 2 mols. of the amine or 1 mol. of the amine plus $^1/_2$ mol. of sodium carbonate; accordingly, the theoretical amounts for 32 g. of benzyl chloride are 28 g. of the hydrated ammonium carbonate, 22 g. of aniline and 28 g. of methyl aniline or toluidine, plus 13 g. of sodium carbonate.

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[1] H. Limpricht, *Ann.*, 144, 305 (1867).

[2] Mason, *J. Chem. Soc.*, 63, 1312 (1893).

[3] *Friedlaender*, 6, 256; D. R. P. 115,653.

TABLE V.

$(NH_4)_2CO_3.H_2O$ or amine.	G.	Benzyl chloride. G.	Temperature of oil-bath. ° C.	Time of run. Hrs.	Yield of amine. Monobenzyl, %.	Dibenzyl, %.	Tribenzyl, %.
$(NH_4)_2CO_3.H_2O$...	28	32	110	5.5	9	9	62
$(NH_4)_2CO_3.H_2O$..	71	32	80–85	5	19	18	50
$(NH_4)_2CO_3.H_2O$..	213	96	85–90	6	16	20	44
$C_6H_5NH_2$........	23	32	95–100	4	56	21	..
$C_6H_5NH_2$........	23	64	95–100	4	13	60	..
$C_6H_5NH.CH_3$....	27	32	95–100	4	90	..	..
p-$CH_3.C_6H_4NH_2$..	21.5	50	95–100	4	..	76.6	..
m-$CH_3.C_6H_4NH_2$.	21.5	50	95–100	4	..	71.4	..

Benzyl Chloride and Sodium Cyanide.

From the time of Cannizzaro[1] it has been customary to use alcohol in carrying out the reaction between benzyl chloride or any of its analogues and sodium or potassium cyanide, for fear that if water be used, hydrolysis of the chloride would occur. The fear is not ungrounded, but, we think it is exaggerated. In some cases it has been observed[2] that the addition to the alcohol of a certain amount of water is desirable, not merely in order to induce greater solubility of the sodium salt, but for the reason that, otherwise, the reaction is likely to proceed in a different sense. For the preparation of benzyl cyanide, itself, Meyer and Jacobson's[3] direct that 2 parts of alcohol and 1 part of water be used. Unfortunately, the yield of the cyanide obtainable under such conditions has not been indicated. In our experiment with aqueous solutions of sodium cyanide we obtained yields of benzyl cyanide equal to 50 and 60%. In the experiments given in Table VI, we used 32 g. of benzyl chloride in each case, which required, theoretically, 12 g. of sodium cyanide; the salt was

TABLE VI.

32 G. of Benzyl Chloride Used in Each Experiment.

Run No.	Sodium cyanide. G.	Temperature of oil-bath. ° C.	Time of run. Hrs.	Yield of cyanide. G.	%
1........................	24	70–75	3	5	17
2........................	36	110–115	4	11	40
3........................	36	105	2	15.5	53
4........................	36	110–115	1.5	15	51
5........................	24	105	1	10.5	36.2
6........................	24	105	1	20	70
7........................	16	110–115	2.5	15.5	53
8........................	16	105	1	19.5	67
9........................	16	105	1	17.5	60
10........................	16	102–105	1	18	63
11........................	16	105	1	13.5	46.5
12........................	16	105	1	15	51

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[1] Cannizzaro, *Ann.*, **96**, 246 (1855).

[2] Br. Radziszewski and P. Wishek, *Ber.*, **18**, 1282 (1885).

[3] Meyer and Jacobson, "Organischen Chemie," II, 1, 597 (1902).

dissolved in 100 cc. of water. It will be noticed that too great an excess of sodium cyanide seems to be detrimental rather than beneficial; presumably it induces hydrolysis of the benzyl cyanide to phenyl-acetic acid as well as some benzyl alcohol. For the same reasons, prolonged boiling should be avoided. The results are summarized in Table VI. In the first 4 runs, the benzyl chloride was added all at one time; in the remaining runs, it was added from a dropping funnel during the course of $^1/_2$ to $^3/_4$ hour. The reaction seems to be extremely sensitive to the influence of various factors, and the yields of the cyanide vary in different experiments, notwithstanding the fact that these experiments have been carried out under as nearly identical conditions as possible.

Benzyl Alcohol.

Cannizzaro,[1] in 1853, showed that benzaldehyde under the influence of a strong solution of potash, suffers auto-oxidation and that half is converted into acid and half into alcohol. This reaction still continues to serve as one of the standard methods for the preparation of benzyl alcohol. R. Meyer[2] substituted water for alcohol as a solvent and Missenheimer[3] improved the procedure of purification. In the development of the methods for obtaining the alcohol from benzyl chloride, two lines have been followed, first, the direct hydrolysis of the chloride; second, previous conversion of the chloride into an ester, usually the acetate, with subsequent hydrolysis of the latter. For obtaining it by the indirect method, Cannizzaro[4] used alcoholic potash for saponification of the acetate. Seelig[5] used the same substance but only 1 mol.; and, recently, Klever[6] patented a process of hydrolyzing the ester by means of water containing sodium acetate or sodium carbonate. In this connection, Mettler's[7] indirect method, one possibly of wide application, may also be mentioned. It consists in the electrolytic reduction of the esters of benzoic acid to benzyl alcohol.

The hydrolysis of benzyl chloride directly to the alcohol has also received considerable attention. Lauth and Grimaux[8] boiled the chloride for a short time with water containing freshly precipitated lead oxide; Niederist[9] boiled it with water alone for a long period; Meunier[10] used one

[1] Cannizzaro, *Ann.*, 88, 129 (1853).

[2] R. Meyer, *Ber.*, 14, 2390 (1881); see also Kohn and Tranton, *J. Chem. Soc.*, 75, 1155 (1899).

[3] Missenheimer, *Ber.*, 41, 1420 (1908).

[4] Cannizzaro, *Ann.*, 96, 246 (1855).

[5] Seelig, *J. prakt. Chem.*, [2] 39, 166 (1889).

[6] *C. A.*, 9, 694 (1915); Brit. Pat. 20,504.

[7] *Friedlaender*, 8, 144; D. R. P. 166,181.

[8] Lauth and Grimaux, *Ann.*, 143, 81 (1867).

[9] Niederist, *ibid.*, 196, 353 (1879).

[10] Meunier, *Bull. soc. chim.*, 38, 159 (1882).

mol. of potassium carbonate in 10 parts of water; and, lately, Klever[1] patented a procedure wherein benzyl chloride is heated in the presence of an excess of water, intimately mixed with magnesium hydroxide, or hydroxides of alkaline earths, or other basic hydroxides; also, by heating the chloride with water and alkaline carbonates.[2] Although the ground appeared to be fairly well covered, it seemed not without interest to make a few trials to obtain benzyl alcohol directly from the chloride according to our procedure, and to determine, if possible, under what conditions of hydrolysis the most favorable yields of the alcohol may be expected. The results are summarized in Table VII.

TABLE VII.

32 G. of Benzyl Chloride Used in Each Experiment.

Run No.	Alkali.	G.	Temperature of oil-bath. ° C.	Time of run. Hrs.	Yield of alcohol. G.	Yield of alcohol. %.
1	$Na_2B_4O_7.10H_2O$	144	110–115	8	4	15
2	Na_2CO_3	40	110–115	10	18	66
3	Na_2CO_3	40	110–115	6	21	78
4	Na_2CO_3	26	110–115	4	20.5	76
5	Na_2CO_3	26	110–115	2.5	22	81.5
6	Na_2CO_3	13	110–115	2	22	81.5
	NaOH	10				
7	NaOH	20	120–125	1	21.5	80

Obviously, the data at hand are not sufficient to warrant drawing very definite conclusions. Nevertheless the results indicate (*a*) that the shorter the period of boiling during hydrolysis, the better the yield of the alcohol, presumably because there is likely to be less oxidation of the alcohol to aldehyde and acid; (*b*) that it is preferable to employ sodium hydroxide rather than the carbonate, as the hydrolysis will thus be completed in a briefer period.

Summary.

(1) It has been shown that benzyl chloride, heated with the dry salts of various organic acids in the presence of copper as a catalyst, gives fair yields of the corresponding esters. Some benzyl chloride is lost through decomposition under the influence of the catalyst.

(2) The same benzyl esters may be obtained in purer state and in better yields, up to 85%, when benzyl chloride and aqueous solutions of the salts of the corresponding acids are heated and thoroughly stirred at the same time.

(3) Benzyl chloride condenses with sodium phenolates in aqueous solution and gives fair yields of mixtures of benzyl ethers and benzyl phenols; the formation of the latter under these circumstances is surprizing.

(4) Benzyl chloride gives good yields of mono-, di-, and tribenzyl amines

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[1] Klever, *C. A.*, 8, 2781 (1914); Fr. Pat. 462,438.

[2] *C. A.*, 9, 694 (1915); Brit. Pat. 20,504.

when heated with aqueous solutions of ammonium carbonate; good yields of the corresponding benzyl anilines when treated, similarly, with aniline, methyl aniline, toluidine, etc.

(5) Benzyl cyanide is obtainable in 50 to 60% yields from benzyl chloride and sodium cyanide in aqueous instead of alcoholic solution.

(6) It has been shown what conditions of procedure are likely to prove most serviceable in the hydrolysis of benzyl chloride to benzyl alcohol.

ANN ARBOR, MICHIGAN.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY.]

THE INTERACTION OF CARBON DISULFIDE WITH AMMONIUM CARBONATE.

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The work described in this paper represents one phase of an extensive investigation now in progress in the Sheffield Laboratory, dealing with the chemistry of carbon disulfide, and was undertaken by the writer at the suggestion of Professor Treat B. Johnson.[1]

In the development of the researches on pyrimidines and hydantoins which have been conducted in the above laboratory for several years, a wide use has been made of thio-urea for the synthesis of a great number of new combinations in these 2 cyclic series of organic compounds. The reagent has been used in large quantities for this work, and the largest proportion of it has been prepared by co-workers in the laboratory by molecular rearrangement of ammonium thiocyanate. The yield so obtained is not satisfactory, the best result that one can expect to obtain being about 25%.[2] Evidence has been obtained, however, which indicates that the velocity constant of the reversion of these 2 isomers is a varible factor, and that the equilibrium percentage of thio-urea is influenced, not only by the presence of other salts, but is also concerned with other important experimental factors or conditions which are not well understood.[3]

Inghilleri[4] has recently described in a paper entitled, "A New Process for the Preparation of Ammonium Sulphocyanate and Thio-urea," a method for synthesizing thio-urea, which gives, according to him, prac-

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[1] In our future work, we will take up the study of high temperature reactions with carbon disulfide, the influence of catalysts on well known reactions of this reagent which proceed with slow velocity, and also an investigation of photochemical influences at low and high temperatures. (T. B. J.)

[2] Reynolds and Werner, *J. Chem. Soc.*, 83, I (1903).

[3] Atkins and Werner, *ibid.*, 101, 1982 (1912); Johnson, Hill and Bailey, THIS JOURNAL, 37, 2406 (1915); Claus, *Ann.*, 179, 128 (1875); Waddell, *J. Phys. Chem.*, 2, 525 (1898).

[4] Inghilleri, *Gazz. chim. ital.*, 39, 634 (1909).

tically quantitative yields of this reagent. The method is based on the reactions which take place when carbon disulfide is heated with ammonium carbonate. According to Inghilleri the complete transformation proceeds in 3 stages, as follows, first, carbon disulfide adds ammonia with formation of ammonium dithiocarbamate (I); second, this salt then loses hydrogen sulfide with formation of ammonium thiocyanate (II); and third, the thiocyanate undergoes quantitative conversion into thio-urea (III).

$$\underset{\text{(I).}}{NH_2CS.S.NH_4} \longrightarrow \underset{\text{(II).}}{NH_4SCN} \longrightarrow \underset{\text{(III).}}{CS(NH_2)_2}$$

The first change is brought about by heating at 100° to 110°, the second from 120° to 130°, and the third by heating at 160°. By heating at 160°, he states that *sym*-diethyl-thio-urea melting at 77° is formed instead of thio-urea, if alcohol is present in the mixture.

The quantitative formation of thio-urea by application of Inghilleri's method of synthesis incited an interest in its practical application, not only because it offered an easy method of obtaining this reagent in quantity, but because it revealed for the first time experimental conditions which not only are productive of a pronounced increase in the velocity of change, but also lead to the maximum equilibrium percentage of thio-urea thus far obtained.[1]

In order to determine whether the products of reaction formed by heating carbon disulfide with ammonium carbonate, according to the conditions of Inghilleri's experiments, contribute to the success of this transformation into thio-urea by increasing the stability of this compound at 160°, it was decided to repeat his work and determine quantitatively the amount of ammonium thiocyanate and thio-urea formed, and also study the influence of different factors concerned in the production of the reaction-equilibrium. This study necessitated first the working out of reliable methods for determining quantitatively ammonium thiocyanate and thio-urea in the presence of each other. The thio-urea was determined successfully by application of the method devised by Reynolds and Werner,[2] namely, titration of aqueous solution with a standard solution of iodine. For the determination of ammonium thiocyanate in presence of thio-urea, we tried different methods which have been recommended for this purpose,[3] but found all of them unsatisfactory. A suitable method was finally developed after many trials on standardized solutions of the 2 reagents, which enabled us to determine with accuracy the amount of thiocyanate present. It is efficient, however, only when less than 40% of thio-urea is present in the mixture. Larger proportions of this reagent

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[1] See Atkins and Werner, *J. Chem. Soc.*, 101, 1171 (1912).

[2] Reynolds and Werner, *ibid.*, 83, 1 (1903).

[3] See Experimental Part of this paper.

mask the silver by formation of stable double combinations, rendering accurate titration with silver nitrate impossible. Whether a method of titrating accurately with silver salts for thiocyanate in the presence of large proportions of thio-urea can be developed, must be decided by further study of various factors influencing the reactions involved.

We now find that carbon disulfide and ammonium carbonate interact with formation of ammonium thiocyanate and finally thio-urea, but the yield of thio-urea is much lower than theory demands. In fact, the best yield that we were able to obtain was about 11%, which is 14% less than that which can be obtained by direct heating of ammonium thiocyanate as originally recommended by Reynolds.[1] In some experiments, the yield of this product was as low as 1.2%. It is apparent from our results that reversion to ammonium thiocyanate is favored by the hydrogen sulfide formed during the reaction. In other words, the results obtained in a quantitative study of this reaction do not recommend the method as a practical one for the synthesis of thio-urea. A description of the analytical procedure and other details of this research is recorded in the Experimental Part of this paper.

Experimental Part.

The thio-urea used in the analytical work discussed below was a very pure imported product, which gave no color with ferric alum. The ammonium thiocyanate employed was first recrystallized from alcohol, carefully dried, and its purity confirmed by titration against a standard silver nitrate solution. Seven mixtures of thio-urea and ammonium thiocyanate in definite ratios were prepared for experimental work. Each mixture, weighing 6 g., was dissolved in water, the solution diluted to a volume of 250 cc. and aliquot parts of these solutions then taken for the various titrations.

Determination of Ammonium Thiocyanate.—The method first employed for the determination of thiocyanate was that recommended by Krall.[2] This method of analysis did not give satisfactory results (Curve A; Fig. 1), especially with mixtures containing more than 15% of thio-urea, and when the percentage of thio-urea reached 60% of the mixture, the 40% of thiocyanate titrated as 60.4% or 151% of that actually present.

The second method employed for the determination of the thiocyanate was direct titration with silver nitrate. Analyses were made on the same mixtures as used above, and the procedure was as follows. A 10 cc. aliquot part of the solution was used, to which were added 20 cc. of water and 5 cc. of dil. nitric acid of the same concentration as stated above. Two drops of ferric alum indicator were added, and the titration made directly with standard silver nitrate solution, which was run in very slowly

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[1] Reynolds and Werner, *loc. cit.*

[2] Krall, *J. Chem. Soc.*, 103, 1385 (1913).

and with constant shaking to avoid the presence of an excess of silver nitrate in the solution at any time. The point at which the pink color disappears is best determined by comparison with an over-titrated standard.

The results of the direct titration of the 7 mixtures used above, supplemented by results from several other determinations made by the same method, are shown in Curve B, Fig. 1. The values obtained show that direct titration against silver nitrate gives concordant results for mixtures containing not more than 40% of thio-urea. But between 40% and 50%, the curve turns sharply upward, and values obtained for thiocyanate in the presence of larger proportions of thio-urea are far too great. Results of analyses made by each of the 2 methods described above, are recorded in Table I.

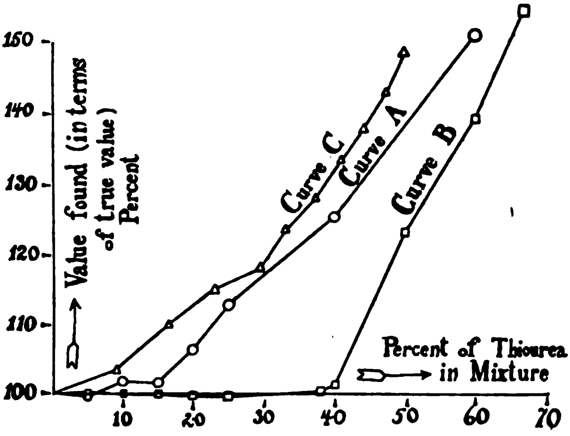

Fig. 1.

TABLE I.—ANALYSES.

Actual thio-urea. %	Actual NH_4CNS. %	Thiocyanate found. Krall's method. %	Thiocyanate found. Direct titration. %	NH_4SCN found (in terms of true value). Krall's method. %	NH_4SCN found (in terms of true value). Direct titration. %
0	100	100.0	100.0	100.0	100.0
5	95	94.6	95.2	99.6	100.2
10	90	91.7	90.0	101.9	100.0
15	85	86.4	85.0	101.6	100.0
20	80	85.0	79.8	106.3	99.8
25	75	84.5	74.8	112.7	99.7
38	62	...	62.2	...	100.3
40	60	75.1	60.8	125.2	101.3
50	50	...	61.5	...	123.0
60	40	60.4	55.6	151.0	139.0
67	33	...	51.3	...	155.5
80	20	...	54.6	...	273.0

The data in Table I were used in constructing the 2 Curves, A and B, shown in Fig. 1. The per cent. of thio-urea in the mixture is plotted along the horizontal axis, and the value found (in terms of true value) on the vertical axis. From these 2 curves it is evident that Krall's method[1] is not reliable for mixtures containing more than 15% of thio-urea, while direct titration will give accurate results for those containing up to 40%

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[1] *Loc. cit.*

of thio-urea. No method was devised for the correct estimation of thiocyanate in mixtures where more than 40% of thio-urea was present.

A third procedure was tried for determining quantitatively the influence of thio-urea on the reaction of thiocyanate with silver nitrate. Aqueous solutions of pure thio-urea and ammonium thiocyanate were prepared of equal strength and an aliquot part of the standard thiocyanate solution titrated with silver nitrate to a colorless end-point. The addition of thio-urea solution to this colorless solution was found to restore at once the pink color, which could again be discharged by further titration with silver nitrate. Following this procedure, successive additions of thio-urea solution were made, titrating with silver nitrate after each addition. The results of these titrations are given in Table II.

TABLE II.—INDIRECT TITRATIONS METHOD.

Actual thio-urea. %.	Actual NH_4CNS. %.	NH_4CNS found. %.	Value found (in terms of true value). %.
0	100.0	100.0	100.0
9.1	90.9	94.1	103.5
16.7	83.3	91.6	110.0
23.1	76.9	88.4	115.0
28.6	71.4	84.3	118.0
33.3	66.7	82.3	123.5
37.5	62.5	80.0	128.0
41.2	58.8	78.4	133.3
44.4	55.6	76.6	137.8
47.4	52.6	75.2	142.9
50.0	50.0	74.2	148.4
54.5	45.5	72.2	158.7
60.0	40.0	69.4	173.5
66.7	33.3	65.5	196.4
71.4	28.6	63.0	220.2
75.0	25.0	60.8	243.1
77.7	22.3	60.7	272.4
80.0	20.0	59.4	297.2

The above results are plotted as Curve C in Fig. 1, in which they are compared with results of the direct titration method, and Krall's excess silver nitrate methods, respectively. Curve C is comparable with Curve A (Krall's method), and gives incorrect values for thiocyanate, even with very low concentrations of thio-urea.

In all the 3 analytical methods outlined above, it was observed that the amount of precipitated silver thiocyanate decreased rapidly with increasing concentration of thio-urea, and finally when the thio-urea was increased to about 55%, the precipitate did not appear, but oily drops gathered on the side of the titration flask. These could be made to solidify to a white crystalline solid by rubbing with a stirring rod. Their composition was not determined, but they undoubtedly consist of silver thiocyanate combined with thio-urea.

The action of silver nitrate on a solution of pure thio-urea was also investigated. When equal molecular proportions of thio-urea and silver nitrate in aqueous solution were mixed, and the silver nitrate titrated for in the usual way with standard potassium thiocyanate solution, it was found that only about 50% of the original silver could be accounted for. The other half mole was masked by the one mole of thio-urea present. When 2 moles of thio-urea were added to one mole of silver nitrate solution, the silver was then entirely masked by the thio-urea. Direct titration gave the same results as were obtained in the indirect titration. In each case one mole of silver was masked by 2 moles of thio-urea.

Determination of Thio-urea.—The method of Reynolds and Werner[1] was employed for the determination of thio-urea by titration with iodine. According to Werner,[2] this method gives low results if the concentration of the thio-urea exceeds 0.02 g. per 100 cc. of the titration mixture. Several titrations were made of solutions containing mixtures of thio-urea and ammonium thiocyanate, the results of which are recorded in Table III.

TABLE III.—DETERMINATION OF THIO-UREA.

G. of thio-urea per 100 cc. of titration mixture.	Apparent per cent. of actual thio-urea present.
0.0450	84.7
0.0290	88.6
0.0190	90.7
0.0120	94.3
0.0096	94.8
0.0072	96.8
0.0048	100.8
0.0024	102.0

From these results it is apparent that concentrations of more than 5 mg. of thio-urea per 100 cc. of titration mixture cannot be correctly estimated. Ammonium thiocyanate did not interfere in the determination of thio-urea by this method. According to Reynolds and Werner[3] the proportion must be greater than 16 parts of thiocyanate to one of thio-urea before it seriously influences the titration.

The Action of Ammonia on Carbon Disulfide.—Inghilleri found that carbon disulfide and ammonium carbonate interact when heated in sealed tubes, and yield thio-urea, ammonium thiocyanate, hydrogen sulfide, and carbon dioxide. His method of operating was to heat at 100° to 110° for 6 hours, and for the same period at 125° to 130° for 2 hours at 160°, releasing the pressure in the tube after each operation. At the end of the 100° period, he identified carbon dioxide but no hydrogen sulfide. After the 130° period, hydrogen sulfide and ammonium thiocyanate were identified, and after heating at 160°, thio-urea was obtained as a final product

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[1] Reynolds and Werner, *J. Chem. Soc.*, 83, 6 (1903).

[2] Werner, *ibid.*, 101, 2166 (1912).

[3] *Loc. cit.*

melting at 169°. No quantitative analysis was made for the determination either of the thio-urea or of the thiocyanate produced in the reaction.

Inghilleri used 6 g. of carbon disulfide and 8 g. of unanalyzed ammonium carbonate, and reported his yield of 1.1 g. of thio-urea as almost quantitative. Basing calculations on the weight of the carbon disulfide a quantitative yield of thio-urea would be 6 g., thus Inghilleri's calculations are at fault, and his yields much lower than theory demands.

In our work the carbon disulfide was purified by allowing to stand for 12 hours over anhydrous copper sulfate, shaking with mercury, drying over anhydrous sodium sulfate, and finally distilling. A product distilling uniformly at 46.3°, uncorr., was obtained. The ammonium carbonate used was analyzed and found to contain 25.08% of ammonia.

TABLE IV.

Expt.	CS_2. G.	Ammo. carb. G.	Calc. NH_3. G.	Heated.		H_4CNS titrat. G.	Thio-urea titrat. G.	Total NH_4CNS and thio-urea. G.	Composition of final product.		Yield of total HN_4-CNS and thio-urea based.		Time left standing in closed tube under pressure before opening.
				Hrs.	At °C.				NHC_3NS. %.	Thio-urea. %.	On CS_2. %.	On NH_3. %.	
1.....	5.05	9.50	2.38	6 7½ 2	100 135 160	4.26	0.281	4.54	93.8	6.2	90.0	...	4 hrs.
2.....	5.10	9.54	2.39	6 6 2	100 135 160	4.35	0.133	4.48	97.0	3.0	87.8	...	15 hrs.
3.....	3.80	7.16	1.79	6 6 2	100 135 160	2.96	0.036	3.00	98.8	1.2	78.9	...	5 days[b]
4.....	3.80	7.16	1.79	6 6 2	100 135 160	2.90	0.037	2.94	98.7	1.3	77.4	...	5 days[b]
5.....	3.80	7.16	1.79	6 6 2	100 135 160	3.04	0.110	3.15	96.5	3.5	82.9	...	..
6.....	6.00	8.00	2.00	..	..	4.11	0.355	4.47	92.1	7.9	..	100.0	..
7.....	6.44	8.67	2.17	6 2½ 3½	100 130 160	..	...	..	93.2	6.8	..	...	..
8.....	6.41	8.01	2.00	6 6	100 160	3.80	0.465	4.27	89.1	10.9	..	95.5[a]	4 hrs.
9.....	6.42	8.00	2.00	6 6	100 160	4.32	0.524	4.85	89.2	10.8	..	108.0	4 hrs.

The tubes in Expts. 1, 2, 3, 4 and 5 above were charged with ammonium carbonate equivalent to an excess of 5% of ammonia, while those in Expts. 6, 7, 8 and 9 contained 33%, 33%, 43% and 43%, respectively, of an excess of ammonia.

[a] This value is too low on account of loss of material when tube was opened.

[b] There was very little internal pressure in these tubes when opened.

The results of our experiments are recorded in Table IV. The method of operating was, in general, that used by Inghilleri, but contrary to his statement, heating at 100° was always productive of large quantities of hydrogen sulfide, which was determined by passing the mixed gases into a solution of copper sulfate when the tube was opened, and precipitating as copper sulfide. The precipitated cupric sulfide was filtered, dried, ignited in hydrogen, and weighed as Cu_2S. According to this method of determination, heating at 100° produced in Expt. 1 a volume of 750 cc. of hydrogen sulfide and 1275 cc. of carbon dioxide, the gases being measured at 20°.

The yield of total thiocyanate and thio-urea, based on carbon disulfide in the presence of a 5% excess of ammonia, varied between 77.4% and 90.9%. Based on ammonia in the presence of 33% excess disulfide, the yield was about quantitative. The difficulty of accurately estimating yields based on ammonia content is apparent from Expt. 9 where the ammonia carbonate used was obviously richer in ammonia than that used in the analysis upon which yields were calculated.

In no case did the percentage of thio-urea in the equilibrium mixture approach the value found by Reynolds and Werner to be about 25%. The highest value found was 10.9%, and other values ranged as low as 1.2%. The lowest percentages of thio-urea were found in those tubes which had been permitted to stand for some time at room temperature after heating at 160°, in the presence of the hydrogen sulfide and carbon dioxide generated at that temperature. In these tubes also the yield of total thio-urea and thiocyanate was lower than in those which were opened immediately after cooling. These results seem to indicate that hydrogen sulfide influences the equilibrium, reverting thio-urea to ammonium thiocyanate. It apparently affects also the formation of the ammonium salt. The action of hydrogen sulfide on these 2 isomeric substances will receive further attention at a later date.

Summary.

1. Quantitative determinations of ammonium thiocyanate in the presence of thio-urea cannot be carried out accurately by indirect titration with excess of silver nitrate if the thio-urea exceeds 15% of the mixture.

2. Direct titration for ammonium thiocyanate with silver nitrate can be applied successfully in mixtures containing as high as 40% thio-urea. This interference in titration is apparently due to the solubility of silver thiocyanate in thio-urea solutions with formation of a complex ion.

3. Thio-urea can be determined by titration with iodine if the concentration of thio-urea does not exceed 5 mg. per 100 cc. of the titration mixture.

4. Carbon disulfide and ammonium carbonate interact at 160° giving a mixture of ammonium thiocyanate and thio-urea; the equilibrium de-

pending upon the concentration of reagents used, temperature, time of heating and finally upon the concentration of hydrogen sulfide formed in the reaction. The reaction is not productive of a quantitative yield of thio-urea.

NEW HAVEN, CONN.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF LELAND STANFORD JUNIOR UNIVERSITY.]

THE ALKYL AMINES AS SOLVENTS.

BY HOWARD MCKEE ELSEY.

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That primary amines are ionizing solvents has been shown by the work of Gibbs[1] and others, and by analogy we would expect that a salt soluble in ammonia would be less soluble in methylamine, still less soluble in ethylamine and dimethylamine, and perhaps insoluble in propylamine and trimethylamine. Indeed Shinn[2] found potassium iodide, a salt very soluble in liquid ammonia and fairly soluble in methylamine, to be entirely insoluble in ethylamine, the next higher ammono alcohol. From this, it would seem that the higher amines would be very poor solvents for inorganic substances.

The salts used in the present solubility determinations were of the ordinary commercial variety, dried as thoroughly as was possible without danger of decomposition. Excepting in a very few cases those compounds only were taken from which all the water was known to have been removed.

The ethyl-, methyl-, propyl- and isopropylamines used as solvents were water-free imported samples. To ensure their remaining dry, they were stored over metallic sodium. The dimethyl and trimethylamines were purchased as the water solutions. They were recovered as the water-free substances by distilling from a flask through an inverted condenser and then a soda-lime tube and finally condensing in a glass container cooled by a liquid ammonia bath. Several pieces of freshly cut sodium were added to the container to remove the last traces of moisture present and to absorb any that might later be introduced. Some difficulty was encountered in preventing loss of the amine by leakage through the stopcock of the container. The value of the amines as organic solvents is shown by the ease with which they dissolved any lubricant which was placed on the stopcock; and it was finally found necessary to keep the tube, holding the stock of amine, in an ice-bath while working, and to seal the stopcock off at night.

Since the lower amines are gases under operating conditions the solubility determinations were made in hermetically sealed glass tubes. For

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[1] Gibbs, THIS JOURNAL, 28, 1395 (1906).

[2] Shinn, *J. Phys. Chem.*, 11, 537 (1907).

this purpose a glass tube was closed at one end, a small amount of substance introduced and the tube placed in an ammonia bath. Solvent was then distilled in and the upper end of the tube sealed off. If, after the temperature rose to room temperature and after agitation, no marked solvent action could be observed, the tube was cooled with liquid ammonia to precipitate, if possible, any dissolved material. In most cases these solutions have very high temperature coefficients, and the change from room temperature to —33.5° is often sufficient to cause crystallization at once from a solution which is by no means saturated at the higher temperature.

In later experiments, these straight tubes were replaced by 2-legged tubes in which it was much easier to judge the relative solubilities of the different salts. These tubes were filled in the same way, but after the solvent had been added the tube was constricted at the neck, evacuated and sealed off. Unless the air was removed in this way, distillation from one arm to the other was very slow.

After filling and sealing, the tubes were allowed to stand for several days, being frequently agitated to ensure the attainment of equilibrium. The clear solution was then decanted over into the shorter leg and the long leg was placed in an ice-bath. Due to the difference in temperature, the solvent was distilled out of the second leg and the solubility of the compound could be determined roughly by the amount of residue remaining

This separation of the solute by distilling off the solvent could not be accomplished in all cases on account of the exceedingly high viscosity of concentrated solutions in the amines. Ammonia and the amines as a class have very low viscosities, being much more mobile than water. But even dilute solutions in ammonia and the amines are markedly more viscous, while concentrated solutions in them are apt to have the consistency of the thickest of molasses.

One of the most striking properties of the amines is the ease with which they enter the molecular structure of compounds as amine of crystallization. These aminates usually form immediately on contact of the cold liquid with the solute, causing the salt to swell up into a bulky mass. Often this aminate is very soluble at room temperatures and on removing the tube from the bath it quickly goes into solution. In other cases, the aminate is insoluble or only slightly soluble at room temperature and it remains as a solid phase. As a rule the addition product is sufficiently soluble to go over slowly to a crystalline structure, the crystals often attaining considerable size.

Since the chemically pure amines are very expensive and our supply of them was somewhat limited, the solubility tubes were of necessity too small to afford quantitative results. However, it is believed that our results are accurate within the limits of error of the method used. The salts are classified as being very soluble, moderately soluble, slightly soluble, or insoluble. A salt is classed as being very slightly soluble where no appreciable residue is left in the second leg and yet where there is some evidence of solubility such as color in the solution.

The solubilities of the different salts in the several amines are tabulated below. For comparison, the measurements of Franklin and Kraus[1] in liquid ammonia and of Gibbs[2] in methylamine are included in the table. The determinations taken from Gibbs' paper are marked thus, *. The following abbreviations are used in the table, very soluble, *v;* moderately soluble, *m;* slightly soluble, *s;* and insoluble, *i.*

A indicates the formation of an aminate on contact of the solvent and solute, the solubility of this aminate being shown by one of the letters above. R indicates marked reaction between solute and solvent.

TABLE I.—SOLUBILITIES OF SALTS IN AMINES.

Solvent. / Solute.	NH_3	CH_3NH_2	$C_2H_5NH_2$	$C_3H_7NH_2$	$CH_3\overset{CHNH_2}{\wedge}CH_3$	$(CH_3)_2NH$	$(CH_3)_3N$
AgBr	*m*	..	*v*	..	..	..	..
AgI	*v*	*v*	*v*	..	..	*v*	A *i*
$AgNO_3$	*v*	*v**	*v*	*v*	*m*	*v*	..
Ag_2SO_3	..	*s*	*s*	..	..	..	..
Ag_2SO_4	*i*	A *i*	A *i*	..	..	..	..
$BaBr_2$	..	..	*v*	..	..	*s*	..
$BaCl_2$	*i*	..	*s*	..	..	..	..
$Ba(ClO_3)_2$[a]	..	..	*m*	..	..	..	..
BaI_2	*s*	A *v*	A *v*	A *v*	A *m*	A *v*	A *s*
$Ba(NO_3)_2$	*m*	*s*	*s*	..	..	*s*	*s*
$Ba(SCN)_2$	*v*	*v*	*v*	..	*m*	*m*	*i*
$BiBr_3$	*v*	..	*m*	..	..	*v*	..
$BiCl_3$	*m*	A *m*	..	..	..	..	..
BiI_3	*s*	A *v*	*v*	..	..	*v*	*s*
Bi_2S_3	*i*	*s*	*s*	..	..	..	..
Br_2[b]	..	*v*	R *v*	..	..	R *v*	..
CaC_2	..	*i*	*i*	..	..	..	..
CaI_2	..	..	A *v*	..	..	*v*	..
$Ca(NO)_2$	*v*	*m*	*v*	..	..	*i*	*i*
$CdBr_2$	..	..	*s*	..	..	A *m*	..
$Cd(CN)_2$	..	..	*m*	..	..	*m*	..

[a] A solution of $Ba(ClO_3)_2$ in $C_2H_5NH_2$ is unlike most of the solutions in these solvents in that it has a very low temperature coefficient of solubility.

[b] Bromine reacts with the dimethylamine with the evolution of heat to form a very soluble crystalline compound. With methylamine and ethylamine, the reaction is much more violent and there is formed in addition to a soluble crystalline product, a black residue.

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[1] *Am. Chem. J.*, 20, 820 (1897).

[1] *Loc. cit.*

TABLE I (*continued*).

Solvent. / Solute.	NH_3.	CH_3NH_2.	$C_2H_5NH_2$.	$C_3H_7NH_2$.	$\genfrac{}{}{0pt}{}{CH_3}{CH_3}\!>\!CHNH_2$.	$(CH_3)_2NH$.	$(CH_3)_3N$.
CdI_2[c]	*s*	..	A *m*	..	..	*v*	*m*
$Cr_2(SO_4)_3$	..	*i*	*i*	..	..	..	..
CuCl	*s*	R*	A *m*	..	..	..	..
$CuCl_2$	*i*	..	A *m*	..	..	..	..
$CuHAsO_3$	*i*	*s*	*s*	..	..	..	..
CuI[d]	*v*	..	*v*	..	..	..	..
CuS	*i*	*s*	*s*	..	..	..	*i*
CuSCN	..	*v*	*v*	..	..	..	..
$CuSO_4$[e]	*i*	*i**	A *i*	..	..	..	..
Fe	*i*	..	*i*	..	..	..	..
$FeCl_3$	..	..	A *s*	..	..	..	..
FeI_2	..	..	A *i*	..	..	*m*	..
$Fe_2(SO_4)_3$	*i*	A *i*	*i*	..	..	..	..
$Hg(CN)_2$	*v*	*v**	..	..	..	*v*	..
$Hg(CON)_2$[f]	*v*	..	R	..	..	..	..
HgI	*v*	..	*m*	..	..	..	..
HgI_2	*v*	*v**	*v*	..	..	*v*	*m*
HgS	*i*	..	*i*	..	..	..	..
$Hg(SCN)_2$	*v*	*s*	*m*	..	..	..	*s*
I[g]	*m*	*v*	*v*	..	..	*v*	*s*
$KAg(CN)_2$	..	..	*s*	..	..	*s*	..
KCN	..	..	*s*	..	..	*s*	..
$K_4Fe(CN)_6$	*i*	..	*s*	..	..	..	..
KI	*v*	..	*s*	*s*	*i*	*s*	*i*
$KMnO_4$	*v*	..	R	..	..	..	..
KNO_3	*v*	*s*	*s*	..	..	..	..
K_2PtCl_4	..	..	*s*	..	..	*s*	..
K_2PtCl_6	..	*s*	*s*	..	..	..	..
KSCN	*v*	*v*	*m*	..	..	..	..
LiCl	*s*	*v**	A *v*	..	..	*m*	..

[c] A saturated solution of CdI_2 in $(CH_3)_2NH$ is a fair conductor of the electric current at 20°.

[d] CuI is very soluble, forming a blue solution in $C_2H_5NH_2$. If metallic copper is placed in this solution, the blue color is discharged, due possibly to the reduction of Cu^{++} to Cu^{+}, the cupric salt being present as an impurity.

[e] The blue aminate formed is the only one observed which did not, on standing, become noticeably crystalline in character.

[f] $Hg(CON)_2$ reacts and is reduced to metallic mercury and other products which are soluble.

[g] Iodine is extremely soluble in all the amines tested, with the exception of trimethylamine. On standing, the deep color of the solution fades in color. One solution of iodine in dimethylamine had a resistance of 80 ohms between sealed-in electrodes. The resistance increased to 100 ohms after the solution had become colorless. Iodine is only slightly soluble in trimethylamine but, after some weeks, colorless crystals separate from this solution.

TABLE I (*continued*).

Solvent. / Solute.	NH_3.	CH_3NH_2.	$C_2H_5NH_2$.	$C_3H_7NH_2$.	$\begin{array}{c}CHNH_2\\ /\ \backslash\\ CH_3\quad CH_3\end{array}$	$(CH_3)_2NH$.	$(CH_3)_3N$.
$LiIO_3$	..	..	*i*	..	..	..	..
MgI_2	*v*	..	A *v*	..	..	..	..
$Mg(NO_3)_2$	*v*	..	..	..	..	A *s*	..
NaBr	*v*	..	*s*	..	..	*s*	..
$Na_2C_4H_4O_4$	..	..	*i*	..	..	..	..
$NaClO_3$	*v*	*m*	*s*	..	..	*s*	..
NaI	*v*	..	..	..	..	..	..
NaN_3	..	..	*s*	..	..	..	..
$NaNO_3$	*v*	*v**	..	*s*	*s*	*s*	*s*
Na_2SeO_4	..	*s*	..	..	..	..	..
$NiCl_2$	*i*	..	A *i*	..	..	..	..
$Ni(CN)_2$	..	..	*s*	..	..	*s*	..
$Ni(SCN)_2$	..	..	*v*	A *m*	..	..	..
$NiSO_4$	*i*	*i*	*i*	..	..	..	..
P (red)	*i*	*s*	*s*	..	..	..	*i*
P (yellow)[h]	*m*	*m*	*v*	..	..	..	..
$PbBr_2$	*m*	..	A *v*	..	..	*m*	..
PbI_2[i]	*v*	A *s*	A *m*	A *m*	*m*	A *s*	A *s*
$Pb(SCN)_2$	..	A *v*	A *m*	..	..	..	*m*
$PtCl_2$	*s*	..	*m*	..	..	..	..
PtI_2	..	..	*m*	..	..	*s*	..
S	*m*	*v*	*v*	..	..	..	*s*
SbI_3	R	..	*v*	..	..	*v*	*i*
Se[j]	*m*	..	*s*	..	..	..	..
SnI_4	..	A *i*	A *v*	..	..	*m*	..
$SrBr_2$	..	..	A *v*	..	..	..	..
$SrCl_2$	*i*	..	*m*	..	..	..	..
SrI_2	..	..	*v*	..	..	A *v*	..
$Sr(NO_3)_2$	*v*	*v*	A *s*	..	..	..	..
Te	..	..	*i*	..	..	..	..
TlI	..	..	*i*	..	..	..	..
$TlNO_3$	*m*	*v*	*m*	*m*	*m*	*m*	*s*
Tl_2SO_4	..	..	*i*	..	..	..	..
$UrO_2(C_2H_3O_2)_2$[k]	..	*s*	*m*	..	..	..	..
$UrO_2(NO_3)_2$	..	..	*i*	..	..	..	*i*
ZnS	..	*i*	*i*	..	..	..	..

[h] Yellow phosphorus is soluble in ethylamine and methylamine, forming almost colorless solutions; but on standing the red modification, which is only slightly soluble, separates.

[i] PbI_2 turns white on contact with the amines. By heating the tubes very gently, the original yellow color returns, indicating that the amine of crystallization has been removed. On cooling, the PbI_2 again turns white.

[j] Se in $C_2H_5NH_2$ turns from red to black in color but without visible increase in volume.

[k] A solution of $UrO_2(C_2H_3O_2)_2$ gelatinizes on standing for some days.

The action of the sulfides of the alkali and alkaline earth metals in these amines is interesting. Samples of the commercial variety of these salts when treated with the amines give yellow solutions very similar to a dilute solution of sulfur. The residual salts, which previously were a dirty yellow in color, are reduced to a pure white color and a granular condition. It is suggested that any free sulfur present in the sulfides is dissolved and the polysulfides thus reduced to the normal sulfides. This explanation, if correct, indicates a possible method of purifying these compounds.

Summary.

The results of this study show that the simpler primary and secondary amines at room temperatures are fair solvents for many salts. However, the solubilities have high temperature coefficients and at the boiling-point of liquid ammonia but very few salts are perceptibly soluble in any of the amines.

The work outlined in this paper was done at the suggestion and under the direction of Professor E. C. Franklin, and I wish to thank him for his kind advice and assistance.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.]

ORGANIC MOLECULAR COMPOUNDS. II.

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It was shown some time ago[1] that tetraphenyl-ethylene dichloride, $(C_6H_5)_2CCl.ClC(C_6H_5)_2$, forms well characterized molecular compounds with chloroform and carbon tetrachloride. The existence of these addition-products led to a study of substances of similar and related structures, and it was discovered that organic compounds of certain types possess to a high degree the power to form molecular compounds.[2] Among the substances studied were substitution-products of tetraphenyl-ethylene. Of these *p*-tetrabromo-tetraphenyl-ethylene, $(BrC_6H_4)_2C = C(C_6H_4Br)_2$, was noteworthy as it formed well crystallized compounds with acetone, methylethyl ketone, ether, carbon tetrachloride, ethyl acetate, and benzene.

As a result of an attempt to interpret the facts discovered and the endeavor to guide future work an hypothesis was devised. A large number of molecular compounds, both inorganic and organic, have been described, but no adequate explanation of their structure based on our present views of valence has been proposed. The subject is an important one, and it

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[1] Norris, Thomas and Brown, *Ber.*, 43, 2940 (1910).

[2] Norris, THIS JOURNAL, 38, 702 (1916).

seemed advisable to study it further, especially in the field of organic chemistry, since the chemist has it in his power to change gradually by the use of the proper substituents the nature of the molecule and thus develop or reduce its ability to form addition-products with other substances. In this way by knowing the effect of the substituents introduced on the general properties of the molecule and on its ability to form molecular compounds, relationships might be traced and the factors underlying the addition discovered.

The hypothesis which has served as a guide in a study of these compounds is as follows.

1. The molecular compound is formed as a result of the coming into play of latent affinities residing on an atom in each of the constituents of the compound. For example, the molecular compound of triphenylchloromethane and acetone, $[(C_6H_5)_3C.Cl]_2.(CH_3)_2CO$, is produced as a result of the fact that the chlorine atoms of the methane derivative and the oxygen atoms of the ketone possess latent affinities of such activity that they interact and a molecular compound results.

2. All atoms possess these latent affinities. Whether or not they are of such a nature as to permit the union of a molecule with a second molecule is determined by the extent to which the chemical energy of the atom in question has been expended when the molecule containing it was formed. If an atom in a compound reacts with difficulty when the latter is brought into contact with other substances it is evident that a large part of its energy has been expended and but a little of it remains to take part in reaction. On the other hand, if the atom enters into reaction readily with other substances it is evident that it still possesses available energy. It is probable, therefore, that such active atoms might be able to unite with atoms of a similar nature and form molecular compounds. For example, the chlorine in methyl chloride is firmly bound in the molecule; it does not form stable molecular compounds. Triphenyl-methyl chloride contains a chlorine atom that is very active; the compound is readily hydrolyzed, and reacts in the cold with sulfuric acid, and with silver. The active chlorine, according to the hypothesis put forward here, contains sufficient energy to form molecular compounds with other substances containing active elements. A study of the literature confirms the view that compounds containing unusually active elements or groups form well characterized molecular compounds.

3. Substances which contain inactive double bonds form molecular compounds. In most cases direct addition of atoms or groups at the double bond leads to the formation of ordinary saturated compounds. So-called unsaturated compounds, however, are known in which the unsaturation is so slight that they will not unite with such an active element as bromine. The chemical affinity latent in the double bond is

so small that it cannot hold in combination other atoms or groups linked to it by primary valence bonds. Many such compounds, however, form well-characterized molecular compounds. The available energy of the double bond is not enough to neutralize the energy of atoms and form a true valence bond, but is sufficient to interact with a similar small amount of energy residing in another compound. Many cases of this type have been discovered. For example, *p*-tetrabromo-tetraphenyl-ethylene contains a very inactive double bond; it will not add bromine; but it forms a large number of molecular compounds with a great variety of substances.

With the hypothesis stated above as a guide a number of compounds have been investigated and a variety of new molecular compounds discovered.

It is impossible to test the proposed hypothesis rigidly, as we have at present no quantitative measure of the relative activities of halogen atoms in organic compounds or of the unsaturation of a double bond. The results of the work described below were obtained in connection with a research on the factors which influence the activity of halogen atoms joined to carbon.[1] When a quantitative measure of this activity has been arrived at by the methods now being developed it is hoped that an interpretation of the facts described below will be possible. As the authors are unable to collaborate in the work in the future, it seems advisable to publish the results so far obtained.

The following molecular compounds have been reported in papers already published.

1. From compounds containing active atoms or groups: (*a*) compounds containing tetraphenyl-ethylene dichloride, $(C_6H_5)_2CCl.ClC(C_6H_5)_2$, (M), of the following composition: $M.2CHCl_3$, $M.2CCl_4$, $M.2CHBr_3$, $M.2CBr_4$, $M.2CHBrCl_2$, $M.2SO_2Cl_2$; (*b*) compounds containing *p*-chloro-tetraphenyl-ethylene dichloride, $ClC_6H_4.C_6H_5CCl.ClC(C_6H_5)_2$, (M′): $M'.CHCl_3$, $M'2CCl_4$; (*c*) compounds containing triphenyl-chloromethane, $(C_6H_5)_3C.Cl$, (M″): $4M''.3CCl_4$:[2] $2M''.(CH_3)_2CO$; (*d*) compounds containing triphenyl-carbinol, $(C_6H_5)_3COH$, (M‴): $4M'''.3CCl_4$, $2M'''.(CH_3)_2CO$.

2. Addition-products from compounds containing an inactive double bond, *p*-tetrabromo-tetraphenyl-ethylene, $(BrC_6H_4)_2C = C(C_6H_4Br)_2$, (N): $N.2(CH_3)_2CO$, $N.CH_3COC_2H_5$, $N.(C_2H_5)_2CO$, $N.CCl_4$, $N.CH_3COOC_2H_5$, $N.C_6H_6$.

On account of the unusual ability of tetrabromo-tetraphenyl-ethylene to form molecular compounds the substance has been investigated fur-

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[1] This work of which this paper is a minor part was aided by a grant from the Warren Fund of the American Academy of Arts and Sciences.

[2] The formula for this compound given in the previous paper is incorrect. The analytical results are correctly given, but these correspond more closely to the above formula than to the one given.

ther to determine whether molecules belonging to other classes of compounds than those studied would enter into combination with it, and to discover the effect of the molecular weight of the added compound on the stability of the addition-products. Well-crystallized molecular compounds were obtained containing in each case one molecule of the ethylene derivative and one molecule of one of the following, toluene, *p*-xylene, chlorobenzene, ethyl ether, propyl acetate, ethyl propionate, and ethyl acetate. No compounds were isolated at ordinary temperatures with chloroform, ethyl alcohol, amyl alcohol, bromobenzene, *m*-xylene, iodobenzene, petroleum ether, methyl acetate, or ethyl formate. It was found that the fact that the ethylene derivative formed no compound with alcohol and with *m*-xylene could be used to separate acetone from alcohol and *p*-xylene from *m*-xylene.

In order to determine the effect of the replacement of bromine by chlorine, tetrachloro-tetraphenyl-ethylene was next studied. In this case the ability to form molecular compounds was much reduced. Of the compounds studied addition-products were obtained only with benzene, carbon tetrachloride, and methylethyl ketone.

Monochloro-tetraphenyl-ethylene was next studied. In this case a compound with carbon tetrachloride only was formed. Negative results were obtained with the substances that yielded well-characterized addition-products with the bromine substitution product. Tetraphenyl-ethylene yielded no molecular compounds. It is impossible to say at present whether the falling off in the ability to form molecular compounds is associated with change in molecular weight or the change in the inactivity of the double bond which is associated with the change resulting from the alteration of the substituents. It is improbable that the formation of the molecular compounds can be attributed directly to the halogen atoms in the tetraphenyl-ethylene derivatives, on account of the fact that in the compounds studied in which the formation of double molecules can be traced to the halogen atoms present, chlorine is more efficient in this respect than bromine. Triphenyl-chloromethane, for example, forms molecular compounds, whereas analogues with triphenyl-bromomethane do not exist.

Since molecular compounds had been formed from triphenyl-chloromethane and triphenyl-carbinol it appeared of interest to investigate diphenyl-chloromethane and diphenyl-carbinol. No molecular compounds were isolated. To determine whether increase in molecular weight produced any effect *p*-phenyl-diphenyl carbinol was studied; it yielded a compound with carbon tetrachloride which contained one molecule each of its constituents. *p*-Phenyl-diphenyl-chloromethane formed a molecular compound with carbon tetrachloride containing two molecules of the former to one of the latter. No molecular compound was formed from *p*-bromo-diphenyl-carbinol and carbon tetrachloride nor from *p,p'*-dichloro-diphenyl-carbinol.

A study of the literature is being made with the hope that generalizations of value may be arrived at. Up to the present a large number of compounds have been tabulated.

Experimental Part.

Experiments with *p*-Tetrabromo-tetraphenyl-ethylene.—The substance was prepared from tetraphenyl-ethylene as follows. Five g. of the finely ground hydrocarbon was spread in a thin layer on the bottom of a beaker and treated with 7.5 cc. of bromine. The mixture was allowed to stand overnight and the colorless product crystallized from hot xylene in which it is readily soluble. On cooling the bromine derivative separates in large, well-formed crystals.

Preparation of the Compound p-$(BrC_6H_4)_2C = C(C_6H_4Br)_2.C_6H_5CH_3$.—The bromine derivative was dissolved in boiling toluene, free from benzene. On cooling, radiating, shiny, transparent needles separated, which slowly became opaque on standing. A sample was dried for 10 minutes on a porous plate, weighed, and heated to constant weight at 110°. The loss in weight calculated for the above formula is 12.44% the loss found was 12.29%.

Preparation of the Compound p-$(BrC_6H_6)_2C = C(C_6H_4Br)_2.C_6H_5Cl$.—This compound was formed by crystallizing the bromine derivative from boiling chlorobenzene. It slowly effloresced in the air. The theoretical loss in weight is 14.79%. The loss found depended on the time the crystals stood in the air before being weighed. The percentages obtained were 13.81 and 15.41.

Preparation of the Compound p-$(BrC_6H_4)_2C = C(C_6H_4Br)_2.(C_6H_5)_2O$.—When tetrabromo-tetraphenyl-ethylene was dissolved in boiling ether, in which it is difficultly soluble, and the solution evaporated so that the product separated while the latter was hot, well-defined crystals of the ethylene derivative free from ether were formed. When a cold saturated solution was allowed to evaporate spontaneously at room temperature two kinds of crystals were obtained, transparent and opaque. Neither kind lost weight when heated. When a dilute solution at about —10° was evaporated slowly in a stream of air, shiny, transparent crystals were obtained which became opaque on standing in the air. Some of these crystals after standing on a porous plate for 5 minutes were weighed and heated at 110°. The loss in weight was 9.38%; the theoretical loss for a compound of the above formula is 10.25%.

Preparation of the Compound p-$(BrC_6H_4)_2C = C(C_6H_4Br)_2.p$-$C_6H_4(CH_3)_2$.—The xylene used boiled at 136° to 138° and solidified in ice-water. The compound was obtained when a hot saturated solution cooled to room temperature. It effloresced very slowly in the air. The crystals were weighed 15 minutes after removal from solution; the weight remained constant for 30 minutes, and then the crystals were heated to 110°. The weight lost was 14.85%, while the theoretical loss is 14.06%.

Attempts were made to prepare a molecular compound with *m*-xylene. Crystals were obtained by rapid and slow evaporation, but no compound was formed.

Tetrabromo-tetraphenyl-ethylene was crystallized from commercial xylene. The crystals obtained from a hot solution did not lose weight on heating. Those obtained by spontaneous evaporation lost 11.93% on heating. It is probable that the xylene present in the molecular compound which united with the bromine derivative was *p*-xylene. The *ortho* compound was not available for experimentation.

Preparation of the Compounds $(BrC_6H_4)_2C = C(C_6H_4Br)_2.CH_3COC_3H_7$, $(BrC_6H_4)_2C = C(C_6H_4Br)_2.C_2H_5COOC_2H_5$, $(BrC_6H_4)_2C = C(C_6H_4Br)_2.CH_3COOC_3H_7$.—These compounds were obtained by dissolving the ethylene derivative in the boiling liquids. In the 3 cases transparent crystals which effloresced rapidly in the air separated on cooling. The actual and theoretical losses were, respectively, 11.93 and 11.71, 13.54 and 13.60, and 12.15 and 13.60%.

Attempts to Prepare Molecular Compounds with Other Substances.—No compounds with tetrabromo-tetraphenyl-ethylene were formed at room temperature with ethyl alcohol, *iso*-amyl alcohol, bromobenzene, iodobenzene, petroleum ether. Experiments in which solutions of the ethylene derivative in methyl acetate, ethyl formate, and chloroform were evaporated at —25° yielded no molecular compounds.

Experiments with a Mixture Containing Acetone and Ethyl Alcohol.—Tetrabromo-tetraphenyl-ethylene forms a compound with acetone but not with ethyl alcohol. It seemed of interest to determine what proportion of acetone must be present in the mixture of the ketone and the alcohol to permit the formation of a compound with the former. A study of various mixtures led to the conclusion that a relatively small amount of the alcohol prevented the molecular compound from being formed. When 6 volumes of the ketone and one of the alcohol were present the molecular compound was formed; when 5 volumes was used a mixture of crystals was obtained; and with 4 of the ketone and one of the alcohol no molecular compound separated.

Experiments with a Mixture Containing Acetone and Chloroform.—Tetrabromo-tetraphenyl-ethylene does not form a compound with chloroform. When the former was dissolved in a mixture of 9 volumes of acetone and one volume of chloroform, crystals of the molecular compound with acetone were obtained. These were dried in the air and then gently heated and the acetone given off collected. This was found to be free from halogen compounds. This and the experiment described above indicate that these molecular compounds could be used to prepare pure solvents.

Experiments with *p*-Tetrachloro-tetraphenyl-ethylene, $(ClC_6H_4)_2C = C(C_6H_4Cl)_2$.[1] The ethylene derivative was prepared by a new method which appears to be more satisfactory than the one described. *p-p'*-Dichloro-diphenyl-carbinol was first prepared from the corresponding ketone. Twenty g. of the latter, 20 g. of zinc dust, 12 g. of sodium hydroxide, and 300 cc. of alcohol were boiled for 3 hours and filtered hot. To the solution water was added, when the carbinol was precipitated. This was crystallized from 60 cc. of alcohol, and then melted at 91.5°. The yield was nearly that theoretically possible.

Eight g. of *p-p'*-dichloro-phenyl-carbinol was heated to the boiling-point with 10 cc. of the constant-boiling mixture of water and hydrobromic acid for 3 hours. The product, dichloro-diphenyl-bromomethane, was extracted with carbon disulfide. On evaporation of the solvent it wa taken up in ether, from which it was obtained in crystals which melted at 70–71°. These were heated in a flask in an oil-bath at 150° for 3 hours, and finally cautiously with a small free flame as long as hydrogen bromide was given off. The contents of the flask were then dissolved in boiling carbon tetrachloride in which the compound is difficultly soluble. On cooling a molecular compound of tetrachloro-tetraphenyl-ethylene separated which lost carbon tetrachloride on standing.

Preparation of the Compound $(ClC_6H_4)_2C = C(C_6H_4Cl)_2.2CCl_4$.—This compound was obtained by allowing the ethylene derivative to crystallize from carbon tetrachloride at room temperature. It loses the added chloride very slowly. The percentage loss found was 39.66: the calculated loss is 39.59%.

Preparation of the Compound $(ClC_6H_4)_6C = C(C_6H_4Cl)_2.2CH_3COCH_3$.—At room temperature a molecular compound is not formed. When the solution is evaporated at the temperature of a bath of calcium chloride and ice well-formed crystals of the molecular compound separated. Calculated loss for the above formula, 19.80%; that found was 21.6%. The compound effloresced very rapidly at room temperature, and lost 20% of its weight in 40 minutes.

Preparation of the Compounds $(ClC_6H_4)_2C = C(C_6H_4Cl)_6.C_6H_6$ and $(ClC_6H_4)_2C = C(C_6H_4Cl)_2.CH_3COC_2H_5$.—These compounds were obtained when hot solutions cooled to room temperature. The calculated and obtained losses on heating to 110° were, respectively, 14.23 and 15.35% and 13.28 and 13.58%. No compound was obtained with ethyl acetate.

Experiments with *p*-Chloro-tetraphenyl-ethylene, $ClC_6H_4.C_6H_5C = C(C_6H_5)_2$.—This compound was prepared by an improved method; 15 g. of *p*-chloro-benzophenone chloride and 9 g. of diphenyl-methane were

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[1] The work on this compound was done by Paul G. Woodward.

heated together in an oil-bath for 2 hours at 170°. The temperature was slowly raised during 3.5 hours to 225° at which temperature the heating was continued for 2 hours. The mixture was then heated with a small flame for 2 hours more. On standing overnight the product changed to a mass of crystals, which, after washing with water, were recrystallized from alcohol. The compound melted at 162°; the yield was 15 g.

The monochloro derivative of tetraphenyl-ethylene did not form a compound with carbon tetrachloride at room temperature, but when a solution of the compound in carbon tetrachloride was evaporated at —15° small crystals were obtained which effloresced rapidly at room temperature. The crystals were removed from the solvent and placed on a porous plate, which had been previously cooled in a desiccator. After standing for 3 minutes the crystals were weighed and heated. The loss in weight calculated for a compound of the formula $ClC_6H_4.C_6H_5C = C(C_6H_5)_2.2CCl_4$ is 45.69%; that found was 47.10%. When the molecular compound was kept at room temperature for 15 minutes before the determination in loss of weight was made the value found was 38.90%. There was evident decomposition of the compound. No molecular compounds could be isolated with benzene, methylpropyl ketone, or acetone.

Preparation of the Compound $C_6H_5C_6H_4.C_6H_5CHOH.CCl_4$.—No compound was formed at room temperature but at —10° crystals separated from the solvent that corresponded in composition to the above formula. The loss in weight obtained was 37.47%; that calculated was 37.19%. It is of interest to note in this connection that no molecular compound of diphenyl-carbinol and carbon tetrachloride could be isolated at —20°. This fact is in accord with the general conclusion that increase in molecular weight favors the formation of such compounds.

No addition-product with acetone could be isolated. In general, carbon tetrachloride has been found to have a greater tendency to form molecular compounds than have ketones or esters. Neither *p*-monobromodiphenyl-carbinol nor *p,p'*-dichloro-diphenyl-carbinol formed molecular compounds with carbon tetrachloride or acetone at —15°.

Preparation of the Compound $[C_6H_5.C_6H_4.C_6H_5.CHCl]_2.CCl_4$.—When the diphenylmethane derivative was crystallized from carbon tetrachloride at —15° a very unstable addition product was formed. It lost weight rapidly in the air. When kept 20 minutes in an ice-chest the loss on heating was 17.84%. When it was dried rapidly in the air for 2 minutes the loss on heating was 18.66%. The theoretical loss for a compound of the above formula is 21.66%. No molecular compound with acetone could be isolated. Diphenyl-chloromethane gave no compound with carbon tetrachloride.

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THE REACTION BETWEEN ALCOHOLS AND AQUEOUS SOLUTIONS OF HYDROCHLORIC AND HYDROBROMIC ACIDS. II.

BY JAMES F. NORRIS AND ROBERT S. MULLIKEN.

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In previous papers[1] the action of aqueous solutions of hydrochloric, hydrobromic, and hydriodic acids on a variety of alcohols was described. It was shown that the reaction furnished the most convenient method of preparing alkyl bromides and iodides, and that in certain cases chlorides could be made advantageously in this way. Recently Kahn has found that the addition of sulfuric acid to the solution of hydrobromic acid increases the yield of alkyl bromides obtained, especially in the case of alcohols of higher molecular weight.

The previous work was limited to monatomic alcohols and had to do primarily with the effect of the structure of the alcohols on the ease with which the reaction took place, and with the yields obtained. The action of hydrochloric acid was quite different from that of hydrobromic and hydriodic acids. While the latter formed alkyl halides with all alcohols studied, hydrochloric acid reacted in certain cases only. Chlorides were formed from all tertiary and some secondary alcohols. The acid did not react with any primary saturated aliphatic alcohols; it formed, however, chlorides with benzyl alcohol and allyl alcohol. It was shown that the presence of unsaturated radicals and aryl radicals rendered the hydroxyl group active, and that this influence decreased as the position of these radicals was farther from the hydroxyl group. Phenyl and unsaturated radicals are so-called negative groups; it seemed advisable, therefore, to study more fully the reaction between alcohols containing such groups to determine if they in general possessed this activating influence. It was found in certain cases that when the negativity was markedly increased the alcohol containing such a group failed to react with aqueous hydrochloric acid. This was shown to be the case with the nitrobenzyl alcohols.

It seems probable from work which will be reported later that the reaction between an alcohol and a halogen acid consists in the addition of the two compounds and the subsequent elimination of water. The ease with which these two separate steps occur determines whether reaction takes place or not under the conditions used. If this view is correct the difference in the behavior of hydrochloric acid and that of hydrobromic acid can be explained.

The work described below was a study of the behavior of certain polyatomic alcohols with aqueous solutions of hydrochloric acid and hydro-

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[1] *Am. Chem. J.*, 38, 627 (1907); THIS JOURNAL, 38, 1071 (1916).

bromic acid; a few monatomic alcohols which contained either negative substituents or belonged to classes not previously investigated were also studied. All the compounds investigated reacted with hydrobromic acid; the results serve, therefore, to strengthen the conclusion previously reached, that the acid may be used as test for the alcoholic hydroxyl group. Aqueous hydrochloric acid replaced hydroxyl groups in certain compounds containing negative substituents, although its failure to act in other cases brought out clearly the fact that other influences than those of negativity serve to activate the hydroxyl group.

Ethylene glycol when heated with aqueous hydrobromic acid (sp. gr. 1.49) yielded a mixture of the bromohydrin and ethylene bromide, the proportions of which varied with the conditions used. When propylene glycol was heated with the acid, profound changes occurred which led to the formation of highly colored oils. From trimethylene glycol a yield of 62% of the bromide along with some bromohydrin was obtained. Glycerol gave 46% of the dibromohydrin and 13% of the monobromohydrin. A detailed study of the conditions under which the reactions are carried out would probably result in larger yields. In a number of cases only very small amounts of the alcohols (3 to 5 g.) were employed so that large yields could not be expected.

The chief interest in the work lay in the behavior of the alcohols with aqueous hydrochloric acid, since it was hoped the results would throw light on the factors which activate the hydroxyl group. When ethylene glycol was heated with a large excess of hydrochloric acid (sp. gr. 1.17) 12% of the alcohol was converted into the chlorohydrin. Since ethyl alcohol does not react with aqueous hydrochloric acid in an open vessel the activation in this case may be due to the added negative hydroxyl group. Ethylene bromohydrin did not, however, react with the acid. In this case if negativity is the cause of the activation, the substituting atom is too negative in character, and the effect is lost. The results recall the fact that while benzyl alcohol reacts readily with hydrochloric acid, the nitrobenzyl alcohols do not.

When propylene glycol was heated with hydrochloric acid, deep-seated changes took place, as might be expected; but 5% of chlorohydrin was obtained. Trimethylene glycol gave a trace of the chloride and about 28% of the chlorohydrin. Trimethylene chlorohydrin was converted to a small extent into the chloride when boiled with hydrochloric acid; the bromohydrin behaved in a similar manner. In these cases the halogen was in the β-position to the hydroxyl group, whereas in ethylene bromohydrin which yielded no chloride the strongly negative halogen atom was in the α-position.

Glycerol reacted to a slight extent only with the acid to form chlorohydrins; a trace of dichlorohydrin and about 9% of monochlorohydrin were formed. Pinacone hydrate reacted slowly at room temperature with hydrochloric acid (sp. gr. 1.17) and gave the chloride.

A few cyclic alcohols were studied to learn the effect of ring structure on the activity of the hydroxyl group. Cyclohexanol gave a yield of 93% of the corresponding chloride. In its activity the alcohol resembles secondary and tertiary alcohols. Menthol reacted much more sluggishly and gave a yield of 41% of the chloride. The increase in the molecular weight or the radical in the *ortho* position may be the cause of the difference between the activity of cyclohexanol and its derivative. Borneol gave but 30% of chloride. Cumin alcohol resembled in activity benzyl alcohol and gave practically a theoretical yield of the chloride.

Unfortunately so many factors are involved in the reaction between alcohols and aqueous solutions of the halogen acid used that no definite general conclusion can be drawn with the facts at present available. It is planned to continue the work with special attention to the physical conditions which come into play. The fact that the alcohols and their halides vary in solubility and volatility no doubt is an important factor which has not been investigated. Quantitative measurements will be made under conditions which can be used in all cases so that the results obtained are comparable. The qualitative work which has been done was necessary in order to survey the field to determine which compounds would serve best in a detailed quantitative study of the reaction.

The results already obtained have led to practical methods of preparation of halides which have proved of great value. The main problem—the interpretation of the mechanism of the reaction—will be actively investigated, since it is of the greatest importance in organic chemistry to know more about the manner in which molecules interact.

Experimental Part.

Ethylene Glycol.—A mixture of 20.3 g. of the glycol and 271 cc. of conc. hydrochloric acid (one molecule of the glycol to 9 of the acid) was heated at its boiling-point for 4.5 hours. The product was then fractionated with a Le Bel-Henninger tube. The fractions containing the chlorohydrin and the glycol were neutralized and extracted with ether. The ethereal solutions were dried over anhydrous potassium carbonate and distilled. Yield of chlorohydrin was 12%; b. p. 127.6–128.6°; d^{20} 1.194. The glycol recovered weighed 10.5 g.

Ethylene Bromohydrin.—A mixture of 5.7 g. of the hydrin and 22.7 cc. of conc. hydrochloric acid was kept near its boiling-point for 6.5 hours. Some decomposition occurred but there was no evidence of the formation of an insoluble halide.

Trimethylene Glycol.—A mixture of 5 g. of the glycol and 53 cc. of conc. hydrochloric acid was slowly distilled. The distillate was neutralized and extracted with ether. After drying with sodium sulfate the ethereal solution yielded 1.8 g. of the chlorohydrin, which boiled at 160.5° and contained 36.55% of chlorine, the calculated value for the compound being 37.55%. The yield of chlorohydrin was thus 28%.

A mixture of 3 g. of the glycol and 13.4 cc. of constant-boiling hydrobromic acid (molecular ratio one of glycol to 3 of acid) was heated near its boiling-point for several hours and then distilled. The oil which separated was distilled and shown to be trimethylene bromide. From the aqueous distillate was isolated 0.5 g. of a liquid which had the specific gravity of the bromohydrin. The yields of the bromide and bromohydrin were 62 and 8% respectively.

In another experiment conditions were used which favored the formation of the bromohydrin. Four g. of trimethylene glycol was heated with 7.14 g. of constant-boiling hydrobromic acid (mol. ratio 1 to 1.2) at 70° for an hour. The mixture was then raised to the boiling-point for a few minutes until an insoluble oil began to form; it was then cooled, neutralized, and extracted. The ethereal solution left on evaporation 3.3 g. of a liquid which possesses the properties and solubility in water of ethylene bromohydrin. Since it contained 54% of bromine and the pure compound contains 57.5% the sample was not quite pure. The yield was 43%.

A small sample of trimethylene bromohydrin was distilled with conc. hydrochloric acid. A small amount of an insoluble oil was obtained which was no doubt formed as the result of the displacement of the hydroxyl group by chlorine.

Glycerol.—A mixture of 105.4 g. of 95% glycerol and 898 cc. of hydrochloric acid of sp. gr. 1.178 (molecular ratio 1 to 9.4) was kept at the boiling-point (about 85°) for 4 hours and then slowly distilled through a Le Bel-Henninger column. After the excess of acid had distilled over, the temperature rose to above 110°, the residue in the flask darkened rapidly, and drops of oil appeared in the distillate. The distillation was continued under diminished pressure. At the end of the distillation the flask contained a thick, very viscous residue which weighed 58 g. and contained no chlorine. The distillate was fractionated and yielded 10.8 g. monochlorohydrin, which is a 9% yield.

A number of experiments were carried out to determine the behavior of glycerol with aqueous hydrobromic acid (sp. gr. 1.49). Three molecular weight equivalents of the acid to one of the alcohol were used. The mixtures were distilled slowly until the temperature rose to above 126° when the distillation was continued under diminished pressure. As the temperature increased the material in the flask darkened and finally a tarry residue was left. By fractionating the volatile material obtained when 50 g. of glycerol was used 66 g. of a mixture was obtained which yielded approximately 11 g. of monobromohydrin and 55 g. of dibromohydrin. This corresponds to a yield of 13% of the former and 46% of the latter. The dibromohydrin had d_{21}^{21} 2.1348; b. p., 87° (corr.) 8.5 mm. pressure and 214.8° (corr.). at 760 mm. The percentage of bromine found was 72.66, that calculated being 73.35%. The constants reported for the symmetrical dibromohydrin are as follows, b. p. 105° at 16 mm., 124° at 38 mm., and 219° at 760 mm., d^{18} 2.11. The constants for the unsymmetrical compound are, b. p. 118° at 17 mm. and 212–214° at 760 mm., d^0 2.1682. It is impossible from these constants to determine which dibromohydrin was formed as the results of the experiment described above. It is possible that the product was a mixture. The solubility of the compound in water makes it appear probable that it was the symmetrical dibromohydrin. It was soluble in about 30 parts of cold water and in a slightly less volume of hot water. The solubility of the unsymmetrical dibromohydrin is reported as one part in 9 parts of water at 19° and 6 parts of water at 72°.

The monobromohydrin was probably the one of the structure $CH_2OH.CHOH.CH_2Br$. It boiled at 120–123° at 10 mm. pressure. It dissolved 1.5 volumes of cold water, and was soluble in about 50 parts of cold water. It was miscible in all proportions with boiling water. The symmetrical compound $CH_2OH.CHBr.CH_2OH$ has not been described. The boiling-points recorded for the known bromohydrin are as follows, 134° at 16 mm., 138° at 17 mm., 145° at 30 mm. and 160° at 60 mm.

The fractionation of the product was difficult as in the presence of the acid changes took place slowly. It is probable that some of the monobromohydrin was being converted into the dibromohydrin or that molecular rearrangements were taking place. The reaction deserves further study.

Pinacone.—It has been shown by previous workers[1] that pinacone is converted into the corresponding dibromides and dichlorides when treated with aqueous solutions of the halogen acid saturated at 0°. After standing at room temperature for some time yields of about 75% of the halides were obtained. When pinacone is distilled with the acids pinacoline and other ill-defined products, some of which contained halogen, were formed.

Cyclohexanol.—When 3 g. of the alcohol was treated with 25 cc. of conc. hydrochloric acid at room temperature it dissolved. The solution soon clouded. On heating, an oil continued to separate and in one hour the reaction appeared to be complete. The oil was separated, washed with a solution of sodium carbonate and dried over calcium chloride. The yield was 3.3 g. or 93%. The oil boiled at 142.7–145° (corr.) at 760 mm. The recorded boiling-point is 143° at 758 mm.

Menthol.—A mixture of 5 g. of menthol and 28 cc. of conc. hydro-

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[1] Thiele, *Ber.*, **27**, 455 (1894); Kondakow, *J. prakt. Chem.*, **54**, 429 (1896); **62**, 169 (1901).

chloric acid (mol. ratio 1 : 9) was gently boiled for several hours. The layer of insoluble oil was separated, dried and analyzed. It was found to be a mixture of chloride and unchanged alcohol. The yield of chloride in the mixture was 41.3%.

Borneol.—When 7.5 g. of borneol was heated with 40 cc. of constant-boiling hydrochloric acid the solution soon clouded. After boiling for 4 hours the solid product was separated and dried over sulfuric acid. It melted at 163.5–170°. Borneol melts at 204° and its chloride at 157°. The product was evidently a mixture. A halogen determination showed that it contained about 33% of the chloride. A fractional crystallization of the product from petroleum removed most of the unchanged borneol.

Cumin Alcohol.—When the alcohol was mixed with constant-boiling hydrochloric acid, the acid layer soon clouded showing that reaction was taking place at room temperature. After boiling the mixture for 2 hours it was neutralized and extracted with ether. The product boiled at 227–228°; the recorded temperature is 225–229°. The yield was practically that theoretically possible.

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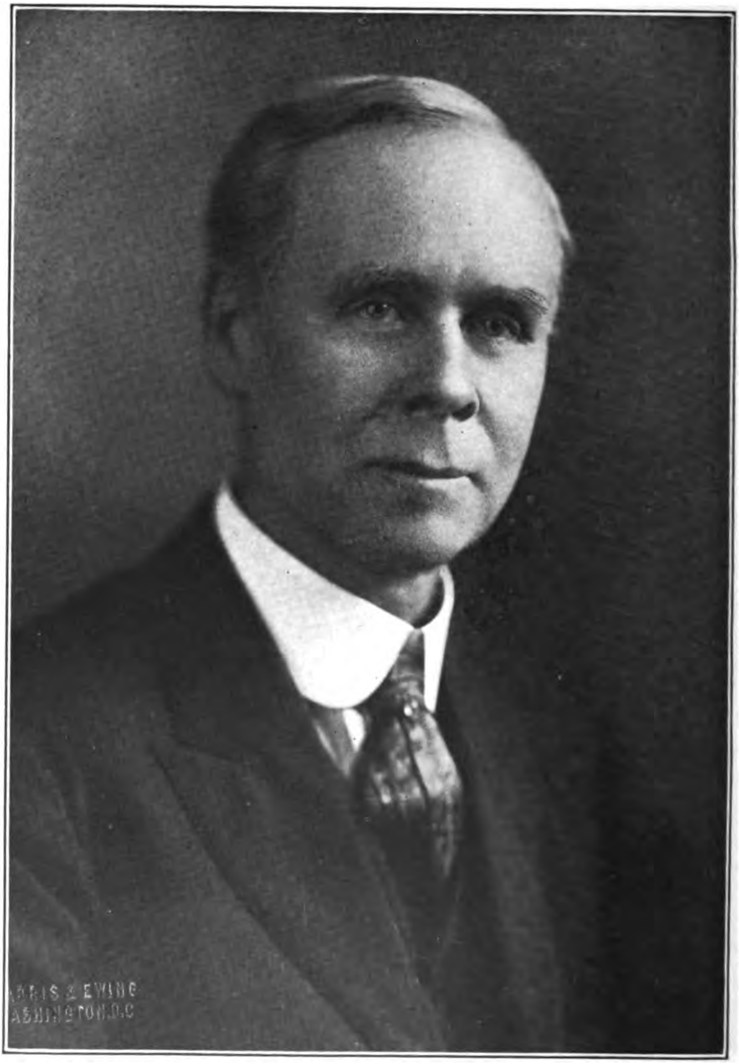

William Albert Noyes

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American Chemical Journal
(Founded by Ira Remsen)

CHEMICAL PUBLICATIONS.[1]

BY WILLIAM A. NOYES.

In an address which has been given before the members of a number of the Local Sections of our Society I have emphasized the training of our young men in methods of research and the discovery of new facts and new principles, as the indispensable foundation upon which the development of chemistry must rest. But research work and discoveries are barren so long as they remain the exclusive possession of an individual. The very rapid development of our science during the last half century depends in no small degree upon the improved facilities for publication which have made new discoveries very quickly available for all who wish to use them.

Through the middle ages and at their close the alchemists and iatrochemists had no journals or organized methods of publication. Their researches, if we can dignify their random experiments by such a name, were published in books, usually in the Latin language. Many of the alchemists used mystical symbols and expressions and some of their writings were designed rather to conceal than to reveal their knowledge—an art which has not been altogether lost in the writing of German and sometimes of other patents.

It is very significant and interesting for us as a Society to recall that the beginning of a different and better form of publication had its origin in the organization of national societies, about the middle of the seventeenth

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[1] President's Address delivered at Chicago, September 8, 1920.

century. Between 1650 and 1670 such societies were begun in London, Vienna, Florence and Paris. The Royal Society, which grew from the union of small scientific societies in Oxford and London has been, perhaps, the most effective of the group in its influence upon the growth of science. The meeting of small groups of kindred spirits in these societies gave an opportunity for the announcement of new results and for the exchange of ideas upon scientific topics which was most useful, not only in the dissemination of new knowledge, but perhaps still more in that growth of ideas which comes from the action of keen minds upon each other. We miss something of this very valuable side of society life in the large meetings of the present time. It is better represented, now, by the discussions among small groups in our laboratories.

The publication of the *Philosophical Transactions of the Royal Society,* begun in 1665, represents a new function of the Society which became of vastly greater importance than the scientific meetings. It would be difficult to overestimate the value of those *Transactions* in their effect on the growth of science. In their pages are to be found the first notice of the microscopic organisms which we now call bacteria. There, too, we find an account of the epoch-making discoveries of Davy and of Faraday and of others who did some of the fundamental work of the nineteenth century.

The publication of the *Comptes rendus* in France was begun in 1776, the year of our American Independence. Like the *Transactions of the Royal Society* it publishes articles in many different lines of science. In other respects the policies of the two Journals are very radically different. The Royal Society aims to publish papers which are the finished product, frequently of years of work, and publication has often been long delayed. Publication in the *Comptes rendus* is prompt but the papers are very brief and frequently lack details which are essential to make them useful. Both kinds of publication are desirable but for the permanent growth of our science and for the future, publication of the form used in the *Transactions* is much more valuable.

As far as I can learn, the first journal devoted to chemistry apart from other sciences was Crell's *Chemische Annalen,* which began as the *Chemisches Journal* in 1778. The oldest chemical journal which has had a continuous existence is the *Annales de chimie,* which was begun in 1789, the year of the French Revolution, by de Morveau, Lavoisier, Berthollet, de Fourcroy and four others, less well known. The subtitle of the journal was "ou Recuiel de Memoires concernant de Chimie et les Arts qui en Dependent." In the introduction the value of chemistry for the arts is emphasized, also the purpose of making new work in chemistry, wherever undertaken, available to all. Another object was, undoubtedly, to give untrammelled expression to the new ideas advocated by Lavoisier at a time when the *Journal de Physique* was still controlled by adherents of the phlogiston theory. This journal must have been one of the factors which made Paris a chief center for the development of chemistry for fifty years following. Four volumes were published the first year, at 12 francs each. Volume 18 was published in July, 1793, and we find in it some signatures of blue paper, a reflection, doubtless, of the troublous times when it was printed, for that was the beginning of The Terror. After that there is a hiatus for four years and Volume 19 appeared in 1797 "Par les Citoyens Guyton, Monge, Berthollet, etc." We miss the name of Lavoisier, who was executed in 1794. In resuming publication the editors explain the interruption by saying that it was because of the necessity of busying themselves with the defense of the Republic, the events of the Revolution and the public occupations and functions of the authors. In 1816 the second series of the journal was commenced under the name *Annales de chimie et de physique.* The ninth series began in 1914, once more under the original name *Annales de chimie.* The other part of the ninth series is published as *Annales de physique.*

A second journal of very great importance was founded in 1832 under the name *Annalen der Pharmacie.* The editors were Brandes, Lorenz, Geiger and Liebig. Volume 25, published in 1838, bears the names of Dumas of Paris, Graham of London and Liebig, evidently an attempt to make the journal international. Apparently this did not prove successful, for with Volume 41, four years later, we find only the names of Wöhler and Liebig. In 1840 the name was changed from *Annalen der Pharmacie* to *Annalen der Chemie und Pharmacie* and this name continued till the death of Liebig in 1873. In 1874 we find the name which is still retained, Justus Liebig's *Annalen der Chemie.* Through the middle of the nineteenth century the *Annalen* was doubtless more valuable than any other journal for the development of chemistry. It remains one of our most valuable journals but its relative value has decreased for three reasons—the growth of the journals of national societies, the establishment of special journals for various fields and the fact that it has become exclusively a journal of organic chemistry.

Silliman's Journal, which later became the *American Journal of Science*, was organized in 1818. This has published some chemical articles throughout its history but when Professor Remsen and others began the intensive study of organic chemistry in the seventies they did not find that journal a very suitable medium of publication. This led to the establishment of the *American Chemical Journal* in 1879. For the following thirty years that journal contributed much toward the development of chemistry in America and to the recognition of the work of American chemists abroad. During that period it was more often quoted than any other American journal. In 1913 we had the good fortune to incorporate it in our own *Journal.*

Just as it was in England that the first scientific journal, the *Philosophical Transactions*, appeared, so it was in England, again, that the first representative of the group of journals which has become the most important of all, was published. The *Quarterly Journal of the Chemical Society of London* began in 1847.[1] It was followed by the *Bulletin de la societe chimique de Paris* in 1864, the *Berichte der deutschen chemischen Gesellschaft* in 1868, the *Gazzetta chimica italiana* in 1871, and our own *Journal of the American Chemical Society* in 1876. These journals fulfil, more nearly than any others the function of the older volumes of the *Annalen* in furnishing their readers with an account of researches from all fields of chemistry. I believe we are justified in thinking our own *Journal* performs this function more fully than any other journal published at the present time. In these days of intense specialization it is very important for us to retain some knowledge of fields remote from our own. President Remsen once told me that in his student days he read the older volumes of the *Annalen* till he was familiar, in a general way, with all of the important researches recorded in them. Even as late as the 80's we heard of chemists who read the *Berichte* from cover to cover and I am sure that some of those who did so gained a breadth of view that is too rare today. I should consider it a very great misfortune, especially for our younger men, if there were any important branch of chemistry which was not occasionally represented by papers in our *Journal.*

In spite of this, the special journals, which we now have in such profusion serve a very important function. In talking with young men and women who are trying to acquire a working knowledge of French and German I often point out that there should be two rather distinct elements in their study. There must be an intensive study of grammar and of a few articles or books till these are thoroughly mastered and then there must be a large amount of more superficial reading, best in elementary chemistries dealing with subjects with which they are familiar. In studying a foreign language we sometimes forget that we have not looked up in a dictionary one word in a thousand of those we understand in our mother tongue. We have acquired a knowledge of the meaning of these words by meeting them over and over again in a great variety of connections and each time we see the word we add something to our knowledge of its meaning. It is for this reason that the words of our mother tongue have for us a wealth of meaning that the words of a foreign language can never acquire until we have lived with them intimately for many years. But a knowledge of the meaning of words in a foreign language may be acquired by extensive reading and use, without a dictionary, exactly as we

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[1] The Chemical Society had published previously, however, the "*Memoirs and Proceedings,*" Vols. I to III, 1841–43, 1843–5, 1845–47, containing original papers and some abstracts.

acquire our own language. There may even be some question whether our teachers of language do not overdo the study of grammar. Young children do not study grammar.

A truly professional knowledge of chemistry must be acquired in somewhat the same manner as a language. We must have an intensive study of the fundamental principles and some knowledge of the more common facts. But Ostwald is right when he says that we have not done as well as the physicists in organizing our instruction. They have directed their teaching more toward general principles. We have allowed ourselves to be burdened with too great a mass of details. We should direct our elementary teaching more toward the great underlying principles of the science, using the details rather as the necessary setting by means of which the principles can be understood in their various relationships. But it is a great mistake to think that one of these principles can be acquired by learning a *definition* and understanding one or two illustrations of its application. We must live with it, just as we live day after day with the words of our mother tongue. It is here that the extensive, general reading that I have referred to is so useful. It is here, too, that teaching of general chemistry is such a valuable experience. The older professors in the German universities have been accustomed to give elementary courses both in general chemistry and in organic chemistry. I suspect that the compelling motive was the fees from courses attended by large numbers of students but, nevertheless, they gained in that way an intimate knowledge of those things which are most fundamental in our science. In this manner their attention was often directed to gaps in our knowledge and problems for research were suggested.

To some extent, therefore, the journals of our national societies may well furnish articles covering a wide range, and every chemist should read them, while the special journals may well publish articles suitable for intensive study in a narrow field. I will come back to this point again.

In some sense the special journals in chemistry bear the same relation to the national and other journals which publish articles from all fields, that the chemical journals, when they were first established, bore to the *Philosophical Transactions*, *Comptes rendus*, *Silliman's Journal*, and other journals covering many lines of science.

The first of these special journals was, I think, Fresenius's *Zeitschrift für analytischen Chemie*, started in 1862. Hoppe-Seyler's *Zeitschrift für physiologischen Chemie* was begun in 1877, Dr. Hart's *Journal of Analytical Chemistry* in 1887, Ostwald's *Zeitschrift für physikalischen Chemie* in the same year, the *Zeitschrift für anorganischen Chemie* in 1892, the *Journal of Physical Chemistry* in 1896, and the *Journal of Biological Chemistry* in 1905. As with other journals spoken of in this address, the list is not intended to be exhaustive, and any one else who prepared similar lists would almost surely make, in part, a different selection. Each of these journals has been useful and some of them have played a very important part in the growth of our science.

Of a somewhat related character, in that they may be considered partly special, are the industrial journals. Wagner's *Jahresberichte über chemische Technologie* was founded in 1855, *Die chemische Industrie*, published by the Verein zur Wahrung der Interessen der chemischen Industrie Deutschlands, in 1878. This journal is published by a society of Manufacturers and Manufacturing Companies. The Society for Chemical Industry was organized in 1881 and the first volume of its *Journal* was published in 1882. Dr. Hart's *Journal of Analytical Chemistry* became the *Journal of Analytical and Applied Chemistry* in 1890. In 1893, that *Journal* was combined with our *Journal* under the editorship of Dr. Hart, beginning a new era in the publications of our Society. Our *Journal of Industrial and Engineering Chemistry* began in 1909 under the editorship of W. D. Richardson. The new French journal, *Chimie et industrie*, published by La Société de la Chimie Industrielle, began in 1918 in the midst of the Great War, and is a reflection of the extraordinary part played by chemistry in the war. These journals and the meetings of the societies which they represent have done something toward transferring to chemical industry that habit of freely publishing new discoveries which has long been second nature to scientific men. The spirit of the older industry was to guard trade secrets most carefully and every competitor was looked upon as a rival whose advancement was considered as an injury to others who manufactured the same or similar articles. To that older time trade and industry were war, the battle was to the strong and the weak must be ruthlessly crushed. It was natural under such a regime that the manufacturer should consider almost exclusively his own interest and should care little for the interests of his workmen, to say nothing of the interests of the public. Where such an attitude was at its worst we can not wonder that workmen became indifferent to the interests of their employers.

I am optimist enough to believe that a better day is dawning when coöperation among manufacturers is replacing destructive competition, when there will be a fairer division of profits and losses between employees and employers and, fully as important as either, when the public interest will be considered and treated equitably by both. The command of nature's resources given us by the scientific advances of the last century is certainly such as to make possible a fair livelihood for every one who is willing to give a proper return in productive labor. As scientific men we must certainly put ourselves on the side of those forces which aim to reduce war and ruinous competition between individuals, or manufacturers, or nations. A useful direction for us to work as chemists is to promote the spread of useful information gained in our industrial life. These are questions in which I am intensely interested, but over which we must not linger.

The growing volume of chemical literature led to the desire for some authoritative medium which should furnish a brief record of the advances each year and which should, at the same time, serve as an index for the literature of the year. For this purpose Liebig and Kopp published in 1849 the *Jahresberichte über die Fortschritte der reinen, pharmaceutischen und technischen Chemie*. During the last half of the nineteenth century this was the indispensable guide for any careful search of the literature. Gradually the task of compilation became so great and the publication was so delayed that the volumes have lost much of their usefulness.

To furnish more prompt reports of current work the London Chemical Society, the Deutsche chemische Gesellschaft and other societies began the publication of abstracts. The *Chemisches Centralblatt* was begun for the same purpose in 1856. In fact, it began as the *Pharmaceutisches Centralblatt* in 1830 and continued as such until 1850, when it became known as the *Chemisch-Pharmaceutisches Centralblatt*, then was changed to *Chemisches Centralblatt* in 1856. In 1897 it was taken over by the Deutsche chemische Gesellschaft and took the place of the abstracts which that Society had been publishing in the Berichte. The *Centralblatt*, however, was sent only to members who subscribed and paid for it in addition to their dues for the Society. This plan of publication cannot be considered a success, as nearly one-half of the members failed to subscribe, with the result that they were deprived of the use of the abstracts and the latter became unduly expensive. The membership of the Society fell off and the circulation of the *Zentralblatt*[1] has never exceeded about 2000 copies. Twenty years ago the question of publishing an abstract journal was often discussed in our Council. An abstract journal for American research which had been started by Professor A. A. Noyes was taken over and continued by our Society for a few years. At that time we felt that a general abstract journal was financially impossible. In 1905, however, an attempt was made to unite the London Chemical Society, with a membership of about 3000, the Society for Chemical Industry, then with a membership of about 4500, and our own Society, with a membership of nearly 3000, in the publication of a common journal. The three societies comprised about 8000 individuals and it was thought that this would give the necessary financial support at a very moderate rate for each. The English Societies were unwilling to enter into such a combination and a year later we decided to establish the journal alone, beginning in 1907. Profiting by the experience of the German Society we increased our dues by $3.00 and furnished *Chemical Abstracts* to all of our members. This policy, and the same policy applied to our *In-*

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[1] The spelling was changed to "*Zentralblatt*" in 1907.

dustrial Journal, has been phenomenally successful. The attraction of our *Journals* together with the loyalty of our members in the local sections, and the very efficient work of our Secretary, have caused the membership of our Society to grow far beyond that of any other in the world.

The mass of details which have been accumulated by chemical research has made necessary the publication of compendia of various kinds. The earliest of these were the chemical dictionaries, Watt's "Chemical Dictionary" in England and somewhat similar dictionaries in France and Germany. Dr. Andrew Ure, Professor of the Andersonian Institution, compiled a "Dictionary of Chemistry," "on the basis of Mr. Nicholson's," and the first American edition of this dictionary, edited by Dr. Robert Hare and Dr. Franklin Bache, was published in Philadelphia in 1821.[1]

Later, in 1881–83, we have Beilstein's "Handbuch der organischen Chemie." The second edition was published in 1886–90 and the third in 1893–99 and five volumes of supplements from 1901 to 1906. The preparation of the fourth edition was begun by the German Chemical Society in 1907 and the publication of this edition, which will cover the literature of organic chemistry only to 1910 was begun in 1919. It will be several years before the publication is completed. More than 150,000 compounds will be described briefly in this monumental work. Before printing began, 250,000 marks (over $60,000) had been spent under the direction of the Editors Bernhard and Prager Paul Jacobson. There are to be 15 volumes of about 1000 pages each. Dr. Jacobson writes me that a large amount of material has been accumulated for supplements, which are planned to cover the period 1910–1925.[2] In the spirit of nationalism which is often evil and full of danger, and not of patriotism, which is good, but which should always be compatible with hearty coöperation between nations—in a spirit of nationalism, I repeat, some Englishmen and Americans have wished to replace Beilstein's "Handbuch" by a book of the same scope in English. A sober second thought must, I think, lead us to question seriously the wisdom of this, for two reasons, first, is it wise for us to duplicate the colossal amount of work which has gone into the preparation of this book; I think it is a very moderate estimate to say that it would take a staff of twenty chemists five years to collect the materials for the book before printing could be commenced and that the cost of the complete work would be at least $250,000. It might easily be two or three times that. Second, we should consider carefully whether a quite different type of book would not meet our future needs better.

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[1] There is a copy of this work in the library of the Department of Chemistry at the University of Illinois, and according to an inscription which was made on the fly leaf on March 19, 1833, it was the property, at that time, of the old Dominican Monastery at Kaskaskia, Illinois. (Kaskaskia was the oldest settlement in Illinois.)

[2] An interesting article by Dr. Jacobson on Beilstein's Handbuch is to be found in *Die Naturwissenschaften* for April 4, 1919, p. 222.

Do we not need, most, a book which shall give all the classes of organic compounds with their methods of preparation and properties, followed, in each case, by a table giving a carefully selected list of the more important compounds of the given class with their physical constants and references to the literature for each constant selected? When I was abroad in 1912 I expressed to some of my friends the wish that there might be found some way to annihilate those portions of our literature which are worthless. The thought met with a very hearty response. German scholars have been past-masters in accumulating all of the data to be found in the literature about a given topic. They have not always been as successful in selecting that which is important and rejecting things which are worthless or obsolete. A critical selection of compounds, given by classes in a series of tables, would be more useful for many purposes than the more complete account of all compounds given in Beilstein's "Handbuch." We must still have, of course, a complete catalog of all known compounds. For the future such a catalog is probably better given in a formula lexicon.

Gmelin-Kraut's "Handbuch der anorganischen Chemie" has very much the same function for inorganic chemistry as that of Beilstein for organic. Abegg's "Handbuch" is more of the nature of a critical compendium and for most purposes it is more useful. Meyer and Jacobson's "Lehrbuch der organischen Chemie" serves somewhat the same purpose.

The first of the formula lexicons was published by Richter in 1884. It registered 20,000 organic compounds. The second edition, published in 1900 gave 74,000 compounds, and the third, in 1910–12, 150,000. The formula indexes of the *Berichte* and *Annalen* have always seemed to me of very little value. We scarcely look for any given compound in a journal of that type unless we remember that there has been an article upon it in that particular journal. Even if we do know that, we often use the index of *Chemical Abstracts* rather than that of the special journal to locate the article we wish. I am sure that the formula index which is to be published for the first time this year in *Chemical Abstracts* will very soon prove itself so useful that we shall wonder how we ever got on without it. That index will not copy the Richter system exactly but will follow a more logical and consistent system devised by Mr. E. A. Hill of our Patent office.[1] Mr. Hill's system differs from that of Richter primarily in that it includes inorganic as well as organic compounds.[2]

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[1] THIS JOURNAL, 22, 478–94 (1900).

[2] Mr. Crane, editor of *Chemical Abstracts*, has prepared the following statement: "Since the Hill system is less familiar than the Richter system, it may be explained that according to the former the symbols in formulas are arranged in a purely alphabetical order except that in carbon compounds C always comes first, followed immediately by H, if hydrogen also is present. The number of atoms of any specific kind influence the order of compounds (*e. g.*, all compounds with C, come before those with C_2), but

Richter system.

1.	CH_4	18.	$C_6H_4Br_2$
2.	CO	19.	$C_6H_4I_2$
3.	CS_2	20.	$C_6H_5N_3$
4.	CBe_2	21.	C_6H_5Cl
5.	CMn_3	22.	C_6H_5Br
6.	CHN	23.	$C_7H_8O_4N_2S$
7.	$CHCl_3$	24.	$C_7H_8O_5NAs$
8.	CH_2O	25.	$C_7H_8O_6N_2S$
9.	CH_2N_4	26.	$C_7H_8O_6NAs$
10.	CH_2Cl_2		
11.	CH_2Br_2		
12.	$COCl_2$		
13.	$C_2H_6O_2Hg$		
14.	$C_2H_6O_4N_2$		
15.	$C_2H_6O_5Cl_2$		
16.	C_2H_6ClBr		
17.	C_6H_6		

Hill system.
With a few inorganic compounds added.

	$AgBr$	15.	$C_2H_6Cl_2O_5$
	$AgNO_3$	13.	$C_2H_6HgO_2$
	Ag_2HO_4P	14.	$C_2H_6N_2O_4$
	$BrCl$	18.	$C_6H_4Br_2$
4.	CBe_2	19.	$C_6H_4I_2$
12.	CCl_2O	22.	C_6H_5Br
7.	$CHCl_3$	21.	C_6H_5Cl
6.	CHN	20.	$C_6H_5N_3$
11.	CH_2Br_2	17.	C_6H_6
10.	CH_2Cl_2	24.	$C_7H_8AsNO_5$
9.	CH_2N_4	26.	$C_7H_8AsNO_6$
8.	CH_2O	23.	$C_7H_8N_2O_4S$
1.	CH_4	25.	$C_7H_8N_2O_6S$
5.	CMn_3		$ClKO_3$
2.	CO		ClO_2
3.	CS_2		Cl_2Cu
16.	C_2H_6BrCl		O_4SZn

I have a hope that when the time comes for another *Decennial Index* we may have a complete American formula index, including all known chemical compounds. It will be a very large task to prepare such an index but such indexes will, most likely, furnish chemists of the future the best means available of finding their way to the practical use of that vast, and ever increasing, mass of detailed information which the industrious chemists of the world have accumulated.

no attention is paid to the number of kinds of atoms in the molecule. Examples of both systems are given below. It has been my experience that the Hill system does not seem as good as the Richter system at first, particularly if one is accustomed to the latter system, but its appeal grows. The object is not to classify but to index. Former editor Patterson, who is always ready generously to help us with our problems, has written as follows regarding the two systems: 'The Richter system has usage in its favor; however, this may not be a sufficient reason for retaining a system of German origin if there is a better and simpler one, and if not, this is the best time to change. I submit the following arguments that occur to me: 1. *Richter:* (*a*) Usage: (*b*) Partial classification in each series, the hydrocarbons being brought together at the beginning, and compounds of many elements being relegated to the end. 2. *Hill:* (*a*) Simplicity; a purely alphabetical order of symbols is used except that by putting C and H first the organic compounds are thrown together. Neither must the number of kinds of elements be taken into account (we do not have to determine the number of kinds of different letters in a word in order to look it up in a dictionary). (*b*) Applicability without change to inorganic as well as organic compounds. (*c*) Usage: This system is already in use in a Government card index of several hundred thousand cards which has cost about $60,000 to date. At present this index is of limited use, due to neglect but I believe could and should be made very valuable to the chemists of the country. It might eventually form the basis of subscription cards like the Library of Congress cards. (*d*) I have found by experimenting that, in spite of my familiarity with the Richter system, cards can be more rapidly and certainly arranged and looked up by the Hill system. The question does not touch the arrangement of isomers; under either system these could be arranged by any scheme desired.' "

Another type of publication which has become very important is represented by the Landolt-Börnstein "Tables of Physical Constants." American chemists have undertaken to prepare a book of this character. Here, again, the superabundance of material and the fact that many constants to be found in the literature are now entirely worthless because they have been superseded by better, recent determinations, constitute the most difficult part of the task. When only one value can be true, it is important to select among many values the one for which we have the best evidence that it approaches closely to the truth. This demands an impartial, critical judgment and a breadth of knowledge that very few possess. Let us hope that the right man may be found to supervise this difficult task.

Detailed knowledge of scientific facts accumulates very rapidly. Our most fundamental theories have been subject, recently, to many changes and new points of view are frequently proposed. Such words and phrases as radioactivity, half-life of an element, atomic numbers, isotopes, vitamines, polypetides, metabolism of amino acids and many others that might be given suggest topics about which our knowledge had scarcely begun twenty years ago. The knowledge of many, older topics is also developing and changing in such a manner that only those intimately acquainted with them can keep abreast with the times. It is of very great service to other chemists when an expert in such a field is willing to digest and coördinate the knowledge that is available and present it in a reliable, interesting form. The form of publication most recently undertaken by our Society is to serve this purpose. In conjunction with the Chemical Catalog Company we are to issue two series of monographs, one scientific and one technical. In the Technical Series, Dr. H. S. Taylor is preparing a monograph on "Industrial Hydrogen" and Dr. H. C. Porter one on the "Carbonization of Coal." In the Scientific Series a monograph on "Enzymes" by Dr. K. G. Falk will appear shortly. One on the "Chemical Effects of Alpha Particles and Electrons" by S. C. Lind is nearly completed. Others in process of preparation are on "Conductance" by Dr. C. A. Kraus, "Organic Mercurials" by Dr. Whitmore, "The Animal as a Converter" by Professor H. P. Armsby, "Silicates" by Dr. R. B. Sosman. We also hope for a monograph on "Thyroxin" by Dr. E. C. Kendall and one on "Vitamines" by Professor H. C. Sherman. I wish to ask your hearty support for this new undertaking.

This has been called the Reconstruction Meeting of our Society. It is a period of rapid, far-reaching changes in a time when we should take stock of what has been accomplished and forecast carefully the directions for further development and change. Our three *Journals* form, undoubtedly, the most important activity of our Society and through these journals we contribute more to the advance of our science in America and, each year, in a very rapidly increasing degree, throughout the world, than by means of all our other activities combined.

The *Journal of the American Chemical Society* contributes chiefly to the development of a better theoretical foundation for our knowledge and to the accumulation of an accurate knowledge of facts upon which the chemists of the future must build. An author who publishes an account of his researches in this *Journal* or in our *Industrial Journal* reaches a larger circle of readers than it is possible to reach by means of any other journal of the same type published in the world. Motives of economy have led the Editors of both of our *Journals* to insist on careful restrictions in the methods of presentation. As Professor Lamb has put the matter, "Authors should write their papers for an audience of experts familiar with the particular field under discussion, and should not attempt to prepare essays or monographs addressed to the general chemical public." There should be a clear, brief statement at the beginning of the paper giving the purpose for which the investigation was undertaken. References to previous work should be confined, as closely as possible to a *critically selected* set of references to the literature. Experimental results should be given in as concise a form as is compatible with a clear presentation and *only those results which are of permanent value* should be included. When one has worked for many months, or sometimes for years over a topic there is often a great temptation to present the results in a chronological order and to include material which may have been very useful in exploring the field and in finding the way toward the final conclusion, but which, nevertheless, is of no real value to others. Many chemists find the writing of papers irksome and many others fail to understand the amount of time and the painstaking care required before matters which seem clear to themselves can be made clear and useful to others.

While our Editors must insist on brief papers, where brevity is consistent with adequate presentation of valuable material, Professor Lamb writes, very justly, "I do not think we should insist invariably on brief papers, at least not in the absolute sense If a man really has done a lot of work of permanent value, it should be published and rendered accessible."

Professor Lamb also writes, "The *Journal* should safeguard zealously the freedom of its pages; that is, nonconformity with current opinions should in no sense hinder the publication of a paper. On the other hand, this nonconformity should not relieve the author at all from compliance with the regular standards of the *Journal*, both as to form and as to matter." Articles should almost always close with a clear, concise summary of the results obtained in the investigation.

It is the aim of *Chemical Abstracts* to give an abstract of every chemical article published in the world, if the article contains *new* results. It reaches this aim more nearly than any other abstract journal now published. With our present financial resources the length of the abstracts is necessarily restricted and the abstracts frequently contain less information than our Editor would be glad to include. Dr. Crane writes, "For example, if funds were available, we could rather frequently publish tables of new data which would be very useful, rather than merely refer to the tables as existing in the original papers. The indexes of *Chemical Abstracts* ought to be, along with the abstracts, complete records of new information of chemical interest published in the periods covered. Our present policy of indexing subjects from the body of abstracts thoroughly has taught us some things regarding the preparation of abstracts. If we felt free to do so, we could expand many abstracts in such a way as to improve their value from the indexing standpoint, and therefore, from the standpoint of their use as a record.

"*Indexes.*—The indexes to chemical publications destined to be used for reference work are very important parts of these publications. This is particularly true of an abstract journal. A great deal of our study and special effort here has been in connection with indexing, and in attempting to improve abstracts the subject index is kept prominently in mind. I believe that the indexes to many chemical publications are weak and that the fundamental faults have been the failure on the part of the one in authority to realize that a trained indexer only should undertake to prepare an important index and the failure on the part of the compiler to bear in mind that a so-called subject index should be an index of *subjects* and not one of *words*. There are many word indexes. Indexing is a science and profession. While I do not want to make any claim that perfection has been approached in our recent indexes to *C. A.* (they can be improved I am sure), I might point out that the weakest points with reference to the early volumes of *C. A.* were the tendency to word-index and the lack of uniformity in nature and quality of the indexes from year to year. The *Decennial Index* has perhaps served to remedy this fault somewhat. The formula indexes to be published annually and perhaps later in collective form will round out our indexes and strengthen them more than any other additional effort could. For the future it will be a wise policy for the indexes of *C. A.* to continue to receive special attention and in the interest of quality and uniformity in them the Society would, I believe, do well to recognize that, to use the words of Dr. J. C. Cain, Editor of the *Journal of the Chemical Society*, indexing is 'a very specialized and difficult job,' one requiring special training and experience to accomplish well, and help me to hold in this rather exacting work the experienced helpers who have been through the *Decennial Index* mill with me and who are dropping away into things which pay better. Better financial recognition of the professional chemical indexer, who must be chemist and indexer both and who is in somewhat the position of the teacher nowadays, is the burden of my thought; the field is a narrow but a very important one."

"*Titles.*—I believe that it would be an improvement in our chemical literature if greater care were to be used by authors of papers in selecting their titles. Too often titles do not adequately tell what the papers are about. Occasionally titles are too long. A good index does not depend on titles for its subjects but good titles will usually suggest the main subjects of the work being described. In recent years there has been an unfortunate tendency in engineering and trade journals to use titles which resemble newspaper headlines. I can perhaps illustrate the form, at least, by quoting a recent headline in one of our local newspapers: 'Combustion Causes Costly Conflagration.' Conservative titles, which are not too long nor detailed, but which avoid leaving the reader with a vague notion only as to the contents of the paper are needed in some cases to replace unsatisfactory ones."

What has been said with regard to articles to be published in the *Journal of the American Chemical Society* applies equally to the original articles which are to appear in our *Journal of Industrial and Engineering Chemistry*. Professor Herty has asked me to emphasize, especially, what has been said with regard to the concise presentation of the results of an investigation. Both of our Editors frequently find it necessary to return papers to authors for abbreviation. In almost all cases such shortening of papers is an advantage both to the author and to readers of our *Journals* as well as a saving in expense to the Society.

About one-third of the pages of our *Industrial Journal* is used for other purposes than the publication of research. Of these other features Professor Herty writes:

"The Society should have one journal which can be a news publication. In adopting Dr. Whitaker's plan and principle it was decided that there should be a definite editorial policy. There should be personals, industrial notes, space for correspondence, such letters as we are now printing from Washington, London, and Paris, accounts of various scientific societies, book reviews, market reports (why not in a journal of this character?), and such addresses as it is believed will be of help to the average member of the Society.

"For instance, we printed Dr. Whitney's Chandler Memorial lecture. Dr. Whitney is an authority in this field. He spent a great deal of his valuable time and intelligent effort on the preparation of this survey of the field which he discussed. It was a splendid piece of work and one which the great majority of the members of the Society could read and be largely benefited thereby. It is true that the authorities of Columbia University could have published that lecture, but not one member in a hundred of the A. C. S. would have seen it. By printing it we put it in the hands of every member.

"In other words, *This Journal* must be made attractive and readable by inclusion of various types of matter which will keep the average member of the Society in close touch with developments of all kinds. My position in this matter is that rather than curtail this many-sidedness of the *Journal*, we should further extend it, as for instance by the inclusion of important articles on chemical engineering by high authorities in that field. An especial appropriation was made for this purpose by the Directors when I first became Editor, but the tax of war service on the men best qualified to write such articles was so great that it was impossible to carry out the plan. Consequently I did not ask for a renewal of the appropriation on the scale on which it has been originally given. But it is my intention to urge the Directors, now that I think such articles can be secured, to renew that policy.

"But apart from all these considerations, it must be remembered that the Society looks upon *This Journal* as the agency to secure additional income through advertising. You may rest assured that if through a policy of retrenchment we restrict the *Journal* chiefly to publication of research in the industrial field, the goose that lays the golden eggs will surely be killed, and advertising will drop at a rate which will amaze you. The hard part of the work for me is to resist the constant pressure to modify the *Journal* from its present standard of being a scientific publication by adopting some of the practices of trade journals. This I will not agree to so long as I am Editor. I do not think it necessary to adopt such practices in order to get advertising business, but in order to do so and at the same time to maintain that standard, the *Journal* must certainly be made attractive and readable not only to scientific men but to men in the plants, business offices, etc., by the inclusion of a wide variety of matter."

During the present year we have greatly enlarged our News Service. Of this, Mr. John W. Harrington, its technical manager, writes:

"The purpose of the A. C. S. News Service is to give to the newspaper and magazine press accurate reports concerning chemical developments in the United States. The Service was founded in 1916, when it was noted that the press of the country was flooded with inaccurate and often exaggerated statements concerning chemistry. At the suggestion of a group of New York newspaper men, a publicity committee was established and bulletins were issued from time to time to a limited number of newspapers.

"It was found, however, that there were many technical reasons, such as the gauging of news values, which made it more practical to have this work in charge of a man of newspaper training. The misunderstanding between science and the newspapers has been due largely to differences of nomenclature. The public and the scientist often speak different languages. The gulf has been bridged by the A. C. S. News Service, providing statements and bulletins concerning discoveries in chemistry, which are expressed in as nontechnical diction as is consistent with precision.

"The News Service seeks to interpret chemical activities in relation to the news of the hour and the thought of the day. It takes nothing for granted and endeavors to reach what the newspaper and magazine editors call 'the standard average reader,' the intelligent laymen. Its function is to translate chemistry into terms of everyday life.

"The News Service performs for chemistry what every other interest and industry in the United States has found it necessary to do, in order that its work and its motive should not only be understood—but not misunderstood. Undoubtedly, the remarkable services which chemistry performed in the war, would have been ignored or submerged had not the American Chemical Society seen to it through this channel that due credit was given to the Chemical Warfare Service, of which it was the sponsor before the nation. The attempt to destroy the identity of the Chemical Warfare Service, in fact, was frustrated largely because the Society was able to explain to the public through the newspapers what the result of such an action would have been.

"It is partly because the bulletins of the A. C. S. News Service are prepared in accordance with the usage of the 'newspaper shop' and partly because they contain nothing commercial and make no attempt to gain any notice for statements which are properly matter for the advertising columns, that the A. C. S. News Service is appreciated and recognized by newspaper editors. They have confidence in it because they know that it exploits the wares of no man and that it is guided by a desire to truthfully and accurately express the ideals and aims of the American chemist. Were this Service conducted with any commercial intent, which, of course, is foreign to the purposes of the American Chemical Society, it would cost far more than the modest and inadequate appropriation which at present is assigned to it.

"An association of industrial companies had, until recently, a budget of $125,000 a year, and still maintains a staff of experts and an extensive publicity service, in addition to what expenditures are made in this direction by individual companies. The A. C. S. News Service, far-reaching as are its results, has given little or no individual attention to newspapers and magazines and has, in fact, only been able to scratch the surface. Its technical manager is retained on a part time basis only and the bulk of the appropriation is spent for secretarial and office expenses and for postage and supplies.

"As far as its relations with the American press are concerned, the A. C. S. News Service is conducted on a policy of give and take. It endeavors, with its limited facilities, to provide material, free of charge, as acceptable as paid contributions would be and devoid of propaganda. It therefore, has the good-will of the American press to such an extent that when crises have arisen in which the interests of the chemical profession were affected, it has, as the editorial and news columns of every leading American newspaper testify, a friend at court in the Fourth Estate."

Members often ask the question whether it might not be possible to furnish our members a choice among our Journals at a reduced rate for dues. As our Council has decided that it is necessary to increase our dues, this question is likely to be raised again. The question has been partially answered in the reference to the experience of the German Chemical Society in connection with the *Chemisches Centralblatt*. The fact that we have furnished our members with an abstract journal larger than the *Centralblatt* and also with the *Journal of the American Chemical Society* and *Journal of Industrial and Engineering Chemistry* for $10 dues to American members and $12.50, including postage, to foreign members, while the *Berichte* and *Centralblatt* cost foreign members about $19.00 before the war, and the *Journal of the Chemical Society* (London) and the *Journal of the Society of Chemical Industry* cost, together, $16.25, is a further demonstration of the economy to our members of the policy which we have followed. Those who wish to receive and pay for only one or two of our three journals forget that the cost of collecting the material for the *Journals*, editing and type-setting is the same whether a small or large number of copies are printed. After this initial work is done it costs only about $2.00 a year to print and send an additional copy of the *Journal of the American Chemical Society* to a member or subscriber and about $3.50 each to send copies of *Chemical Abstracts* or of our *Industrial Journal*. It is evident that these are the maximum rebates which we could possibly offer to members who do not care for one of the journals we publish. And the question is not as simple as even these statements of cost would indicate. Any decrease in the circulation of our *Industrial Journal* would be immediately reflected in our income from advertising. We must certainly continue that splendid spirit of coöperation in supporting all of the varied interests of our Society and our profession which has made our present commanding position possible. The following table shows clearly the phenomenal success of the policies adopted by the Society. At a time when all other costs have increased so much we feel sure that the chemists of the country will stand united behind the Society in the work it is doing.

Year.	Income.	Expense.	Surplus.	Deficit.	Excess of assets aver. liabilities.	Mem-bers.
1880............	......	......	......	.....	......	288
1890............	1,915.21	1,915.21	.....	.....	......	256
1900............	10,190.87	9,943.95	246.92	None	5,155.81	1715
1905............	16,532.37	15,353.76	1,178.61	None	7,027.51	2888
1906............	23,106.67	20,494.44	2,612.23	None	13,875.74	3047
1907............	33,275.25	27,248.89	6,026.36	None	17,490.06	3361
1908[a]...........	29,785.94	41,302.86	.....	11,516.92	5,171.53	3978
1909............	55,985.65	51,175.20	4,810.45	None	14,316.09	4460
1910............	61,760.91	52,483.64	9,277.27	None	19,659.17	5011
1915............	109,377.71	101,286.41	8,091.30	None	34,820.06	7332
1916............	136,557.65	123,375.77	13,181.88	None	51,038.25	8265
1917............	196,210.57	173,195.10	23,015.47	None	87,407.37	10504
1918............	203,483.32	165,158.92	38,324.40	None	126,601.27	12099
1919............	232,935.53	227,731.94	5,203.59	None	150,068.24	13568
1920[b]...........	272,160.66	290,498.96	.....	18,338.30	131,729.94	15577

[a] Part of 1906 dues were credited to 1907 and there was no decrease in receipts in 1908.

[b] Estimate September 1, 1920.

[Contribution from the Chemical Laboratories of Columbia University. No. 343.]

THE DETERMINATION OF THE HYDROGEN-ION CONCENTRATION IN PURE WATER BY A METHOD FOR MEASURING THE ELECTROMOTIVE FORCE OF CONCENTRATION CELLS OF HIGH INTERNAL RESISTANCE.

By H. T. Beans and E. T. Oakes.

Received May 16, 1919.

The present investigation was undertaken for the purpose of developing a method of measuring the hydrogen-ion concentration of pure water as directly as possible. It was desired to carry out this work in such manner as to avoid, as much as possible, the use of data obtained from the investigation of various solutions of salts, acids or bases. The object was to make the primary measurements on pure water in such a way as to be translated into hydrogen-ion concentration through the use of only such data as are substantiated by such proof, both experimental and theoretical, as to make it readily acceptable to everyone.

The only investigation of this question so far carried out in which measurements were made on pure water was that of Kohlrausch and Heydweiller who measured the conductivity of pure water, but in order to calculate hydrogen-ion concentration use was made of the ionic mobilities as determined in solutions of acids, bases and salts. These mobilities may or may not hold true for pure water. A more complete discussion of the possible objections to be raised against this method as well as the additional objections to the various other methods will be given later.

Since it was desired to make the measurements on pure water the only other method that presented itself was that of determining the electromotive force of a cell such as Hg | HgCl KCl (saturated) | pure H_2O | H_2. Heretofore the main difficulty encountered in this measurement was that due to the extremely high resistance of pure water, making the use of the potentiometer, or any other instrument previously employed for such measurements, out of the question. The problem then became one of developing and applying a method of measuring potential differences in which the resistance of the circuit would not affect the accuracy of the results and which at the same time would not require an excessive amount of current for operation. This latter requirement is necessary in order not to change materially the concentrations in the cells during the process of measurement. In other words, the new method must have all the advantages of the potentiometer method with the additional advantage of being independent of the internal resistance of the cell. Such a method as this being accomplished, the measurement of the voltage of the cell Hg | HgCl KCl (saturated) | H_2O | H_2 becomes a comparatively simple operation. From these results the hydrogen-ion concentration of pure water may be readily calculated by making use of Nernst's formula ($E = 0.0002T \log C/K$), and the established value for the saturated calomel electrode.

It is also to be noted that the application of such a method would not be limited to the cell mentioned above. The same method could be applied to all concentration cells, finding its greatest use, however, in connection with the measurement of the electromotive force of cells having such a high internal resistance as to render them impossible of measurement so long as the potentiometer method is the only one available. The new method would also open up a procedure for the investigation of very dilute solutions. By this means experimental evidence could be brought to bear on many of the numerous assumptions regarding the applicability of the laws of moderately dilute solutions to those that are extremely dilute. In addition, as will be shown later, the method as developed makes an ideal arrangement for electrometric titrations.

Up to the present time there has been no measurement of the hydrogen-ion concentration of water based solely upon the results of an investigation of pure water. So far results have been based on (1) measurement of the electromotive force of concentration cells; (2) conductivity measurements; (3) hydrolytic dissociation of salts; (4) velocity of reaction; (5) by use of colored indicators.

In only one of these methods (2) have any measurements actually been made on pure water. Even in that method the ionic concentrations could be calculated only by means of data resulting from a number of other investigations in which not pure water but various solutions were employed.

The following table, giving the results of previous investigations, is a summary of what has been accomplished thus far.

Date.	Investigator.	Method used.	Hydrogen-ion concentration.	Temp. ° C.
1893	Arrhenius[a]	Hydrolytic dissociation of 0.1 *M* sodium acetate solution. Taking Shields' values of 0.008% hydrolyzed at 25°	1.125×10^{-7}	25
1893	Arrhenius[b]	Calculated the e. m. f. of H_2 | *M* HCl | *M* NaCl | *M* NaOH | H_2 to be 0.806 volts neglecting contact-potential difference and assuming α HCl = 0.854 α NaOH = 0.776	1.125×10^{-7}	25
1893	Bredig[c]	Conductivity of aqueous solutions containing aniline	6.2×10^{-7}	25
1893	Ostwald[d]	E. m. f. H_2 | *M* acid | *M* base | H_2 Neglecting contact difference potential and assuming 100% ionization of both acid and base	9×10^{-7}	Room temp.
1893	Wijs[e]	Velocity of saponification of methyl acetate in water	1.4×10^{-7}	25
1894	Kohlrausch and Heydweiller[f]	Specific conductivity of pure water. Mobilities of ions at 26° taken as: H ion = 325, OH ion = 189; or at 18° H ion = 289, OH ion = 165.	1.10×10^{-7}	26
1894	Nernst[g]	Recalculated hydrogen-ion concentration from the average e. m. f. obtained by Ostwald and LeBlanc[h] correcting for contact potential difference, using mobilities as found by LeBlanc. Na ion = 32, Cl ion = 54, H ion = 272, OH ion = 143.	0.8×10^{-7}	18
1896	Lowenherz[i]	E. m. f. H_2 | 0.1 *M* HCl | 0.1 *M* LiCl | 0.1 *M* NaOH | H_2, also 0.1 *M* KOH correcting for contact potential differences using ionic mobilities. H ion = 325, OH ion = 167, Cl ion = 70.2, Na ion = 49.2, Li ion = 39.8.	NaOH cell 1.19×10^{-7} KOH cell 1.13×10^{-7}	26
1907	Lunden[j]	Measured dissociation constant and degree of hydrolysis of *p*-nitrophenol and trimethylpyridine	1.05×10^{-7}	25

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[a] Arrhenius, *Z. physik. Chem.*, 11, 805 (1893).

[b] Arrhenius, *ibid.*, 11, 808 (1893).

[c] Bredig, *ibid.*, 11, 830 (1893).

[d] Ostwald, *ibid.*, 11, 521 (1893).

[e] Wijs, *ibid.*, 12, 514 (1893).

[f] Kohlrausch and Heydweiller, *ibid.*, 14, 330 (1894).

[g] Nernst, *ibid.*, 14, 155 (1894).

[h] LeBlanc, *ibid.*, 8, 299 (1891).

[i] Lowenherz, *Z. physik. Chem.*, 20, 283 (1896).

[j] Luden, *J. chim. phys.*, 5, 574 (1907).

Date.	Investigator.	Method used.	Hydrogen-ion concentration.	Temp. ° C.
1907	Kanolt[a]	Hydrolytic dissociation of ammonium salt of diketo-tetrahydro-thiazole	0.91×10^{-7}	
1907	Noyes[b]	Conductivity measurements of various aqueous solutions	0.91×10^{-7}	
1909	Lorenz[c] Böhi	E. m. f. $H_2 \mid 0.1\ M\ HCl \mid 0.1\ M\ KCl \mid 0.1\ M\ KOH \mid H_2$, correcting for contact potential differences, using ionic mobilities of Kohlrausch. K ion = 74.5, H ion = 352.1, Cl ion = 75.3, OH ion = 195.9, at 25°	1.1×10^{-7}	25
1915	Fales[d] Nelson	Indicator method similar to Sorenson[e] Using *p*-nitrophenol as an indicator and comparing to mixtures of citrate solutions and 0.1 *M* sodium hydroxide	15.8×10^{-7}	25
1915	Sherman[f] Thomas	Confirmed Fales and Nelson results by the same method	15.8×10^{-7}	25

[a] Kanolt, THIS JOURNAL, **29**, 1492 (1907).

[b] Noyes, *Carnegie Inst. Pub.*, 1907.

[c] Lorenz and Bohi, *Z. physik. Chem.*, **66**, 733 (1909).

[d] Fales and Nelson, THIS JOURNAL, **37**, 2769 (1915).

[e] Sorensen, *Biochem. Z.*, **21**, 131 (1909).

[f] Sherman and Thomas. THIS JOURNAL, **37**, 623 (1915).

No attempt will be made to give the complete theory of each of the above methods, since they are readily accessible in the original works and in all standard texts on physical chemistry. The mere mention of the method employed serves to recall the numerous assumptions surrounding the calculation of the results from the experimental data. The most interesting and remarkable feature of these results is that data from such entirely different sources furnishes values for the hydrogen-ion concentration of water so comparable to each other. However, upon examination of the original data represented above we find that without exception the accuracy of each of the individual results is seriously affected either by the method employed or its execution or both, and each makes use of a multiplicity of assumptions which may or may not be justified.

Considering first only the determinations from electromotive-force measurements, it is to be noted that while all these electromotive-force measurements give values for the concentration of the hydrogen ion in water between 9×10^{-7} and 1.2×10^{-7} none of the measurements was made on pure water and in the computations data were selected from a wide range, no two investigators selecting the same data for the same purpose. Furthermore, the conditions which were accepted for comparatively concentrated solutions were assumed to hold for pure water itself.

With the exception of the conductivity determinations by Kohlrausch and Heydweiller, the other methods outlined can at best serve only as corroborative evidence of the validity of values obtained by the electromotive-force method, for these contain so many more assumptions. It is interesting to note that Kanolt, who claims no additional accuracy for his own work, in 1907, after discussing the previous attempts, concludes thus, "Although these entirely different measurements have all given for the ionization of water values of the same order of magnitude and have thereby furnished one of the most striking evidences of the ionic theory, yet for none of these values can any considerable percentage of accuracy be claimed."

Considering now the conductivity measurements of Kohlrausch and Heydweiller, a number of questions might properly be raised: (*a*) Do the hydrogen and hydroxyl ions have the same mobilities in pure water as in solutions, and what is the ionizing effect of the electric field of force from the current? (*b*) Is the surface effect on the electrode negligible? (*c*) Do the ions carry the entire current? (*d*) Is the secondary ionization of hydroxyl into oxygen and hydrogen ions negligible in pure water? (*e*) Is it not possible that this secondary ionization takes place to a rather great extent at the surface of the electrode?

According to theory, in order that the alternating current be carried, a minute quantity of ion must be discharged and then recharged. In the case of the hydroxyl ion this would have to ionize further into oxygen and hydrogen ions before the oxygen could be discharged. The resultant of these effects depends upon their relative magnitude.

These factors, while supposedly negligible, may or may not be without considerable effect and are especially alluded to because they apply to the only work so far accomplished on this subject in which the measurements were carried out on pure water. In the works of Taylor and Acree,[1] in 1916, and of Newbery,[2] in 1918, this question has been attacked from 2 different angles. These investigators have shown that the above factors are not without effect on the results.

The main difficulty connected with the use of the potentiometer for measuring the electromotive force developed by cells of the type $Hg \mid HgCl\ KCl \mid X \mid H_2$, where X is a poor conductor, results from the lack of sufficient amperage to allow of accurate galvanometer readings. The problem then developed into devising a method whereby such a quantity of electricity as would accurately actuate the galvanometer, could be withdrawn from the cell, stored up, and instantaneously discharged through a ballistic galvanometer.

From a consideration of the relations of quantities of electricity and current strength and of current strength, voltage and resistance the solution to the above problem becomes apparent. Where the resistance is

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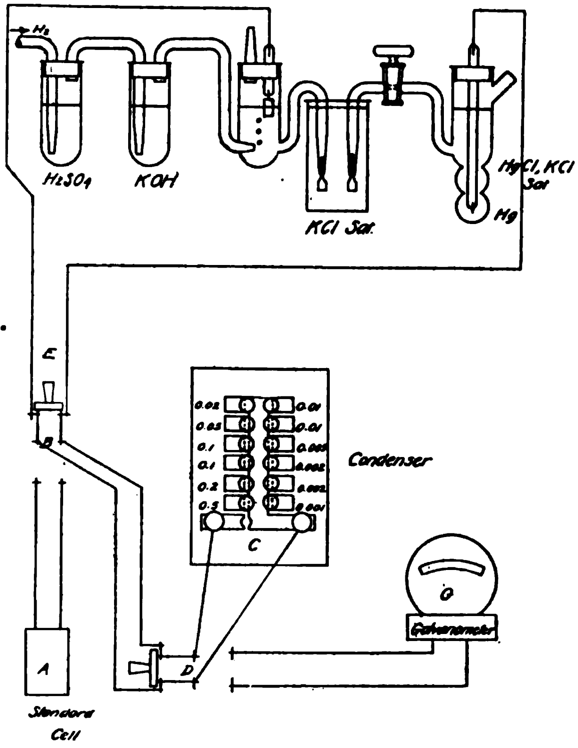
[1] Taylor and Acree, This Journal, 38, 2396 (1916).

[2] Newbery, *J. Chem. Soc.* (*London*), 113, 701 (1918).

very great it is only necessary to connect the cell to a condenser of sufficient capacity and allow it to run until the required number of coulombs is delivered, and then to discharge the condenser through the galvanometer in one pulse. Accordingly, the arrangement represented by the figure was tried. (In the actual work a charge and discharge key was used.) With the switches B and D, as indicated, the concentration cell E is charging the condenser C with a quantity of electricity equal to the product of the voltage of the cell times the capacity of the condenser, or $Q = E\,C$. By reversing Switch D this quantity of electricity is discharged through the ballistic galvanometer G and the deflection noted as d_1. By reversing Switch B with D in its original position the standard cell charges the condenser with a known quantity of electricity which may then be discharged through the galvanometer and the deflection noted as d_2. Since these deflections are proportional to the quantities of electricity passing through the instrument which in turn equals the product of the capacity of the condenser and the voltage of the cell we have $E_1\,C/E_2\,C = d_1/d_2$ or $E_1/E_2 = d_1/d_2$, where E_1 and E_2 are the voltages of the concentration cell and the standard cell, respectively, and d_1 and d_2 are the galvanometer deflections resulting from the discharge of the quantities of electricity $E_1\,C$ and $E_2\,C$. Substituting the known value of E_2 and the observed values of d_1 and d_2 we can readily solve for E_1. In practise it is much easier to calibrate the galvanometer over the particular range of deflections to be observed, calculating the electromotive force of the unknown cell from the micro-coulomb sensitivity so determined or reading it from a chart constructed from these values. The former method was the one employed in this work, and the results were checked at frequent intervals by using condensers of different capacities so as to get the same



deflection of the galvanometer with the standard cell and the unknown cell. This, of course, eliminated any slight variations due to imperfections of the scale divisions or to errors in estimating fractions of divisions. The results were then calculated directly from the formula $E_1C_1 = E_2C_2$, where E_1 and E_2 are the voltages of the unknown and standard cells, respectively, and C_1 and C_2 are the capacities of the condensers used in connection with the cells. Throughout this work no differences were obtained by using the two methods so that the second method, which is slightly longer, need be resorted to only when there are special reasons for checking the results obtained by the first method.

From a consideration of the equation $E_1/E_2 = d_1/d_2$ it is seen that the capacity of the condenser need not appear as a factor in the calculations. This makes it possible to use a single unit condenser of unknown capacity, calibrating the galvanometer for various voltages by means of a standard cell and such a condenser, using the necessary shunts in parallel with the galvanometer in order to secure deflections throughout the scale range. Such an arrangement would naturally result in a very material reduction in the cost of the apparatus. The very moderate cost of the apparatus thus modified as compared to that of the potentiometer equipment furnishes an additional argument for its use.

A Leeds and Northrup low sensitivity galvanometer was used for this work. The same standard cell and condensers were used in its calibration as were used in the investigation. A much more sensitive galvanometer is to be preferred. Although, as will be shown later, the galvanometer used gave results accurate to one millivolt, it required an undue amount of effort not needed if a more sensitive instrument were employed or if greater magnification of deflections of the scale were secured. With the scale at 0.5 meter from the galvanometer the following calibration was effected by discharging a standard Leeds and Northrup Weston cell through various capacities. This cell was checked against 2 other standard cells of the same make and found to develop an electromotive force of 1.01823 volt.

The condenser was manufactured by Jas. G. Biddle. The calibration certificate furnished with the instrument was checked in the Ernest Kempton Adams physical laboratory of Columbia University and found to be correct. The condenser was made up of units from 0.001 microfarad to 0.5 microfarad, the sum totaling 1.000 microfarad, so that capacities from 0.001 to 1.000 microfarad could be obtained.

All glassware was of the Non-sol brand and all bottles, flasks, beakers, etc., were subjected to the action of live steam for 3 hours before using, and twice thoroughly rinsed with the solution to be contained in them before introducing the main portion of the solution.

Condenser capacity. Microfarads.	Deflection, millimeters. Left.	Right.
1.00	50.0	50.0
	50.0	....
	49.8	50.0
	50.0	....
0.50	25.0	25.0
	25.0	25.0
	25.0	25.0
0.40	20.0	20.0
	20.0	20.0
	20.0	20.0
0.30	15.0	15.0
	15.0	15.0
	15.0	15.0
0.20	10.0	10.0
	10.0	10.0
	10.0	10.0
0.10	5.0	5.0
	5.0	5.0
	5.0	5.0

The water used in this work for making up the calomel cell and for one series of hydrogen electrodes was obtained by twice distilling ordinary distilled water from an alkaline permanganate solution through a block-tin condenser which condensed only about $^1/_3$ of the steam. For another series the ordinary distilled water was distilled once from an alkaline permanganate solution and then from a solution containing a small amount of phosphoric acid.

The mercury used in the preparation of the calomel cells and for contacts in the electrodes was purified by first dropping through a 1.5 meter tower of nitric acid according to the method of Hildebrand,[1] filtering through a dry cloth and then distilling under reduced pressure in a current of air as described by Hulett.[2]

The hydrochloric acid was prepared by distilling from a resistance glass flask through a quartz condenser and collecting the middle fraction in a quartz receiver, transferring it to a Non-sol bottle after it had cooled. This was then used in the preparation of the calomel and the standard 0.1 *M* hydrochloric acid solution. This latter was standardized by titration against sodium carbonate solution, using methyl orange as the indicator and was found to be 0.09996 *M*.

The calomel was prepared by the electrolytic method of Ellis.[3] After thoroughly washing it with pure water and then with saturated

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[1] Hildebrand, THIS JOURNAL, 31, 933 (1907); 35, 847 (1913).

[2] Hulett, *Z. physik. Chem.*, 33, 611 (1900).

[3] Ellis, THIS JOURNAL, 38, 737 (1916).

potassium chloride solution it was stored in a 500-cc. Non-sol bottle containing 400 cc. of the saturated potassium chloride solution. From these bottles it could then be transferred directly to the electrode.

The potassium chloride was purified by twice recrystallizing from distilled water Baker's analyzed potassium chloride and then fusing in platinum.

Compressed hydrogen was used, after it was passed through a solution of sodium hydroxide to insure the absence of carbon dioxide. The fact that the voltage of the cell did not change during long periods of use indicates that the hydrogen contained nothing to affect the cell.

The hydrogen electrodes were of platinum, platinized with platinum black. They were of plate form 2 × 1 × 0.025 cm.

All measurements were made at a temperature of 25° ± 0.01°.

In order to compare the accuracy of the condenser method with that of the potentiometer a cell was arranged as follows and the electromotive force measured by both methods,

$$\text{Hg} \mid \text{HgCl KCl (saturated)} \mid \text{KCl (saturated)} \mid 0.1\ M\ \text{HCl} \mid H_2.$$

The electromotive force of this cell was measured after the hydrogen had been bubbling through the hydrogen electrode for 5 hours and gave a voltage on the potentiometer of 0.3203 volt.

When measured by the condenser method, the cell 0.1 *M* HCl | calomel and the standard cell gave at 1.000 and 0.315 m. f., respectively, the galvanometer deflection 15.5, and at 0.500 and 0.157 m. f. the deflection 7.8, by 3 or more successive readings.

These results give a value of 0.3207 volt for the electromotive force of the above combination. Potentiometer measurements gave 0.3203 volt after 5 hours. Condenser measurements gave 0.3207 volt after 5 hours, 10 minutes. Potentiometer measurement gave 0.3200 volt after 5 hours, 20 minutes. Hence the condenser method with the set-up employed gives the voltage correct to ±0.0005 volt.

Since the voltage of the cell at the time these measurements were taken was undergoing a slow change the values recorded above are not to be taken as the true values for this cell, but were made for the sole purpose of indicating the accuracy of the condenser method.[1]

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[1] Using a galvanometer of very much greater sensitivity the electromotive force of the cell Hg | HgCl 1.0 *M* KCl | Sat. KCl | 0.1 *M* HCl | H_2 where a capacity of 1.5 m. f. gave a deflection of 88.8 mm. as against a deflection of 87.2 mm. for a standard cell of 1.01844 volts through 0.5 m. f., a voltage of 0.3457 to 0.3461 was obtained where a potentiometer gave 0.3460 to 0.3462 volt. While this voltage is not the true one for this cell it serves to show the order of accuracy of the method. A reading of this same cell after it had come to equilibrium gave a voltage of 0.3471 on the potentiometer, thus checking the value 0.3470 ± 0.0002 volt obtained by Fales and Vosburgh (THIS JOURNAL, **40,** 1293, (1918)), and published in 1918. This preliminary work was done in November, 1916.

Having fully demonstrated the applicability of the method for measuring the electromotive force of cells of this type where the internal resistance is not great, it remained to be determined whether the same method would apply to cells of high internal resistance such as Hg | HgCl.-KCl | KCl | H_2O (pure) | H_2. Accordingly a quantity of ordinary distilled water was twice distilled from alkaline permanganate solutions and the cell Hg | HgCl.KCl (satd.) | KCl (satd.) | H_2O | H_2 prepared. The hydrogen was admitted into the electrode chamber and allowed to flow over the electrode half immersed in the water. The actual progress of the determination of the electromotive force of a single cell is given in Table I. In this table the third column gives the time in minutes required by the cell to reach equilibrium. The second column indicates the length of time required by the cell to charge the condenser fully. Both of these factors must be determined by repeated tests, as it is obvious that constant readings cannot be secured until both of these conditions are satisfied. The low reading recorded after the cell had reached equilibrium when only one minute was allowed for charging the condenser indicates that this time was not sufficient to completely charge the condenser.

Table I.—Electromotive Force of a Single Cell.

Condenser capacity. Microfarads.	Time for charging condenser. Min.	Time of hydrogen flow. Min.	Galvanometer deflections. Mm.	
			Right.	Left.
1.000	2	14	24.8	....
.....	5	19	24.8	....
.....	5	25	24.8	....
0.802	6	38	20.0	....
.....	5	45	20.0	....
1.000	6	59	24.9	....
.....	5	64	25.0	....
.....	2	66	25.0	....
		Reversed cell.		
.....	2	70	....	25.0
.....	1	71	....	24.0
.....	9	80	....	25.0
0.800	5	86	....	20.0
0.600	2	88	....	15.0
		Reversed cell.		
0.600	2	92	15.0	....
.....	3	95	15.0	....

Maximum voltage reached in 64 minutes = 0.5091 volt.
Hydrogen-ion concentration = $10^{-44.4}$.

The average deflection for this cell after reaching maximum voltage is 25.0 mm. for one microfarad capacity. Since the standard cell of 1.01823 volts gives a deflection of 50.0 mm. when used with a capacity of one microfarad, the voltage of this cell is 25.0/50.0 of 1.01823 volts or 0.5091 volt.

This cell, using pure water in the hydrogen electrode element, reached a maximum voltage of 0.5091 volt in one hour, and this voltage had not changed in another half-hour. However, the same hydrogen electrode was used in this cell as was used in the 0.1 *M* hydrochloric acid cell and it was thought that some slight amount of acid might have been retained in the electrode even though it had been carefully washed several times with pure water. Accordingly the electrode was thoroughly washed again, this time in 3 lots of boiling water and a cell made up of pure water from the same lot as was used in the previous cell. This time the following results were obtained.

TABLE II.—CELL WITH WASHED ELECTRODE.

Condenser capacity. Microfarads.	Time for charging condenser. Min.	Time of hydrogen flow. Min.	Galvanometer deflections. Mm.
0.600	3	16	16.0
.....	4	20	17.3
.....	4	25	17.4
.....	7	32	17.6
.....	8	40	18.0
.....	4	51	18.0
1.000	2	66	28.0
.....	7	73	30.0
.....	37	110	30.0
0.800	4	126	24.0
.....	7	142	24.0

Maximum voltage reached in 40 minutes.
Average deflection for one m. f. after reaching maximum voltage 30.0 mm.
Electromotive force = 0.6109 volt.
Hydrogen-ion concentration = $10^{-6.24}$.

Following this a large number of cells were made up from water redistilled from alkaline permanganate solutions and from alkaline permanganate solutions followed by distillation from dilute solutions of phosphoric acid. The following table gives the results of a number of these experiments and indicates the futility of trying to secure water free from acid fumes under ordinary laboratory conditions even though a constant flow of uncondensed steam surrounds the mouth of the receiving vessel during the entire distillation.[1]

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[1] In order to check up again on the apparatus and calomel electrode the following combination was made up:

$$Hg \mid HgCl.KCl\ (satd.) \mid KCl\ (satd.) \mid 0.1\ M\ HCl \mid H_2.$$

After 6 hours this cell was measured by both the potentiometer and the condenser methods with the following results:

Potentiometer, 0.3115 volt. Condenser, 0.3116 volt.

After 7 hours this cell developed an electromotive force of 0.3113 volt and after 15.5 hours 0.3111 volt. This value (0.3111 volt) was then taken as the true voltage of the cell.

TABLE III.—CELLS MADE UP WITH WATER REDISTILLED FROM ALKALINE PERMANGANATE AND PHOSPHORIC ACID.

Number of alkaline permanganate distillations.	Time to reach max. voltage. Min.	Deflections at max voltage. using 1.0 m. f. Mm.	E. m. f. of cell. Volts.	Hydrogen-ion concentration.
1	35	28.2	0.5742	$10^{-5.58}$
1	50	28.2	0.5742	$10^{-5.58}$
2	35	28.0	0.5702	$10^{-5.52}$
2	30	27.8	0.5661	$10^{-5.45}$
2	60	28.5	0.5804	$10^{-5.69}$
1	40	28.2	0.5742	$10^{-5.58}$
1	30	28.5	0.5804	$10^{-5.69}$
1	30	28.5	0.5804	$10^{-5.69}$
1	40	29.2	0.5946	$10^{-5.92}$
2	40	29.2	0.5946	$10^{-5.92}$
2	60	29.4	0.5987	$10^{-5.99}$
One alk. permanganate followed by one acid distillation	70	28.2	0.5742	$10^{-5.58}$
Duplicate on last sample	40	25.1	0.5111	$10^{-4.52}$

The last cell recorded above was made up from the same sample of water as the cell recorded next above it. However, while the cell was being washed out a beaker of conc. hydrochloric acid was accidentally brought within about 2 feet of the unstoppered small-necked bottle containing the water. As soon as the odor of the fumes gave warning of the presence of the acid the bottle was stoppered and the cell taken to another room free from fumes. Here the cell was carefully washed out several times and filled from the bottle which had been exposed to the acid fumes for perhaps one-half minute. The electromotive force of this cell dropped to 0.5111 volt, a difference of 0.063 volt, due to the acid fumes, or in terms of hydrogen-ion concentration the change was from $10^{-5.58}$ moles per liter to $10^{-4.52}$ moles per liter. It is to be noted that the constant flow of hydrogen through the water in the cell and the maintaining of an atmosphere of hydrogen above the water should result in the complete removal of such gases as carbon dioxide and ammonia. This was observed to be true in the case of carbon dioxide, although it required days for the complete removal of very small quantities of this gas.

A large number of samples of water were prepared by distilling in a room where only ordinary precautions were taken against fumes. It was found impossible to duplicate results from water distilled under these conditions.[1,2] The distilling apparatus was therefore removed to a room free from all acid fumes when little difficulty was experienced in securing samples of water that gave the same electromotive force values. There

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[1] Kendall, THIS JOURNAL, 38, 1480 (1916).

[2] Kendall, *ibid.*, 38, 2460 (1916).

was no difference in the results obtained from water prepared by distilling ordinary distilled water once from an alkaline permanganate solution and from that distilled twice from an alkaline permanganate solution. Samples prepared by distilling ordinary distilled water once from an alkaline permanganate solution and once from a solution containing a few drops of phosphoric acid did not give such reliable results as those distilled from alkaline permanganate solution alone. The results given in the table below were obtained on samples of water from entirely different distillations. In every case the results on each sample were checked by measuring the voltage of a number of cells made up from the same sample of water. Such cells rarely exhibited a measurable difference in voltage. The cells requiring an excessive length of time to develop their maximum voltage were those in which fresh hydrogen electrodes were used. When the electrode was already thoroughly saturated with hydrogen the cells reached their maximum voltage in less than 40 minutes.

TABLE IV.—EFFECT OF DISTILLATION FROM ALKALINE PERMANGANATE SOLUTION.

Number of alkaline permanganate distillations.	Time to reach maximum voltage. Min.	Deflection at maximum voltage. Mm.	E. m. f. of cell. Volts.	Hydrogen-ion concentration.
2	300	35.1	0.7149	$10^{-7.94} = 1.15 \times 10^{-8}$
2	720	35.0	0.7129	$10^{-7.91} = 1.23 \times 10^{-8}$
1	20	35.0	0.7129	$10^{-7.91}$
1	10	35.0	0.7129	$10^{-7.91}$
1	60	35.0	0.7129	$10^{-7.91}$
2	40	35.0	0.7129	$10^{-7.91}$

Using a galvanometer having a ballistic period of 8 seconds and a sensitivity of 0.0003 micro-coulomb per mm. a sample of water having a specific conductivity of 0.9×10^{-6} reciprocal ohms was tested with the following results:

Capacity of condenser. M. f.	Deflection with standard cell. Mm.	Deflection with calomel pure water cell. Mm.	E. m. f. of cell. Volts.	Hydrogen-ion concentration.
0.1	164.1	.....	1.0187	....
...	164.0	.....	1.0187	....
...	164.1	.....	1.0187	....
0.2	328.0	.....	1.0187	....
0.2	.....	229.5	0.7128	$10^{-7.91} 1.23 \times 10^{-8}$

In the above determinations of the e. m. f. of the pure water cell the following 9 readings were made over a period of 4 hours: 230.0, 229.7 229.3, 230.0, 230.2, 229.2, 229.5, 230.0, 229.0. Average, 229.5.

In this series the deviation from the mean is, therefore, about two parts per thousand.

The apparatus assembled by Leeds and Northrup as set forth in a recent catalogue is a direct result of our work. However, we recommend a galvanometer of a sensitivity of 0.0003 micro-coulomb per mm. such as was used in this more recent work.

Consider now the cell $\underbrace{\text{Hg} \mid \text{HgCl.KCl}}_{E_1}$ (satd.) | KCl (satd.) | (0.1 *M* $\underbrace{\text{HCl} \mid \text{H}_2}_{E_2}$, the voltage of which, as determined in this investigation is 0.3111 volt and 0.3094 volt as determined by Nelson and Beegle.[1] The contact potential difference at the juncture of the saturated potassium chloride and hydrochloric acid solutions is zero. This is evidenced by the work of Fales and Vosburgh.[2] When pure water is substituted for the hydrochloric acid solution this contact potential difference is still zero. This is evidenced by practically all of the results for the mobilities of the potassium and the chloride ions. While various investigators have obtained different results all agree in that the mobility of the potassium ion is sensibly equal to that of the chloride ion.

Since the contact potential difference at the juncture of solutions is due to a difference in the mobilities of the ions if these mobilities are equal the contact potential difference is zero.

It is evident then that the measured electromotive force of 0.3111 volt is the resultant of E_1–E_2. Fales and Vosburgh[3] have measured this voltage E_2 and found it to be 0.2179 volt. It is, therefore, evident that since $E_1 - 0.2179$ volt $= 0.3111$ volt, then $E_1 = 0.5290$ volt. Hence by subtracting 0.5290 volt from the observed voltage of the cell Hg | HgCl.KCl (satd.) | KCl (satd.) | H_2O | H_2 we obtain the voltage of the element H_2O | H_2. Substituting this value in the Nernst equation, $E = 0.0002T \log C_{H^+}/K$, where $T = 25°$, $C = 298°$ absolute, and $K = 10^{-4.820}$(4,5,6,7,8) we can solve for C_H. It was in this way that the concentrations of hydrogen ions were calculated from the voltages of the cells whose electromotive forces were measured in this work.

The value of $10^{-7.91}$ moles per liter for the hydrogen-ion concentration in water was obtained from the experiments in which water of the highest degree of purity was used. The other results recorded above are published merely to show the variations to be expected unless extreme care is exercised in all operations. For example, failure to boil out the hydrogen electrode thoroughly after using it in 0.1 *M* hydrochloric acid resulted in

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[1] Nelson and Beegle, This Journal, 41, 559 (1919). (Private communication.)

[2] Fales and Vosburgh, *ibid.*, 40, 1293 (1918).

[3] Fales and Vosburgh, This Journal, 40, 1293 (1918).

[4] Loomis and Acree, *Am. Chem. J.*, 46, 585 (1911).

[5] Ellis, This Journal, 38, 737 (1916).

[6] Fales and Vosburgh, *ibid.*, 40, 1293 (1918).

[7] Wilsmore, *Z. physik. Chem.*, 36, 91 (1900).

[8] Nelson and Beegle, This Journal, 41, 559 (1919).

an increase of the hydrogen-ion concentration of $10^{1.8}$, even though the electrode had been washed several times with pure water. Also less than one minute exposure of the water contained in a small-necked bottle to fumes from a beaker of conc. hydrochloric acid caused an increase of 10^1 in the hydrogen-ion concentration.

In order to test the applicability of this method for measuring the electromotive force developed in organic cells a cell was set up with ethyl bromide dissolved in dry ether. A platinum strip was used for one electrode and a magnesium rod for the other. Due to the high resistance of the ether solution of ethyl bromine a much longer time was required to charge the condenser than was the case with pure water. However, the measurements made proved that this method can be successfully used with cells of this type where the internal resistance is many times greater than that of a cell of pure water.

In using this method for electrometric titrations it is first necessary to calibrate the galvanometer. This may be done either by means of calibrated capacities and a single voltage or by means of an unknown capacity used in conjunction with the standard voltage and the proper galvanometer shunts. From the results obtained by either method a graph may be constructed whereby the voltage corresponding to any deflection may be read directly.

With regard to the effects of polarization on the results obtained by this method it need only be pointed out that if a condenser of one microfarad is used and the electromotive force of the cell is one volt, then one hundred billionth of an equivalent of ion is discharged. This is still less than the amount which would ordinarily be discharged during the adjustment of the instrument when a potentiometer is used. The fact that the voltage of the cell does not exhibit a measurable change over periods as great as 24 hours, during which frequent measurements are taken, indicates the reliability of the method and the lack of effects due to polarization.

Summary.

1. A new method of measuring the electromotive force of concentration cells has been applied with an accuracy of 0.5 millivolt.

2. The hydrogen ion concentration of pure water has been measured and found to be 1.23×10^{-8} or $10^{-7.91}$.

3. The time required by the cell $Hg \mid HgCl.KCl \mid KCl \mid H_2O \mid H_2$ to charge a condenser of one microfarad capacity is from 3 to 5 minutes.

4. For a cell of low internal resistance such as $Hg \mid HgCl.KCl \mid KCl \mid HCl \mid H_2$ only an instant is required to charge the condenser.

5. The cell $Hg \mid HgCl.KCl$ sat. $\mid KCl.$ sat. $\mid H_2O \mid H_2$ reaches its maximum voltage in from 40 minutes to one hour and then remains constant for at least 24 hours.

6. Without sacrificing accuracy the new method makes possible the use of a much less expensive equipment than is used in the potentiometer method.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF COLUMBIA UNIVERSITY, No. 341.]

THE FORMATION OF ADDITION COMPOUNDS BETWEEN 100% SULFURIC ACID AND THE NEUTRAL SULFATES OF THE ALKALI METALS.

JAMES KENDALL AND MARY LOUISE LANDON.

Received April 27, 1920.

An extensive study of the freezing-point curves of various pairs of organic substances[1] and of water solutions of acids and bases[2] has gradually yielded increasing evidence in support of a general rule for compound formation—namely, that "the stability of an addition compound increases with the difference in character (*i. e.*, the positive or negative nature of the constituent groups) of its 2 components." In the application of this rule to compound formation in aqueous solutions, the complex nature of the question of salt hydration has been briefly treated,[3] and the difficulty of bringing it into line with other work discussed. The proposal was made to attack this question by first investigating the extent of compound formation in systems of the types HX–RX and ROH–RX. If the results of this work should lead to the formulation of any general rules for these cases, then it was suggested that a comparison of these results with those from a study of the systems HX–H_2O and ROH–H_2O might make possible the statement of general rules for the system RX–H_2O.

It was in initiation of this broad plan that the present work was undertaken, the type of system investigated being HX–RX. Because of its relatively high freezing point, 100% sulfuric acid was chosen as the acid component. As salts the anhydrous normal sulfates of sodium, potassium, lithium and ammonium were selected.

Previous Work.—The data available on the formation of addition compounds of the neutral sulfates of the alkali metals with sulfuric acid are very incomplete.[4] Most of the results are in the form of isolated observations which have been incidental in the study of other problems,

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[1] Kendall, THIS JOURNAL, 36, 1222, 1722 (1914); 38, 1309 (1916); Kendall and Carpenter, *ibid.*, 36, 2498 (1914); Kendall and Gibbons, *ibid.*, 37, 149 (1915); Kendall and Booge, *ibid.*, 38, 1712 (1916).

[2] Kendall, Booge and Andrews, *ibid.*, 39, 2303 (1917); Kendall and Booge, *ibid.*, 39, 2323 (1917).

[3] Kendall, Booge and Andrews, *loc. cit.*, p. 2304.

[4] References to previous work will be found later, under each particular system examined.

and apparently in no case has there been a systematic investigation of the question. In the methods of preparation noted for the various acid salts which have been reported, the acid used has been spoken of ordinarily as "concentrated" or as "a hydrate," showing that 100% acid had not been employed. In some cases the properties of the resulting products are given as definitely relating to the anhydrous substance, but this has not been done always, leading one to conclude that the compound may have been a hydrate, and so of no value for comparison in the present problem. Variation in the concentration of the acid, the proportion of the acid to the salt, and the temperature used in the reaction have naturally resulted in the formation of different compounds. Sometimes no melting point is given for the compound claimed, and frequently it is stated as "about" or "above" a certain value. Where more than one determination is available, there is little concordance, as a rule, between the results.

Experimental.

The method employed for this work was essentially the freezing-point method[1] previously used, though the conditions made certain alterations necessary.

The 100% sulfuric acid was prepared as described by Kendall and Carpenter.[2] Most stringent precautions were taken to prevent the acid from absorbing water from the atmosphere at any stage of the work. In spite of all precautions, however, the work was held up frequently for days at a time by unfavorable weather conditions which made it impossible to work with the acid.

The salts used were carefully analyzed sulfates of sodium, potassium, lithium and ammonium. Any impurities present were certainly insufficient in quantity to affect the measurements within the error of the experiment. All salts were dried to constant weight and then kept absolutely free from moisture.

For the lower range of the work—that is, up to 100°—a modified Beckmann apparatus was used. The inner tube, which had no side tube, was 15 cm. long and 3 cm. inside diameter; the outer tube was 17 cm. long with an inside diameter of $4^1/_2$ cm., Pyrex glass having been used for both. A 2-liter Pyrex beaker held the freezing mixture as long as that was needed, and later served as the container for the water-bath. The bath was stirred by a stream of compressed air. Mercury thermometers were used. Up to about 60° one graduated in 0.1° was employed; above 60°, a set of Anschütz short-stem thermometers graduated in 0.2° was substituted. The thermometers were standardized by taking the freezing and boiling points of water, by comparison with a standard thermometer

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[1] This method, as a means of studying compound formation, has been discussed fully in the earlier articles to which reference has been made above.

[2] Kendall and Carpenter, This Journal, 36, 2500 (1914).

between these 2 temperatures, and by means of fixed points above 100°. The standardization was checked at frequent intervals during the work.

At first the introduction of the solids into the tube containing the acid gave considerable trouble because, in their very dry condition, they could not be made into pills and so scattered badly over the thermometer, stirrer and sides of the tube. To overcome this difficulty, a glass-stoppered weighing-bottle with a long delivery tube attached was made and found to be most satisfactory. The length of the delivery tube was sufficient to allow it to reach nearly to the surface of the liquid in the freezing-point tube, and still not so great as to prevent the bottle from standing on the balance pan.

For the range of temperature above 100° the open tube could not be employed to advantage because of the decomposition of the 100% acid. It became necessary, therefore, to enclose the materials in sealed bulbs.[1] Special care was taken in filling and sealing these bulbs to ensure no absorption of water by the acid. The proportions of acid and salt in each mixture were established by direct weighing. The mixture was always melted completely 2 or 3 times and thoroughly shaken before any attempt was made to take freezing-point readings.

The bath used for this higher temperature work varied according to the temperature under investigation. Up to about 190° the bath was conc. sulfuric acid with 25% of ammonium sulfate added to reduce the fuming.[2] From this point up to 230° the bath was a mixture of fused lithium and potassium nitrates (65 mol per cent. of potassium nitrate), while from 230° to 300° a 50 mol per cent. mixture of fused potassium and sodium nitrates was used.[3] Above 300° the bath was of fused zinc chloride.[4] In all cases the bath was stirred by compressed air. The material in the sealed tube was kept thoroughly agitated by energetic rotation during determinations.

At the lower temperatures, it was usually possible to determine the freezing point by reading the temperature to which the thermometer rose after a slight degree of supercooling. In cases where there was persistent supercooling, it was necessary to employ the seeding process.[5] At higher temperatures the point recorded was that at which the last

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[1] See Smith and Eastlack, THIS JOURNAL, 38, 1262 (1916); Kendall and Davidson, *ibid.*, 42, 1142 (1920).

[2] The addition of ammonium sulfate to the hot acid removed the discoloration that had appeared on heating. Afterwards only the slightest darkening was apparent even after prolonged heating. The acid alone is useless for work requiring a transparent bath.

[3] A little conc. nitric acid was added at intervals to the molten mixture to remove the cloudiness that appears after continued heating.

[4] Scudder, THIS JOURNAL, 25, 161–163 (1903).

[5] See Kendall, *ibid.*, 36, 1226 (1914).

crystal disappeared, the temperature being allowed to rise very slowly in a mixture containing only a few minute crystals. A light placed behind the beaker made it possible to determine this point with accuracy. At least 3 readings were taken for each point, the variations obtained being within the following limits:

Limits.	Possible error.
—35° and —10°	0.2 to 0.5°
—10 and 100	0.1 to 0.2
100 and 200	0.2 to 0.5
200 and 300	0.5 to 1.0

In each of the systems investigated, it was possible to carry the work to a temperature of about 300°, at which point the curve was rising very rapidly. In the cases of potassium, sodium and lithium, it was found that, with mixtures containing just a little more salt than the last one used for obtaining a reading, it was impossible to dissolve the material even at the temperature of boiling sulfur. It had been hoped in the beginning of the work that the curve for ammonium sulfate might be carried through to 100% ammonium sulfate, but this proved to be impossible.

When a compound was indicated which was too unstable to give a maximum on its freezing-point curve, it became necessary to perform an analysis to determine its composition. A mixture was made up slightly richer in acid than that corresponding to the upper temperature limit of the curve, and allowed to cool to a temperature just above the lower limit. The solid phase which had separated out in the interval was then filtered off at this temperature by suction, a hot funnel being used when necessary. In order to have as small a surface as possible in the funnel during filtration a perforated plate from a Gooch crucible was fitted into a small glass funnel of the right size to fit into the hot funnel. A layer of asbestos was poured over the plate in such a way as to cover thoroughly any small cracks between it and the sides of the funnel. The compound was freed from excess acid, and wieghed portions of it titrated against standard alkali. This work was done in very cold dry weather when the mositure content of the air was small. In some cases extra protection was given to the material by drawing the air through calcium chloride.

When an unstable compound was formed beyond the range of the open tube work, no attempt was made to determine the composition of the solid phase because of the obvious change in conditions that would have resulted in any attempt to filter the material. The separation of the crystals in a centrifuge was impracticable owing to the high temperature that it would have been necessary to maintain in the machine.

The addition compounds obtained in every case were well-defined crystals, usually in the form of needles which arranged themselves in star-shaped clusters. In some cases it was possible to confirm change in solid phase directly by observing changes in appearance of the crystallized mass. In the case of the potassium system, the solid in the sealed tubes was clear and transparent as long as the 75% compound was the solid separating. When the eutectic was passed and the 50% compound crystallized out, the solid was white and opaque. In the same way the 2 crystalline modifications of the compound $Na_2SO_4.2H_2SO_4$ could be easily distinguished, the unstable form separating out in long needles, the stable in short plates.

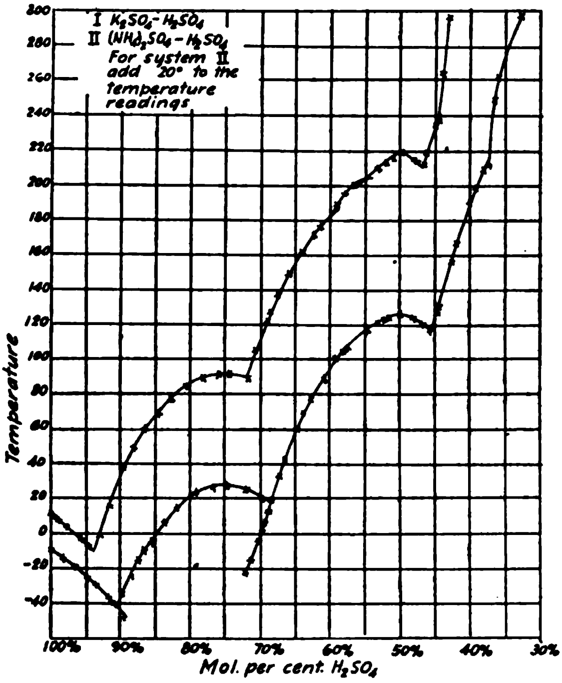

Fig. 1.

Results.

System K_2SO_4-H_2SO_4.—As a consequence of previous work 8 acid potassium sulfates have been claimed — K_2SO_4, $6H_2SO_4$ melting at about 55°;[1] K_2SO_4,$3H_2SO_4$ melting at about 95°;[2] K_2SO_4, H_2SO_4 with recorded melting points of 197°,[3] 200°,[4] 210,[5] and 315.5°;[6] $4K_2SO_4$, $3H_2SO_4$; $5K_2SO_4$, $3H_2SO_4$; $2K_2SO_4$, H_2SO_4 and $3K_2SO_4$, H_2SO_4 all given with no melting points;[7] and $4K_2SO_4$, H_2SO_4 with no melting point.[8]

The freezing point results of the present investigation are tabulated below; their significance is more clearly indicated by the accompanying diagram. Compositions are expressed in molecular percentages throughout.

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[1] Bergius, *Z. physik. Chem.*, 72, 338–63 (1910); Arzelier, *Compt. rend.*, 147, 129 (1908) claims that it is impossible to have an acid salt of potassium sulfate with more than 3 molecules of sulfuric acid to one of the salt.

[2] Schultz, *Pogg. Ann.*, 133, 137 (1868).

[3] Jacquelain, *Ann. phys. chim.*, 70, 311 (1839).

[4] Mitscherlich, *Pogg. Ann.*, 18, 152, 173 (1830).

[5] Schultz-Sellack, *Jahresber.*, 24, 218 (1871).

[6] See Gmelin and Kraut, "Handbuch der Anorg. Chem.," II, 1, 56.

[7] Stortenbecker, *Rec. trav. chim.*, 21, 400–402 (1902).

[8] Mitscherlich, *Pogg. Ann.*, 39, 198 (1836).

(*a*) Solid phase, H_2SO_4.

% acid	100.00	99.70	98.90	97.63	95.77	94.49
T	10.4	9.5	7.2	3.4	−3.2	−7.9

(*b*) Solid phase, $K_2SO_4.3H_2SO_4$.

% acid	93.13	91.66	89.60	88.02	86.47	84.61
T	−0.8	15.4	36.5	48.9	59.1	69.6
% acid	82.79	80.97	78.20	75.95	74.47	71.73
T	77.1	83.3	89.2	91.5	91.6	89.0

(*c*) Solid phase, $K_2SO_4.H_2SO_4$.

% acid	70.71	69.07	68.63	67.51	66.14	64.03	62.44
T	105.4	122.1	126.7	136.7	149.5	162.0	171.5
% acid	61.72	60.78	59.15	58.27	56.69	53.23	52.06
T	176.4	178.3	188.4	195.3	200.2	210.0	213.8
% acid	51.38	49.94	49.64	48.30	47.81	46.86	46.73
T	215.7	218.6	218.2	214.1	213.6	212.3	212.5

(*d*) Solid phase, X?

% acid	46.42	45.48	45.18	44.76
T	219.8	235.9	235.6	237.5

(*e*) Solid phase, Y?

% acid	44.29	43.41	41.53
T	264.3	296.8	300+

It will be seen that no confirmation is given for the compound K_2SO_4, $6H_2SO_4$ claimed by Bergius.[1] The 75% compound gives a well-defined maximum on the freezing-point curve, showing a melting point for the pure substance of 91.5°. At 182° and 202° there are clear evidences of changes in the crystalline habit of the 50% compound. These breaks are in accord with results of Bridgman[2] who, in working on the polymorphism of potassium hydrogen sulfate at high pressures, found 2 not very well defined transition points, one at 180° and the other at 200°. The compound gives a very well defined maximum at 218.6°. Beyond the region of the 50% compound, there is clear evidence of the formation of another compound, which, at 238°, gives a transition point to the next compound richer in potassium sulfate. While it is impossible to put great faith in the composition of Stortenbecker's salts, since there is a decided possibility that they are hydrates,[3] there may be salts of the composition $4K_2SO_4,3H_2SO_4$ and $5K_2SO_4,3H_2SO_4$. Either of these formulas might represent the composition of the substance indicated on the freezing-point curve. Stortenbecker's other salts lie beyond the range of this work.

System $(NH_4)_2SO_4$-H_2SO_4.—Previously there have been only 2 acid

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[1] The work of Bergius was not of the exact nature to justify his statement that this compound was formed.

[2] *Proc. Am. Acad. Sci.*, 52, 124 (1916).

[3] Stortenbecker himself states in a later article that the compound $3K_2SO_4.H_2SO_4$ previously described should have the formula $3K_2SO_4.H_2SO_4.H_2O$ (*Chem. Zentr.*, 1911, I, 1405.

salts of ammonium claimed—$(NH_4)_2SO_4.H_2SO_4$, melting at about 146°,[1] and $3(NH_4)_2SO_4.H_2SO_4$ to which no melting point has been given.[2]

The present work gave the following results. (See also Fig. 1).

(*a*) Solid phase, H_2SO_4.

% acid	100.00	98.31	96.53	94.61	93.56	91.64	90.59	89.52
T	10.4	6.2	1.3	—5.0	—8.5	—16.3	—20.7	—26.7

(*b*) Solid phase, $(NH_4)_2SO_4.3H_2SO_4$.

% acid	90.59	89.90	88.52	87.64	86.86	85.67	83.79	81.86	79.33	76.88	74.76	72.12	69.59
T	—20.7	—13.1	—3.9	5.3	10.5	17.6	26.7	35.1	42.7	46.9	47.9	45.8	39.8

(*c*) Solid phase, X?

% acid	72.02	71.40	70.38	69.67	69.59	69.13
T	—2.6	4.8	16.0	21.4	22.0	26.1

(*d*) Solid phase, $(NH_4)_2SO_4.H_2SO_4$.

% acid	68.79	68.37	67.35	66.52	64.94	63.81	62.69	60.87	59.33	58.19	57.53	54.82	53.18	52.40	51.92	50.05	48.16	46.92	45.73
T	32.9	39.4	53.5	63.1	79.8	89.1	97.4	109.5	120.8	124.3	126.4	136.8	141.1	142.6	144.9	146.9	144.1	141.7	137.2

(*e*) Solid phase, $2(NH_4)_2SO_4.H_2SO_4$(?)

% acid	44.95	44.57	43.83	42.82	42.02	40.22	39.38	38.36	37.62
T	147.2	151.7	159.3	176.7	187.7	210.2	218.5	229.2	232.0

(*f*) Solid phase, Y?

% acid	36.55	36.02	32.63
T	269.2	281.5	318.0

The data recorded above give distinct evidence of a substance not noted before, the compound $(NH_4)_2SO_4.3H_2SO_4$. This substance is stable at its melting point, having a well-defined maximum at 48°. The 50% compound gives a marked maximum at 146.9°, in close accord with the melting point noted by Smith.[3] It is of interest to note that the melting point given in the literature for the *normal* salt is 140°, a value obtained by Marchand.[4] This apparent contradiction is explained by Smith in objecting to the reference of Hodgkinson and Bellairs to their use of dried and carefully melted ammonium sulfate. Ammonium sulfate itself will not melt, but, on being heated, one equivalent of ammonia is expelled and it is the *acid* salt that melts at about 146°. This, of course, suggests that Marchand heated his material in an open tube which gave an opportunity for escape of ammonia. Bridgman also worked with acid

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[1] Smith, *J. Soc. Chem. Ind.*, 14, 629 (1895).

[2] Marignac, *Jahresber.*, 10, 134 (1857); Mitscherlich, *loc. cit.*; van Dorp, *Z. physik. Chem.*, 73, 284–289 (1910).

[3] *Loc. cit.*

[4] *Pogg. Ann.*, 42, 556 (1837).

ammonium sulfate and his record shows that his sample was entirely melted at 150°,[1] though no exact melting point was obtained. Below the eutectic between the 75 and 50% compounds there is a branch of the curve showing a metastable modification of unknown composition. Persistent efforts to carry this branch further met with failure. Above the 50% compound, there is a distinct break in the curve, and a slight extrapolation from the curve suggests that the compound formed is $2(NH_4)_2SO_4.H_2SO_4$. The transition point from this substance to the one next richer in ammonium sulfate comes at 234°. The compound containing 3 molecules of ammonium sulfate to one of the acid lies beyond the range of the present work.

System Na_2SO_4-H_2SO_4.—As the result of previous work 6 acid salts of sodium sulfate have been recorded—$Na_2SO_4.8H_2SO_4$ melting at about 40°;[2] $2Na_2SO_4.9H_2SO_4$ for which no melting point is given;[3] $Na_2SO_4.3H_2SO_4$ melting at about 100°;[4] $Na_2SO_4.H_2SO_4$ melting at about 315°;[5] $2Na_2SO_4.H_2SO_4$ and $3Na_2SO_4.H_2SO_4$ with no melting points.[6]

The results of the present work are given below, and also shown more clearly in Fig. 2.

(*a*) Solid phase, H_2SO_4.

% acid	100.00	98.02
T	10.4	4.3

(*b*) Solid phase, $2Na_2SO_4.9H_2SO_4$.

% acid	96.31	95.21	94.16	92.96	91.09	89.62	87.37	84.89
T	10.8	21.2	28.9	36.8	45.4	49.9	55.0	57.4

(*c*) Solid phase, $Na_2SO_4.2H_2SO_4$.

% acid	83.71	82.52	80.79	79.05	76.86
T (unstable modification)	62.9	70.4	79.7	87.0	93.6
T (stable modification)	71.5	78.6	88.5	95.7	102.1

(*d*) Solid phase, $Na_2SO_4.H_2SO_4$.

% acid	74.64	73.63	71.10	70.62	69.57	68.63	66.01	65.72
T	112.5	122.3	136.5	139.8	148.2	148.2	159.0	160.6
% acid	62.73	58.73	56.59	55.88	51.75	49.77		
T	170.0	177.8	180.7	180.9	185.5	185.8		

(*e*) Solid phase, X?

% acid	49.03	48.63	46.04	45.40	44.26	43.28	41.17
T	190.9	194.3	223.3	230.2	243.2	254.2	274.5

As in the case of the potassium system, no confirmation is obtained of the work of Bergius, claiming the compound $Na_2SO_4.8H_2SO_4$. For the

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[1] *Loc. cit.*, pp. 125–126.

[2] Bergius, *loc. cit.*

[3] d'Ans, *Z. anorg. Chem.*, 80, 236–238 (1913).

[4] Schultz, *loc. cit.*

[5] von Thomson, *Pogg. Ann.*, 6, 80 (1826).

[6] von Thomson, *ibid.*; Mitscherlich, *Pogg. Ann.*, 39, 198 (1836); Pascal and Ero, *Bull. soc. chim.*, [4] 25, 35 (1919).

compound $2Na_2SO_4.9H_2SO_4$ noted by d'Ans there is very distinct evidence,[1] extrapolation from the freezing-point curve indicating that its melting point would be about 60°. It gives transition points to the next compound at 57° and 58°. The compound $Na_2SO_4.3H_2SO_4$ noted by Schultz was not obtained. In its stead, the new compound $Na_2SO_4.2H_2SO_4$ appeared, a substance existing in 2 crystalline modifications.[2] This salt decomposes before its melting point is reached, giving transition points to $Na_2SO_4.H_2SO_4$ at the temperatures of 95° and 109°, respectively, for its 2 modifications. This compound is just barely stable at its melting point, and cannot be separated from a solution containing a greater percentage of sodium sulfate. The melting point of 186° found here is quite out of accordance with the value of 315.5° given in the literature. $2Na_2SO_4.H_2SO_4$ and $3Na_2SO_4.H_2SO_4$, for which no melting points are recorded, lie outside the range of this work. The slope of the upper portion of the curve indicates, however, that com-

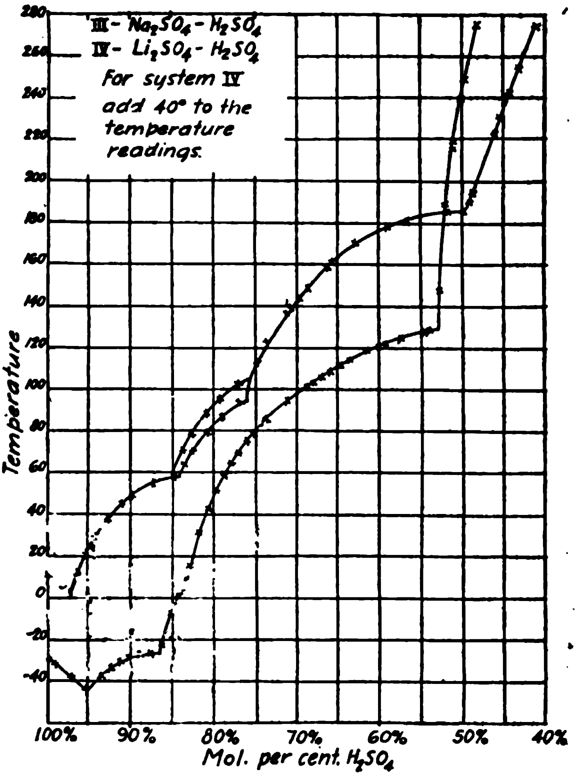

Fig. 2.

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[1] The analytical results, upon which the decision concerning the composition of this substance is based, agree within the limit of error in the acid titration. Computation from these results gave percentage molecular compositions of 81.85%, 81.34%, 81.34%, 81.37% (calculated, 81.81% acid). It was felt in the beginning that it was possible that this percentage corresponded to an 80% compound with some excess acid, but, since persistent filtering did not reduce the proportion of acid and since the substance was in the form of light needle-shaped crystals which did not pack down into a hard mass that opposed the passage of the air through it, there finally seemed to be no reason for not giving the compound the formula $2Na_2SO_4.9H_2SO_4$ previously recorded by d'Ans.

[2] Schultz's compound was very probably this substance, insufficiently freed from excess acid.

pounds of this type would be formed before the melting point of the normal salt could be reached.

System Li_2SO_4-H_2SO_4.—From previous work there are 3 acid salts of lithium sulfate claimed—$Li_2SO_4.7H_2SO_4$ melting at about 12°;[1] $Li_2SO_4.2H_2SO_4$ melting at above 110°;[2] and $Li_2SO_4.H_2SO_4$ melting at 120° according to Lescoeur,[3] and at 160° according to Schultz.[2]

The results of the present work are tabulated below. (See also Fig. 2.)

(*a*) Solid phase, H_2SO_4.

% acid	100.00	99.19	97.15	95.37
T	10.3	8.0	2.0	—3.6

(*b*) Solid phase, $Li_2SO_4.7H_2SO_4$.

% acid	93.58	92.37	91.25	90.27	88.76	87.68	87.50	87.15
T	3.0	6.5	9.7	11.4	12.9	13.1	13.3	13.0
% acid	86.98							
T	13.0							

(*c*) Solid phase, $Li_2SO_4.2H_2SO_4$.

% acid	86.36	85.09	84.69	84.13	83.77	83.42
T	17.9	32.6	36.7	40.9	44.3	48.9

(*d*) Solid phase, $Li_2SO_4.H_2SO_4$.

% acid	82.99	81.61	80.68	79.94	78.84	77.89	76.55	76.08
T	55.3	70.9	82.7	91.2	99.0	105.2	109.3	114.7
% acid	75.27	73.59	71.05	68.72	67.70	66.69	66.03	64.88
T	117.7	125.4	135.8	142.5	144.5	147.1	148.6	152.4
% acid	63.99	61.67	59.89	59.24	57.40	54.90	54.00	
T	155.2	159.4	161.3	161.5	164.7	167.8	168.5	

(*e*) Solid phase, X?

% acid	52.40	51.90	51.45	51.21	50.15	49.52	48.20
T	186.5	229.9	256.0	258.6	279.9	289.0	315.0

The present results confirm in general all the salts previously claimed. The compound containing 7 molecules of sulfuric acid, for which Bergius gives a melting-point of "about 12°," shows a clearly defined maximum at 13.3°. The melting-point of 110° for $Li_2SO_4.2H_2SO_4$ recorded by Schultz is in error, since this compound is shown on the freezing-point curve to be unstable at its melting-point and gives a transition point to $Li_2SO_4.H_2SO_4$ at a temperature of 50°. The latter compound is also unstable at its melting-point, but a slight extrapolation from the curve indicates that the value for the melting-point is 170.5°, much higher than any previously given. The stable portion of the curve ends with a transition point at a temperature of 169.7° to a compound with a larger per cent. of lithium sulfate with a maximum beyond the range of the present work. No such compound has as yet been recorded.

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[1] Bergius, *loc. cit.*

[2] Schultz, *loc. cit.*

[3] Lescoeur, *Bull. soc. chim.*, 24, 516 (1875).

Consideration of Results.

Reference to the diagrams will show at once a strong similarity between the curves for potassium and ammonium salts; the course of compound formation with sodium and lithium sulfates is also much alike. This result is not at all surprising when one remembers the general similarity between the compounds of these respective pairs of radicals. In all cases there is evidence for extensive compound formation, the compounds varying considerably in complexity and stability.

Bergius,[1] in some very rough preliminary work, showed that other sulfates, such as those of barium and strontium, are much less active in forming compounds with sulfuric acid, the majority being, indeed, only very slightly soluble. While Bergius' work is merely qualitative in character, it does indicate clearly that the tendency toward compound formation with sulfuric acid is greatest with the alkali metals here examined.

This is in exact accordance with the results of previous articles, since according to the rule already stated[2] we would expect the sulfates of the most electropositive metals to form most stable compounds with sulfuric acid. In this acid, in fact, the salts here investigated should give results analagous to those obtained with the corresponding hydroxides in aqueous solution.[3] A systematic study of the remaining metal sulfates in sulfuric acid is now in progress, and it is hoped to obtain, by means of compound formation, solubility and conductivity data in these systems, results which will enable us to establish definitely the general relationships existing between the position of the metal in the electromotive series and compound formation in the first place, and between compound formation and ionization in the second. Extended discussion of the present results will consequently be deferred to the succeeding article of this series.

In conclusion here, the fact may be noted that the freezing-point curves obtained are not without interest in connection with certain industrial problems, such as the utilization of nitre cake, or the treatment of gas liquor.[4]

Summary.

A complete investigation has been made by means of the freezing-point method upon compound formation in systems containing sulfuric acid and the anhydrous neutral sulfates of potassium, ammonium, sodium and lithium from the eutectic point of each system up to a temperature of 300° (approximately).

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[1] *Loc. cit.*

[2] P. 2131.

[3] A sulfate in sulfuric acid being not a salt, but a base.

[4] See, for example, Johnston, *J. Ind. Eng. Chem.*, 10, 468 (1918); Dawson, *J. Chem. Soc.*, 113, 675 (1918); Pascal and Ero, *Bull. soc. chim.*, [4] 25, 35 (1919); Foote, *J. Ind. Eng. Chem.*, 11, 629 (1919).

The results obtained may be summarized as follows (compounds of undetermined composition being omitted):

Salt formula.	Acid compounds isolated.
K_2SO_4	(*a*) $K_2SO_4.3H_2SO_4$; m. p., 91.5°.
	(*b*) $K_2SO_4.H_2SO_4$; m. p., 218.6°; existent in three modifications, with transition points at 182° and 202°.
$(NH_4)_2SO_4$	(*a*) $(NH_4)_2SO_4.3H_2SO_4$; m. p. 48.0°.
	(*b*) $(NH_4)_2SO_4.H_2SO_4$; m. p. 146.9°.
Na_2SO_4	(*a*) $2Na_2SO_4.9H_2SO_4$; unstable at m. p. (60°, by extrapolation), transition points to the two modifications of (*b*) occurring at 57° and 58°.
	(*b*) $Na_2SO_4.2H_2SO_4$; existent in two modifications both unstable at their m. p., transition to (*c*) occurring at 95° and 109°.
	(*c*) $Na_2SO_4.H_2SO_4$; m. p., 186°.
Li_2SO_4	(*a*) $Li_2SO_4.7H_2SO_4$; m. p., 13.6°.
	(*b*) $Li_2SO_4.2H_2SO_4$; unstable at m. p., transition to (*c*) occurring at 50°.
	(*c*) $Li_2SO_4.H_2SO_4$; unstable at m. p. (170.5°, by extrapolation).

The bearing of the results here obtained upon the general problem of the factors affecting compound formation in solutions has been briefly pointed out, but full discussion is reserved for a later article, in which the compound formation, solubility and ionization relationships of a more complete series of metal sulfates in sulfuric acid will be considered.

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COLLOIDAL ADSORPTION.

BY ARTHUR MUTSCHELLER.

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From the work of Stokes, Einstein, von Smoluchowski, The. Svedberg, and others, we have a clear notion of the properties of the unstable colloids when suspended in a fluid; for in their case all the conditions upon which Stokes' law is based seem to be realized. On the other hand, the properties of the gelatinizing and swelling colloids are so much at variance with the requirements for the validity of Stokes' law, that it seems clearly impossible to consider the metallic and the gelatinous colloids in one class, and separate efforts to establish a securely based view-point from which the mechanism of the action of the latter might be considered, does not seem to have hitherto been made.

To make generalizations and general deductions safely, requires a set of accurately determined experimental facts obtained under uniform standard conditions and sufficiently complete so that by coördinating the variations in properties a complete set of descriptive data on the system are secured showing the changes in the properties of the substance under investigation when certain changes in the surrounding conditions are forced upon it.

In view of the fact that such uniform experimental data on the gelatinous or swelling colloids are not directly available nor found in the literature, the investigations herein recorded were carried out with the same typical colloid, with an electrolyte added in varying concentrations, and under uniform experimental conditions. An attempt was made to study all such physical or physico-chemical properties of a typical colloid as are capable of investigation by modern methods and as seem to have a bearing in defining the properties of the colloid.

The distinctions, heretofore made, between suspensoids, and emulsoids, between irreversible and reversible colloids, between unstable and stable colloids, between anhydrophils and hydrophils, etc., are undoubtedly all based upon differences in the properties of the 2 classes of colloids, which it becomes interesting to investigate. When considered together with the general properties of colloids, these differences between the 2 classes of colloids would form an important item in a set of data from which it should be possible to derive general principles applying to both classes or if that is not possible, to describe models of colloidal particles which exhibit the properties of both classes.

When a colloid is precipitated the properties which characterize it as a colloid generally vanish. It appears, therefore, that a study of the properties of colloids would have to be directed toward investigating the factors of stability or, on the other hand, of the conditions under which a colloid is coagulated or precipitated. Since the factors upon which the stability of a colloid system depends are quite numerous, and coagulation or precipitation can be initiated by any one of a great number of factors, it appears that the study of the factors of stability of colloidal systems should cover the most important properties which characterize colloids.

Nearly all of the aforesaid factors seem to be connected with or dependent upon changes in the concentrations of electrolyte which is generally present. Thus, the addition of gradually increasing quantities of electrolyte to a colloidal solution is known to produce many changes such as adsorption of ions and salts, changes in the migration velocity of the particles in the electrostatic field, surface tension, viscosity or internal friction, swelling and shrinking, etc.

As far as possible, the writer's experimental work covers the changes above outlined and, therefore, the topics given below. Unless otherwise stated, the experiments of all sections were performed with identical series of solutions, at the same temperature, and as far as possible, under identical experimental conditions.

The topics of the investigation were (1) the migration velocities of the ions as influenced by the presence of a reversible colloid; (2) the concentration of the anions and cations as influenced by the presence of a reversible colloid; (3) the migration velocity of the colloid as influenced by increasing concentrations of electrolyte; (4) the surface tension of emulsoid solutions as influenced by increasing concentrations of electrolyte; (5) the viscosity or internal friction of emulsoid solutions as influenced by increasing concentrations of electrolyte; (6) the swelling of gelatin as influenced by increasing concentrations of electrolyte.

EXPERIMENTAL PART.

Preparation and Composition of the Solutions.

In view of the variety of determinations and observations planned, all with the same series of mixtures, it became necessary to select a colloid and a salt both adapted to the carrying out of such determinations and observations. To avoid complications and to obtain the results as simply as possible, it seemed desirable to select a salt ionizing into equivalent ions, the concentrations of which could be determined by electromotive-force measurements.

In previous experimental work it was found that gelatin, which is a typical representative of the emulsoids, is suitable for the experiments planned, and also that zinc sulfate is satisfactory as an electrolyte, both the sulfate and the zinc-ion concentrations being determinable independently by electromotive force measurements by means of electrodes, one (first kind) for the zinc ion and one (second kind) for the sulfate ion. The experiments were, therefore, made with 1% solutions of gelatin containing increasing concentrations of zinc sulfate as indicated in Col. 2 of the tables.

Standard solutions of zinc sulfate were prepared from the chemically pure salt and distilled water; they were standardized by precipitating the zinc and weighing it as zinc ammonium phosphate. The gelatin solutions were prepared from a good quality of gelatin previously dialyzed and again desiccated. For each day's work, fresh solutions were prepared containing 2 g. in every 100 cc. of distilled water. The mixtures were slowly heated while stirring when the gelatin went rapidly into solution, and heating was continued until boiling just *began*. After cooling and while the gelatin solution was still fluid the mixtures were finally prepared by adding an equal volume of the properly diluted standard zinc sulfate solution to make the gelatin content of the mixtures uniformly 1% and then allowing them to stand at 25° for *one hour*. This uniform method of preparing the mixtures was found necessary, for otherwise varying results were obtained.

A series of solutions of concentrations as indicated in the tables and prepared as stated above was employed for all experiments reported in this paper, unless otherwise stated. The working temperature was uniformly maintained near 25°. The reaction vessels were placed into a carefully regulated thermostat until this temperature was attained, and the measurements were then made and repeated until found constant. Thus all experimental work was performed under identical conditions, such as the preparation of the solutions, the regulation of the temperature, the lapse of time, etc., unless the contrary is indicated. The experimental data reported are the result of several measurements, and, as a rule, the average of at least 2 measurements made at different times is given in the tables.

The Migration Velocities of the Ions as Influenced by the Presence of a Reversible Colloid.

In a previous publication experiments were described which show that the migration velocities of the silver and the nitrate or the copper and the sulfate ions are changed considerably when certain quantities of an emulsoid are added to their solutions.[1] Thus the silver and the nitrate ions of a pure silver nitrate solution migrate with relative migration velocities of 0.562 for the nitrate ion and 0.438 for the silver ion. These relative migration velocities are generally determined by estimating the changes in the concentrations at the 2 electrodes when a certain quantity of the metal is electrically deposited on the cathode. Thus it is found that while one equivalent of silver is deposited on the cathode there have arrived by migration only 0.438 equivalent; hence there is a decrease in the concentration of silver ions at the cathode. It is then also found that at the anode there have only arrived 0.562 equivalent of nitrate ions, so that there is also a decrease in the concentrations of silver nitrate. Moreover, the deposit on the cathode is not smooth but rather crystalline, forming the so-called silver trees. The height of these silver trees probably indicates the thickness of the layer of fluid near the cathode in which impoverishment of the silver content has developed.

Marked changes in the migration velocities of these ions are observed, however, if to their solutions addition of certain quantities of gelatin is made. Thus a small quantity of gelatin added to a normal solution of silver nitrate causes a decrease in the migration velocity of the nitrate ions and a proportional increase in the velocity of the silver ions. At the same time, the tendency to form silver trees and a loose deposit on the cathode is decreased, the deposit being quite smooth, well adherent to the cathode, and less crystalline. Furthermore, a small amount of organic material having the appearance of coagulated gelatin had gathered around the anode.

Quite different results are observed when larger additions of gelatin are made to a normal silver nitrate solution. The deposit on the cathode is then smooth and well adhering and a layer of gelatin is found to have gathered around the cathode; the deposit on the cathode consists in this

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[1] Mutscheller, *Met. Chem. Eng.*, 13, 353–7 (1915).

case of a mixture of silver and gelatin. The migration velocity of the silver ions is found to be either unit or more, according to whether the organic deposit on the cathode was weighed with the silver or whether it was removed and the silver only had been weighed. The migration velocity of the nitrate ions, however, is found to be zero.

Under ordinary conditions gelatin without the addition of electrolyte, migrates to the negative electrode, hence carries a positive charge. When a small quantity of it is added to a normal silver nitrate solution, then there is adsorption of negative ions until the charge of the gelatin particles is reversed, at which time they migrate to the anode instead of as before to the cathode.[1] If the quantity of gelatin added is larger, the negative ions in the solution which are being adsorbed are not sufficient to reverse the charge of the gelatin particles and they still continue to migrate to the cathode. There is, naturally, a point when the gelatin particles are just neutralized and they do not migrate either to the cathode or to the anode.[2]

Experiments to determine the migration velocities of the zinc and the sulfate ions in the series of solutions of zinc sulfate of increasing concentrations containing 1% of gelatin were carried out for the purpose of finding at what concentration the negative sulfate ions are just sufficient to neutralize the positive charge of the gelatin particles of a 1% solution. The apparatus employed for this work is the same as that formerly employed. The entire cathode compartment was emptied into a weighing

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[1] That there is a reversal in the direction of migration of the anions when gelatin is present in the solution has already been observed by A. Carpentier (*Compt. rend.*, 136, 1652 (1903)). He found that when the solution is of a chromate or dichromate placed upon a film of 10% gelatin, the reddish-yellow chromate ion migrates with great velocity, not to the anode but to the cathode. While Carpentier does not give an explanation, this observation is evidently in agreement with the theory of adsorption as expounded in this paper.

[2] Paul Richter (*Z. physik. Chem.*, 80, 449, (1912)) determined the influence of certain colloids upon the migration velocities of several electrolytes and found only slight decreases when increasing additions of colloid were made. He analyzed the anode fluid and in all cases he neglected the presence of the colloid or he assumed that no changes in the concentration of the colloid could occur. But, as will be shown, when a small quantity of colloid is added its charge is reversed and made negative so that the colloid migrates to the anode. When larger additions of colloid are made, however, more and more of the colloid migrates toward the cathode for its charge then becomes more and more positive. Thus, when larger additions of colloid are made, the anode fluid will have a lower specific gravity after the electrolysis than before, so that at the rate at which the additions are increased, the anode fluid loses progressively in specific gravity. This gives the impression that the anode fluid is of smaller volume than it actually is, and the chlorine ion concentration is found to be higher with the result that the differences before and after the electrolysis appear larger and the migration velocities also larger than they are. This error in the case of a 0.05 *N* solution of monovalent ions is much larger than it would be in the case of a molar solution of polyvalent ions.

flask and its exact weight was determined. From this weight, that of the zinc sulfate as found later by analysis, was subtracted. From the remaining weight and the specific gravity of the solution the exact volume of the cathode fluid was calculated. Finally, from the data obtained by analysis (*i. e.*, precipitating and weighing the zinc as zinc ammonium phosphate) the relative migration velocities of the sulfate and the zinc ions were calculated. These results are reported in Table I.

TABLE I.—CHANGES IN THE RELATIVE MIGRATION VELOCITY OF THE ZINC ION IN SOLUTIONS OF VARIOUS CONCENTRATIONS BY 1% GELATIN.

Zinc anode, platinum cathode; volts 12, from storage battery; time, 2 to 3 hours.

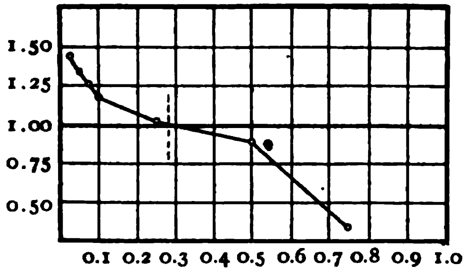
Solution No.	$ZnSO_4$ added molar.	Conc. of free ions.[a]	Deposit on cathode.	Zn^{++} migrated to cathode.[c]	Relative migration velocity of Zn^{++} calculated.	Form of the deposit.	Gelatin.
4....	0.025	0.0142	0.0118[b]	0.0169	1.438	Dark color; impure	Thick layer dep. on cathode
5....	0.05	0.0234	0.0136[b]	0.0180	1.323	Gray with tendency to peel off	Layer of gel. dep. on cathode
6....	0.075	0.0326	0.0381[b]	0.0483	1.269	Slightly gray	Film of gel. dep. on cathode
7....	0.10	0.0397	0.0624[b]	0.0734	1.177	Well adherent; slightly dull	Small amt. of gel. gathered at cathode
8....	0.25	0.0803	0.0297	0.0302	1.016	Brilliant, pure, adherent	No accumulation of gelatin
9....	0.50	0.141	0.0585	0.0517	0.884	Pure, tendency to form striae	Small quan. of gel. gathered around anode
10....	0.75	0.185	0.0421	0.0143	0.340	Pure, forming striae and bubbles	Layer of gel. gath. around anode
11....	1.00	0.229	0.0560	0.362	0.154	Very poor, forming craters and striae	Gel. precipitated upon add. of *N* $ZnSO_4$ sol.

[a] Calculated from the conductivity measurements of Jones and West, *Am. Chem. J.*, 34, 357 (1905).

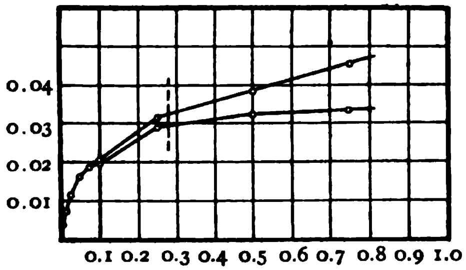
[b] Deposit of zinc and organic material.

[c] Zinc deposited minus the loss of zinc in the cathode compartment.

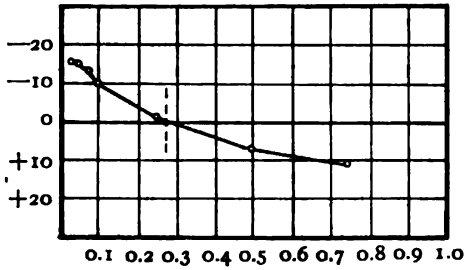
The results which are plotted in Fig. 1 Curve 2, show that concentrations higher than 0.28 molar zinc sulfate furnish, probably through progressive ionization, more sulfate ions than the colloid added is capable of adsorbing. The migration velocities of the zinc ion in the solutions containing zinc sulfate in higher concentration than 0.28 molar are, as the experimental data show, less than unity and the deposit is less smooth and less adherent as the concentration of the zinc sulfate in the solutions increases. At the point where the addition of zinc sulfate just amounts to 0.28 molar the migration velocity of the zinc ions is unity and the



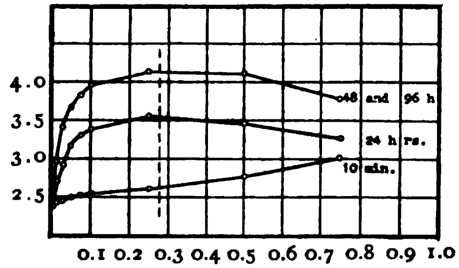
Curve 2 showing changes in the relative migration velocity of the Zn^{++} ion.



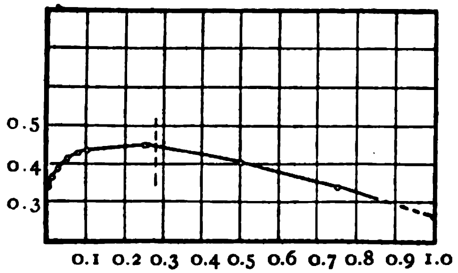
Curve 2a showing the $SO_4^{=}$ and the $Zn^{++} + SO_4^{=}$ adsorbed.



Curve 4 showing the changes of the migration velocity of the gelatin particles.



Curve 5 showing the viscosity of the solutions after various intervals of time



Curve 6 showing the extent of swelling of gelatin in the various dilutions of $ZnSO_4$.

Fig. 1.—Molar concentration of $ZnSO_4$ added

velocity of the sulfate ion is zero. At lower than 0.28 molar concentrations of zinc sulfate the migration velocities of the zinc ion are apparently higher than unit velocity since the deposit of organic material was weighed along with the zinc deposited on the cathode. The deposition of gelatin on the cathode probably takes place due to the fact that gelatin when negatively charged adsorbs positive ions as shown in the next section, and may thus be deposited on the cathode.

The results of this series bring into evidence again the fact that the particles of gelatin adsorb negatively charged ions, rendering them electrically neutral, so that at proper proportions the current which is transported across the electrolyte is then carried by the positive ions. This is indicated by the fact that the positive ions actually migrate with increased velocity for the concentration of positive ions around the cathode is found to remain constant when just the proper quantity of gelatin sufficient to adsorb the free negative ions is present. The results of this series show that the negative ions of a 0.28 molar zinc sulfate solution are approximately neutralized by 1% of gelatin with the result that the zinc ions migrate with unit velocity and they deposit as a smooth and non-crystalline layer on the cathode.

The Concentration of the Free Anions and Cations as Influenced by the Presence of a Reversible Colloid.

The results of the foregoing series of experiments indicate that a union takes place between the colloidal particles and the negatively charged ions when a neutral salt is added to the solution of the colloid. The storage of electrolyte in finely divided substances is an old and a well-known phenomenon generally called adsorption. The relation of the adsorbed to the unadsorbed quantities of electrolyte, in the case of a number of suspensoids has been investigated by H. Freundlich and many others. Freundlich[1] found that the ratio of distribution of the electrolyte between the colloid and the solvent is well represented within certain limits, by the equation

$$x/m = Bc^{1/q}$$

where x/m is the quantity of electrolyte adsorbed by m grams of the colloid, c is the concentration of electrolyte remaining in solution, and B and $1/q$ are constants. Since taking the logarithms of both sides of this equation gives an equation for a straight line, plotting the logarithms of the experimental data must give a straight line, if they satisfy the adsorption equation.[2] Freundlich,[3] however, found that the logarithmic plot of the points corresponding to larger additions of electrolyte bends somewhat and tends to run parallel with the log-c axis. The curve of

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[1] "Kapillarchemie," 1909, p. 143ff.

[2] Freundlich, *Z. physik. Chem.*, 57, 391 (1907).

[3] "Kapillarchemie," p. 94.

this plot, therefore, is only a straight line when smaller additions of electrolyte are made to the colloid.

In order to test the ratio of adsorption of ions by the emulsoid chosen for this investigation a series of determinations of the concentrations of the free zinc and sulfate ions was made, first in a series of pure solutions of zinc sulfate of increasing strengths, and then in a similar series of solutions containing in addition 1% of gelatin. Differences found in the results evidently indicate the formation of a neutral combination consisting of colloidal particles and ions, and the numerical values of these differences represent the adsorbed quantity of ions. These values and those of the ionic concentrations found in the solutions can then be suitably plotted to determine whether they represent an adsorption equilibrium.

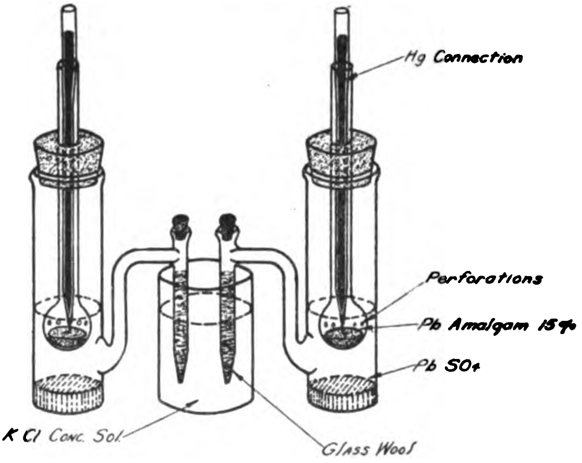

Fig. 2.

The apparatus employed for determining the concentration of the zinc ion and the sulfate ion in solutions of zinc sulfate consists of a potentiometer as a balancing instrument, an electrometer as a zero instrument, a standard cadmium element as a standard of electromotive force and an accumulator as a constant electromotive force. All determinations were made at 25°, the temperature of the cells being controlled in a carefully regulated thermostat. The type of cell representing the combination is

$$\mathrm{Zn}\left|\frac{\mathrm{ZnSO_4}}{C_1} \text{ — conc. KCl — } \frac{\mathrm{ZnSO_4}}{C_2}\right|\mathrm{Zn}$$

where C_1 and C_2 are the concentrations of Zn^{++}, respectively, in the 2 solutions.

A concentrated solution of potassium chloride served as a connecting fluid between the 2 electrode halves.

The electromotive force of this cell is given by the formula

$$E = \frac{0.0000198T}{2} \times \log\frac{C_1}{C_2}.$$

The concentration of C_2, the concentration sought was calculated from

$$\log C_2 = \log C_1 - \log \psi$$

where

$$\log \psi = \frac{E}{0.0000198T/2}.$$

The concentrations of the sulfate ion was determined with the aid of a cell represented by

$$\text{Pb} \left| \frac{\text{PbSO}_4}{\text{ZnSO}_4/C_1} - \text{conc. KCl} - \frac{\text{PbSO}_4}{\text{ZnSO}_4/C_2} \right| \text{Pb}$$

Metallic lead as an electrode was employed in the form of a 15% amalgam. The electrode vessels illustrated in Fig. 2 were found to be most satisfactory, especially for operation with solutions containing colloidal matter.

The electromotive force of this cell is given by

$$E = \frac{0.0000198T}{2} \times \log \frac{C_2}{C_1}$$

and is calculated from

$$\log C_2 = \log C_1 + \log \psi$$

where log ψ is again equal to

$$\frac{E}{0.0000198T/2}.$$

Thus Fig. 3 is a direct plot of the experimental results recorded in Table II and Fig. 4 (*a*) is the logarithmic plot of the ratio of distribution of the sulfate ion between gelatin and the solvent; Fig. 4 (*b*) is the logarithmic plot of the sum of the concentrations of the sulfate and the zinc ions and is clearly a straight line.

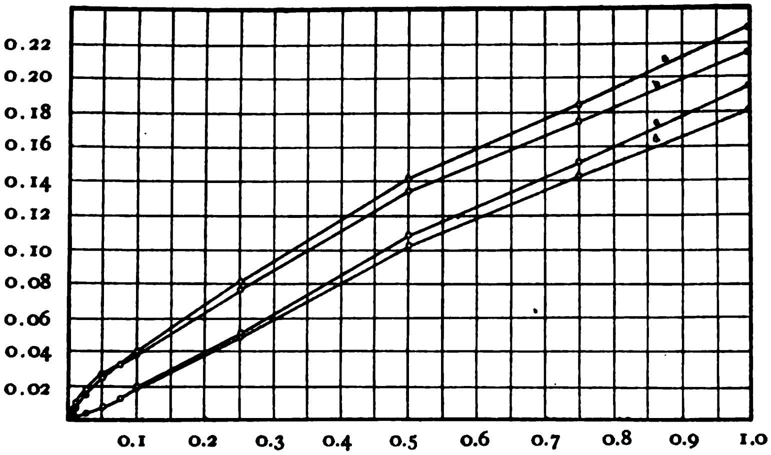

Fig. 3.—Showing (*a*) the concentrations of the $SO_4^{=}$ and of the Zn^{++} in the pure solutions; (*b*) the concentrations of the Zn^{++} when 1% of gelatin is added; (*c*) the concentrations of the $SO_4^{=}$ when 1% of gelatin is added; (*d*) the loss of $Zn^{++} + SO_4^{=}$ when 1% of gelatin is added.

TABLE II.—CHANGES IN THE CONCENTRATION OF THE SULFATE AND ZINC IONS PRODUCED BY THE ADDITION OF 1% GELATIN.

			Found by e. m. f. measurement.						
			No additions. Concentrations.		1% gelatin solutions.		Adsorbed by gelatin.		
Solu- No.	$ZnSO_4$ added molar.	Conc. of free ions.[a]	Zn^{++}.	$SO_4^{=}$.	Zn^{++}.[b]	$SO_4^{=}$.	Zn^{++}.	$SO_4^{=}$.	$Zn^{++} + SO_4^{=}$[c].
2....	0.005	0.0035	0.003	0.0035	0.0045	0.0002	—0.00094	0.0042	0.0042
3....	0.01	0.0063	0.0062	0.0063	0.00872	0.0007	—0.00238	0.00701	0.00701
4....	0.025	0.0142	0.0136	0.014	0.0180	0.0031	—0.0038	0.0111	0.0111
5....	0.05	0.0234	0.0247	0.034	0.0248	0.0077	—0.0014	0.0159	0.0159
6....	0.075	0.0326	0.033	0.0326	0.0324	0.0134	+0.0002	0.0192	0.0194
7....	0.10	0.0397	0.0394	0.0395	0.0385	0.0199	+0.0010	0.0196	0.0206
8....	0.25	0.0803	0.0813	0.0803	0.0775	0.0517	+0.0028	0.0286	0.0314
9....	0.50	0.141	0.141	0.141	0.135	0.109	+0.0060	0.032	0.038
10....	0.75	0.185	0.184	0.188	0.176	0.155	+0.0120	0.033	0.045
11....	1.00	0.229	0.219	0.229	.....	....	....	.....	.....

[a] Calculated from the conductivity measurements of Jones and West, *Am. Chem. J.*, **34**, 357 (1905).

[b] With regard to the dissociation of zinc sulfate, it must be considered to exist in accordance with the equilibrium

$$\frac{(Zn^{++})(SO_4^{=})}{(ZnSO_4)} = K.$$

If the colloidal particles remove $SO_4^{=}$ from the solution, there will be a rearrangement of the equilibrium so that if x moles per liter of $SO_4^{=}$ are removed,

$$\frac{(Zn^{++} + x)\ SO_4^{=} - x)}{(ZnSO_4 - x)} = K.$$

There is, therefore, an increase of zinc ions due to the further ionization of zinc sulfate initiated by the removal of sulfate ions. Thus we find such an increase of zinc ions as recorded in Table I below 0.1 molar dilutions. From there on, however, there is then a decrease of zinc ions which shows that from that point on, the colloid has also adsorbed some zinc ions. Assuming that y moles were adsorbed, then there is again a rearrangement of the equilibrium so that

$$\frac{(Zn^{++} + x - y)\ (SO_4^{=} - x + y)}{(ZnSO_4 - x + y)} = K.$$

The amount of Zn^{++} and $SO_4^{=}$ actually adsorbed is, therefore, in all probability considerably larger than that found by difference from the remaining concentrations. That is, the removal of zinc ions and sulfate ions is followed by further ionization of zinc sulfate through which loss in these ions is made to appear smaller. The actual extent of this difference cannot be accurately determined, the difference would appear in the constants of the adsorption equation, which, however, at the present has no definite meaning. The result might be a slight difference in the slope and the intersection of the logarithmic curve with the log x/m axis but the differences, in all probability, are only slight.

[c] These increases in the case of the zinc ion in the solution are not added as negatively adsorbed for they are probably due to the readjustment of the equilibrium of the zinc and sulfate ions when the latter are withdrawn from the solution by the colloid.

The results brought into evidence by this series of determinations are two-fold. First, it is shown that the sulfate ion (not the zinc ion) maintains a typical adsorption equilibrium between the solvent and the gelatin present in the solution in the sense of H. Freundlich's criteria; second, it is shown that the logarithmic plot of the ratios of distribution of the sulfate and the zinc ion taken as their sums and plotted against the concentrations of $^1/_2$ the sums of the concentrations of the sulfate and the zinc ions in the solutions is better represented by the adsorption equation used by Freundlich, than the ratio of the sulfate-ion concentrations alone without including the zinc (positive) ion also. (Fig. 1. Curve *2a*.)

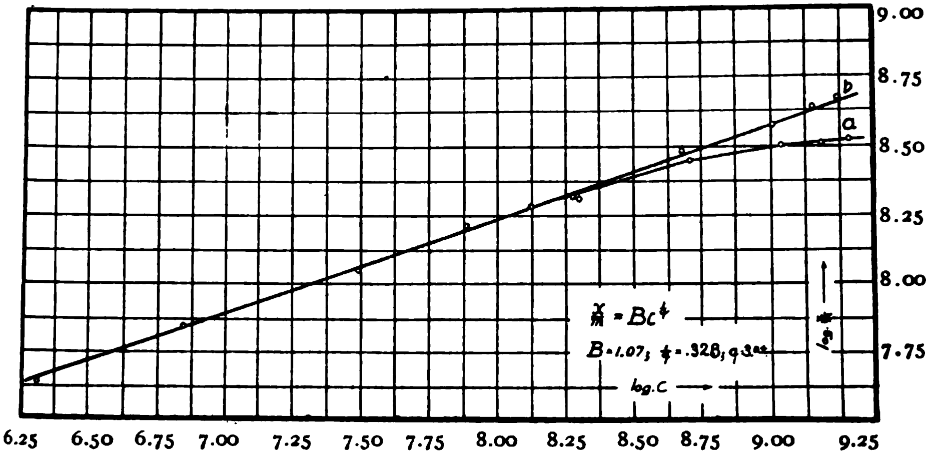

Fig. 4.—Logarithmic plot of (*a*) the $SO_4^=$ and of (*b*) the $Zn^{++} + SO_4^=$ as distributed between the colloid and the solvent.

The Velocity of Motion of Colloidal Particles as Influenced by the Presence of Increasing Concentrations of Electrolyte.

That many colloidal particles migrate when subjected to the force of an electrostatic field and that this motion is the result of the action of the field on the electrical charges carried by the particles, is a fact known for many years and which has been the subject of lively investigation. The work of Wiedemann and Perrin[1] brought out the fact that if 2 different mutually insoluble substances, especially when present in different phases, come in contact, that there is generally a difference of electrical potential at or near the surface of contact.

Although the mechanism of the action of a field on a charged particle and the factors upon which the motion imparted to the particle by the field depends are rather clearly understood, there are still quite a number of theories under consideration regarding the origin of the charge of the particles. The chemical theories seem to fail utterly to account for the original charge of the particle and to explain the existence of a charge when

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[1] *J. chim. phys.*, 2, 607 (1904).

electrolyte is present in the solution. The theory of Helmholtz and Lamb, however, has in recent time received very good support from the work recently performed on the structure of solids to which reference is made later in another article.

When testing the electrical properties of suspensoids it is, as a rule, possible to obtain definite and well agreeing results, but with emulsoids there seem changes of a more complicated nature to be going on around the electrodes so that the same interpretations do generally not apply. But this series of experiments was carried out for the sole purpose of finding the point at which the charge of the gelatin particles is neutralized by the added electrolytes.

For the determinations the same tube as that used for the determinations of the changes of migration velocities of the ions was employed. The distance between the electrodes is 12.4 cm.; the voltage of the current applied to the electrodes is 44.6 volts, so that there existed a potential drop across the electrodes of 3.6 volts per centimeter. The time of running was generally about 30 minutes. The estimation of the gelatin that migrated was carried out by determining the changes in the gelatin content at the 2 electrodes. From determinations of the total nitrogen content of a given volume of the well mixed content of the cathode vessels the velocity of the gelatin particles that migrated was calculated for an existing drop of one volt per centimeter in one second of time.

TABLE III.—CHANGES OF MIGRATION VELOCITY OF GELATIN PARTICLES WITH INCREASING ADDITIONS OF ELECTROLYTE.

Solution No.	$ZnSO_4$ added molar.	Conc. of free ions.[a]	Velocity of motion cm./sec. pot. drop volt/cm.
3	0.01	0.0063	-16×10^{-5}
4	0.025	0.0142	-15×10^{-5}
5	0.05	0.0234	-13×10^{-5}
6	0.075	0.0326	-10×10^{-5}
7	0.10	0.0397	-3×10^{-5}
8	0.25	0.0803	7×10^{-5}
9	0.50	0.141	11×10^{-5}

[a] *Loc. cit.*

The numerical data of Table III, which are plotted to Fig. 1, Curve 4, bring out the fact that the colloidal particles are deprived of all their charge when 0.28 molar zinc sulfate is present in the solution. This point, therefore, represents the isoelectric conditions of the colloidal gelatin particles as indicated by the fact that, at that point, they are unsusceptible to the force of an electrostatic field.

The Surface Tension of a Solution of an Emulsoid as Influenced by Increasing Concentrations of Electrolyte.

It has been observed experimentally that the surface tension of water is decreased by a class of colloids which includes gelatin, albumin, dextrin, agar-agar, gum arabic, soaps, rosins, etc., as against being increased by metallic colloids. The results of H. Freundlich and W. Neumann[1] show that some of these substances, when dispersed in water, decrease the surface tension, but when dispersed in alcohol they cause a rise in the surface tension. These differences in the effects upon the surface tension of the pure solvent, can, therefore, be considered as constituting a property characteristic of emulsoids.[2]

The surface tension of a gelatin solution, as G. Buglia[3] and W. Frei[4] show is further decreased by the addition of H^+ (positive ions) and is increased (*i. e.*, the difference between the surface tension of the gelatin solution and the pure solvent is made smaller) by the addition of OH^- (negative ions). As is shown by W. Frei, the order in which the anions increase the surface tension of gelatin solutions and in which the cations decrease it, is in the order of the Hofmeister series. Furthermore, as is characteristic of the Hofmeister series, the order is reversed when the reaction of the solution is changed by the addition of either an acid or an alkali.

It seems indicated to mention that these and the observations described in the following are in agreement with W. Gibbs' well-known theorem; for, as reported by W. Frei,[5] the anions cause a decrease in the difference between the surface tension of the pure solvent and that of the gelatin solutions, as the result of which the anions are adsorbed by the gelatin particles.

The surface tension of the solutions described in the introduction was measured by the capillary-rise method.[6] A capillary of uniform cross section was employed; a thread of mercury in this capillary 10 cm. long weighs 0.1053 g. As a criterion of cleanness, it was observed that the capillary rise and fall should not differ by more than one mm. The data recorded in Table IV are calculated with the aid of the formula, $n = {}^1/_2\, rhsg$, where r is the radius of the capillary calculated from the weight of the thread of mercury, h the height of ascent in cm., s the specific gravity, and g the constant of gravity equal to 980.6.

The results show a decrease in the surface tension of water caused by the solution of 1% of gelatin. But, within the limits of experimental error attainable by the capillary rise method, it is not possible to find any change in the surface tension of the solutions due to the addition of increasing quantities of zinc sulfate to the gelatin solution. This, at first, might be contrary to the expectations, but since the effectiveness of the

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[1] Freundlich and Neumann, *Kolloid Z.*, 3, 80 (1908).

[2] Wo. Ostwald, "Kolloidchemie," 1912, p. 227.

[3] Buglia, *Biochem. Z.*, 11, 311 (1908).

[4] Frei, *Diss.*, Zürich, 1907.

[5] *Loc. cit.*

[6] Ostwald-Luther, "Physico-chemische Messungen," 1904, p. 234.

ions varies in the order of the Hofmeister series, and since the zinc ions and the sulfate ions as decreasing and increasing the surface tension of the gelatin solution might be nearly equivalent, it is probable that the changes which might actually exist are too small as to be discernible by this method.[1]

TABLE IV.—SHOWING THE SURFACE TENSION OF 1% GELATIN SOLUTIONS WITH INCREASING CONCENTRATIONS OF ZINC SULFATE.

Solution No.	$ZnSO_4$ added molar.	Conc. of free ions.[a]	Sp. gr.	Capillary ascent, cm.	Surface tension.
Water	......	......	1.000	9.60	741×10^{-5}
1% Gel.	......	......	0.9936	8.20	629×10^{-5}
2	0.005	0.0035	0.9946	8.30	631×10^{-5}
3	0.01	0.0063	0.9950	8.20	629×10^{-5}
4	0.025	0.0142	0.9966	8.20	630×10^{-5}
5	0.05	0.0234	1.0021	8.15	630×10^{-5}
6	0.075	0.0326	1.0058	8.15	632×10^{-5}
7	0.10	0.0397	1.0103	8.10	631×10^{-5}
8	0.25	0.0803	1.0304	7.85	629×10^{-5}
9	0.50	0.141	1.0723	7.60	629×10^{-5}
10	0.75	0.185	1.1042	6.30	630×10^{-5}
11	1.00	0.229	coagulated	....	......

[a] *Loc. cit.*

The conclusions from this series of determinations are that the addition of increasing quantities of zinc sulfate to 1% gelatin solutions is not accompanied by any great changes in the surface tensions of the original pure gelatin solution.

The Viscosity or Internal Friction of a Solution of an Emulsoid as Influenced by Increasing Concentrations of Electrolyte.

Viscosity measurements of colloidal solutions were hitherto used mostly for the purpose of comparing different qualities and different sols, yet they seem also to indicate changes in such physical properties which are the result of changes in the internal structure of the dispersed component of the system. The Faraday Society, in 1913, called a meeting for the discussion of the theme "The Viscosity of Colloids."[2] A large part of the discussions at this meeting were on 2 formulas which should represent the viscosity of suspensoids and emulsoids, respectively. These formulas, the Einstein-Hatschek formula for a suspension of rigid spheres in any liquid in terms of the viscosity of the pure liquid, and a second formula deduced by Hatschek for the variation in the viscosity of the emulsoids, differ in that in the latter, there is taken into consideration the fact that in emulsoids the dispersed phase consists of a deformable aggregate formed by the dispersed substance in association with a large and varying proportion of the dispersion medium. This formula, which has received

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[1] *Biochem. Z.*, 11, 311 (1908), and *Diss.*, Zürich, 1907.

[2] *Trans. Faraday Soc.*, 9, 34 (1913).

a considerable amount of experimental verification expresses that, if the viscosity of the system increased, the ratio of the total volume to the volume of the dispersed phase becomes larger; hence an increase in the association of the dispersed phase with the dispersion medium, generally called swelling, is indicated by an increase in the viscosity.

The influence of electrolyte addition to gelatin solutions were studied and demonstrated in a set of curves by P. von. Schroeder.[1] His curves show that the sulfates in general cause an increase in the viscosity, but that the chlorides and nitrates of the alkali metals decrease the viscosity of a gelatin solution. The addition of sulfates, however, were carried only to 0.5 *N* concentration and the viscosity determinations were made one hour after the mixing of the solutions.

In the series of solution upon which the experiments herein reported are made, the concentration of the salt added was increased to normal concentration. Also the determinations of the viscosities were made after different intervals of time and these differences in the procedure gave interesting results that were not brought out by Schroeder.

For the determination of the viscosity of the series of gelatin solutions with increasing additions of zinc sulfate a viscosimeter as described by Ostwald[2] was employed. The temperature of the bath in the thermostat was, as in all other cases, very near 25°. The time of outflow and the relative viscosity, taking the viscosity of pure water at 25° as unity, are given in Table V. These results are also plotted in Fig. 1, Curve 5, which shows that the viscosity and consequently the degree of hydration are decreased when the additions of zinc sulfate approach the point where precipitation begins, *i. e.*, at concentrations higher than 0.5 *N*. The plot of the data obtained, after different lengths of time of standing of the solutions after mixing, brings out the fact that the shape of the curve changes consid-

TABLE V.—CHANGES OF VISCOSITY OF 1% GELATIN SOLUTIONS WITH INCREASING CONCENTRATIONS OF ZINC SULFATE.

Solution No.	$ZnSO_4$ added molar.	Conc. of free ions.[a]	Shortly after mixing.	Standing 24 hours.	Standing 48 hours.	Standing 96 hours.
1% Gel	.....	......	2.38	2.44	2.52	2.46
2	0.005	0.0035	2.39	....	2.80	2.78
3	0.01	0.0063	2.41	2.70	3.07	2.95
4	0.025	0.0142	2.43	2.90	3.50	3.40
5	0.05	0.0234	2.48	3.16	3.77	3.68
6	0.075	0.0326	2.50	3.30	3.86	3.80
7	0.10	0.0397	2.53	3.37	4.00	3.95
8	0.25	0.0803	2.60	3.55	4.20	4.12
9	0.50	0.141	2.75	3.45	4.10	4.10
10	0.75	0.185	3.00	3.25	3.77	3.68

[a] *Loc. cit.*

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[1] *Z. physik. Chem.*, 45, 75 (1903).

[2] "Phys. Chem. Mess.," p. 232, 3rd Ed.

erably with the time. Thus from an upward bent curve obtained immediately after the mixing of the solutions, this curve changes to a downward-bending curve upon standing for 24 and 48 hours. There is also a considerable increase in the viscosity of the various solutions except in those which have the larger additions of the zinc sulfate. The results obtained 96 hours after the mixing of the solutions are practically identical with the 48-hours results.

These facts plainly indicate that during that time of standing there was going on a readjustment of the equilibrium of hydration or swelling of the gelatin particles in the solutions. This fact is also made more probable by the increasing clarification of the solutions upon standing in the center region of the series. These differences in clearness and turbidity of the solutions were hardly visible immediately after the mixing of the solutions but were most distinct after about 48 hours standing.

The results revealed by viscosity determinations show that there is a maximum of hydration or swelling of the gelatin particles in the region of the series corresponding to the addition of about 0.28 molar zinc sulfate to 1% gelatin solution.

The Swelling of Gelatin as Influenced by Increasing Concentrations of Electrolyte.

Closely following the viscosity measurements should be cited experiments which show how much dry pieces of gelatin swell when submerged in solutions of zinc sulfate in concentrations as used throughout this investigation. If viscosity measurements indicate the extent of swelling of the gelatin particles in the solutions, in other words, if the assumptions upon which the 2 viscosity formulas are based are correct, then we should expect the experiments on swelling to give results that are similar to those obtained by viscosity measurements.

The relative amounts of water adsorbed by dry pieces of gelatin when placed for identical lengths of time[1] into zinc sulfate solutions were determined by cutting from one sheet of gelatin equal pieces and making their weights as nearly equal as possible; these sheets were placed into the previously prepared solutions, which were kept in the thermostat until their temperature was 25°. After remaining in these solutions for exactly 10 minutes the pieces of gelatin were removed, blotted between hard pieces of filter paper and weighed. The increases in weight obtained are recorded in Table VI and the results are plotted in Fig. I, Curve 6, as usual against the concentrations of the solutions into which the gelatin foils were placed.

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[1] The correct length of time to produce the full amount of swelling was determined by experiment, so that the results given are not proportional to swelling velocities but to the maximum extent of swelling in the solutions.

TABLE VI.—WEIGHT OF WATER ADSORBED BY PIECES OF DRY GELATIN PLACED INTO SOLUTIONS OF ZINC SULFATE OF INCREASING CONCENTRATIONS.

Solution No.	$ZnSO_4$ added molar.	Conc. of free ions.[a]	Increase in weight. G.
Water	.....	......	0.346
2	0.005	0.0035	0.350
3	0.01	po.0063	0.362
4	0.025	0.0142	0.388
5	0.05	0.0234	0.411
6	0.075	0.0326	0.425
7	0.10	0.0397	0.438
8	0.25	0.0803	0.443
9	0.50	0.141	0.400
10	0.75	0.185	0.331
11	1.00	0.229	0.254

[a] *Loc. cit.*

The curve obtained is strikingly similar to the curve obtained by viscosity measurements. The last point corresponding to molar concentration of zinc sulfate shows that there was less water adsorbed from this solution than from the pure solvent without the addition of zinc sulfate. From this fact it can be inferred that the precipitation of gelatin from its solution by strong solutions of salts, especially of polyvalent salts, is due to dehydration of the gelatin particles, osmotic withdrawal of solvent from the gelatin particles beyond the point to which they normally hydrate in the pure solvent.

Summary of Conclusions from the Experimental Work.

The arrangement of the curves on page 2148 shows the results of the various experimental series and the various changes taking place when increasing concentrations of electrolyte are added to uniform solutions of gelatin. Considering the sign of the electrical charge of the colloidal particles, these curves can be divided into 3 vertical columns. A vertical line at concentration 0.28 of the electrolyte added indicates the condition when the colloidal particles are neutral and possess no charge. To the left of this line, when smaller concentrations of electrolyte were added, the colloidal particles are positively charged; to the right of the line, when larger than 0.28 concentration are added, the colloidal particles are negatively charged.

A—In the zone corresponding to small additions of electrolyte.

(1) The migration velocity of the anions is zero and the velocity of the cations is unity, so that in electrolysis the cations alone seem to carry the current across the electrolyte.

(2) The anions alone are adsorbed, and only near the point where the colloid is neutral, are a small quantity of cations adsorbed by the colloid.

(3) The colloidal particles migrate to the negative pole, which indicates that they are positively charged.

(4) The viscosity or internal friction increases as the charge of the particles approaches the zero point.

(5) The rate of swelling of gelatin increases as the concentration of electrolyte approaches 0.28 molar.

B—In the zone when the concentration of electrolyte added is 0.28 molar.

(1) The migration velocity of the anions is zero and that of the cations is exactly unity: The electrolytic deposit on the cathode is smooth and pure.

(2) The anions and the cations are being adsorbed by the colloid in proportion to their mobilities; as the anions generally migrate faster than the cations there is adsorption of a larger quantity of anions than cations.

(3) The velocity of motion of the colloidal particles in the electrostatic field is zero.

(4) The viscosity of internal friction is a maximum.

(5) The rate of swelling of gelatin is a maximum.

C—In the zone when larger additions of electrolyte are made.

(1) The migration velocity of the anions is increased as the electrolyte additions are increased and the velocity of the cations is decreased in the same proportion.

(2) The adsorption of positive and negative ions continues until the particles assume a negative charge when the cations are then being adsorbed in larger proportions.

(3) The particles migrate to the anode hence are negatively charged.

(4) The viscosity of the solutions gradually decreases as the charge of the particles increases.

(5) The rate of swelling of gelatin decreases as the concentration of the electrolyte added increases. At molar concentration of zinc sulfate gelatin is precipitated.

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THE SALT ERROR OF CRESOL RED.[1]

By Roger C. Wells.

Received May 25, 1920.

In the course of a study of the water of Chesapeake Bay now being made by the U. S. Geological Survey in coöperation with the U. S. Bureau of Fisheries, it was desired to determine the hydrogen ion concentration of the water taken directly from the bay at various points, and for this purpose it was decided to use the colorimetric method involving comparison with standard tubes. As the salinity of the water of the bay is considerably lower than that of sea water it appeared necessary to make new determinations of the salt error of the indicator, cresol red, for the

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[1] Published by permission of the Director, United States Geological Survey.

salinities in question and at values ranging around 7 8 for P_{H}. Similar studies have previously been made for several indicators.[1] As is well known, the presence of much salt affects the color of most indicators to a certain extent, so that in making comparisons allowance should be made for the amounts of salt in the standard and the unknown. The results obtained in the present study show that with the buffer mixtures used—boric acid and sodium borate—there is a considerable difference in the P_{H} values for mixtures having the same color in the presence and absence of salts such as sodium chloride, this difference depending on the concentration of salt and also slightly on the concentration of buffer.

A short description of apparatus and methods will first be given.

Solutions.—Cresol red, or *o*-cresol-sulfone-phthalein, is one of the indicators recommended by Lubs and Clark[2] for the range $P_{\mathrm{H}}{}^{+} = 6.50$ to 8.50. The material used was obtained from Hynson, Westcott & Dunning, Baltimore. It was made up one part to a thousand of 50% alcohol.

The buffer solutions of boric acid and borax were made up 15 g. to a liter and led to burets protected by soda-lime tubes. No precautions were taken to purify these substances, except to filter the solutions, as it was considered better to determine the P_{H} value of certain mixtures than to rely on solutions of definite content.

Practically all of the experiments on the salt error were made with sea-salts which were added in the form of a concentrated sea water containing 107.3 g. per liter. It was later found, however, that sodium chloride gave practically the same results, weight for weight.

Potassium chloride solution for the 0.1 *N* calomel electrode was saturated with calomel by shaking it in the thermostat at 25°.

Apparatus.—The indicator solution was taken in 0.30 cc. portions and made up to a volume of 30 cc. for each experiment. It was measured in the graduated 2 cc. buret shown in Fig. 1.

The calomel electrodes were made up with paste prepared by Hulett's method. Three electrodes gave identical values after a week's standing.

The hydrogen electrode was mounted in a Clark cell[3] obtained from A. H. Thomas & Co. This cell could be shaken as long as desired by means of a motor and an eccentric rotating support constructed in the laboratory. The various cells were kept in a large double-chambered air thermostat fitted with observa-

Fig. 1. Graduated 2 cc. buret.

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[1] Prideaux, "The Theory and Use of Indicators," London, 1917, p. 211. See also McClendon, "The Standardization of a New Colorimetric Method for the Determination of the Hydrogen Ion Concentration of Sea-water," *J. Biol. Chem.*, 30, 265 (1917).

[2] *J. Washington Acad. Sci.*, 5, 609 (1915).

[3] *J. Biol. Chem.*, 23, 475 (1915).

tion windows, which ran continuously at 25°, the air being made to circulate continuously from the inner to the outer chamber by means of a small Sirocco fan. Hydrogen, made from zinc and hydrochloric acid, was passed over a hot tungsten filament and through a tower washed with dil. caustic soda solution.

The cadmium cell was compared with one at the Bureau of Standards. Two Leeds and Northrup resistance boxes were used as potentiometer by maintaining a gradient of one millivolt per ohm through 1500.0 ohms by means of an auxiliary resistance box and storage battery. The balance was obtained with a sensitive galvanometer which was read by means of a telescope and scale.

Procedure.—Each solution investigated was first brought as nearly as possible to the same color by comparison with one that was not changed throughout the course of the experiments. This was done by altering the proportions of boric acid and borax. The solutions were eventually made up to 30 cc. in small Erlenmeyer flasks by adding boric acid and borax solutions, and water, keeping the flasks stoppered as much as possible. When the matching was completed a portion of each solution was transferred to the hydrogen-electrode cell, which had first been filled with hydrogen and well rinsed with the solution. After shaking for 15 minutes, the gas was displaced by a stream of fresh hydrogen for 2 minutes, and then the shaking continued 5 minutes longer. Fresh contacts with 4.1 *N* potassium chloride solution were then made in wide tubes with the solutions in the 2 half-cells and the e. m. f. read immediately. The e. m. f. usually rose slightly on standing but the first readings were used.

From the e. m. f. the hydrogen ion concentration was calculated by the equation

$$P_{\mathrm{H}} = -\log[\mathrm{H}^+] = \frac{E - 0.3369}{0.0591}.$$

E represents the e. m. f. observed corrected to represent dry hydrogen at 25° and 760 mm. pressure. This correction, however, ranged only from +0.3 to +0.7 millivolt, as follows:

Pressure of H_2.	Correction.
750	+0.2
740	+0.4
730	+0.6
720	+0.8

Discussion of Results.—The results are shown in Table I and Fig. 2. Expts. 1*c* to 3*b*, inclusive, were made with only buffer present. They show that as the quantity of buffer is increased the solution becomes slightly more acid. The effect of salt is similar, but a given weight of salt, or sea salts, produces a much more acid solution than the same weight of buffer. All of the solutions represent the same color. In other words, the color of cresol red cannot be ascribed entirely to the hydrogen ion concentration, although that is the principal factor.

TABLE I.

Solutions Made up to 30 cc. to have same color with cresol red. P_H from e. m. f. Measurements with hydrogen and 0.1 *N* calomel electrodes at 25° C.

Expt.	Boric acid solution. Cc.	Borax solution. Cc.	Salt solution. Cc.	Buffer. g/l.	Salt. g/l.	E. m. f. of cell.	P_H.
1*c*[a]	0.18	0.08	None	0.13	None	0.8159	8.10
1*d*	0.32	0.13	None	0.23	None	0.8276	8.30
1*e*	0.43	0.20	None	0.32	None	0.8241	8.24
1*ea*[a]	0.50	0.20	None	0.35	None	0.8094	7.99
1*f*	0.88	0.30	None	0.59	None	0.8243	8.25
2	1.35	0.55	None	0.95	None	0.8237	8.24
2*a*	1.80	0.63	None	1.21	None	0.8232	8.23
3	3.02	1.20	None	2.11	None	0.8237	8.24
3*a*	6.00	2.32	None	4.17	None	0.8207	8.18
3*b*	19.90	12.80	None	16.30	None	0.8152	8.09
4	0.57	0.20	0.10	0.28	0.36	0.8161	8.11
4*a*	0.50	0.18	0.20	0.34	0.72	0.8119	8.04
4*b*	1.70	0.70	0.10	1.20	0.36	0.8194	8.16
5	1.51	0.51	0.20	1.01	0.71	0.8169	8.12
6*a*	1.20	0.40	0.40	0.80	1.43	0.8146	8.08
8	0.54	0.21	0.41	0.38	1.47	0.8113	8.03
8*a*	0.62	0.20	0.56	0.41	1.98	0.8087	7.99
9	0.55	0.18	1.12	0.36	4.00	0.8060	7.94
10	1.70	0.62	1.68	1.19	6.00	0.8065	7.94
10*b*	1.10	0.30	2.00	0.70	7.18	0.8048	7.92
11	0.48	0.18	3.30	0.33	11.8	0.8019	7.87
12	6.50	0.20	5.03	0.35	18.0	0.8003	7.84
13	10.13	4.87	7.83	7.50	28.0	0.8007	7.85
18	0.55	0.21	7.83	0.38	28.0	0.7980	7.80
19	1.04	0.30	9.23	0.67	33.0	0.7985	7.81
20	1.04	0.30	11.40	0.67	40.8	0.7988	7.81
21	1.60	0.52	11.46	1.06	41.0	0.7964	7.78
22	0.48	0.28	20.98	0.38	75.0	0.7933	7.72
23	0.76	0.13	28.81	0.45	103.2	0.7897	7.67
24[b]	10.00	5.00	5.03	7.50	18.0	0.8059	7.94
25	0.47	0.20	5.03	0.34	18.0	0.8018	7.88
26	15.00	9.92	5.03	12.5	18.0	0.8063	7.94
27	10.00	5.30	7.54	7.67	27.0	0.8036	7.89
28[c]	10.13	4.87	7.82	7.50	28.0	0.8007	7.85

[a] Probably affected by CO_2 and not shown in Fig. 2.

[b] New standard color.

[c] Last standard color.

It is somewhat difficult to determine the salt effect at low concentrations on account of the necessity of having some buffer present to maintain a stable P_H value. But the total effect is not additive, as the presence of buffer with salt nullifies the effect of the salt to a certain extent. Several experiments (*e. g.*, Nos. 4, 4*a*, 4*b*, 5, 25, 26) were made to determine what allowance should be made for the action of the buffer on the salt but the effect appeared to be only about 0.07 in the P_H value for the extreme cases, so that no corrections seemed necessary when, as in most of the experiments, the weight of salt used was greatly in excess of the weight of buffer.

Fig. 2 is based on the weights of salt without any correction for the weight of buffer, for all experiments in which the weight of buffer was small in comparison with the weight of salt. The P_H values are plotted against $\log_2 S$, S being the salinity in g. per liter of sea salts (or buffer). The logarithm to base 2 was chosen in order to give the various concentrations more nearly equal importance in the figure.

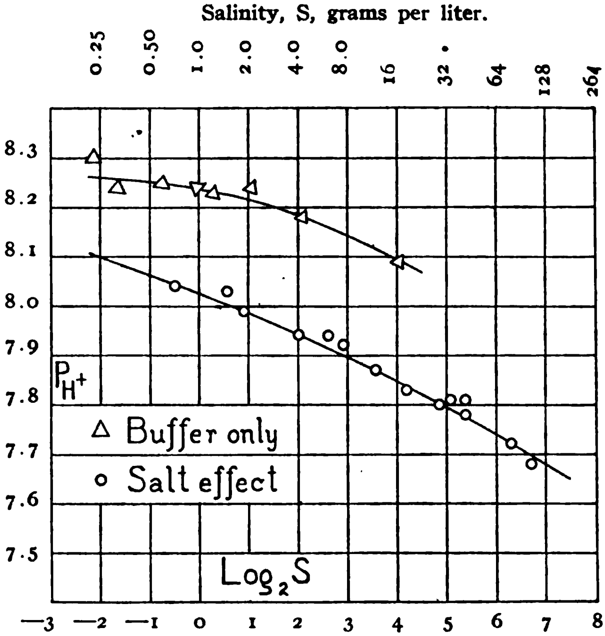

Fig. 2.—Salt effect at constant color.

Several e. m. f. determinations were made using half-saturated potassium chloride as connecting solution, in order to extrapolate according to Bjerrum's method, but the differences found between those obtained with saturated potassium chloride were too small to be worth considering.

Applications.—The principal object of the study was to prepare tubes of standard P_H value. When small amounts of buffer are used the solutions are quickly affected by carbon dioxide of the air or by glass of the containing vessels. It is therefore advisable to use a large amount of buffer and an insoluble glass. Ampules of Pyrex glass that can be closed by sealing have been found serviceable. For the work in hand it was decided to have the standard tubes require no correction when compared with unknown solutions having a salinity of 18 g. per liter of salt and very little buffer, but as the standard tubes were to contain 0.225 g. of buffer in 30 cc. or 7.5 g. per liter the quantity of salt in each standard tube was increased to 1.26 g in order to counterbalance the increased amount of buffer, this being the quantity of salt indicated by the curve of Fig. 2 to make a lowering of 0.07 in the P_H value over that for 18 g. of salt per liter with very little buffer present. Each tube was therefore made up to 30 cc. with water, after adding 0.3 cc. of indicator solution, 15 cc. of buffer solutions, and 1.26 g. of sodium chloride.[1] The correction when such tubes are compared with waters having other salinities are given in Table II.

TABLE II.

Corrections in Using Standard Color Tubes Containing 0.3 cc. of Cresol Red, 0.225 g. of Buffer and 1.26 g. of Salt in 30 cc.

Salinity of unknown g. per liter.	Correction to P_H marked on standard.
0.2	+0.27
0.5	+0.22
1.0	+0.19
2.0	+0.14
5.0	+0.09
10.0	+0.04
15.0	+0.01
18.0	0
20	—0.01
25	—0.03
30	—0.05
35	—0.06
40	—0.07
100	—0.15
200	—0.21

In making comparisons 0.3 cc. of indicator is placed in a tube similar to those containing the standards and made up to the 30 cc. mark with the water to be tested. Different lots of indicators may vary so much that it is best to make all comparisons with the same indicator solution as used in the standard tubes. When the matching of the standard and unknown is completed the value marked on the standard is recorded, to be corrected eventually for the salinity of the sample under scrutiny.

Before making up the standard tubes a few P_H determinations are made with various buffer mixtures, using connecting solutions with both standard and half-saturated potassium chloride in order to extrapolate if necessary. A curve is then constructed so that a mixture of any desired P_H value within range of the buffer solutions can quickly be pre-

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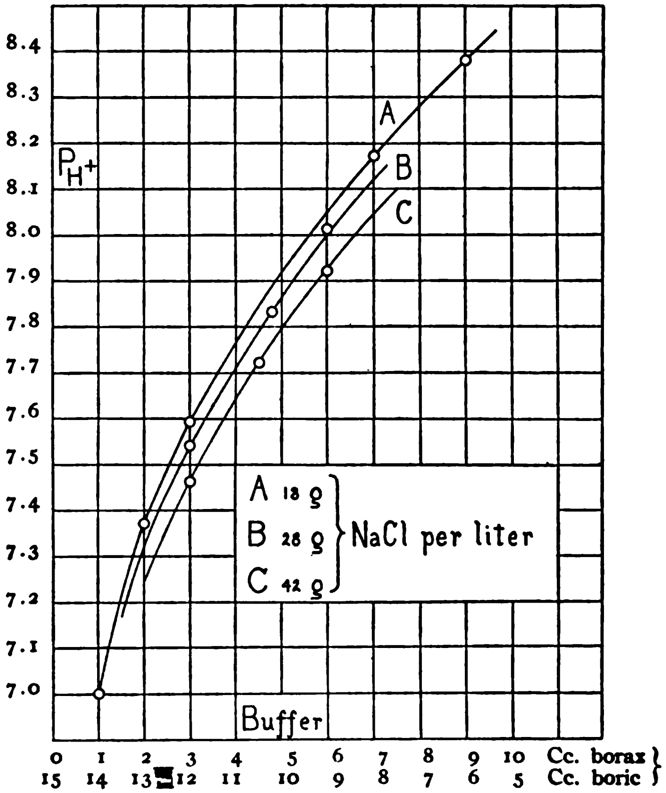
[1] If the action of the buffer here is to reduce the ionization of the sodium chloride it seems that the action should be due more to the borax than to the boric acid, but over the small range of P_H investigated this was not definitely proved.

pared. Some figures obtained in standardizing buffer mixtures are given in Table III, which also shows the variations caused by different amounts of salt while the quantity of buffer remains constant. The results are reproduced in Fig. 3.

TABLE III.—SALT EFFECT WITH TOTAL BUFFER CONSTANT.

Expt.	Water. Cc.	Boric acid. Cc.	Borax. Cc.	Sodium chloride.[a] Cc.	Indicator. Cc.	P_H.
32	12.64	14.00	1.00	2.06	0.30	7.00
33	12.64	13.00	2.00	2.06	0.30	7.37
31	12.64	12.00	3.00	2.06	0.30	7.59
30	12.64	8.00	7.00	2.06	0.30	8.17
34	12.64	6.00	9.00	2.06	0.30	8.38
36	11.51	12.00	3.00	3.19	0.30	7.54
43	11.51	10.20	4.80	3.19	0.30	7.83
35	11.51	9.00	6.00	3.19	0.30	8.01
40	9.90	12.00	3.00	4.80	0.30	7.46
41	9.90	10.50	4.50	4.80	0.30	7.72
42	9.90	9.00	6.00	4.80	0.30	7.92

[a] Containing 0.2628 g. per cc.



made up to 30 cc. together with indicator and salt.

Fig. 3.—Salt effect with buffer constant.

It is possible that the salt effect may be used in certain cases to produce definite hydrogen ion concentrations with certain buffers where the buffer mixtures alone do not cover the P_H value desired.

Remarks.—A few difficulties connected with the work here described may be mentioned. When small quantities of buffer were used the colors were often dimmed by the action of carbon dioxide from the air before the e. m. f. could be measured. Moreover, in the course of the first experiments, extending over about 3 weeks, a slow drift toward the acid side was detected about the third week in the solution serving as the constant standard color for comparison, so that the results were not as concordant as they might have been and were therefore discarded. Whether this was caused by fading of the indicator in the solution serving as standard color, by evaporation of the stock solution of indicator, or by changes in the stock buffer solutions could not be ascertained. It may have been due to all 3 causes. Fresh color standards made up like the first were slightly redder and gave slightly higher P_H values. By starting with a standard having a given P_H value, however, the curves shown in Fig. 2 were constructed before any changes could be detected. Under any circumstances it is probably advisable to keep the standard tubes in the dark when not in use in order to avoid the bleaching action of light. It is not certain that the indicator suffers no change over long intervals but it certainly does not fade out entirely.

It may be noted that to reproduce definite P_H values the dilution of a given borate buffer mixture must be controlled as well as the proportions of boric acid and borax, and the amount of salt.

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THE REACTION BETWEEN CHLORINE AND AMMONIA, II.[1]

BY WILLIAM A. NOYES AND A. B. HAW.

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Some years ago one of us, working with A. B. Lyon,[2] showed that a considerable amount of nitrogen trichloride may be formed by the action of chlorine on a dilute solution of ammonia. An equation representing a somewhat complicated reaction was given to account for the result obtained and in the discussion it was suggested that in this reaction, and probably in others which are not usually considered as ionic, molecules separate into positive and negative parts as they react.

W. C. Bray and C. T. Dowell[3] have pointed out that the complicated,

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[1] Abstract of a thesis submitted to the University of Illinois in partial fulfilment of the requirements for the degree of Master of Science.

[2] Noyes and Lyon, THIS JOURNAL, 23, 460 (1901).

[3] Bray and Dowell, *ibid.*, 39, 907 (1917).

ninth order reaction which was proposed is highly improbable and demonstrated that the nitrogen and nitrogen trichloride formed in Lyon's experiments were formed in independent reactions. The discovery by Raschig[1] that chloroamine, NH_2Cl, is formed by the action of a hypochlorite on ammonia, taken with the experiments described in this and the following papers, render it almost certain that nitrogen trichloride results from a series of reactions analogous, in part, at least, to those which give carbon tetrachloride from methane.

The idea that there are positive and negative parts, either actually or potentially present in molecules, was already somewhat current in the minds of chemists[2] and after it had been given, quite independently, an electronic interpretation by J. J. Thompson,[3] it has been an important factor in many discussions which have appeared in our literature. The questions involved are so fundamental that it seems desirable to accumulate new experimental evidence with regard to the formation and decomposition of nitrogen trichloride, a compound in which the conduct of the chlorine atoms is abnormal and such as to indicate that the atoms are positive in character.

So far as we are aware, all observers except Bray and Dowell and ourselves have prepared nitrogen trichloride by the use of ammonium salts. This might lead to the conclusion that in the experiments described in our first paper chlorine acted upon the ammonium hydroxide in the solution and not upon ammonia. We have, accordingly, studied the interaction of anhydrous ammonia and anhydrous chlorine at low temperatures. We have tried the experiment under the following conditions: (1) in presence of carbon tetrachloride (11 experiments); (2) in presence of chloroform (3 experiments); (3) in presence of pentane (2 experiments); (4) without any solvent (3 experiments).

The chlorine and ammonia were weighed in the liquid state in small sealed bulbs. The chlorine was generated by dropping conc. hydrochloric acid on potassium permanganate. It was passed through a wash bottle containing water and through 2 wash-bottles containing conc. sulfuric acid. It was then condensed in a bulb surrounded with carbon dioxide snow and alcohol. The tube connected with the small bulb in which the chlorine was to be weighed was drawn out to a long, fine capillary which was bent over in such a manner that the end could be dipped in the liquid chlorine, while the small bulb was cooled with carbon dioxide snow in alcohol. After a little of the chlorine had been drawn over and condensed, the bulb was removed from the cooling mixture and the

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[1] Raschig, *Chem. Ztg.*, 31, 926 (1907).

[2] Van't Hoff, *Z. physik. Chem.*, 16, 411 (1895); Stieglitz, THIS JOURNAL, 23, 796 (1901).

[3] *Phil. Mag.*, 7, 237 (1904).

chlorine in it was allowed to evaporate and expel the air. By dipping the bulb into the cooling mixture a second time it was filled nearly full with liquid chlorine. The capillary tube was then sealed, and the bulb allowed to come to ordinary temperature for weighing.

Ammonia was prepared by warming a strong aqueous solution of the gas. It was dried by passing it through a U-tube surrounded with ice, through a tube containing soda-lime and another containing solid caustic potash. It was condensed and transferred to a bulb for weighing in the same manner as described for the chlorine.

Three different methods of bringing the chlorine and ammonia together were used. In the first experiments (1–6) a bulb having a capacity of 100 cc. and bearing a 3-way stopcock was filled about $^1/_5$ full with carbon tetrachloride. After evacuating till the liquid boiled and the air was expelled the bulb was cooled with carbon dioxide and alcohol and one of the bulbs containing a weighed amount of chlorine and which had been cooled to a low temperature was attached to the tube from one arm of the 3-way stopcock and the chlorine was allowed to evaporate and condense in the carbon tetrachloride. The weight of chlorine used was determined by weighing the sealed bulb before it was cooled and opened, and weighing it again after the evaporation of the chlorine. After removing the bulb which had contained the chlorine, a bulb containing liquid ammonia was put in its place and the ammonia allowed to evaporate into the bulb containing the carbon tetrachloride and chlorine. Since considerable nitrogen is evolved from the interaction of the chlorine and ammonia, it was not always possible to introduce all of the ammonia, and losses sometimes occurred, causing unsatisfactory results (Expts. 2 and 6 in the table).

After the gases had been introduced, the bulb was connected with an exhausted bulb cooled with carbon dioxide and alcohol and the carbon tetrachloride and nitrogen trichloride were distilled over and condensed, the original bulb containing the ammonium chloride which was formed being finally heated to 70°. The amount of nitrogen trichloride formed was determined by shaking the distillate with sodium sulfite and determining the amount of ammonia formed by the reduction of the trichloride.[1] The amount of ammonium chloride formed was found in some cases by weighing the reaction bulb after the removal of the carbon tetrachloride and in other cases by dissolving the ammonium chloride in water and determining the ammonia and chlorine in the solution.

The second form of apparatus is shown in Fig. 1. The chlorine and ammonia were weighed in small bulbs, as before; these were attached to the stopcocks A and B, and, while they were still cooled with carbon dioxide snow and alcohol, the apparatus was filled with oxygen, the U-tube

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[1] Dowell and Bray, THIS JOURNAL, 39, 898 (1917).

C was cooled with carbon dioxide and alcohol and a strong solution of sodium sulfite was placed in D. In one experiment with this apparatus (No. 11) no solvent was used, but glass beads were placed in the U-tube C. In other experiments chloroform, carbon tetrachloride or pentane were used as solvents. The chlorine was allowed to evaporate and condense in the U-tube first, and then the ammonia. The nitrogen formed in the reaction was carried out by the current of oxygen and was determined after absorbing the oxygen in an alkaline solution of pyrogallol.

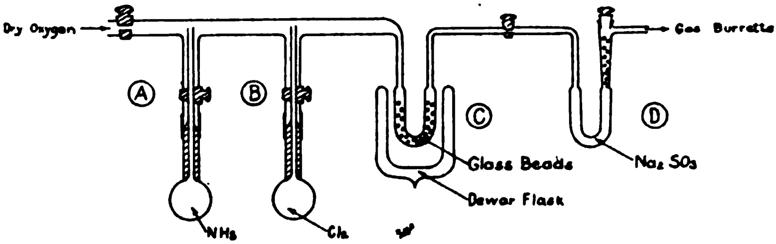

Fig. 1.

After the reaction had taken place and the amount of nitrogen formed had been determined, the contents of the U-tube in C was transferred to a suitable apparatus and distilled under diminished pressure, essentially as in the first method. A part of the nitrogen trichloride was found in this distillate and a part in sodium sulfite solution from D. The ammonium chloride formed was also determined. Expts. 7–12 were carried out in this manner.

In the third series of experiments (13–19) a bomb tube about 40 cm. long and 2 cm. in diameter was used. This was drawn out to a capillary and connected to a stopcock as shown in Fig. 2. The tube was exhausted to 10 mm. pressure or less and placed in a long Dewar tube and surrounded with solid carbon dioxide and alcohol. A weighed ammonia bulb was connected with A and the contents allowed to distil into the tube. A bulb containing carbon tetrachloride was then connected at A and the liquid allowed to distil into the tube, which was held at an angle of 15°. In this way, the tetrachloride was frozen along the side of the tube with the ammonia disseminated through it. The chlorine bulb was then attached and the chlorine was allowed to evaporate into the tube. The tube was then sealed at B, and placed in a horizontal position to warm up overnight.

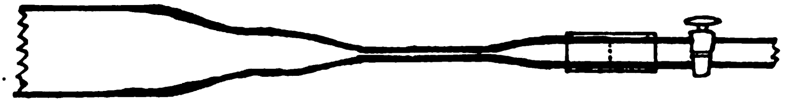

Fig. 2.

Some of the earlier experiments of this series were carried out with the tube in a perpendicular position, the carbon tetrachloride being frozen on top of the ammonia. It was found with this arrangement that the gases had not thoroughly mixed, the ammonia not diffusing up through the carbon tetrachloride. On mixing the contents of the tube in the morning a further reaction took place with evolution of considerable heat.

In the morning, in those experiments (14 and 15) in which a rough estimate of the amount of nitrogen was made, a rubber tube connected with a gas buret set at 50 cc. was wired to the capillary tip and the tip was broken within the rubber tube, while the tube was immersed in ice-water. By taking account of the known capacity of the tube, of the rise or fall of the water in the buret and of the vapor pressure of carbon tetrachloride at 0°, the amount of nitrogen was calculated, approximately. The determination of nitrogen was only a rough approximation in either series.

The tube was then cut off and the carbon tetrachloride was filtered through a Gooch crucible into a solution of sodium sulfite. The various determinations were made essentially as in the other experiments.

The following table, for ease of comparison, the quantities involved in the experiments have been recalculated in their relation to 4 mols of ammonia. The actual quantities used were from 0.66 to 3.67 g. of chlorine and from 0.17 to 0.94 g. of ammonia.

TABLE I.

Results Calculated to 4 Mols of Ammonia.

Expt.	Form of apparatus.	Solvent.	Atoms Cl.	Mols NH_4Cl.	Mols NCl_3.	Atoms N.
1............	1	CCl_4	6.00	2.97	0.338	1.27
2............	1	CCl_4	6.08	1.11	0.137	...
3............	1	CCl_4	3.71	4.06	0.141	...
4............	1	CCl_4	6.14	3.19	0.134	...
5............	1	CCl_4	8.61	3.28	...	...
6............	1	$CHCl_3$	9.12	2.13	0.294	...
7............	2	$CHCl_3$	7.04	2.97	0.406	0.603
8............	2	$CHCl_3$	6.10	2.96	0.132	0.946
9............	2	Pentane	8.00	2.48	0.156	1.016
10............	2	Pentane	5.99	3.04	0.246	0.837
11............	2	None	6.51	2.42	0.240	0.925
12............	2	CCl_4	6.06	2.99	0.333	0.911
13............	3	CCl_4	5.36	2.99	0.077	...
14............	3	CCl_4	6.59	2.98	0.070	0.826
15............	3	CCl_4	5.23	2.98	0.004	0.901
16............	3	None	4.88	2.99	0.013	...
17............	3	None	6.36	2.98	0.034	...
18............	3	CCl_4	10.54	2.92	0.165	...
19............	3	CCl_4	3.28	2.99	0.075	...

The temperature was —90° in all experiments except 8 and 9, in which it was —180°.

An examination of the table shows that the results obtained by the first method were erratic and of little value further than to show that considerable quantities of nitrogen trichloride may be formed by the direct interaction of chlorine and ammonia.

In the second series, with the exception of Expts. 9 and 11, the ratio of the mols of ammonia used to the mols of ammonium chloride formed is very closely 4 to 3. The ratios of the third series point still more closely to this value. These results indicate very clearly that the course of the reaction is expressed by the equation

$$4NH_3 + 3Cl_2 = 3NH_4Cl + NCl_3.$$

The reaction doubtless occurs in steps (see the following paper) which rapidly succeed each other, with chloroamine, NH_2Cl, and dichloroamine, $NHCl_2$, as intermediate products.

The amounts of nitrogen trichloride formed are always far below those theoretically possible, either because a large part of the trichloride formed decomposes directly into nitrogen and chlorine or because it reacts with some of the ammonia

$$NCl_3 + NH_3 = 3HCl + N_2.$$

Since the hydrochloric acid formed would combine with ammonia until the latter was exhausted, neither the decomposition of the trichloride or its interaction with ammonia would affect the ratio between the mols of ammonia and mols of ammonium chloride as given in the first equation.

The fact that the ratio of the ammonia to the ammonium chloride is very nearly independent of the amount of chlorine used shows that the action of the chlorine is almost exclusively upon the ammonia and not upon the ammonium chloride. In Expt. 18, where a large excess of chlorine was used, there is a little indication that some of the ammonium chloride is attacked, but not much weight should be attached to the single experiment. Expt. 19 gives some indication of the interaction between nitrogen trichloride and ammonia, suggested above, since the amount of nitrogen trichloride formed is much less than in the preceding experiment, where an excess of chlorine was used.

Summary.

1. Anhydrous ammonia and anhydrous chlorine react to form nitrogen trichloride and ammonium chloride.

2. A considerable part of the trichloride always decomposes into chlorine and nitrogen, either directly or by interaction between the trichloride and ammonia.

3. The ratio of the mols of chlorine used to the mols of ammonia may be varied between wide limits without affecting, appreciably, the ratio between the mols of ammonia and the mols of ammonium chloride. This ratio is 4 to 3.

4. The chlorine reacts primarily with the ammonia. It reacts only to a trifling extent, or not at all, with the solid ammonium chloride which is formed.

URBANA, ILL.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

THE REACTION BETWEEN CHLORINE AND AMMONIA. III. PROBABLE FORMATION OF TRICHLOROAMMONIUM CHLORIDE.

BY WILLIAM ALBERT NOYES.

Received July 12, 1920.

With the exception of the experiments described in the preceding paper, and those of Bray and Dowell[1] and of Noyes and Lyon,[2] nitrogen trichloride seems always to have been prepared by the action of chlorine;[3] a hypochlorite,[4] or hypochlorous acid,[5] on ammonium chloride. Even those who have used chlorine have considered that hypochlorous acid is at first formed and that this acid then reacts with the ammonium salt.[6] The results described in the preceding paper demonstrate that nitrogen trichloride may be prepared by the direct interaction of chlorine and ammonia, in the absence of water. Experiments to be described in this paper show that nitrogen trichloride reacts quantitatively with hydrochloric acid, in the absence of water, giving ammonium chloride and chlorine. Also, when hydrogen chloride is passed into a solution of nitrogen trichloride in carbon tetrachloride[7] an immediate precipitation of ammonium chloride is caused.

In the light of these results it seems clear that the decomposition of nitrogen trichloride by hydrochloric acid is *not* an hydrolysis, under the conditions just described.

The most rational explanation of the formation of nitrogen trichloride from ammonium chloride seems to be that chlorine adds itself to ammonia, which is doubtless present in small amounts from the dissociation of the ammonium chloride to ammonia and hydrochloric acid. The chloro-

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[1] Bray and Dowell, THIS JOURNAL, 39, 905 (1917).

[2] Noyes and Lyon, *ibid.*, 23, 460 (1901).

[3] Gattermann, *Ber.*, 21, 751 (1888); Hentschel, *ibid.*, 30, 1792 (1897); Chapman and Vodden, *J. Chem. Soc.*, 95, 141 (1909).

[4] Hentschel, *Ber.*, 30, 1434 (1897).

[5] Balard, *Ann. chim. phys.*, [2] 57, 258 (1894); Hentschel, *Ber.*, 30, 1792 (1897); Dowell and Bray, THIS JOURNAL, 39, 896 (1917). Balard speaks of using other ammonium salts but gives no details. He also used a solution of ammonia.

[6] Seliwanoff, *Ber.*, 27, 1012; Chapman and Vodden, *loc. cit.*

[7] This experiment was suggested by Professor Washburn in a conversation in which the author expressed the opinion that the decomposition of nitrogen trichloride by conc. hydrochloric acid is not an hydrolysis.

ammonium chloride, $NH_3Cl^+Cl^-$, formed in this manner, would dissociate easily into chloro-amine,[1] NH_2Cl, and hydrochloric acid. The chloro-amine would then add another mol of chlorine, giving dichloro-ammonium chloride, $NH_2Cl_2^+Cl^-$. A repetition of the dissociation and addition and a third dissociation would give nitrogen trichloride.

Seliwanoff, Chapman and Vodden, and others, have shown, qualitatively, that the interaction of nitrogen trichloride and hydrochloric acid gives ammonium chloride and chlorine, but they have considered the decomposition as primarily an hydrolysis of the trichloride. Seliwanoff states that the trichloride is scarcely affected by sulfuric acid, and he explains the different effect of the hydrochloric acid by saying that the hypochlorous acid formed by the hydrolysis reacts with the hydrochloric acid to give free chlorine. He fails to explain why the free chlorine does not react with the ammonium chloride in the solution to give nitrogen trichloride again. In the experiments described below, it was shown that by shaking a solution of nitrogen trichloride with conc. hydrochloric acid more than 99% of the nitrogen of the trichloride passed into the aqueous phase, as ammonium chloride. On shaking a similar solution with sulfuric acid (1 cc. = 0.6 g. of H_2SO_4) only a trace of the nitrogen was converted into an ammonium salt.

When a similar solution of nitrogen trichloride was shaken with a saturated solution of salt to which 5% by volume of conc. hydrochloric acid was added only a very small amount of the trichloride was converted to ammonium chloride.

It seems difficult to explain these results on the supposition that the decomposition is an hydrolysis.[2] They are easily explained on the basis that nitrogen trichloride is, in reality, trichloro-amine and that a mol of chlorine may separate into one positive and one negative chlorine atom. On this supposition nitrogen trichloride would add a mol of hydrogen chloride exactly as ammonia does. The resulting compound, trichloro-ammonium chloride, $NCl_3^+H^+Cl^-$, might dissociate either by loss of hydrogen chloride or by loss of one positive and one negative chlorine atom as free chlorine. The dissociation to nitrogen trichloride and hydrogen chloride would occur in the presence of dil. hydrochloric acid, or of the acid salt solution or of sulfuric acid as mentioned in the last paragraph, just as

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[1] Raschig, *Chem. Ztg.*, 31, 926 (1907).

[2] Professor Bray, who has been kind enough to read this paper, points out that the possibility of hydrolysis, as a rapid reaction, is not excluded for these cases when water is present. In the presence of water the mechanism of the reaction may be different from that of the reaction in the absence of water. In the light of the experiment described here, he does not, however, take the ground that hydrolysis is the more likely mechanism when water is present. Even in 1917 (*loc. cit.*, p. 905, footnote 2) he stated that we had no means of deciding. He further states that the new results of this paper greatly weaken the case for hydrolysis.

some organic amines form salts only in the presence of concentrated acids. In the presence of conc. hydrochloric acid, however, the tendency would be to dissociate to dichloro-amine, $NHCl_2$, and free chlorine and a repetition of this process would give ammonium chloride and chlorine as the end-products.

It seems probable that the action of hypochlorous acid on ammonium salts is similar to that of chlorine, as explained above. Hypochlorous acid would add itself to ammonia, giving chloro-ammonium hydroxide, $NH_3Cl^+OH^-$, exactly as it adds to ethylene to give ethylene chlorohydrin, $CH_2Cl.CH_2OH$. Chloro-ammonium hydroxide would, of course, dissociate to chloro-amine, NH_2Cl, and water, and repetitions of the process would give nitrogen trichloride.

Action of Chlorine on Ammonium Salts.—The experiments reported in the folllowing table were carried out, partly by shaking a solution of chlorine in carbon tetrachloride, of known concentration, with solutions of ammonium salts (Expts. 1–16) and partly by passing chlorine into a layer of carbon tetrachloride beneath a solution of an ammonium salt. The solutions were shaken from one to five minutes in most cases, equilibrium being reached rather quickly. The nitrogen and total chlorine were determined in the carbon tetrachloride solution in most cases, by reduction with sodium sulfite, as described by Bray and Dowell.[1] In some of the later experiments, however, the nitrogen of the chlorides of nitrogen was determined by shaking the carbon tetrachloride solution with about an equal volume of conc. hydrochloric acid. This method gives a practically quantitative conversion of the chlorides of nitrogen to ammonium chloride with less danger of loss of nitrogen than when sodium sulfite is used. In a number of cases higher results were found with the use of hydrochloric acid than with the use of sodium sulfite. This may be particularly true when chloro-amine or dichloro-amine is present, but that has not been fully demonstrated.

In every case where the aqueous solution was examined at once after separating it from the carbon tetrachloride it was found to contain some substance which would liberate iodine from potassium iodide. The amount of iodine liberated was determined by titration with sodium thiosulfate and the results calculated on the supposition that the oxidizing compound was chloro-amine, NH_2Cl. As yet it has not been shown, however, whether the compound present was chloro-amine, dichloro-amine or nitrogen trichloride.

In the table which follows, the results are calculated on the basis of the mols of ammonium (NH_4) reacting with 6 atoms of chlorine. It gives the number of mols of each product formed, also the ratio of chlorine to nitrogen in the carbon tetrachloride solution.

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[1] *Loc. cit.*

TABLE I.

Results Calculated to 6 Atoms of Chlorine.

Expt.		Molar conc. NH_4.	Atomic conc. Cl.	Mols NH_4.	Mols NCl_3.	Mols NH_4 recovered.	Atoms N lost.	Mols NH_2Cl.	Cl:N in CCl_4 solution.
1	NH_4Cl	1.0	0.46	0.79	0.35	0.41	0.04	..	11.9
2	NH_4Cl	0.1	0.59	0.98	0.74	0.09	0.07	0.08	5.8
3	NH_4Cl	0.1	0.59	1.96	0.71	0.84	0.37	0.04	5.1
4	NH_4Cl	1.0	0.59	1.56	0.14	1.24	0.17	..	33.5
5	NH_4Cl	0.1	0.35	1.03	0.81	0.19	0.01	0.03	3.88
6	NH_4Cl	0.1	1.09	0.95	0.59	0.25	0.03	0.08	5.96
7	NH_4Cl	0.1	0.45	1.03	0.52	0.33	0.11	0.06	7.03
8	NH_4Cl	0.1	0.77	0.97	0.79	0.03	0.11	0.05	4.09
9	NH_4Cl	0.03	0.56	0.98	0.79	0.02	0.09	0.09	3.84
10	NH_4Cl	0.1	0.56	3.06	0.94	2.04	..	0.08	2.97
11	NH_4OH	0.1	0.27	1.00	0.66	0.23	0.11	0.01	3.93
12	NH_4PO_4	0.1	0.31	2.80	0.92	1.96	..	0.06	2.74
13	NH_4PO_4	0.1	0.58	2.92	0.98	1.72	0.15	0.09	2.52
14	NH_4PO_4	0.1	0.74	1.05	0.94	0.10	0.01	..	3.92
15	NH_4PO_4	0.1	0.73	0.93	0.70	0.05	0.17	..	6.00
16	$(NH_4)_2SO_4$	2.0	4.0	3.0	0.94	1.90	0.15	0.01	3.06
17	$(NH_4)_2SO_4$	0.2	0.32	3.6	0.85	2.50	0.16	0.09	3.13
18	NH_4Cl	2.0	1.60	3.3	0.78	2.18	0.24	0.10	3.70
19	$(NH_4)_2SO_4$	2.0	3.21	3.32	1.02	2.19	0.11	0.01	2.82
20	$(NH_4)_2SO_4$	0.1	1.61	2.86	0.90	1.73	0.05	0.18	3.06
21	$(NH_4)_2SO_4$	2.0	..	8.4	0.87	7.22	0.26	0.05	3.55
22	$(NH_4)_2SO_4$	2.0	..	8.4	0.92	7.17	0.26	0.05	3.21
23	$(NH_4)_2SO_4$	2.0	..	7.43	0.87	6.21	9.29	0.05	3.51

These results seem to justify the following conclusions.

When a normal solution of ammonium chloride is treated with 6 atoms of chlorine for one mol of ammonium, the hydrochloric acid formed becomes so concentrated as to interfere seriously with the formation of nitrogen trichloride (Expts. 1 and 4). For the theoretical reaction the hydrochloric acid would become 4 *N*.

With a 0.1 *N* solution of ammonium chloride the per cent. of nitrogen trichloride formed is much larger.

In all cases, an appreciable amount of a chloro-amine remains in the aqueous solution. In proportion to the chlorine used this is much larger in the dilute solution.

Solutions of sodium ammonium phosphate and of ammonium sulfate give a larger per cent. of nitrogen trichloride, in proportion to the chlorine used, than solutions of ammonium chloride do. This is evidently because the resulting solutions contain a lower concentration of hydrochloric acid.

In Expts. 13, 14 and 20 the ratio of nitrogen to chlorine is considerably below 3 to 1 in the carbon tetrachloride solution. Gattermann[1] and

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[1] Gattermann, *Ber.*, 21, 751 (1888).

Hentschel[1] have reported similar ratios when nitrogen trichloride is prepared by the action of chlorine on ammonium chloride. The experiments of Hentschel[2] and of Dowell and Bray[3] indicate that the conversion to the trichloride is complete when hydrochlorous acid is used. The low ratio must, of course, be due to the presence of some chloro-amine, NH_2Cl, or dichloro-amine, $NHCl_2$. The explanation of the formation of the chloro-amines and nitrogen trichloride as due to the addition of chlorine to ammonia and splitting off of hydrogen chloride in the one case and to the addition of hypochlorous acid and splitting off of water in the other agrees excellently with these results. In the 2 equilibria,

$$NH_2Cl^+Cl^- \rightleftarrows NH_2Cl + HCl,$$

and

$$NH_2Cl^+OH^- \rightleftarrows NH_2Cl + HOH,$$

it is evident that the equilibrium would be much farther toward the formation of the chloro-amine in the second case than in the first. Whether the substance present in the carbon tetrachloride solution, or in the aqueous solution, is chloro-amine, dichloro-amine, nitrogen trichloride, or a mixture, when chlorine is used, has not been determined. Experiments on this point will be undertaken later.

There is usually a considerable loss of nitrogen. The results are somewhat erratic, but, in general, the loss is greater when the ammonium salt is in excess. It also seems to be greater in the phosphate than in the ammonium chloride solutions. This is probably connected with the lower hydrogen ion concentration in the phosphate solution.

Action of Hydrogen Chloride on Nitrogen Trichloride.—The precipitation of ammonium chloride when hydrogen chloride is passed into a solution of the trichloride in carbon tetrachloride has been mentioned above.

In another experiment nitrogen trichloride was prepared by passing chlorine into a solution of ammonium sulfate contained in an inclined bulb connected with a serpentine tube at the top, which was in turn connected both with an exit for the gases and a return tube which carried the liquid pushed forward by the gas back to the bottom of the bulb. The whole was surrounded with a wooden box to protect the trichloride from the light and as a precaution in case of explosion. The chlorine was almost completely absorbed by the ammonium sulfate solution and the nitrogen trichloride collected in a globule in the lower part of the bulb. A current of air was then passed through the bulb and the mixture of air and vapor of the trichloride was passed through a wash bottle containing conc. sulfuric acid to dry it and then through a U-tube surrounded by a

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[1] Hentschel, *Ber.*, 30, 1792 (1897).

[2] Hentschel, *ibid.*, 30, 2642 (1897).

[3] This Journal, 39, 896 (1917).

freezing mixture. This method of separating pure nitrogen trichloride without the use of a solvent is much easier of manipulation and safer than the method described by Gattermann.[1]

After about 0.37 g. of the trichloride (calculated from the ammonium chloride formed by its decomposition) had collected in the U-tube, dry hydrogen chloride was passed through the tube. The chlorine liberated was passed through a small coil containing water to remove the excess of acid and into a solution of potassium iodide. There was left in the U-tube 3.01 mg. mols of solid ammonium chloride, 0.028 mg. mols of ammonium were found in the potassium iodide solution and 18.95 mg. of iodine was liberated by the chlorine, as determined by titration with sodium thiosulfate. The ratio is one mol of ammonium chloride to 6.075 atoms of free chlorine. The nitrogen trichloride had been converted quantitatively into ammonium chloride and free chlorine.

In another experiment, performed on a hot day, the product condensed in the U-tube was found to boil below 30° and the ratio between the mols of ammonium chloride and atoms of chlorine obtained by treating it with hydrogen chloride was very nearly 1 : 4. This may, possibly, indicate that the product was dichloro-amine, $NHCl_2$. This will be investigated further.

Sixteen g. of a solution of nitrogen trichloride in carbon tetrachloride gave 1.173 mg. mols of ammonium chloride on shaking once with 15 cc. of conc. hydrochloric acid. Sixteen g. of the same solution gave 1.185 mg. mols of ammonia when treated with 25 cc. of a sodium sulfite solution. In another experiment 20.2 g. of a solution of nitrogen trichloride in carbon tetrachloride gave 1.87 mg. mols of ammonium chloride when shaken with 10 cc. of conc. hydrochloric acid, while the carbon tetrachloride solution containing chlorine which was separated from the acid solution. gave only 0.004 mg. mols of ammonia by reduction with sodium sulfite. In other words, 99.8% of the original trichloride had been converted to ammonium chloride. In a number of comparative determinations, treatment of nitrogen trichloride solutions in carbon tetrachloride with conc. hydrochloric acid gave either the same amount of ammonia or a larger amount than when the same solutions were reduced with sodium sulfite.

Summary.

1. Dry hydrogen chloride converts nitrogen trichloride quantitatively to ammonium chloride. The reaction may occur either with a solution of the trichloride in carbon tetrachloride or without any solvent. This demonstrates that the decomposition is not an hydrolysis, in the absence of water, and probably not an hydrolysis in the presence of water.

2. It seems probable that the action consists primarily in the formation of trichloro-ammonium chloride, NCl_3HCl, followed by the loss of

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[1] Gattermann, *Ber.*, 21, 751 (1888).

an atom of positive chlorine combined with an atom of negative chlorine.

3. The formation of nitrogen trichloride by the action of chlorine on an ammonium salt seems to be the reverse of the reaction just described. Ammonium sulfate is much more suitable than ammonium chloride for the preparation of the trichloride.

4. Chloro-amine or dichloro-amine are formed, as well as nitrogen trichloride, when ammonium salts are treated with chlorine.

5. Treatment of an ammonium salt with hypochlorous acid is better than treatment with chlorine for the preparation of pure nitrogen trichloride free from other chloro-amines.

6. Nitrogen trichloride may be separated from a solution in which it is prepared by passing a current of air through the solution, drying the air and vapor of the trichloride with conc. sulfuric acid and condensing the trichloride in a U-tube surrounded with a freezing mixture.

Three of the most fundamental questions now before chemists for consideration are:

1. Are all, or nearly all, reactions essentially ionic in character? When two atoms or radicals separate and recombine, is one of the atoms usually positive and the other negative?

2. If the first question is answered in the affirmative, are the positive and negative character of atoms retained in compounds?

3. Is the simplest bond of union between two atoms due to one electron or two?

The experiments which have been described seem to throw some light on the first 2 questions. If the interpretation given is true, trichloroammonium chloride, NCl_3HCl, contains one chlorine atom which is bound to the nitrogen atom, or to the group, in an essentially different manner from the combination of the other 3. This chlorine atom tends to separate from combination carrying an extra electron, while either of the other 3 chlorine atoms tends to separate from the nitrogen atom with the loss of an electron, *i. e.*, as a positive atom. The negative chlorine atom may then combine with the positive atom to form free chlorine.

The experiments throw little or no light on the question whether in free chlorine one atom remains positive and the other negative, or as to whether the 2 atoms are bound by a single electron or by two.

URBANA, ILL.

[Contribution from the Chemical Laboratory of the University of California.]

SOLUBILITY. IV. SOLUBILITY RELATIONS OF NAPHTHALENE AND IODINE IN THE VARIOUS SOLVENTS, INCLUDING A METHOD FOR EVALUATING SOLUBILITY DATA.

By Joel H. Hildebrand and Clarence A. Jenks.

Received July 29, 1920.

In the preceding papers of this series[1] a theory of solubility has been presented according to which Raoult's law, which is taken as expressing the behavior of an ideal solution, will be obeyed by substances which, in the liquid state, have the same internal pressures, provided the substances are relatively non-polar and do not tend to form compounds with each other. Positive deviations from Raoult's law, under the same conditions, are shown wherever the substances have different internal pressures. Since solubilities can be calculated on the basis of Raoult's law, substances will be less soluble in each other the greater the difference in their internal pressures in the liquid state.

In the earlier papers the solubility relations of naphthalene and iodine were briefly discussed. It is the purpose of the present paper to do this more fully, with the aid of a new method for criticising solubility data, and utilizing additional experimental material.

Method for Evaluating Solubility Data.

In evaluating solubility data, it is possible to use a procedure frequently applied in connection with vapor pressures. From the form of the ideal equation, $\log N = L/4.57\,T + I$, where N is the mol-fraction of the solute in solution, L its heat of solution, and I a constant of integration, it is evident that when $\log N$ is plotted against $1/T$, a straight line should result whose slope gives the heat of solution of the solute (which is identical with the heat of fusion of the solute when Raoult's law is obeyed). Moreover, when the 2 substances in the liquid form are miscible in all proportions, as is the case where Raoult's law is even approximately obeyed, N becomes unity at the melting point of the solute. It follows, therefore, that for solutions in which molecular changes do not play very important roles, the solubility data when plotted in the above fashion will give a family of curves converging to the melting point and approaching the ideal value calculated from the heat of fusion as Raoult's law is approached. Figs. 1 and 3 illustrate this method.

Since the internal pressures of different substances do not retain precisely the same relative values at all temperatures, the solubility lines are not strictly parallel. This is, however, a second order effect. It is possible, therefore, to make the following predictions for solutions of non-polar substances.

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[1] This Journal, 38, 1452 (1916); 39, 2297 (1917); 41, 1067 (1919).

1. From the melting point of the solute and its solubility at any one temperature (in terms of mol-fraction) it is possible to predict its solubility at all temperatures rather closely by drawing a straight line through the 2 points on the plot of log N against $1/T$. Where the 2 substances differ greatly in internal pressure, which can readily be determined according to the criteria used in the third paper of this series, this line should be slightly concave upwards.

2. When the solubility of the solute in other solvents is known at any temperatures, a family of curves similar to those in Figs. 1 and 3 can be drawn. It is then possible to predict approximately its solubility in any other solvent at any temperature by noting the relation of the internal pressure of the new solvent to that of the others, and by drawing a line in the proper position. This will be illustrated in the subsequent discussion of existing data.

3. When solvation exists solubility will be greater than would otherwise be expected, but will have a smaller temperature coefficient.

4. The temperature coefficient of solubility will be greatest for substances differing most in internal pressure.

Solubility Relations of Naphthalene.

At the time of the publication of the first paper of this series, we were not aware of an important paper upon solubility by Schroeder[1] in which he published, apparently for the first time, the formula for calculating the solubility of a substance from its heat of fusion and melting point upon the assumption that Raoult's law holds. He further represented his results by plotting log N against the difference between the melting point of naphthalene and the temperature of each solubility determination. This method is similar to the one here employed, but does not give straight lines. The data he obtained using solutions of naphthalene in benzene, chlorobenzene and carbon tetrachloride, agree fairly well with the formula. We wish, however, to take account of the minor deviations of solubility in these and other solvents and to show that they are essentially such as have been predicted on the basis of internal pressure. In addition to the data of Schroeder, we have determinations of the solubility of naphthalene in hexane, carbon disulfide and chloroform by Etard[2] and by Speyers[3] in chloroform and toluene. All of the above determinations cover a considerable range of temperature. The data of Etard and Speyers for chloroform agree fairly well. A single determination by Bechi[4] in toluene agrees with the values by Speyers.

The experimental values have been plotted in Fig. 1. The ideal solu-

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[1] Schroeder, *Z. physik. Chem.*, 11, 449 (1893).

[2] Etard, *Bull. soc. chim.*, [3] 9, 82 (1893).

[3] Speyers, *Am. J. Sci.*, [4] 14, 294 (1902).

[4] Bechi, *Ber.*, 12, 1978 (1879).

bility calculated from the heat of fusion is also indicated. For this purpose, the heat of fusion of naphthalene and its specific heats in the solid and liquid forms have been taken from the work of Bogojawlenski.[1] His value of the heat of fusion is a little lower than the ones given by older observers, but the comprehensive character of the investigation and the greater purity of the naphthalene used, as indicated by its higher melting point, are evidence that this work is the most accurate. If other values were taken into account the line would be slightly higher, but the validity of the theory would not be affected thereby.

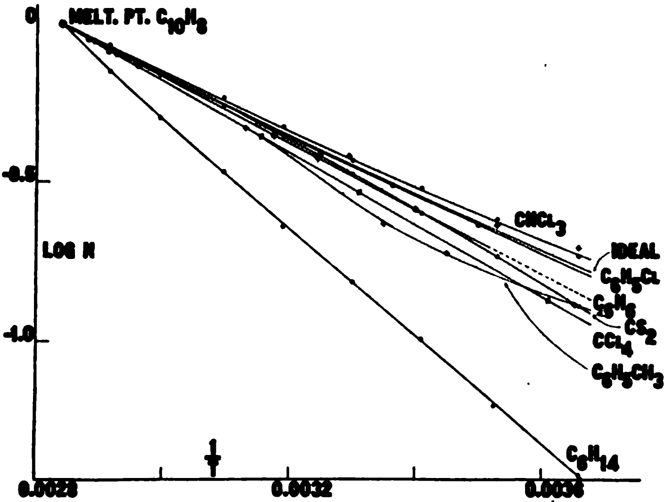

Fig. 1.—Solubilities of naphthalene.

It will be seen that, except for chloroform and toluene, the solvent powers of the various substances considered are exactly in the order given in the table of relative internal pressures in the third paper of this series, where the values are shown to increase in the following order: hexane, carbon tetrachloride, toluene, benzene, chloroform, chlorobenzene, naphthalene, carbon disulfide. We would expect from this that the solubility of naphthalene in chloroform would be between its solubilities in benzene and chlorobenzene. The fact that its solubility in this solvent is greater than Raoult's law would lead us to expect, may be evidence of the existence of solvation such as will be seen in the case of iodine in benzene, and, at lower temperatures, in carbon disulfide.

The curve for toluene should, theoretically, fall slightly above that for carbon tetrachloride, and be almost straight, like those for the other solvents. The fact that it falls below for part of its course would constitute a more serious contradiction if the experimental values were more regular.

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[1] Bogojawlenski, *Chem. Zentr.*, [5] 9, II, 945 (1905).

It is unlikely that the true curve would have the inflections of the one drawn in the figure, which was drawn through the experimental points. If an approximately straight line were drawn to satisfy these points it would fall very close to the one for carbon tetrachloride.

It is evident that, except for unforeseen instances involving solvation, the solubility of naphthalene in other solvents could be approximately predicted by the aid of Fig. 1. For example, ethylene bromide, which falls between carbon disulfide and naphthalene, should have a solvent power somewhat greater than that of carbon disulfide, but less than the ideal. Again, xylene, which has an internal pressure between those of toluene and hexane, should show a solvent power which would be indicated by drawing a line somewhat below the line for toluene, in Fig. 1.

TABLE I.

Solubilities of Naphthalene—Mol-Fraction.

Solvent.	Temperature. 0°.	10°.	20°.	25°.	40°.	50°.
Hexane	0.0375	0.0622	0.100	0.124	0.234	0.340
Carbon tetrachloride	0.117	0.1645	0.226	0.262	0.405	0.515
Toluene	0.13	0.16	0.20	0.23	0.40	0.51
Benzene	0.139	0.190	0.254	0.290	0.432	0.540
Chloroform	0.184	0.237	0.291	0.334	0.473	0.575
Chlorobenzene	0.164	0.217	0.281	0.316	0.453	0.557
Ideal	0.172	0.224	0.287	0.323	0.455	0.561
Carbon disulfide	0.129	0.183	0.252	0.293	0.441	0.553

In Table I are given values of the solubilities of naphthalene at various temperatures in terms of mol-fraction. These values were taken from a careful plot of Fig. 1 and represent the smoothed out experimental data. The values for benzene at the lower temperatures represent some extrapolation, shown in the figure by the dotted line. This table illustrates numerically the conformity of the solubilities of naphthalene to the internal pressure theory.

Solubility of Iodine.

Experimental.—Solubilities of iodine over any range of temperature are given in the literature for only a few solvents. It was accordingly necessary for our purpose to determine the solubility in several others, including benzene.

The iodine used was subjected to a purification to eliminate particularly the other halogens and cyanogen. For this purpose we used with but slight modification the method of Baxter.[1]

Commercial "C. P." benzene was first distilled and then shaken repeatedly with sulfuric acid, in order to remove thiophene. It was then frozen 4 times. The samples from the last 2 operations showed no differ-

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[1] Baxter, *Proc. Am. Acad.*, 40, 421 (1904).

ences in freezing point greater than 0.001°. The benzene was finally dried with phosphorus pentoxide and redistilled.

The carbon tetrachloride used was first shaken with a concentrated solution of sodium hydroxide and then distilled from the phosphorus pentoxide, a constant-boiling distillate being obtained.

The heptane was obtained from material kindly donated by Mr. D. F. Fryer, Santa Rosa, Calif. It was treated 3 times with sulfuric acid, diluted with $^1/_2$ of its volume of water. It was then distilled, nearly all coming over between 98.3° and 98.6°. The distillate was again shaken 3 times with sulfuric acid diluted with $^1/_4$ of its volume of water. The sulfuric acid used in this treatment remained colorless. It was then shaken with conc. sulfuric acid, treated with phosphorus pentoxide and distilled, all distilling at 98.4°. The density of the resulting liquid was 0.6827 at 20.1°. Both the boiling point and the density agree well with the values given by other observers for normal heptane. The boiling points of the other heptanes are 90° or lower.

The solubility determinations were made in an apparatus shown in Fig. 2. The bulb was supported in the thermostat in a nearly horizontal position and rotated in such a way as to rock the contained liquid from one end to the other. After equilibrium was obtained the apparatus was tilted so that the exit tube was in a vertical position and a portion of the solution was forced up into the pipet by blowing gently into the side arm provided with a stopcock. The construction of the bulb is such that the solid is kept away from the tip of the pipet, minimizing the danger of forcing particles of the solid into the pipet. The bulb was kept under the surface of the water in the thermostat during the filling of the pipet. The pipet was then removed from the bulb and weighed. Its contents were washed into a flask and titrated with sodium thiosulfate solution. The weights and burets used were carefully standardized.

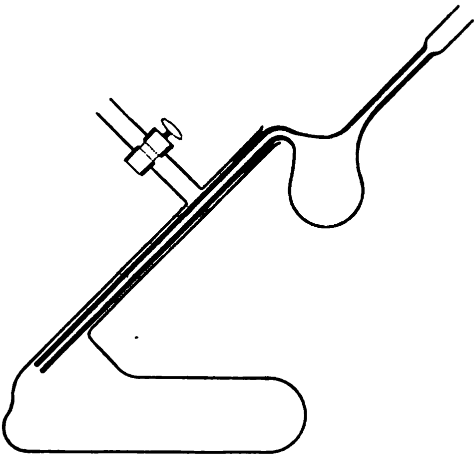

Fig. 2.

Results.

Tables II, III and IV give the experimental results upon the solubilities of iodine in benzene, carbon tetrachloride and heptane, respectively. These results are plotted in Fig. 3, along with the experimental values obtained by Arctowski for the solubility of iodine in carbon disulfide[1] and in benzene[2] at lower temperatures. The figure includes also solubilities in chloroform obtained by Hantzsch and Vagt[3] and the single value of Jakowkin[4] in carbon tetrachloride at 25°, which falls almost exactly upon our own curve. There exist values by Bruner[5] for the solubilities of iodine in chloroform and carbon tetrachloride in the neighborhood of 15°, but examination of his paper shows his values to be rather unreliable, and they are not here included.

TABLE II.

Solubility of Iodine in Benzene.

Temp.	25°.	30°.	35°.	40°.	45°.	50°.	54.64°.
G. I_2 per 100 g. solution	14.00	16.06	17.93	20.01	22.74	25.51	28.25
	14.15	16.14	17.74	20.09	22.82	...	28.27
	14.12	...	18.03	...	22.79	...	...
Mean	14.09	16.10	17.90	20.05	22.78	25.51	28.26
Mol-fraction	0.0480	0.0558	0.0629	0.0716	0.0832	0.0953	0.1081

TABLE III.

Solubility of Iodine in Carbon Tetrachloride.

Temp.	0°.	35°.	50°.
G. I_2 per 100 g. solution	0.6880	2.621	4.364
	0.6875	2.599	4.344
	0.6866	2.597	4.346
	....	2.594	...
Mean	0.6877	2.603	4.351
Mol-fraction	0.00418	0.01594	0.02683

TABLE IV.

Solubility of Iodine in Heptane.

Temp.	0°.	25°.	35°.	50°.
G. I_2 per 100 g. solution	0.6192	1.703	2.501	4.200
	0.6149	1.701	2.497	4.192
	0.6164	...	2.476	...
	0.6199	...	...	...
Mean	0.6176	1.702	2.491	4.196
Mol-fraction	0.00245	0.006786	0.00998	0.01699

Marden and Dover[6] have published a single determination of the solubility of iodine in chloroform at 25° which does not agree very well with

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[1] Arctowski, *Z. anorg. Chem.*, 6, 404 (1894).

[2] *Ibid.*, 11, 276 (1895).

[3] Hantzsch and Vagt, *Z. physik. Chem.*, 38, 728 (1901).

[4] Jakowkin, *ibid.*, 18, 590 (1895).

[5] Bruner, *ibid.*, 26, 145 (1898).

[6] Marden and Dover, THIS JOURNAL, 38, 1235 (1916).

the values of Hantzsch and Vagt. Hertz and Rathmann[1] give solubilities of iodine in chloroform at 25° in terms of weight of iodine per unit volume of the solutions. Lack of data concerning the densities of these solutions makes it impossible to recalculate solubility to a weight basis. The solubility of iodine in molten sulfur is given by the freezing-point determinations of Smith and Carson.[2] The formula S_8 was used in calculating the mol-fraction of iodine.

TABLE V.

Solubilities of Iodine—Mol-Fraction.

Solvent.	Temperature. 0°.	10°.	20°.	25°.	40°.	50°.
Heptane	0.00245	0.00376	0.00565	0.00679	0.0119	0.0170
Carbon tetrachloride	0.00418	0.00631	0.00920	0.0110	0.0169	0.0268
Chloroform	0.0093	0.00135	0.00193	0.0228	(0.0380)	(0.0530)
Benzene	...	0.0306	0.0420	0.0482	0.0718	0.095
Carbon disulfide	0.0250	0.0341	0.0487	0.0570	0.0925	0.127

Table V gives the smoothed-out values of the solubility of iodine at various temperatures in carbon disulfide, benzene, chloroform, carbon tetrachloride, and heptane, obtained from a careful plot of the data after the manner shown in Fig. 3.

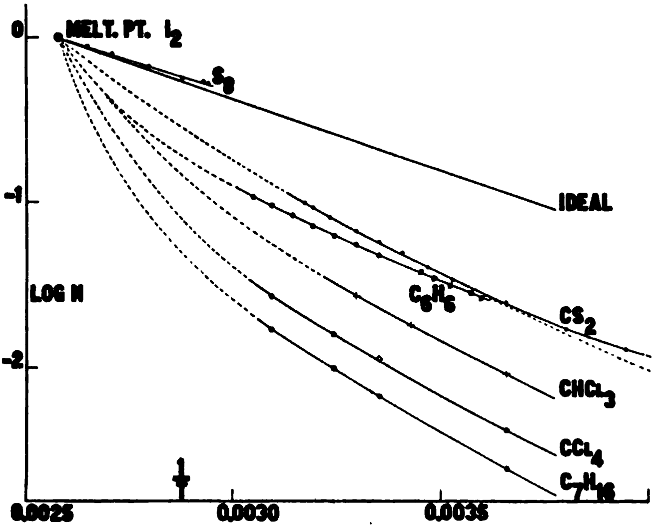

Fig. 3.—Solubilities of iodine.

Discussion.—It is evident that the solubilities of iodine plotted as in Fig. 3, give, except for benzene, a family of closely parallel curves similar to those for naphthalene shown in Fig. 1. The dotted lines represent the hypothetical portions at higher temperatures as the curves converge

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[1] Hertz and Rathmann, *Z. Elektrochem.*, 19, 887 (1913).

[2] Smith and Carson, *Z. physik. Chem.*, 61, 200 (1907).

to the melting point of iodine where it becomes soluble in all proportions, *i. e.*, $N = 1$.

Excepting for benzene, the order of solubility in the various solvents follows the order of internal pressures. Sulfur, whose internal pressure and solubility relations will be discussed more at length in a future communication, falls very close to iodine, and, since there is little or no tendency for the elements to combine, dissolves iodine almost exactly to the extent corresponding to an ideal solution.

In the first papers of this series, figures were given which showed that the solubility of iodine, in accord with the theory, falls off in the following solvents in the order named: bromoform, carbon disulfide, chloroform, carbon tetrachloride, hexane. The solubility in benzene, however, was found to be nearly as great as in carbon disulfide, instead of being near that in chloroform, as might be expected. A statement was made in the first paper attributing this discrepancy to the formation of a solid solution of iodine and benzene, reported by Beckmann and Stock.[1] Prof. E. W. Washburn kindly directed our attention some time ago to the fact that this was a mis-statement, for it is evident that the formation of a solid solution would not increase solubility, but rather decrease it. Upon second thought, it seemed that the true explanation of the discrepancy lies in the solvation of iodine in benzene as shown by the fact that this solution has a brownish-red color instead of the violet shown by solutions in the other solvents above named.

Evidence that brown solutions of iodine contain solvated iodine, has been given by Hildebrand and Glasscock.[2] If a solution of iodine in benzene is cooled, the red color deepens, while if it is warmed, the color approaches the violet of iodine vapor, indicating that the solvation decreases with rising temperature, as would be expected. This changing solvation with the temperature is very strikingly shown by solutions in amyl acetate, where the color may be made to vary all the way from violet to brown. When solvation occurs, the activity of the solute is diminished, allowing more of it to go into solution than would otherwise be the case, so that as the temperature rises and solvation decreases, the solubility should approach that expected from the position of the solvent in the table of internal pressures.

The effect of temperature upon the solubility of iodine in benzene is as expected from this point of view. Fig. 3 shows that as the temperature is increased the solubility in benzene approaches the solubility in chloroform. There is little doubt, therefore, that if no solvation occurred

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[1] Beckmann and Stock, *Z. physik. Chem.*, **17**, 107 (1895).

[2] Hildebrand and Glasscock, THIS JOURNAL, 31, 26 (1909). See also P. Waentig, *Z. physik. Chem.*, **68**, 513 (1909) and J. H. Hildebrand, *ibid.*, **74**, 679 (1910).

the solubility in benzene would be represented by a line parallel and close to the line for chloroform.

The same behavior is shown by carbon disulfide solutions, which begin to turn brown below 0°, indicating solvation and producing a higher solubility than would otherwise be found. The dotted lower extension of the curve for this solution shows approximately the course the curve would take in the absence of solvation. *We wish to emphasize that it is the deviation of the actual curve from this dotted curve, and not from the line of the ideal solution higher up which should be used for any estimate of the amount of solvation.* The well-nigh universal practice of concluding that all deviations from Raoult's law, or, still worse, from van't Hoff's law for osmotic pressure or from any of the laws derived from them, indicate changes in the molecular species present in the solution, is far from being justifiable, as the present illustration clearly shows. The considerable deviation of solutions of iodine in heptane from Raoult's law that would be shown by molecular weight determinations as well as by the solubility curve, might be "explained" by assuming that iodine is "associated" in heptane, or, if one prefers, that heptane is associated—either will work. However, either is unjustifiable, for there is no more effect of this sort in heptane than there is in carbon disulfide.

The above results are at most but slightly influenced by any tendency of benzene to form solid solutions in iodine. A solution of iodine in benzene was slowly evaporated at approximately 45° and the iodine crystals remaining were analyzed. They were found to contain 98.7% iodine. Since some benzene may have been occluded, the amount in solid solution must have been very small. Evidently the solubility of benzene in solid iodine is much less than that of iodine in benzene.

The curves in Fig. 3 would enable one to construct the whole solubility curve for any solvent for iodine which gives violet solutions provided a single point is known. Thus the solubility of iodine in hexane has been determined at 15° by E. T. Ellefson in this laboratory,[1] giving $N = 0.0045$, a value a little less than the corresponding one for heptane. A curve drawn through this point parallel to the curve for heptane would undoubtedly give very closely the solubility in hexane through the corresponding range of temperature. Jakowkin[2] gives a value for the solubility of iodine in bromoform at 25°. Unfortunately, it is not clear whether his figures refer to amount of iodine per liter of solvent or of solution. Since the solubility is large it makes a considerable difference which is used in calculating to mol. fraction. If the former is correct $N = 0.062$, while if the latter is correct, and assuming that the volume of the solution is the sum of the volumes of bromoform and liquid iodine, $N = 0.066$. In

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[1] E. T. Ellefson, THIS JOURNAL, 39, 1301 (1917).

[2] Jakowkin, *Loc. cit.*

either case the solubility is greater than that in carbon disulfide, in accord with the greater internal pressure of bromoform, and the entire solubility curve could be drawn parallel to that for carbon disulfide.

If we consider a solvent for which we have no solubility data, such as ethylene bromide, we can predict the solubility with a fair degree of approximation by noting that this solvent has an internal pressure a little less than that of carbon disulfide, hence its solvent power for iodine should also be a little less, and its solubility curve should be drawn a little below that for carbon disulfide and parallel to it, since it gives violet solutions showing no solvation.

When polar solvents are used, or those giving brown solutions, the solubility curve will be more unique, behaving like the benzene curve but in a more exaggerated form, and in a position more difficult to predict.

Summary.

1. A method for criticising solubility data has been outlined, according to which the solubilities of a substance in solvents where no molecular changes are involved, when plotted as log N against $1/T$, give a family of approximately straight lines converging to the melting point of the solute where $N = 1$. The position of these lines corresponds to the internal pressures of the solvents and is approximately predictable from them.

The effect of solvation upon the solubility and also upon its temperature coefficient has been outlined.

2. The above mentioned has been illustrated by means of solubility data of naphthalene in various solvents,

3. Solubilities of iodine in benzene, carbon tetrachloride and heptane have been measured at various temperatures.

4. The solubility relations of iodine have been discussed by the aid of the above method, and it is shown that the violet solutions give the expected family of parallel curves, whereas the brown solutions show deviations in the direction expected.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC COMPANY.]

RADIATION AS A FACTOR IN CHEMICAL ACTION.

BY IRVING LANGMUIR.

Received August 16, 1920.

Jean Perrin, in his book "Les Atomes" (1913), advanced the thesis that the action of light plays an essential part in all chemical reactions. In a more recent article[1] he shows that Arrhenius' equation for reaction velocity can be derived from the Planck or Wien radiation law upon the assumption that the chemical action depends on the absorption of a nearly monochromatic radiation. Thus the increase in the velocity of a reaction with rising temperature is supposed to be due to the increasing intensity of some particular part of the so-called black-body radiation. According to Wien's radiation law, the natural logarithm of the intensity of any monochromatic black-body radiation is a linear function of the reciprocal of the absolute temperature. The slope of the line representing this relation is $—h\nu/k$ where h is the quantum 6.6×10^{-27} erg seconds, ν is the frequency of the monochromatic radiation, and k is the gas constant per molecule, or 1.37×10^{-16} erg per degree. According to Arrhenius' equation, an exactly similar relation holds between the natural logarithm of the *reaction velocity* and the reciprocal of the temperature. Trautz, Marcelin, Wm. McC. Lewis and others, from analogy with van't Hoff's equation, have identified the slope of the line obtained from the Arrhenius equation with Q/R where R is the gas constant and Q is the energy (per gram molecule) required to *activate* the reacting substance. The quantity Q/R thus has the same relation to Arrhenius' equation that $h\nu/k$ has to the Wien equation. To correlate the two laws it is only necessary to equate these quantities

$$\frac{h\nu}{k} = \frac{Q}{R}. \tag{1}$$

But $R = Nk$ where N is the Avogadro constant 6.1×10^{23} molecules per gram molecule. Therefore

$$Q = Nh\nu. \tag{2}$$

In other words, the heat of activation per molecule is $h\nu$, a result in accord with the quantum theory.[2]

The radiation hypothesis, together with the quantum theory, thus furnishes a very simple explanation of the relation between the Arrhenius equation for reaction velocity and the Wien radiation law. According to this hypothesis, all chemical reactions are to be regarded as essentially

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[1] *Ann. phys.* [9] 11, 5–108 (1919).

[2] Haber, *Verh. deut. physik. Ges.*, 13, 1117 (1911), proposed a relation like that of Equation 2 for calculating the heats of chemical reactions from the natural frequencies of vibrations of the electrons in atoms and molecules.

photochemical reactions in which the energy of radiant heat or light is transformed into chemical energy or *vice versa.*[1]

Perrin has given one of the strongest arguments in favor of the hypothesis. In a unimolecular reaction the amount of substance reacting in a given time is proportional to the amount present. The chance that any molecule shall react during any small time interval is thus *independent of the pressure.* But the number of collisions which the molecule makes with others is proportional to the pressure. Therefore, as Perrin points out, the reaction of any molecule must be a phenomenon which is independent of collisions between molecules. If the reaction is not due to collisions, it seems almost necessary to conclude that it is caused by radiation.

There are two consequences of the radiation hypothesis which should serve as a test of its validity. In the first place, it is necessary that the reacting substance shall absorb the radiation which causes the reaction. Therefore, there must be an absorption band which includes the radiation in question. It is also to be expected that the frequency of this radiation should be the same as that obtained from the specific heat, the compressibility or the melting-point by the relations of Nernst, Einstein, or Lindemann.

In the second place, the total amount of energy absorbed from the radiation must be sufficient to activate the requisite number of molecules. Before any molecule can undergo reaction, it must become activated and this requires the absorption of the energy $h\nu$ or Q/N, an amount which can be determined experimentally for any given reaction from the temperature coefficient of the reaction velocity. As far as I have been able to find, no one has tested the radiation hypothesis from this point of view, although it would seem to constitute a decisive test. It is the principle object of this paper to compare the energy absorbed in a few thermal reactions with the total available radiant energy.

Trautz, Lewis and Perrin have attempted to correlate the frequencies calculated from Equation 2 with those of absorption bands or with the natural frequencies found from the specific heats, etc. The results taken as a whole do not seem to furnish satisfactory evidence for the radiation hypothesis. In a few cases the calculated frequencies do come within the range of absorption bands, but in most of these cases (for example, iodine)

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[1] The radiation hypothesis was proposed by Trautz in 1911, and has been developed in detail by him in a series of papers since then. A summary of Trautz' work with reference to the earlier papers, is given in the *Z. anorg. allgem. Chem.*, 102, 81–129 (1918); and 106, 149 (1919). During the last few years Wm. McC. Lewis has published numerous papers on this subject in the *J. Chem. Soc.* See particularly *J. Chem. Soc.*, 111, 389, 457, 1086 (1917); *Phil. Mag.*, 39, 26 (1920). In this last paper Lewis points out a serious difficulty in reconciling the radiation hypothesis with either Planck's or Einstein's views regarding the mechanism of radiation.

there is a very great number of bands and there is no way of predicting in advance which of the bands corresponds to the activation of the molecule. In many other cases there is not the slightest trace of an absorption band observed in the neighborhood of the calculated frequency. For example, according to Lewis' calculation, the critical frequency for the dissociation of hydrogen into atoms corresponds to a wave length of 325 $\mu\mu$ which is in the ultra-violet region just slightly beyond the visible. There is, however, no measurable absorption of light of this frequency by hydrogen. The following data on the heats of activation of various dissociations will be given by Dr. Dushman in a forthcoming paper, PH_3 — 73,000; As_4 — 45,000; P_4 — 50,000; and $COCl_2$ — 61,000 g. cals. per mol. The heat of activation of nitric oxide in its decomposition into oxygen and nitrogen is 65,000 cal. The value for the decomposition of nitrous oxide is 60,000 cal. These values correspond to wave lengths of 390 $\mu\mu$ for PH_3, 630 for As_4, 570 for P_4, 474 for N_2O, 467 for $COCl_2$, and 437 for NO, which, according to the radiation hypothesis, should lie within absorption bands. It is evident that this conclusion cannot be correct, for the above wave lengths are in the visible spectrum, while the gases are all colorless and therefore do not absorb perceptible amounts of radiation in this range.

Is the Radiant Energy Absorbed by Gases Sufficient to Account for the Observed Reaction Velocities?

The only unimolecular gas reaction whose velocity has been directly measured, is the dissociation of phosphine.[1] At a temperature of 948° K. the velocity constant is 0.012 per second. This means that 1.2% of the phosphine present at any time decomposes within the next second. Under the conditions of the experiment the reaction was wholly irreversible. From the temperature coefficient of the reaction velocity Lewis has calculated that the heat of activation lies between 70,000 and 80,000 calories per molecule. Dushman will show that excellent agreement with the experimental data is obtained if we take 73,000 for the heat of activation. According to Equation 2, this corresponds to a frequency of 7.7×10^{14}, or to a wave length of 392 $\mu\mu$.

According to the radiation hypothesis, the energy required to activate the molecule before dissociation can occur, is supplied by the absorption of radiant energy having a wave length in the neighborhood of 392 $\mu\mu$. From the heat of activation and the reaction velocity we can calculate the rate at which energy must be supplied to bring about the reaction. From Wien's law we can also determine how much radiation there is at 948° within a given range of wave lengths, and in this way we can see if there is enough radiant energy to cause the observed reaction.

One cc. of phosphine at atmospheric pressure and 948° K. contains

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[1] Trautz and Bhandarkar, *Z. anorg. allgem. Chem.*, **106**, 95 (1919).

1.27×10^{-5} g. mols. The amount that dissociates in one second is 0.012 of this, or 1.52×10^{-7} g. mols. Taking 73,000 as the heat of activation, the energy which must be supplied per cc. per second is 0.0111 calorie, or 465,000 ergs.

According to the Stefan-Boltzmann law, the total radiation from a black body at 948° is 4.56×10^7 ergs per second per sq. cm. All but a minute fraction of this energy lies far in the infra red part of the spectrum. The Wien displacement law $\lambda_M T = 0.290$ cm., shows that the wave lengths corresponding to the maximum of the distribution curve is 3060 $\mu\mu$. Wien's radiation law gives for the energy radiated per sq. cm. per second between the frequencies ν and $\nu + d\nu$ the expression

$$E_\nu d\nu = \frac{2\pi h\nu^3}{c^2} e^{-h\nu/kT} d\nu. \qquad (3)$$

Here c is the velocity of light, 3.00×10^{10} cm. per second.

The radiation hypothesis gives no definite information regarding the width of the band $d\nu$ which should be absorbed except that the radiation must be reasonably nearly monochromatic in order to account for the similarity between the Wien and the Arrhenius equations. To calculate the total energy available in the radiation, let us assume that all energy of wave length shorter than 400 $\mu\mu$ can be used for activating molecules. This wave length corresponds to a frequency of 7.5×10^{14} per second. By integrating the expression in Equation 3 between this frequency and infinity, we find that the total energy radiated from a black body at 948° with a wave length less than 400 $\mu\mu$ is 1.3×10^{-5} erg per second per sq. cm. This is only $3. \times 10^{-13}$ of the total energy radiated (in all wave lengths) at this temperature, and is about 4×10^{10} times less than the amount of radiant energy needed to cause the reaction in one cubic cm. of phosphine (465,000 ergs. per sec.). In other words, a black body at 948° K. (675° C.) radiates so little energy in the neighborhood of 392 $\mu\mu$ that this energy would only be sufficient to activate molecules of phosphine in a layer having a thickness not greater than 3×10^{-11} cm., *even if all the radiation were absorbed within this layer.* The observed reaction velocity, therefore, cannot be due to the absorption of radiation of the wave length needed to account for the observed temperature coefficient.

Another fact which should make the radiation hypothesis in its present form untenable is that the decomposition of phosphine is not brought about at measurable rate by ordinary daylight, although the intensity of blue and violet light in daylight is enormously greater than in the radiation from a body heated to 675° C.

The above objections to the radiation hypothesis apply not only in the case of the dissociation of phosphine, but to all unimolecular reactions.

It will be shown by Dr. Dushman[1] that the velocity of any unimolecular reaction is given by the expression

$$k_1 = \nu e^{-h\nu/kT}. \tag{4}$$

The "frequency" ν can be determined experimentally from the temperature coefficient of the reaction velocity. The "heat of activation" is related to ν by Equation 2.

By means of the above equation we can now test the radiation hypothesis for the general case. Imagine a large vessel, bounded by plane walls, which contains a gas undergoing a unimolecular reaction. According to the radiation hypothesis, each molecule which reacts absorbs the energy $h\nu$ from the black body radiation having a frequency approximately equal to ν. Let us consider the reaction which takes place within a very short distance dx of one of the plane walls of the vessel. Since the number of molecules per cc. in a gas is p/kT we obtain the following expression for the energy required to activate the molecules which react within the distance dx of the wall (per second and per sq. cm. of wall)

$$\frac{ph\nu^2}{kT} e^{-h\nu/kT} dx. \tag{5}$$

Let us now calculate how much energy will be absorbed by the gas within dx of the wall. If α is the absorption coefficient of the gas for light of the frequency ν the total energy absorbed by the gas in a slab of thickness dx is $2\alpha E_\nu d\nu dx$ where E_ν is given by Equation 3. The coefficient 2 comes into the expression because part of the radiant energy passes diagonally through the slab and is, therefore, more strongly absorbed than that passing normally. Let us assume that the gas can absorb energy from a band of finite width. We therefore, place $d\nu = \beta\nu$ where β expresses the width of the band as a fraction of the corresponding frequency. It does not seem reasonable that β should exceed say 0.1. The total energy absorbed in the slab (per second and per sq. cm.) is thus:

$$\frac{4\pi h\nu^4\alpha\beta}{c^2} e^{-h\nu/kT} dx. \tag{6}$$

By equating Expressions 5 and 6, we obtain (in C.G.S. units)

$$\alpha\beta = \frac{pc^2}{4\pi\nu^2 kT} = 5.2 \times 10^{35} \frac{p}{\nu^2 T}. \tag{7}$$

This expression gives the absorption coefficient which is required if radiation is to supply the energy for the activation of the molecules. Assuming a reaction in which the heat of activation is 100,000 calories (hence, $\nu = 1.05 \times 10^{15}$), and placing $p = 10^6$ (one atmosphere) and $T = 1000°$, we obtain $\alpha\beta = 4.8 \times 10^8$. If we take $\beta = 0.1$, this gives

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[1] A short abstract covering Dushman's theory has already been published in the *J. Franklin Inst.*, April, 1920.

an absorption coefficient of 5. × 10^9 per cm. In other words, the energy would be sufficient only for a gas layer of the order of 10^{-10} cm. in thickness. If we should choose reactions occurring at lower temperatures or having lower heats of activation, we see by Equation 7 that the absorption coefficient would be still larger.

Dissociation of Hydrogen.—The experiments on the dissociation of hydrogen into atoms which were carried out by Mr. G. M. J. Mackay and the writer[1] furnish strong evidence that this reaction is not caused by the absorption of radiation. When a tungsten filament is heated to high temperature in hydrogen, the heat carried away by the gas is many times greater than can be accounted for by ordinary heat conduction or convection.

TABLE I.

Heat Dissipation from Tungsten Filaments in Hydrogen in Watts per Centimeter.

	Absolute temperature, ° K.		
	2500.	3000.	3400.
At 0.0 mm. pressure:			
W_r, heat radiated	1.92	4.46	9.41
At 50 mm. pressure:			
W_c, conduction and convection	6.5	9.1	11.0
W_d, dissociation	12.5	48.0	107.0
Ratio $W_d : W_r$	6.5	10.7	11.4
At 750 mm. pressure:			
W_c, conduction and convection	14.4	20.2	25.0
W_d, dissociation	6.3	29.0	69.0
Ratio $W_d : W_r$	3.3	6.5	7.3

A few typical results are summarized in Table I, which gives the heat losses from a tungsten filament of 0.0071 cm. diameter in hydrogen at 2 pressures. W_r represents the total energy radiated per second, W_c the energy carried by normal heat conduction and convection, while W_d gives the energy carried away as a result of the dissociation of the gas.

The effect of the dissociation is to cause a transfer of heat from the hot filament to the walls of the surrounding vessel, amounting in some cases to more than 10 times the total heat radiated from the filament.

According to the radiation hypothesis, the dissociation of the hydrogen is produced by the absorption of a radiation of a wave length of approximately 325 $\mu\mu$. It is clear, however, that the absorption of the radiation from the filament by the gas cannot be made to account for an increase in the heat carried from the filament. In fact, such absorption must decrease the heat loss, for whatever heat is absorbed by the gas in causing dissociation, will be reradiated when the atoms recombine, and some of this heat will thus be returned to the filament, while if there is no absorption, the radiated heat travels away with the velocity of light.

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[1] THIS JOURNAL, 36, 1708 (1914); and 37, 417 (1915).

The evidence that radiation does not play an appreciable part in the reaction is even more striking when we consider the small proportion of radiation present in the shorter wave lengths. Calculation by means of Wien's equation indicates that of the total energy radiated by the filament, only the following fractions are of wave lengths less than 325 $\mu\mu$: at 2500° K. — 0.00006; at 3000° K. — 0.0006; at 3400° K. — 0.002. The observed rate of dissociation is thus thousands of times greater than could be accounted for by the absorption of radiation even if the hydrogen absorbed the radiation in question completely.

It may be objected that the dissociation of hydrogen takes place in contact with the tungsten filament and that the radiation hypothesis has not usually been applied to reactions involving solid bodies. It would seem, however, that the radiation hypothesis is of such a fundamental nature that if true for gases it should also be applicable for liquids and solids. Moreover, the difficulty is not removed even in this way, for although the dissociation occurs in contact with the solid, the recombination certainly takes place in the gas phase, and this, on the basis of the radiation hypothesis, would produce a radiation of an intensity greater than that of a black body at the same temperature. This result for an endothermic reaction, is in conflict with the principles of thermodynamics.

Dissociation of Iodine.—Isnardi[1] has studied the heat conductivity of iodine vapor in contact with a heated platinum wire having an effective surface of 0.25 sq. cm. With the wire at 1080° K., the total energy carried by normal conduction corresponded to 0.70 watt, while that caused by dissociation (W_d) amounted to 3.49 watts. These results were obtained by subtracting the radiated energy from the total energy loss, but Isnardi does not give the amount of this correction. The radiation from a black-body surface of 0.25 sq. cm. at 1080° K. is 1.95 watts. Since platinum at this temperature radiates about 11% as much as a black body, the radiation in Isnardi's experiments must have been about 0.2 watt. The heat carried from the wire by the dissociation was thus about 17 times greater than the total heat radiated from the wire.

Dissociation of Nitrogen Peroxide.—Nernst[2] developed a quantitative theory of heat conduction in dissociating gases and applied it to experimental data obtained by Magnanini for the heat conductivity of nitrogen peroxide at various temperatures. At 190° C. the nitrogen peroxide is practically completely dissociated into nitrogen dioxide, and the heat conductivity is about the same as that of carbon dioxide, but at 40°, where the degree of dissociation is only about 30%, the heat conductivity is greater than that of hydrogen and is about 6.7 times as great as at the higher temperature. The experimental results furnish

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[1] Isnardi, *Z. Elektrochem.*, 21, 405 (1915).

[2] "Boltzmann-Festschrift," p. 904, Leipzig, 1904.

quantitative confirmation of Nernst's theory, which treats the problem as involving dissociation of the gas in a hot region and diffusion of the dissociation products to a cold region, where recombination takes place. The following analysis will make it clear that the observed facts are in radical disagreement with the radiation hypothesis.

According to the data given by Nernst, the heat conductivity κ of nitrogen peroxide at 40° is 0.00041 calorie per cm. sec. degree. Of this, the conductivity 0.00037 is due to the dissociation, while 0.00004 is ordinary heat conduction. Let us consider 2 parallel plane surfaces one cm. apart, differing in temperature by one degree and having an average temperature of 40°. If the space between the planes is filled with nitrogen peroxide, 0.00037 calorie per sq. cm. per sec. will pass across the space because of the dissociation. This corresponds to 0.00155 watt per sq. cm. According to the Stefan-Boltzmann law, the total heat transferred by radiation should be 0.00070 watt per sq. cm., which is less than half of that caused by the dissociation.

If the medium between the 2 plane surfaces does not absorb radiation, the heat transferred by radiation is independent of the distance between the surfaces, although the heat conducted is inversely proportional to this distance. When the medium absorbs the radiation, as it must, according to the radiation hypothesis, if a chemical reaction takes place, the transfer by radiation also varies inversely as the distance between the planes. Let us calculate how much heat can flow in this way. The problem involves the multiple scattering of heat rays.

Consider the radiation of heat between 2 parallel plane surfaces having a gas between them which absorbs heat in accordance with the radiation hypothesis. For example, consider a dissociating gas in which the reaction velocity is so high that chemical equilibrium prevails at every point in the gas. The absorption of the radiation causes the dissociation, while the recombination must produce an equal emission of radiation of the same wave length. Under these conditions the radiation of heat from molecule to molecule becomes strictly analogous to the energy carried between molecules in heat conduction in gases. We are thus justified in saying that the average distance that the heat rays travel before being absorbed is $1/\alpha$ where α is the absorption coefficient. The distance $1/\alpha$ corresponds to the mean free path of the molecules. Similarly, the radiation which arrives at any point may be considered as having come from a point at the average distance $1/\alpha$.

Let us choose a coördinate system in which the flow of heat takes place parallel to the X axis, so that the planes YZ are isothermal surfaces. Let T be the temperature at a plane having the coördinate x. Consider the radiation passing through a unit area of this plane in a direction making an angle θ with the X axis. Since $1/\alpha$ is the effective distance from which this radiation comes, we may take the temperature of its source as being

$$T - \frac{dT}{dx} \cdot \frac{\cos\theta}{\alpha}.$$

Let R be proportional to the heat radiated by a unit area of a black body at the temperature T. Then the energy in the radiation considered is

$$R - \frac{dR}{dT} \cdot \frac{dT}{dx}\,\frac{\cos\theta}{\alpha}.$$

The spherical angle from which this radiation falls on the unit area is proportional to $\sin\theta . d\theta$ and the energy that can pass through this unit area is proportional to $\cos\theta$. Hence the total flux of radiation through the unit area is

$$dw = \left(R - \frac{dR}{dT} \cdot \frac{dT}{dx} \cdot \frac{\cos\theta}{\alpha}\right) \sin\theta \cos\theta \; d\theta. \qquad (8)$$

The total flux obtained by integrating this expression from $\theta = 0$ to $\theta = \pi/2$ and placing $dT/dx = 0$ must equal the energy radiated per unit area per second from a black body at the temperature T. If we call this quantity W_1 we find $W_1 = 2R$. By integrating from 0 to π we obtain

$$W = \frac{2}{3\alpha}\,\frac{dR}{dT} \cdot \frac{dT}{dx} = \frac{4}{3\alpha}\,\frac{dW_1}{dT}\,\frac{dT}{dx}. \qquad (9)$$

This represents the rate at which heat flows between the 2 parallel surfaces. Since it depends on the temperature gradient between the planes rather than the temperature difference, the flow of heat follows the laws of heat conduction. The coefficient of heat conductivity due to this scattered radiation is

$$\kappa_r = \frac{W}{dT/dx} = \frac{4}{3\alpha}\,\frac{dW_1}{dT}. \qquad (10)$$

In this equation dW_1/dT represents the heat flow per sq. cm. per second between 2 surfaces differing by one degree in temperature when there is no absorbing medium between the plates. With surfaces separated by the distance x and with the absorbing gas between them, the rate of heat flow will be $\kappa_r \div x$ or $\frac{4}{3\alpha x}\, dW_1/dT$. Thus with surfaces one cm. apart and with an absorption coefficient of 1000, the effect of the gas would be to decrease the flow of radiant energy in the ratio 3000:4. Of course the above equation must be applied only to that part of the radiation which is strongly absorbed.

We have already seen that to account for chemical reactions on the basis of the radiation hypothesis it is necessary to assume very large values for the absorption coefficient and the existence of relatively broad absorption bands. From the foregoing reasoning it is apparent that this must lead to a marked decrease in the heat that can be transferred through the gas. It is evident, then, that if chemical reactions take place in accordance with the radiation hypothesis, dissociation of a gas should decrease rather than increase the total heat flow. Even if it be admitted that part of the heat may be carried by the diffusion and subsequent recombination of the dissociation products, there will still be less heat flow than if the energy had been radiated through the gas instead of having been absorbed. It would seem that the only increase of heat conductivity in a dissociating gas which would be consistent with the radiation hypothesis is that due to the increased heat conductivity of the dissociation products resulting from their lower molecular weight. This should never cause an increase of more than about 40%, whereas experimental values show several-fold increase.

Discussion.

The evidence of the preceding pages seems to prove beyond question that the energy involved in chemical reactions is not in general derived from the absorption of radiant heat or light. Must we then consider that the similarity between the Wien relation law and the Arrhenius equation is a mere coincidence, and how are we to explain the fact that in a unimolecular reaction the velocity is independent of the collision frequency?

Among any large number of molecules in thermal equilibrium at the temperature T the probability P that a given molecule shall have the energy E or an energy lying between E and $E + \mathrm{d}E$ is qiven by

$$P = ce^{-E/kt}, \qquad (11)$$

where c is either independent of the temperature or varies with the temperature at a rate which is negligible, compared with the variation of the exponential factor. Maxwell's distribution law of molecular velocities is a special case of the above statistical law applying to kinetic energy. The equation also holds for potential energy of position and for internal energy of molecules, even under conditions where the equipartition law is not applicable. Einstein[1] has shown, for example, that the Planck radiation equation may be derived by a very simple method from a fundamental statistical law of the above type.

It would seem, therefore, that the similarity in form between the Arrhenius and the Wien equations may very probably be due to the dependence of both of these relations upon the statistical laws. In fact, the Arrhenius equation follows directly from Equation 11 if we assume that the chance that a given molecule will undergo a chemical reaction is proportional to the probability that it contains a specified amount of energy. The exponential factor $e^{-E/kt}$ gives the fraction of the molecules which have an energy in excess of E and which may thus be called "active" molecules. This factor, however, is a pure number and does not involve

[1] A. Einstein, *Physik. Z.*, 18, 121 (1917).

time. The velocity of a unimolecular reaction is measured by $(1/n)\ dn/dt$ where dn is the number of molecules which react in the time dt and n is the total number of molecules of the reacting substance. This quantity has the dimensions of a frequency. The velocity of a reaction may thus be expressed by

$$k_1 = \frac{1}{n}\frac{dn}{dt} = \nu_0 e^{-E/kt}, \tag{12}$$

where ν_0 is a frequency (dimensions t^{-1}) characteristic of a particular reaction, but which is at least approximately independent of the temperature.

In interpreting this equation we must keep in mind that Equation 11, upon which it is based, depends upon the assumption of thermal equilibrium. In order that Equation 12 may hold, it is, therefore, necessary that the number of molecules which dissociate per second shall be very small compared to the number that become active. The active molecules must thus remain active for only very short periods of time. Let τ be the average duration of these periods.

There are 2 types of mechanism which may underlie Equation 12.

I. We may assume that ν_0 represents the rate of dissociation of the active molecules. Thus $\nu_0 dt$ is the chance that a given active molecule will dissociate in the time dt. As we have seen, however, the chance that any molecule will dissociate during any single period of activity must be very small. Therefore, $\nu_0\tau$ must be small compared to unity or

$$\tau << 1/\nu_0. \tag{13}$$

II. We may assume that a regular periodic phenomenon of frequency ν_0 is taking place in all molecules, so that there are ν_0 "crises" in each molecule per second. Whenever a crisis occurs in an *active molecule* dissociation results. The chance that a crisis shall occur during any single period of activity of a molecule is, in this case also, equal to $\nu_0\tau$ so that the condition of Equation 13 must be fulfilled.

To obtain a more concrete conception of the mechanism of a unimolecular reaction, let us consider again the dissociation of phosphine at 948° K., at which temperature the velocity of the reaction is 0.012 per second. Taking the heat of activation as 73,000 calories per g. molecule, we find that the exponential factor of Equation 12 is equal to 1.6×10^{-17}, and therefore, since $k_1 = 0.012$, the value of ν_0 is 7.5×10^{14}. It follows, then, from (13), that τ, the average period of activity, must be *very small* compared to 1.3×10^{-15} seconds. At atmospheric pressure each molecule of phosphine makes only 4.2×10^9 collisions per second with other molecules. The average time between collisions is thus 2.4×10^{-10} seconds. In other words, the duration of a free path is many millions of times greater than the period during which the molecules remain active.

It is natural, then that the rate of reaction should not be dependent upon the number of collisions. This result may also be reached in the following manner.

Suppose we should assume that the activation of molecules is brought about only by collisions. Since the proportion of active molecules is given by the exponential factor whose value is 1.6×10^{-17}, it follows that the only one collision out of 6.2×10^{16} could result in the formation of an active molecule. But each molecule makes only 4.2×10^{9} collisions per second, so that it would become active only once every 1.5×10^{7} seconds (170 days). The average life of a molecule of phosphine is, however, only 83 seconds (the reciprocal of the reaction velocity). The equilibrium between active and inactive molecules must therefore be brought about enormously more rapidly than is possible by the direct action of collisions.

This brings us face to face with a fundamental difficulty. It is generally assumed that the activation of a molecule depends on the acquisition of an amount of energy corresponding to the heat of activation. In the case of the dissociation of an elementary gas into atoms, the heat of activation has been found to be equal to the heat of dissociation. The question arises, How does the molecule acquire this energy? We have just seen that by means of collisions at 948° K. the molecule of phosphine can receive enough energy for activation only once every 170 days. Since the actual life of the molecule is very short compared to this, it is evident that the molecules which do dissociate must have acquired the energy for activation subsequently to their last collisions. We have already proved that the radiant energy (assuming full black-body radiation) is millions of times too small to supply the energy needed for the dissociation. This discrepancy is further magnified when we consider that the number of molecules which become active per second must be much greater than the number which dissociate. The radiation hypothesis, therefore, does not help us out of the difficulty.

Unless we are to assume some new and unknown agency by which energy may be transmitted to isolated molecules, or are willing to renounce the conservation of energy, it seems necessary to conclude that each molecule must contain within itself the energy required for its own dissociation. This must be true no matter what the temperature may be. We are thus forced to assume a "Nullpunktsenergie" or zero temperature energy. The difference between the active and inactive molecules is thus not one of total energy content, but lies rather in the availability of the internal energy for the purposes of chemical action. The exponential factor of Equations 11 and 12 must then represent the probability that the energy is in a form that renders the molecule active.

We must thus conceive of a thermal equilibrium between the electrons or other parts of a molecule, brought about by the collisions between molecules. This thermal agitation inside the molecule will presumably be governed by statistical laws and by quantum relations and will not even approximately be in accord with the equipartition law, and, therefore, the energy will be relatively small in amount. The distribution of this energy among the different parts of the molecule determines, however, the availability of the comparatively large store of zero temperature or latent energy within the molecule. According to this view it is not surprising that τ, the period during which molecules remain active, should be small even when compared to 10^{-15} seconds.

As far as I am aware, the above reasoning has not previously been applied to chemical reactions, although it resembles in many points some of the physical theories of radiation, photoelectric effect, etc. For example, in the theory of heat radiation it has been necessary to conceive of temperature as applying to the oscillations of single electrons in atoms. The velocity of electrons emitted in the photoelectric effect is independent of the intensity of the light, so that it has seemed necessary to assume, at least, for low intensities, that the energy must have resided in the atom, and that the effect of the light is to render the energy available to the electron by some sort of trigger action. In this case, radiation plays a part analogous to that of the collisions in chemical reactions. Thus in the photoelectric effect, the energy of the electron emitted by any atom may be very great compared to the radiant energy absorbed by *that atom*, although the total energy of the electrons emitted by any large surface is always less than the toal radiant energy absorbed. Similarly, in a chemical reaction, the energy required to activate a molecule may be very great compared to the energy that is transferred to *that molecule* by a collision, although the total energy required for the chemical reaction in a mass of gas is always less than the total energy that is transferred by collisions, but is usually enormously greater than the total energy transferred by radiation. Both in the photoelectric effect and in chemical reactions, it is necessary to assume a kind of trigger action by which an energy of low intensity is able to control the disposition of an energy of high intensity.

The difficulties of explaining the photoelectric effect have seemed nearly insuperable. Planck and later, Nernst,[1] have assumed a "Nullpunktsenergie" in order to help explain this and other phenomena. The conception of Nernst bears many resemblances to that which has been developed in the present paper. Nernst assumes, however, that the zero temperature energy owes its origin to a zero temperature radiation of great intensity which passes through all bodies without absorption, except insofar as it can be rendered available by a trigger action depending upon certain

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[1] *Verh. deut. Physik. Ges.*, 18, 83 (1916).

thermal changes in bodies. It hardly seems necessary to assume this zero temperature radiation to explain chemical reactions. But by doing so, we would have a new radiation hypothesis for chemical action which would be free from the objections that we have raised against the old one.

As an illustration of the difficulties that have arisen in connection with the photoelectric effect, I may refer to a recent paper by D. L. Webster,[1] in which it is proposed to abandon the conservation of energy except as a statistical result, in order to explain some of these difficulties. Webster's reasoning can be applied with nearly equal force to the case of chemical reactions, but it seems that the assumption of a zero temperature energy which we have made above is preferable to an abandonment of the conservation of energy. The problem, however, is by no means solved, but it seems probable that the final solution will clear up both the chemical and the photoelectric problem.

The similarity between the Wien radiation law and the Arrhenius reaction velocity law is in many respects analogous to the relation between the laws of photoelectric and thermionic electron emission. It has been found by Richardson that the thermionic emission from a heated body increases with the temperature according to an equation similar to the Wien or Arrhenius equation. Also he found that the distribution of velocities among the electrons is given by Maxwell's distribution law. On the other hand, the number of photoelectrons emitted is proportional to the intensity of the light and the energy of the electrons is proportional to the frequency of the light. But if we let the total radiation from a heated black body fall on a metal, the number of photoelectrons emitted should increase with the temperature of the black body in accord with Wien's equation, and the energy of the electrons should increase in proportion to the temperature, and thus in accord with Maxwell's law, because the average frequency of the light from a black body increases in proportion to the temperature. As a matter of fact, A. Becker[2] has recently shown that the distribution of velocities, as well as the most probable velocity, among the photoelectrons emitted from any substance as a result of illumination by black-body radiation (temperature T) is the *same* as that found among the electrons emitted by thermionic emission when the emitting body has the temperature T. It is thus natural to assume that the thermionic emission from a heated body is caused by the photoelectric effect of the radiation emitted by the body. Experiments show, however, that the number of electrons emitted thermionically is of the order of a million times greater the number that can be produced by the photoelectric effect from black-body radiation of corresponding

[1] *Phys. Rev.*, 26, 31 (1920).

[2] *Ann. Physik.*, 60, 30 (1919).

temperature.[1] This result is probably closely related to the fact that chemical action follows laws similar to those of radiation, but the amount of chemical action is millions of times greater than can be explained by radiation.

Summary.

In order to account for the close similarity between the Arrhenius equation for the velocity of chemical reactions and the Wien radiation law, and also to explain the fact that the velocities of unimolecular reactions cannot be dependent upon the number of collisions between molecules, it has been proposed by Trautz, Wm. McC. Lewis, Perrin, and others, that molecules can take part in chemical reactions only after they have become activated, and that this activation is brought about by the absorption of a nearly monochromatic radiation. There seems to be ample evidence in support of the activation of molecules, but the *radiation hypothesis*, by which this activation depends upon the absorption of radiation, does not rest upon such a firm foundation.

There are two decisive tests of the validity of the radiation hypothesis: (1) the reacting substance must absorb radiation of the frequency required to produce activation, and there must, therefore, be an absorption band which includes this frequency; (2) the total amount of radiant energy absorbed must be sufficient to supply the known heat of activation to the molecules which react.

Examination of the available data indicates that there is little evidence that absorption bands occur which include the frequency corresponding to the activation. Thus in the dissociations of the following substances, phosphine, nitrous oxide, nitric oxide, phosgene, and the vapors of phosphorus and arsenic, the activation frequencies lie within the range of the visible spectrum, but the fact that the gases are all colorless proves that there are no absorption bands in this region.

An analysis of the experimental data on the velocity of dissociation of phosphine proves that the energy actually required for activation in one cc. at 948° K. is 4×10^{10} times greater than the amount that can be supplied by radiation from one sq. cm. of surface at 948° K. Further-

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[1] Richardson, Becker and others have given evidence of this kind. In 1912 I made some very careful experiments (unpublished) to see whether photoelectric emission from tungsten could explain the thermionic emission. Tungsten filaments were heated nearly to their melting-point in highly evacuated bulbs immersed in liquid air. The vaporized tungsten produced an exceptionally high vacuum as a result of the clean-up effect, and formed an opaque conducting film on the glass which was made to serve as a gas-free electrode for collecting electrons emitted thermionically or for emitting photoelectrons. The photoelectric effect of the light from the filament on the clean film of distilled tungsten was easily detected, and increased with the temperature in the manner expected, but the magnitude of the photoelectric currents was of the order of one-millionth of the corresponding thermionic currents.

more, when the intensity of the radiation in question is increased enormously (as by using daylight), the reaction velocity does not show a corresponding increase.

Experiments with nitrogen peroxide, hydrogen, and iodine vapor have proved that the heat conductivity of dissociating gases is many times greater than that of similar gases which do not dissociate. The increase in heat loss from small wires, due to the dissociation of a surrounding gas, is often more than 10 times the total energy radiated from the wire. On the basis of the radiation hypothesis, however, the dissociation entails an absorption of radiation and thus could produce only a decrease in the heat lost from the filament. These experiments furnish conclusive evidence against the radiation hypothesis.

The similarity between the Arrhenius and the Wien equation thus results from the fact that both reaction velocity and radiation are fundamentally dependent upon phenomena involving probability. Both equations can be derived from the same statistical law. It is shown that the energy for the activation of molecules must be derived from *internal* energy of the molecules. This conclusion involves certain very fundamental difficulties, but it is shown that these are of the same nature as those that are encountered in the theory of the photoelectric effect, thermionic emission, and other phenomena involving quantum relations.

SCHENECTADY, N. Y.

[FORTY-SECOND CONTRIBUTION FROM THE COLOR LABORATORY, U. S. BUREAU OF CHEMISTRY.]

THE INDEPENDENT ORIGIN OF ACTINIUM.

BY ELLIOT QUINCY ADAMS.

Received August 27, 1920.

Actinium has been shown[1] to be derived from Antonoff's "uranium Y,"—isotopic with uranium X_1 (and thorium)—through a long-lived intermediate variously known as uranium Z, eka-tantalum and protactinium. This element, as the second name indicates, is homologous to tantalum and is isotopic only with brevium (uranium X_2). The production of uranium Y from chemically pure uranium shows that it must be derived by an α-ray transformation from uranium or an isotope of uranium. Hahn and Meitner[2] believe that Hönigschmid's value (206.05) for the atomic weight of uranium-lead proves uranium Y to be derived from uranium II, since 3% of actinum-lead of atomic weight 210 (if uranium Y were derived from uranium I) would raise the mean to 206.12. The suggestion

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[1] Frederick Soddy and John A. Cranston, *Proc. Roy. Soc.* **94A**, 384–404 (1918); Otto Hahn and Lise Meitner, *Ber.*, **52B**, 1812–28 (1919); *Physik. Z.*, **20**, 529–33 (1919).

[2] *Loc. cit*

of Piccard[1] that uranium Y is derived from actino-uranium, an isotope of uranium, has been held by Soddy and Cranston[2] to involve the assumption that the periods of uranium I and actino-uranium must be the same.

This assumption is by no means necessary, as the following considerations will show. For the actinium-uranium ratio to remain constant with respect to *time* would, indeed, require equality of period of uranium I and actino-uranium. The experimental results, however, do not show constancy with respect to *time;* they demonstrate approximate constancy with respect to *place*. If the isotopes were thoroughly mixed before the beginning of the geologic history of the earth, and if neither of them has since been supplied from another source (as the disintegration of an unknown radio-element of comparable period), their ratio should be the same everywhere on the earth at any time, but should everywhere change progressively at a rate dependent on the difference in period of the 2 isotopes. The enormous periods make the detection of such a "secular change" in the ratio a matter of extreme difficulty.

By analogy with uranium-lead (206.00) and thorium-lead (208.00), actinum-lead should have an atomic weight of 207, giving for (uranium + 3% actinium)-lead a mean value of 206.03, which agrees well with Hönigschmid's 206.05, particularly as the presence of thorium-lead or any ordinary lead would make the experimental figures too high.

The relation between the 3 series is shown in the table. For the sake of symmetry the actinium series begins with a *hypothetical* β-ray element of valence 5. Since the longest-lived of the known β-ray elements, radium D, has a half-period of only 24 years, the assumed element must, ages ago, have disintegrated quantitatively to form actino-uranium. The table gives the atomic weight and valence of each element and the type of radiation given out in each transformation. The 2 sub-groups of the Mendeleeff table are indicated by the letters A and B. The names "radium emanation," "actinium emanation" and "thorium emanation" have been shortened, respectively, to "radon," "actinon" and "thoron," names which suggest that the element in question is an inert gas.[3] The valences given in black-faced type point out the return to the original valence after 3 transformations and, with change from the A to B sub-group, after 7 more transformations. The valences given in *italics* show a similar repetition of the valence IV, 3 and 10 steps *before* the final product (lead).

Since each line represents a step in the disintegration, where both α-

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[1] A. Piccard, *Arch. Sci. Phys. Nat.* [4], 44, 161 (1917).

[2] *Loc. cit.*

[3] The name "niton" suggested by Ramsay fails to show the relation of the element to radium. It might be well, similarly, to change "helium" to "helion." The former name was given by Lockyer to what he believed to be a *metallic* element in the sun.

and β-changes occur with the same element the products will be given together on the line below, the one occurring in smaller amount being in parenthesis. It will be noted that radium D is given as the common product of radium C′ and radium C_2, thorium-lead as the common product of thorium C′ and thorium D, etc. While such identity has not been proved,—and indeed could be proved only in the first instance, until means are perfected for detecting and separating non-radioactive isotopes,—it seems unreasonable to assume unnecessarily the possibility of isotopes of the same atomic weight. No instance of such elementary isomerism has yet been established.[1]

Table I.

		Uranium series.			Actinium series.			Thorium series.
238	VI A	Uranium I	...		....	...		....
α								
234	IV A	Uranium X_1	...		....	...		....
β								
234	V A	Uranium X_2	235	V A	(hypothetical)	...		....
β			β					
234	VI A	Uranium II	235	*VI* A	Actino-uranium	...		....
α			α					
230	*IV* A	Ionium	231	*IV* A	"Uranium Y"	232	IV A	Thorium
α			β			α		
226	II A	Radium	231	V A	Protactinium	228	II A	Mesothorium 1
α			α			β		
222	O	Radon	227	III A	Actinium	228	III A	Mesothorium 2
α			β			β		
218	VI B	Radium A	227	IV A	Radio-actinium	228	IV A	Radio-thorium
α			α			α		
214	IV B	Radium B	223	II A	Actinium X	224	II A	Thorium X
β			α			α		
214	V B	Radium C	219	O	Actinon	220	O	Thoron
$\beta(\alpha)$			α			α		
214 (210)	VI B (III B)	Radium C′(C_2)	215	VI B	Actinium A	216	VI B	Thorium A
$\alpha(\beta)$			α			α		
210	*IV* B	Radium D	211	*IV* B	Actinium B	212	*IV* B	Thorium B
β			β			β		
210	V B	Radium E	211	V B	Actinium C	212	V B	Thorium C
β			$\alpha(\beta)$			$\beta(\alpha)$		
210	VI B	Radium F	207 (211)	III B (VI B)	Actinium D (C′)	212 (208)	V B (III B)	Thorium C′ (D)
α			$\beta(\alpha)$			$\alpha(\beta)$		
206	*IV* B	Uranium-lead	207	*IV B*	Actinium-lead	208	IV B	Thorium-lead

The atomic weight and valence relations are simply explained by the assumption that (1) the hypothetical first member of the actinium series and (2) thorium differ from uranium by the replacement of, respectively,

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[1] If actinium were a branch product of uranium I or II, there would be several such cases.

one and two α-particles by hydrogen ions. The latter are not lost in the radioactive disintegration and increase correspondingly the atomic weight of the lead finally resulting. It is interesting to note that in the actinium series (with presumably an *odd* number of hydrogens in the atomic nucleus) the tendency shown in the uranium and thorium series for β-particles to come off in successive transformations is replaced by a tendency to come off in alternate transformations.

As Soddy and Cranston have pointed out[1] the actinium series differs from the uranium series so markedly,—particularly in the constant of the Geiger-Nuttall relationship between period of transformation and range of α-particles emitted,—as to favor the "suggestion that the actinium and radium families may be quite distinct."

Summary.

1. The assumption (made by Piccard) that the actinium series is derived neither from uranium I nor from uranium II, but from a third isotope (actino-uranium) does not require (as Soddy supposed) the identity of period of the first and third.

2. The relation of the 3 series (uranium, actinium and thorium) becomes more symmetrical if a hypothetical isotope of protactinium (= eka-tantalum = uranium Z) be assumed as the parent of actino-uranium by a β-ray transformation.

3. This element, and likewise actino-uranium are predicted to have an atomic weight 235, corresponding to protactinium 231, actinium 227 and actinium-lead 207.

4. This last value agrees well with Hönigschmid's value of 206.05 for the atomic weight of uranium-lead containing approximately 3% of actinium lead.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN.]

PERCHLORIC ACID AS A DEHYDRATING AGENT IN THE DETERMINATION OF SILICA.

BY H. H. WILLARD AND W. E. CAKE.

Received August 30, 1920.

In the determination of silica the latter is usually rendered insoluble by evaporating the hydrochloric acid solution to dryness and dehydrating the residue at 100° to 120°. This method requires considerable time, and a small amount of silica passes into solution when the salts are dissolved out by acid. Efforts have been made to dehydrate the silica in other ways which would be more rapid and equally or more effective. Drown[2] first suggested the use of hot conc. sulfuric acid as a dehydrating

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[1] *Loc. cit.*

[2] Drown, *J. Inst. Min. Eng.*, 7, 346 (1879).

agent for the determination of silicon in steel, where rapidity is essential, and this method is widely used at the present time. It has several disadvantages, however. Insoluble ferric sulfate separates, causing bumping unless great care is taken, and this sulfate often does not readily dissolve after the solution is diluted. The use of acetic anhydride was suggested by Gooch, Reckert, and Kuzirian[1] but offered no advantages and was no more effective than evaporation to dryness.

The dihydrate of perchloric acid, $HClO_4.2H_2O$, boils at 203° and at this temperature is a powerful dehydrating agent. It seemed probable, therefore, that it could replace sulfuric acid in the method mentioned above, and to great advantage, since its salts are nearly all readily soluble both in the concentrated acid and in water. This was found to be true. Without danger of forming insoluble salts it can be used with all silicates, metals and alloys which are soluble in acids, while sulfuric acid is utterly useless in the presence of lead, barium, strontium and calcium, and is difficult to use in many other cases. Moreover, it is more effective in rendering the silica insoluble than the usual method of evaporation to dryness, and it is extremely rapid. It is, however, without action on those silicates which are not decomposed by hydrochloric acid.

The method in general consists in dissolving the metal or silicate in hydrochloric or nitric acid, adding perchloric acid, or dissolving directly in perchloric acid, evaporating to dense fumes of the latter, boiling gently for 15 or 20 minutes to dehydrate the silica, cooling and diluting with water. All salts are instantly soluble and the silica is filtered off and determined as usual. It contains less impurity than when separated by the usual methods.

The perchloric acid used in this work was prepared from ammonium perchlorate by the method described by one of the authors,[2] and purified by distillation under reduced pressure. If distilled under atmospheric pressure there is some decomposition which is greater the slower the rate of distillation. When 500 cc. of acid containing 67% of perchloric acid was distilled in 50 minutes, the loss by decomposition was about 3.5%. When the time was extended to 135 minutes, the loss was 13%. In the method referred to above it should be noted that the proportions of ammonium perchlorate, hydrochloric acid and nitric acid there recommended are satisfactory when a fairly pure salt is used, but the commercial perchlorate requires 10 to 20% more of the acids.

The chemically pure acid has been on the market for some time, so that it is no longer necessary to prepare it. The price is still rather high, but if there is sufficient demand, it can be produced cheaply.

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[1] Gooch, Reckert and Kuzirian, *Am. J. Sci.*, 186, 598 (1913).

[2] Willard, THIS JOURNAL, 34, 1480 (1912).

The following procedures are recommended for the differnt classes of materials and these were followed in obtainin the results tabulated below.

Procedure for Metals and Alloys.

Weigh out a sample corresponding to about 10 mg. of silica, using a 100 or 150 cc. beaker. Dissolve it in either nitric or hydrochloric acid, depending on which reagent is more suitable for effecting solution. For steel, 20 to 40 cc. of dil. nitric acid (sp. gr. about 1.17) will be found convenient. After the action has ceased add 8 to 10 cc. of perchloric acid (60 to 70%) for each gram of metal dissolved. The amount of acid required depends upon the solubility of the metal perchlorate in hot conc. perchloric acid. In the case of aluminum and its alloys it is necessary to use as much as 15 cc. of perchloric acid per gram of sample. Support the cover glass on glass hooks to facilitate evaporation, place the beaker on the hot-plate and evaporate to copious fumes of perchloric acid. Remove the glass hooks to prevent unnecessary loss of acid and boil 15 to 20 minutes, so that the acid refluxes down the side of the beaker. Especial care must be taken never to allow the boiling contents of the beaker to become solid, since if this occurs the separation of silica is always incomplete. If there is a tendency for much insoluble perchlorate to separate out, either the heating is not properly regulated or insufficient acid is present. In the case of aluminum, however, there is always a considerable amount of insoluble perchlorate. As the solution cools it usually becomes completely solid. Dilute with 4 or 5 times its volume of water, heat to boiling, filter off the silica, wash it with very dilute hydrochloric acid and finally with water, ignite and weigh as usual. Treat the precipitate with hydrofluoric and sulfuric acids, ignite and weigh the residue to determine the weight of pure silica. This correction is usually very small.

The metal may be dissolved directly in hot conc. perchloric acid but the action is often so violent as to be almost explosive. For this reason it is usually advisable to use some other acid, but dil. perchloric acid may be used if the action is rapid enough.

If a liberal amount of perchloric acid is used, the process is more satisfactory and the separation of silica more certain. The amount suggested is a minimum to economize acid as much as possible.

High per cent. ferrosilicon is not decomposed by perchloric acid.

Procedure for Limestone and Soluble Silicates.

In a 100 to 150 cc. beaker dissolve about 0.5 g. of the material in a mixture of 5 cc. perchloric acid and 10 cc. of water. If the silica content is very high, it is advisable to use more acid. Evaporate to dense fumes of perchloric acid and follow the procedure for metals described above. Insoluble silicates must first be fused with sodium carbonate as usual.

In order to test the accuracy of the process several experiments were carried out using a known weight of silica in the form of quartz sand containing only 0.025% of impurity. It was fused in a platinum crucible with sodium carbonate, the melt dissolved in water in a platinum dish and perchloric acid added. The silica was separated as described above. The filtrate was evaporated to dryness and taken up with hydrochloric acid to recover any silica remaining in solution. The residue left after treatment with hydrofluoric and sulfuric acids was obviously sodium sulfate and was, therefore, converted into its equivalent of oxide before subtracting from the weight of the impure silica. The results appear in Table I.

TABLE I.

Expt.	Weight SiO_2 taken. G.	Weight impure SiO_2. G.	Weight pure SiO_2. G.	Error. Mg.	Weight SiO_2 from filtrate.[a] Mg.
1	0.3613	0.3626	0.3615	0.2	0.0
2	0.1553	0.1545	0.1541	1.2	0.6
3	0.1716	0.1710	0.1708	0.8	0.7
4	0.1400	0.1395	0.1394	0.6	0.4
5	0.1503	0.1496	0.1494	0.9	1.1
6	0.3152	0.3140	0.3138	1.4	1.3

[a] Not used in calculating error.

The removal of silica is remarkably complete considering the amount present, and in all but the most accurate work the amount remaining in solution can be disregarded. In the usual method the latter amounts to several milligrams.[1]

Table II gives the results obtained with limestone and silicates.

TABLE II.

Expt.	Material.	Weight of sample. G.	Weight of impure SiO_2. G.	Weight of pure SiO_2. G.	SiO_2 found. %.	SiO_2 usual method. %.	SiO_2 in filtrate.[a] G.
7	Cement A	0.3337	0.0756	0.0747	22.38	22.48	0.0001
8	Cement A	0.3507	0.0797	0.0790	22.50	22.48	0.0003
9	Cement B	0.6205	0.2244	0.2238	36.07	36.10	......
10	Limestone	0.6693	0.0356	0.0346	5.18	5.20	......
11	Limestone	0.5915	0.0316	0.0306	5.18	5.20	......
12	Willemite[b]	1.5199	0.3911	0.3743	24.63	24.70	0.0010
13	Willemite	1.3331	0.3433	0.3289	24.62	24.70	0.0009

[a] Not used in calculating per cent. of SiO_2.

[b] Contained a little gangue.

The silicon present in iron and steel separates out as the gelatinous precipitate of silicic acid, while in the case of aluminum part of the silicon is precipitated in the form of brown amorphous silicon which is not oxidized by perchloric acid. This is converted on ignition to silicon dioxide.

Table III shows the results obtained with metals.

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[1] Hillebrand, THIS JOURNAL, 24, 366 (1902).

TABLE III.

Expt.	Material.	Weight of sample. G.	Weight of impure SiO_2. G.	Weight of pure SiO_2. G.	Silicon found. %.	Silicon present. %.
14..........	B. of S. Iron D	1.0675	0.0603	0.0600	2.64	2.64
15..........	B. of S. Iron D	0.6496	0.0369	0.0368	2.66	2.64
16..........	B. S. Steel 1% C	3.0897	0.0103	0.0101	0.153	0.153
17..........	B. S. Steel 1% C	3.0406	0.0102	0.0100	0.153	0.153
18..........	B. S. Steel 30*a*	5.1190	0.0265	0.0259	0.238	0.228
19..........	B. S. Steel 30*a*	5.1659	0.0272	0.0259	0.235	0.228
20..........	B. S. Steel 30*a*	2.0565	0.0110	0.0106	0.237	0.228
21..........	Steel 5% W.	2.1036	0.0592	0.0068	0.147	0.135
22..........	Steel 5% W.	2.0120	0.0405	0.0061	0.142	0.135
23..........	"99%" Aluminum	1.1417	0.0076	0.0072	0.28	0.28
24..........	"99%" Aluminum	2.0621	0.0144	0.0124	0.28	0.28
25..........	Nickel wire	3.3265	......	0.0157	0.22	0.21[a]
26..........	Nickel wire	3.1486	......	0.0145	0.22	0.21

[a] Drown's method.

It was noticed that some tungsten steels formed a clear solution in nitric acid and that in a few of these cases the tungsten remained in solution after evaporation with perchloric acid. This allowed the method to be applied to the determination of the silicon in such steels. The steel used in Expts. 21 and 22 was of this character. The silica was contaminated with both ferric oxide and tungsten trioxide. Much more perchloric acid was required in this case to prevent the precipitation of tungstic acid. This method is applicable only in comparatively few cases, since with most tungsten steels the tungstic acid precipitates.

Summary.

1. The silica in metals and silicates can be rendered insoluble by boiling the conc. perchloric acid solution (60 to 70%) for a short time.

2. Less silica remains in the filtrate than by the usual method of evaporating the hydrochloric acid solution to dryness, and the process is far more rapid.

3. The perchlorates formed are dissolved instantly upon dilution with water, leaving pure silica, uncontaminated by difficultly soluble salts.

ANN ARBOR, MICH.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

SOLUBILITY V. CRITICAL SOLUTION TEMPERATURES OF WHITE PHOSPHORUS WITH VARIOUS LIQUIDS.

BY JOEL H. HILDEBRAND AND THEO. F. BUEHRER.

Received September 7, 1920.

Introduction.

According to the theory of solubility advanced by one of us, and supported by extensive experimental data, in the previous papers of this series,[1] Raoult's law expresses the maximum solubility to be expected in the case of solutions of relatively non-polar substances, and where no changes arise in the molecular species present. This maximum solubility is shown whenever the substances are of equal internal pressure in the liquid state, while differences in internal pressure give rise to roughly proportional decreases in solubility.

In the case of non-polar liquids sufficiently unlike in internal pressure to form 2 liquid phases, the critical temperature of mixing of the 2 layers may be taken as a measure of their mutual solubility, as has been previously[2] explained. When one liquid forms 2 layers with several others the critical mixing temperatures can serve to compare the deviations from Raoult's law, or the solvent powers of the first liquid for the several others.

But few of the substances in the table of relative internal pressures given in the third paper are far enough apart in their internal pressures to form 2 liquid layers, so that other methods of studying their solutions must be employed. However, white phosphorus, at the bottom of the list, is so different from most of the other substances there given that a number of 2-layer systems are possible. In the third paper the following statement was made: "It is to be expected that, except as relative internal pressures may be altered by changing temperature, there will be a progressive rise in the critical temperatures of mixing of molten phosphorus with another liquid as we ascend the table." The present paper presents the results of experiments made to test this prediction.

Purification of Materials.

As one ascends in the table of internal pressures to substances above carbon disulfide the critical temperatures of mixing with phosphorus become so high as to make desirable the selection of substances of low pressure. The substances chosen for the investigation were carbon disulfide, ethylene bromide, *p*-dibromobenzene, phenanthrene, naphthalene, chlorobenzene and decane.

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[1] THIS JOURNAL, **38**, 1452 (1916); **39**, 2297 (1917); **41**, 1067 (1919); **42**, 2180, (1920). There has recently come to our attention in a paper by P. Walden, *Z. physik, Chem.*, **66**, 409 (1909), a partial statement of the same theory as governing the solubility of other liquids in water.

[2] *Ibid.*, **38**, pp. 1455–1458. See also paper by Keyes and Hildebrand, *ibid.*, **39**, 2126 (1917).

Since carbon disulfide decomposes on standing, especially when exposed to light, it was purified immediately before use. Some carbon disulfide which had stood in contact with lime for several months was shaken with mercury and then with finely pulverized mercuric chloride, which is somewhat soluble in the liquid and which removes the sulfur. Fractional distillation by the aid of a bead column yielded a product which boiled at 46.1°.

The ethylene bromide used was shaken with a solution of sodium carbonate, washed repeatedly with distilled water, left in contact with calcium chloride for 36 hours and fractionally distilled. The portion distilling between 131.5° and 133° was fractionally crystallized. The material used had a melting-point of 9.5° and a boiling-point of 132.6°.

Very pure samples of *p*-dibromobenzene and phenanthrene were used after recrystallization from benzene.

Naphthalene, already of a high degree of purity, was twice sublimed and then recrystallized, the first crystals from the molten liquid being selected.

Chlorobenzene and decane, already very pure, were used without further purification. The high critical temperatures of these substances with phosphorus made accurate determinations impossible, and careful purification was, therefore, without purpose.

The principal impurities likely to be present in phosphorus are arsenic and oxides of phosphorus. Some high grade red phosphorus was used as a source of material. It was boiled with a solution of sodium hydroxide, washed with distilled water, then with alcohol and finally dried *in vacuo* at about 110°. On distillation in the dark or in ruby light this yielded beautiful colorless crystals of active phosphorus. This distillation was carried out in connection with the filling of the tubes with mixtures to be used, as described in the succeeding paragraphs.

Experimental Procedure.

The filling of the tubes with phosphorus and the respective substances whose critical temperatures of mixing with phosphorus were to be determined, was carried out in an apparatus illustrated in Fig. 1, constructed of Pyrex glass. The purified red phosphorus was put into Compartment A, which was then sealed off at H. Wads of glass wool were placed at the ends of both A and B to avoid dusting over during the distillation. The substance whose mixtures with phosphorus were to be investigated was introduced into E, which was then sealed and evacuated to remove dissolved air. When a solid substance was used it was melted during the evacuation.

White phosphorus distilled into B upon heating the tube A to about 300°. To insure uniform temperatures the tube A was enclosed in a block of aluminum which was heated by a Bunsen burner. A small amount of lime was used in B to retain there any traces of oxides of phosphorus. Upon gently heating B the white phosphorus distilled into J when it was later washed down into the tubes D by the other component distilled from E. When the substance in E was liquid, having an appreciable vapor pressure, its vapor was confined to E during the distillation of the phosphorus by means of the device shown at F and G, suggested by Dr. R. F. Newton, of this laboratory. F is a scratched capillary tube and G contains an iron nail enclosed in glass which could be lifted magnetically so as to break the capillary and allow distillation of the liquid from E to J. This arrangement was not used when E contained such a substance as phenanthrene. After a little practise it was found possible to adjust the contents of the tubes D so that they contained the desired proportions of the 2 components, after which, they were sealed off. The entire operation was carried out in ruby light except for the slight illumination from a hand torch. This procedure yielded tubes entirely free from visible signs of red phosphorus and presumably from other impurities as well. The tubes were kept in the dark until used.

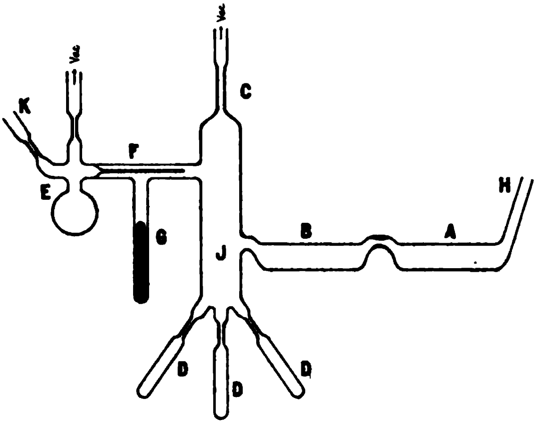

Fig. 1.

In the case of the carbon disulfide mixtures the temperatures of mixing were far below the freezing-point of phosphorus. It was, nevertheless, possible to prevent crystallization of phosphorus in many cases by introducing a trace of alkali, one drop of 3 *N* solution. This alkali probably did not exert a measurable effect upon the observed temperatures, since it is nearly insoluble in both of the other liquid phases present.

Except when carbon disulfide was used the temperatures of mixing were determined in an electrically heated air-bath provided with small windows. The air was vigorously stirred. A ruby lamp was used for the observation. One of the tubes D could be supported in this bath in such a way that it could be rocked in order to stir its contents.

The temperatures were measured by aid of a potentiometer and a 6-junction copper-constantin thermocouple, calibrated by the boiling-points of water and naphthalene and the melting-point of tin. The interpolation table of Adams[1] was found very convenient. Temperatures could be read to 0.1°.

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[1] This Journal, 36, 65 (1914).

The mixtures of phosphorus with carbon disulfide were observed in a jacketed brine-bath whose temperature could be closely adjusted. An ordinarily calibrated thermometer was used.

The temperature of mixing was at first roughly fixed, and then determined within narrower limits by decreasing the rate of heating or cooling of the air-bath so as to avoid lag in either the thermocouple or the tube. The disappearance, but more especially the appearance of the cloudiness indicating the presence of 2 liquid phases, was very sharp. The constancy of this temperature upon repeated observation was considered as evidence that the phosphorus did not react with any of the substances with which it was mixed. At higher temperatures, red phosphorus gradually formed, but except for decreasing the fluidity and transparency of the tubes, making observation more difficult, it did not seem to have any marked effect on the critical temperatures.

The composition-temperature curve for the mutual solubility of 2 liquids is always very flat at the top, so that considerable variation in composition is possible without greatly affecting the temperature of mixing. In order to be sure, however, that the composition was not too far removed from the maximum, tubes were prepared containing the substances in various proportions. The composition of the contents was determined by analysis after the observation of its mixing temperature. The method of analysis used for this purpose was oxidation with potassium iodate and titration of the excess iodate with sodium thiosulfate. A preliminary investigation showed that this method was quite accurate for the determination of either white or red phosphorus, and further that none of the other substances present had any effect with the exception of carbon disulfide. When this was used the phosphorus was determined gravimetrically by the phosphate method after oxidation with iodate.

TABLE I.

Naphthalene.

Mol. % P_4	26	49	56	60	74	75	80
Temp. of mixing, °C	132.8	201.4	195.5	202.7	201.6	200.2	190.4

Ethylene Bromide.

Mol. % P_4	41	44	47	56	63	81
Temp. of mixing, °C	169.6	165.0	163.0	165.5	162.0	151.7

	Phenanthrene.				*p*-Dibromobenzene.				
Mol. % P_4	55	57	73	80	41	49	54	61	70
Temp. of mixing, °C	199.2	199.5	199.1	198.0	154.3	159.4	162.0	163.0	159.2

Carbon Disulfide.

Mol. % P_4	6	34	43	50	59	74
Temp. of mixing, °C	—7.8	—6.7	—5.9	—6.4	—6.4	—6.6

Results.

Table I summarizes the experimental observations. Each temperature recorded represents the mean of from 6 to 10 observations upon the individual tubes. These observations seldom differed among themselves by more than 0.4°. The figures indicating composition have been rounded off to whole numbers, as the effect of composition upon temperature of mixing is small in the region investigated.

The values in Table I were plotted and a smooth curve was drawn through each set of points in order to obtain the critical temperatures shown in Table II. Temperatures are there given only to whole degrees, as any greater accuracy would doubtless be illusory.

Table II.

	Crit. temp. of mixing. ° C.	Rel. internal pressures at 20°.		
		$\gamma/V^{1/3}$.	$(5200 + 30h)/V$.	$a/v^2.10^6$.
Decane	>390	3.8	53	2.5
Chlorobenzene	264	7.1	90	4.9
Naphthalene	202	7.8	96	5.2
Phenanthrene	200	....	98	5.7
p-Dibromobenzene	163	7.9	98	6.0
Ethylene bromide	165	8.7	106	5.5
Carbon disulfide	—6.5	8.7	109	6.1
Phosphorus	....	12.4	199	13.7

The figure for chlorobenzene represents observations upon one tube only, others having burst. From the manner of disappearance of the phases, however, it was evident that the proportions were such as to yield the maximum temperature. Some red phosphorus was formed, but this seems to be so insoluble as to exert little effect.

The value for decane likewise represents a single observation. It was evident from the high interfacial surface tension that the system at 300°, where red phosphorus was rapidly forming, was still far below the critical temperature.

In addition to the figures given in the table a determination was made using anthracene, but without the careful precautions to avoid oxidation or other impurity. This gave a value of about 198°.

An attempt was also made to observe a critical temperature using bromoform. It was impossible, however, to avoid crystallization of the bromoform in the neighborhood of 0°, before separation of 2 liquid phases.

Discussion.

In Table II are given, in addition to the critical temperatures of mixing with phosphorus, the relative values of internal pressures taken from the third paper of this series. It will be seen that the prediction quoted earlier in this paper is well fulfilled by the facts. The slight reversal in the case of *p*-dibromobenzene and ethylene bromide is insignificant in view of the extrapolation involved in the figures for the former because of its high melting-point. Even this may be accounted for by a reversal of position at higher temperatures, for the value of $\gamma/V^{1/3}$ at 100° becomes 6.0 for ethylene bromide and 6.2 for *p*-dibromobenzene.

The only surprise is the great difference between the critical temperatures for ethylene bromide and carbon disulfide mixtures. Until a more quantitative treatment is given we will not attempt to account for this difference.

Summary.

Critical temperatures of mixing of liquid phosphorus withother substances have been determined as follows, decane, >300; chlorobenzene, 264; naphthalene, 202; phenanthrene, 200; *p*-dibromobenzene, 163; carbon disulfide, —6.5. These figures confirm predictions made in a previous paper.

BERKELEY, CALIF.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PRINCETON UNIVERSITY.]

A METHOD OF MEASURING LOW VAPOR PRESSURES, WITH ITS APPLICATION TO THE CASE OF TRINITRO-TOLUENE.

BY ALAN W. C. MENZIES.

Received September 7, 1920.

The method most in favor for the measurement of rather low vapor pressures is perhaps the gas-current saturation method. Against this method may be urged its cumbrousness; the trouble of maintaining constant temperatures far from room temperature over prolonged periods of time; the need of the assumption of a normal molecular weight for the vapor in question; and other objections,[1] varying in seriousness with circumstances. It is, therefore, perhaps of interest to note that a single McLeod gage can be very simply utilized in measuring low vapor pressures, yielding readings for different temperatures as fast as a bath can be adjusted to each new temperature. The present paper indicates how such measurements may be carried out.

Outline of the Method.—Elsewhere,[2] the writer has described a method for measuring vapor pressures involving the use of 2 McLeod gages, one of which actually contained the vapor in question. In the present case, in which one gage only is used, none of the vapor enters the gage.

The apparatus consists of a McLeod gage, immersed in a large vessel of stirred water to secure constancy of temperature, and connected by capillary glass tubing with a bulb, preferably cylindrical, which can be completely submerged in a bath or surrounded by a jacket to give it the temperatures desired. The bulb, which may be of glass, porcelain, platinum or other material, should have as large a volume as convenient relative to that of the gage. This simple system is connected through a mercury seal to a source of dry inert gas and to a vacuum pump. The system

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[1] Cf. Menzies, THIS JOURNAL, 42, 978 (1920).

[2] *Ibid.*, 41, 1783 (1919).

may thus be charged with, for example, dry nitrogen[1] at any pressure desired. If now the temperature of the bulb be raised, the gage should indicate an increased pressure close to that which may be computed by the gas laws from the known temperatures and previously ascertained volumes of the hot and cold parts of the system. Initial and final bulb temperatures may obviously be chosen to suit the case. For vapor-pressure measurement, in addition to the inert gas, the bulb is charged with sufficient of the substance under examination to furnish more than enough of its attenuated saturated vapor to fill the bulb completely. Vapor may be prevented from reaching the gage by sufficiently cooling a portion of the connecting tube. The initial temperature of the bulb is chosen conveniently so low that the vapor pressure of the substance will be small or negligible compared with its vapor pressure at the final temperature. Thus, when the apparatus is operated as before, one obtains a higher final pressure than if nitrogen only were present, and, from this pressure excess, an obvious application of the gas laws enables one to compute the vapor pressure of the substance at the final temperature, provided in particular, that Dalton's law may be assumed.

It would appear that the only investigator who has, in a particular case, made use of a form of this simple method of vapor pressure measurement is Villiers.[2]

The Case of T. N. T.—Knowledge of the vapor pressures of T. N. T. in a short range above its melting-point was desired by the Division of Chemistry and Chemical Technology of the National Research Council, and the case was studied as a War Problem at their request. The sample was furnished through Dr. Comey and was stated to have a melting-point of 80.5°, in agreement with Comey's published work on this melting-point.[3] Any attempt at purification other than desiccation[4] in absence of light was purposely omitted for obvious reasons. The sample is correctly named merely "T. N. T.," not "alpha trinitrotoluene."

Details and Discussion of Procedure and Measurements.—The McLeod gage, together with the cold connecting tubes, had a corrected volume of 10.69 cc., and the bulb a corrected volume of 94.01 cc. The dry nitrogen which was used as the inert gas was given a pressure of 0.5852 mm. of mercury at 23.0°. So far as the determination of the pressure difference with and without vapor is concerned, the greatest sensitiveness would be obtained by using a nitrogen pressure only slightly greater than the highest vapor pressure to be measured; on the other hand, divergence

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[1] Cf. Menzies, THIS JOURNAL, **41**, 1784 (1919).

[2] Villiers, *Ann. chim. phys.*, [8] **30**, 588 (1913).

[3] Comey, *J. Ind. Eng. Chem.*, **2**, 103 (1910). See also Carlton Smith, "T. N. T. and Other Nitrotoluenes," **1918**, p. 75; Bell and Herty, *J. Ind. Eng. Chem.*, **11**, 1124 (1919), where this m. p. is discussed with literature references.

[4] Cf. Huff, *Chem. Met. Eng.*, **21**, 570 (1919).

from Dalton's law is more to be feared with such relatively low pressures of permanent gas. Possible error due to the solution of nitrogen in the molten T. N. T. was minimized by the fact that only a minute quantity, less than a mg., was necessary in the bulb to insure saturation. By employing different nitrogen pressures, this error, had it been serious, could have been completely eliminated, as also could error arising from departure from Dalton's law. Very slow condensation of T. N. T. took place in the capillary tube where it emerged from the heating bath, and care was taken to note that the T. N. T. at the bottom of the bulb did not become exhausted. The heating bath and the thermometry were similar to those formerly described.[1] Readings were taken with the gage at 23.0° in all cases, and with the bulb at 23.0°, 81.6°, 90.1°, and 102.6°, giving vapor pressures of 0.046, 0.067 and 0.120 mm. of mercury at 0°, respectively, for the last 3 temperatures. Correction for thermal expansion of the bulb could be neglected. The observations were completed within 2 hours.

The logarithms of these pressures were plotted against the reciprocals of the corresponding absolute temperatures, and pressures for each whole degree were read off from the straight line that passed very closely through the 3 datum points. These values are given in Table I.

TABLE I.

Vapor Pressures of Liquid T. N. T. in Mm. of Mercury at 0°.

Temperature. ° C.	Pressure. Mm.	Temperature. ° C.	Pressure. Mm.
(80)	(0.042)	92	0.074
(81)	(0.044)	93	0.078
82	0.046	94	0.081
83	0.048	95	0.085
84	0.051	96	0.089
85	0.053	97	0.093
86	0.056	98	0.098
87	0.059	99	0.102
88	0.062	100	0.106
89	0.064	101	0.110
90	0.067	102	0.116
91	0.070		

Confirmation by Gas Current Saturation Method.—As one could not, *a priori*, be certain that the gas laws were followed strictly by the mixture of gas and vapor in the bulb, confirmation of these values was sought by a measurement by the gas current saturation method. For this purpose, the T. N. T. was melted over the surface of several g. of glass wool which had previously been washed with nitric acid, steamed and dried. The very large surface of T. N. T. thus produced was contained within a weighed saturator tube which could be maintained at the boiling-point of water. The loss of weight of this tube gave the weight of vapor

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[1] Menzies, THIS JOURNAL, 41, 1783 (1919).

concerned. The volume of the air current used was measured, not by use of an aspirator as is customary, but by weighing the water it evaporated at 25° from a water saturating train described in another place,[1] where also necessary precautions and corrections are referred to. Preliminary experiments having shown that an air speed of half a liter per hour gave saturation, the experiment was continued for 5 days in order to obtain a satisfactorily large loss of weight (5 mg.) from the saturator. On account of fluctuation in the barometric pressure over this period, the suitably weighted mean of many observations of the actual temperature of the saturator tube was employed. This was 99.5°, while the found vapor pressure was 0.102 mm. The vapor pressure for 99.5° as read from the curve given by the previous observations is 0.104, thus showing a degree of concordance rather closer than could be anticipated.

Either the assumptions involved in the application of each of the 2 methods are justified in this instance, or else the error is fortuitously the same for both in direction and amount. Further comment is reserved for a later publication.

Summary.

A method has been outlined by which low vapor pressures may be measured by the help of a single McLeod gage. This method is much more expeditious than the gas-current saturation method but, like it, is of accuracy subject to the truth of certain assumptions. Its application, with certain precautions necessary to its use, has been illustrated in the case of T. N. T., whose vapor pressures are here reported for each degree from 82° to 102°.

PRINCETON, N. J.

[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY OF HARVARD UNIVERSITY.]

A REVISION OF THE ATOMIC WEIGHT OF ALUMINUM. THE ANALYSIS OF ALUMINUM BROMIDE.
PRELIMINARY PAPER.

BY THEODORE W. RICHARDS AND HENRY KREPELKA.

Received September 27, 1920.

The usually accepted atomic weight of aluminum (27.1) is based chiefly on the work of J. W. Mallet,[2] published in 1880. The earlier researches of Davy, Thomson, Berzelius, Mather, Dumas, Tissier, and Terreil regarding this subject were considered carefully in Mallet's paper and therefore need not be detailed here. Those of Isnard and Baubigny are sufficiently described by Clarke,[3] who gives the bibliographical references to

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[1] Menzies, THIS JOURNAL, 42, 978 and 1953 (1920).

[2] Mallet, *Phil. Trans.*, 171, 1003 (1880).

[3] F. W. Clarke, "Recalculation of Atomic Weights," *Smithsonian Inst. Pub.*, 54, No. 3, 262 (1910).

all the early work. Of course such methods as ignition of aluminum sulfate (Berzelius and Baubigny) or conversion of the metal into nitrate and then into oxide (Tissier and Isnard) are not now acceptable for this purpose. Likewise, the analysis of aluminum halide as it was carried out by Mather[1] and even by Dumas[2] must have given wrong values, because the old method of precipitation and titration of halides was very faulty. The completion of the reaction cannot be accurately ascertained simply by the addition of a standard solution of silver until turbidity is no longer evident. In those days, moreover, no attention was given to the adsorption or occlusion of the dissolved substances by silver chloride in concentrated solutions.

Mallet's work was much more convincing; indeed, it was remarkably good for that time, and received general acclaim. He used 3 methods. First, pure ammonium alum was ignited and the remaining oxide was weighed. Second, aluminum bromide was titrated with a solution of pure silver. Third, metallic aluminum was dissolved in sodium hydroxide solution and (*a*) the volume of the hydrogen evolved was measured; again (*b*) the hydrogen set free was oxidized and weighed as water.

The difficulties connected with the first method were recognized by Mallet himself; it is probably impossible to free ammonium alum from traces of hygroscopic water without loss of crystal water. Two series of experiments with this compound were performed and gave for the atomic weight value 27.153 (as recalculated by F. W. Clarke).[3]

The second method was more promising. Aluminum bromide was prepared on a large scale (more than one kg.), no attention being paid to the purity of the factors (aluminum metal and bromine). The bromide obtained was purified by repeated fractional distillation. The arrangement of Mallet's apparatus caused every successive fraction, except the last one, to come into contact with the outside air, causing formation of oxybromide and acid gas. The contamination of the final portion with oxybromide was not necessarily prevented by the last distillation in a current of nitrogen, because the source of nitrogen used by Mallet in his work was not clearly explained and no evidence is given that it was free from oxygen and moisture. Either impurity would tend toward an elevation of the apparent atomic weight. Likewise his method of breaking the tubes containing aluminum bromide would have the same effect; for he opened his tubes in the air of the room; and by this operation, even working quickly (according to our experience) he must have lost hydrobromic acid. The possible errors tending in the opposite direction were

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[1] Mather, *Am. J. Sci.*, **27**, 241 (1835).

[2] Dumas, *Ann. chim. phys.*, [3] **55**, 151 (1859).

[3] F. W. Clarke, "The Constants of Nature," Part V, "A Recalculation of the Atomic Weights," p. 264.

less significant, since titration is far more accurate with bromide than chloride, even as formerly carried out, and since the silver employed could hardly have contained an important amount of impurity, having been carefully prepared and fused in a Sprengel vacuum. Hence his value might be expected to be too high. This series of experiments gave the value 27.098.

The experiments designed to determine the amount of hydrogen evolved by the solution of metallic aluminum were less fortunate. Impurity in the metal, hydrogen dissolved in the solution of sodium hydroxide, and the unknown tension of the water vapor of this strong solution were possible sources of error which could not be eliminated by the use of large quantities of substance. This set of experiments gave the value 27.099 for the atomic weight. The modification of this method, in which the hydrogen was weighed as water after oxidation, was subject to some of the same errors, together with others.

Nevertheless, in some respects Mallet's work deserves the commendation which it has received for 40 years. He duly considered many details of accurate weighing, and of precision in chemical operations. Because of the numerical agreement of the results obtained by the different methods, the international committee, having to choose between the value of Mallet and the more recent work of Thomsen[1] (26.99), accepted the former. Nevertheless Thomsen's work (which resembled the third series of Mallet) was more carefully executed than Mallet's. He used larger amounts of material, and weighed the loss of dry hydrogen from his apparatus as well as the oxygen needed to oxidize it. Careful corrections were made for the iron and silica found among the products of the reaction, and for the contraction occurring when the metal is dissolved. The fact that his method stood alone whereas Mallet had 4 more or less confirmatory series, doubtless militated against Thomsen's outcome, as already stated.

The most recent determination of the atomic weight of aluminum was performed by Kohn-Abrest.[2] Impure aluminum (98.68%) was dissolved in hydrochloric acid, the hydrogen evolved was burned by the copper oxide, and the resulting water was weighed. Again, impure metal was converted into oxide. The results were, respectively, 27.25 and 27.23. Kohn-Abrest used methods of an early period (without modern precautions), which are sufficiently characterized by Brauner.[3]

Of all the methods used for the determination of the atomic weight of aluminum undoubtedly the best is the analysis of pure halide, which has

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[1] Thomsen, *Z. anorg. Chem.*, 15, 447 (1897).

[2] Kohn-Abrest, *Bull. soc. chim.*, [3] 33, 121 (1905).

[3] See Brauner's article in Abegg's "Handbuch der anorg. Chemie," "At. Weight of Aluminum," III, (1), 59 (1906).

been in contact only with pure, perfectly dry nitrogen and has finally been redistilled *in vacuo*. Either the chloride or the bromide is suitable for analysis; the iodide is unstable, forming an explosive mixture with air.

We followed Mallet's example and used the bromide, because its properties are more convenient than those of the chloride. Its lower melting-point (93°) and relatively lower heat of formation are convenient in both synthesis and purification. The great difference between its melting-point (93°) and boiling-point (265°) gave a wide range for digestion of the liquid in a current of nitrogen in order to effect the elimination of bromine and other volatile impurities. Bromine has less tendency to attack glass than chlorine: another advantage. Finally, the small solubility of silver bromide facilitates accuracy in the analysis of the salt. On the other hand, the bromide, of course, has one disadvantage as material for atomic weight determination, the smallness of its content of aluminum magnifies the effect of any error.

Preparation of Materials.

Aluminum.—The task of preparing this metal in a perfectly pure state presented so many almost insuperable difficulties that we decided to use raw material of only moderate purity, and devote our available time to purifying the bromide made from it. Accordingly the best commercial sample which we were able to obtain was used in the final synthesis: namely, a standard sample of aluminum[1] made available by the Bureau of Standards. As the sample was in the form of a cylinder about 5 cm. in diameter, it was first sawed into thin disks about 3 mm. in thickness. In order to remove any surface contamination (derived from the saw) these disks were set in de Khotinsky cement and turned smooth on a lathe. The polished pieces were then washed in alcohol and cut with clean steel shears into strips about 8 mm. wide. These strips were made the anode in a very dilute solution of sulfuric acid in order to facilitate the removal of a possible trace of iron on the surface, and were then etched with dil. hydrobromic acid, washed many times with boiling distilled water and finally dried in an air-bath at 120°. Any trace of remaining iron must have been removed together with bromide of silicon during the fractional distillation which followed, as described below.

Bromine.—Ordinary C. P. bromine was twice redistilled from a concentrated solution of pure potassium bromide. The middle portion of the second distillate was allowed to react with a solution of pure potassium oxalate. The potassium bromide thus formed was twice recrystallized. In order to remove any iodine which might be present the solution of potassium bromide was digested and evaporated to dryness twice with a little

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[1] According to the analysis made by the Aluminum Co. of America, this aluminum contained 99.71% Al, 0.02% Cu, 0.12% Li, 0.15% Fe (*Circular* of the Bureau of Standards, No. 66).

sulfuric acid and potassium dichromate. Organic matter was removed from the dry bromide by fusion in an electric furnace. From the diluted solution of this fused bromide, the bromine was set free by means of the calculated amount of sulfuric acid and pure potassium dichromate. The bromine thus obtained was dried as usual with calcium bromide and phosphorus pentoxide twice resublimed.

Nitrogen.—The nitrogen was generated in an apparatus which is generally used at Harvard. A current of air was passed through concentrated ammonia water, over red-hot copper gauze, through dil. sulfuric acid, over red-hot copper oxide, and once more over red-hot copper. The nitrogen was then thoroughly dried (finally with resublimed phosphorus pentoxide) and when tested with alkaline pyrogallol was found to contain no appreciable trace of oxygen.

Phosphorus pentoxide used was resublimed twice in an electrically heated Pyrex tube.

Silver employed in this investigation was a preparation made by H. H. Willard, remaining from his work in collaboration with one of us upon the atomic weight of lithium.[1] Samples A and B were employed. The preparation of this silver has been fully described both in the place indicated and in an earlier article,[2] so that further description is unnecessary, except perhaps to state that it was precipitated from silver nitrate by ammonium formate, and fused on lime in a current of hydrogen—all the materials being very pure. The 2 samples (which had been kept more than 10 years in a closed desiccator over fused caustic alkali) were washed in pure ammonia, dil. nitric acid, ammonia again, and much pure distilled water. The clean metal was dried in an electric air-bath at 150°.

Sulfuric acid and nitric acid were twice distilled. The nitric acid was nephelometrically tested.

Potassium dichromate, C. P., was 3 times recrystallized.

Potassium oxalate was prepared by the neutralization of pure oxalic acid by twice recrystallized, C. P., potassium carbonate, the resulting oxalate being recrystallized 3 times.

Distilled water was prepared from ordinary distilled water by 2 additional distillations, first from alkaline potassium permanganate solution and secondly from a trace of sulfuric acid.

Apparatus for the Synthesis of Aluminum Bromide.

Two preliminary trial syntheses (the first with less pure aluminum and bromine) were made to determine the best conditions of working and to study the difficulties to be overcome. The original apparatus was very similar to that used in the final synthesis—but some details of the final

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[1] Richards and Willard, THIS JOURNAL, 32, 18 (1910).

[2] Richards and Wells, *ibid.*, 27, 472 (1905).

arrangement were added in the light of the experience obtained in these earlier experiments. The final form is illustrated in the diagram. The whole apparatus used for the syntheses and for nitrogen was made of glass and sealed together. Where stopcocks for the gas connections were necessary, vacuum stopcocks were used and were lubricated with viscous syrupy phosphoric acid made by moistening phosphorus pentoxide very slightly with water. The caps in which mercury is generally placed were filled with paraffin which was melted when it was necessary to turn the cock. In the train through which the aluminum bromide was distilled, only magnetic valves were used instead of stopcocks.

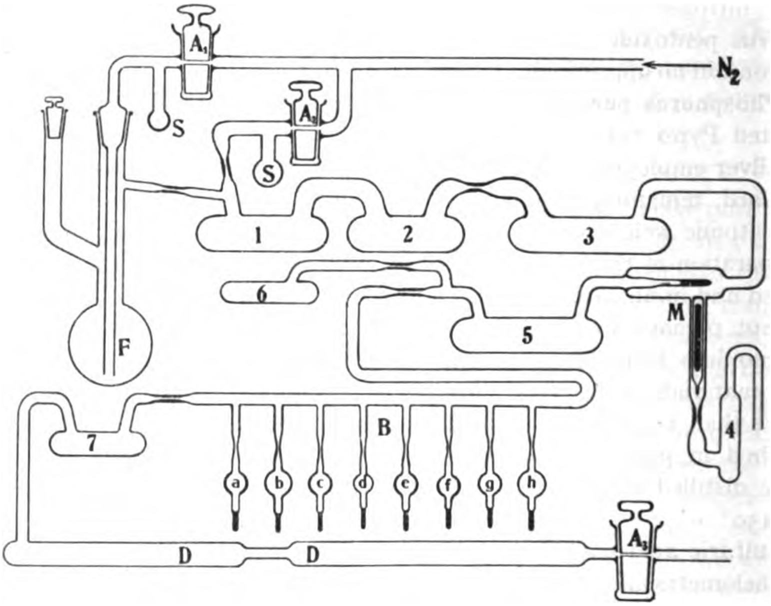

Fig. 1.

The Magnetic Valve M in Fig. 1, was a Richards-Craig[1] modification of a device of Briscoe's.[2] A small closed tube containing an iron nail was used as a hammer, actuated by a very strong electromagnet, in order to break the capillary.

Sampling Bulbs.—The bulbs used for taking samples were not exactly of the shape used by Baxter and Moore,[3] but were rather like those used by Richards and Craig in an analysis of gallium chloride.[4] They were made of soft glass with heavy walls and had tubes extending on opposite sides. These 2-necked bulbs had the following advantages: first, they

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[1] T. W. Richards and W. M. Craig, THIS JOURNAL, 41, 131 (1919).

[2] H. V. A. Briscoe, *J. Chem. Soc.*, 107, 73 (1915).

[3] G. P. Baxter and C. J. Moore, THIS JOURNAL, 34, 1648 (1912).

[4] *Loc. cit.*

were easily broken at the necks; second, no fine pieces of glass resulted from breaking them, and third, the solution of the substance within them could be controlled easily and the bulb could be drained completely. After washing and steaming the separate parts of the apparatus, they were sealed together with great care.

Synthesis of Aluminum Bromide.

The synthesis of aluminum bromide was effected in this apparatus by allowing dilute bromine vapor to react upon metallic aluminum. Thus the violent reaction which results when the bromine is liquid is prevented. The metal had been introduced into the vessels No. 1 and No. 3 before these parts had been sealed to the system. The part of the apparatus comprising Bottle F, Vessels 1, 2 3, Magnetic Valve M, Vessel 4, and drying tubes (cut off from the sample bulbs by means of the valve M), communicated with the outside air beyond Vessel 4 through a phosphorus pentoxide tube, 2 tubes of calcium bromide and a washing flask with distilled sulfuric acid. This part of the apparatus was dried by moderate heating while a current of dry nitrogen was passed through it. The other part, containing Vessels 5, 6, the series of sampling bulbs, *a* to *h*, Vessel 7, and 2 phosphorus pentoxide Tubes (D,D) with vacuum Stopcock A_3, was dried by heating and repeated evacuation.

Before starting the reaction, pure dry nitrogen was passed for 2 hours through the stopcock A_1 (Stopcock A_2 being closed), the empty flask F and the first part of the apparatus as mentioned before. After proving that the apparatus was completely filled with pure nitrogen, the flask F was filled with pure bromine in the following manner. The stopcock A_1 was turned off and Stopcock A_2 opened, the nitrogen stream through the reaction tubes, 1,2, 3, etc., was stopped by closing a stopcock beyond Vessel 4, and its drying system. The stopper in the side arm of Flask F was opened and cold bromine was poured into the flask, which was strongly cooled with a mixture of ice and salt. A counter current of nitrogen prevented the reaction of the bromine vapor with the aluminum and the introduction of outside oxygen while filling the flask with bromine. The side arm was then closed with a well-ground stopper which had been lubricated with phosphorus pentoxide and was firmly secured in place by means of de Khotinsky cement.

Since dry bromine vapor reacts very slowly with aluminum at ordinary room temperatures the vessel No. 1, containing aluminum, was kept at 120° by means of an electric heater. The stopcock A_2 was then turned off and stopcock A_1 opened. The nitrogen thus was bubbled through the bromine in flask F and accordingly carried with it a stream of bromine vapor over the gently heated aluminum. The current of nitrogen was regulated so as to carry only the amount of bromine necessary for convenient speed of reaction. The reaction of bromine with aluminum was continued 22 hours while the vessels 2 and 3 were kept cool. At the end of this time a sufficient quantity of aluminum bromide had been formed, although quite a quantity of uncombined aluminum was left in tube No. 1. The current of nitrogen was then stopped (by means of A_1) and the whole apparatus was allowed to cool.

The flask F, after being cooled, was disconnected from the reaction tubes by sealing the connecting capillary. The contents of Tube 1 were first digested for one hour at 100° in a slow current of nitrogen (Stopcock A_2) and then for one hour at 150°. Perfectly clear colorless, strongly refracting liquid aluminum bromide was obtained, the excess of bromine having been removed partly by the reaction with the excess of metal left in the reaction tube, partly by the current of nitrogen.

After digestion, the vessels 1 and 2 were heated electrically while Tube 3 (containing more aluminum) was cooled with ice-water. The bromide was thus distilled in a slow current of nitrogen at a temperature slightly below its melting-point into Vessel 3. About 20 g. was left in the reaction vessel; this residue must have contained the least volatile impurities, if there were such.

After this first fractional distillation the portion in Vessel 3 was digested in a very slow current of nitrogen at 200° for one hour. Without stopping the current of nitrogen the temperature was raised and the first fraction (15–20 g.) of the distillate was distilled over into the cooled vessel 4. Subsequently the whole apparatus was allowed to cool and stopcock A_2 cut off. Tube 3 was cooled with ice, the capillary connecting tubes 2 and 3 was sealed; and tube 4, containing the most volatile impurities, if any, was disconnected from the magnetic valve by sealing the capillary between them. The remainder of the pure colorless bromide to be further fractioned for analysis was treated as follows.

That part of the system comprising Tubes Nos. 5, 6, the sampling bulbs, Tube F and Drying-system D was evacuated through the phosphorus pentoxide tubes; connection was made between this system and vessel 3 by breaking the magnetic valve M, and the apparatus was again evacuated. Next, Tube 3 and the broken magnetic valve were heated electrically while Tube 5 was cooled with filter paper kept wet with ice-water. The temperature was regulated so as to carry on the distillation at as low a temperature as possible. In an oven kept at 120° the aluminum bromide sublimed *in vacuo*, and at 130° distilled very slowly into the cooled vessel 5. About 10 g. was left behind in Tube 3, thus affording another fractionation as regards less volatile impurities. From this Tube 5, now separated from Tube 3 by sealing an intervening capillary, the bromide was distilled fractionally into the several bulbs in which it was subsequently weighed. Tube 5 and that part of the tubes leading to the sampling bulbs[1] above the capillary were incased in a fixed electric oven (kept at 125–135°) which remained in this position during the entire sampling process. The bulbs and capillaries were heated by means of an adjustable oven which could be moved along so as to heat all the bulbs except that in which a sample was being taken. This adjustable oven was kept at the temperature some 75° higher than was the fixed oven above—a precaution which prevented distillation into bulbs other than the one in which a sample was to be collected. The first portion of distillate, collected and sealed in Bulb 6, was rejected. The capillary of Valve M and the capillary connecting Tube 7 and the sample bulbs became plugged with solid bromide—a portion which constituted another fraction, as it was likewise taken from Tube 5.

When a sample bulb had been filled about $^3/_4$ full of liquid aluminum bromide, the capillary above it was sealed off with a very small flame. The movable oven was then changed in position so as to cool another bulb, and another sample taken as before. In this manner 8 samples were taken.

Method of Analysis.

Each sample bulb (as may be seen from the figure) had on one end a solid rod while on the other end was a capillary, which had been sealed off from the apparatus. This capillary was converted into another solid rod by a small flame. To make proper vacuum corrections the exterior volume of each bulb separately was determined by weighing in water and subtracting this weight from the weight in air, the temperature and pressure being noted. As the specific gravity of single bulbs varied from 1.77 to 2.6, a specially calculated correction for the buoyancy of air for each bulb was used, varying from 0.53 mg. to 0.32 mg. per apparent gram. Each bulb, just before weighing, was scratched with a very sharp razor blade on both ends very near to the solid rods. After scratching it was washed in alcohol, rinsed in distilled water and wiped dry with clean lintless cloth. Before its precise weighing (by substitution) the sample bulb was allowed to remain in a desiccator for several hours.

Great care was necessary in dissolving the sample in water, owing to the great heat of solution and the consequent danger of loss of either bromide or glass. Samples from the first trial synthesis were broken in various ways to determine the best conditions for dissolving the bromide without loss. After the discarding of a number of only partially successful devices, a method was devised which proved altogether satisfactory in that the rate of solution could be adequately controlled and fuming prevented. This method of breaking and solution was used for all the samples analyzed from the final synthesis.

An amount of water, which was roughly sufficient to make a *N* solu-

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[1] Vessel 5 and the sampling bulbs were actually in line with each other.

tion with the bromide contained in the bulb to be broken, was placed in a heavy-walled ground-stoppered flask. The water was frozen with a freezing mixture of ice and calcium nitrate, C. P., (all anions precipitated by silver being for safety excluded). The ice thus formed inside the flask was then further cooled by means of solid carbon dioxide and alcohol. This served to cause the ice to contract and break away from the surface of the glass. When the flask was thoroughly cold the scratched, weighed sample-bulb was carefully introduced and allowed to slip down the side of the flask to the ice. After the stopper had been replaced it was covered with chemically clean cloth and tied down. A slight shaking of the bulb against the ice on the sides of the flask was sufficient to break off both ends of the bulb at the scratches. Sufficient ice was melted to allow the solution to go on very slowly and without any fuming. When the reaction seemed to become too rapid the flask was again strongly cooled. The rate of solution was so well controlled that an hour was generally consumed in the solution of each sample.

The stoppered flask was allowed to stand one hour more after completion of solution. The flask was then opened and diluted, a few drops of nitric acid being added to prevent hydrolysis. The diluted solution was filtered very carefully through a weighed Gooch-Munroe hat-form platinum crucible[1] into a precipitating flask. The crucible with the broken bulb after drying in an air-bath was again weighed and the weight of the empty bulb thus ascertained. The solution of aluminum bromide was diluted so as to be about 0.1 N and was precipitated with silver solution, using the usual Harvard methods. After precipitation 2 or 3 cc. of distilled nitric acid was added to prevent the hydrolysis of aluminum nitrate formed. The end-point of precipitation was then ascertained with the assistance of the nephelometer.

In order to make sure that no powdered glass should be rubbed off from the stopper of the Erlenmeyer flask this stopper had been very carefully ground, first with fine emery, and finally with rouge. After this treatment, a blank experiment (involving about 10-fold as much rubbing as occurred in an analysis) yielded only 0.01 mg. of glass powder which could be caught by the Gooch-Munroe crucible used for the collection and weighing of the shattered bulb. Hence no correction was needed on this account, when the silver bromide was weighed.

Five samples were analyzed. In one case (Sample *b*) the ratio $AlBr_3$: 3AgBr was determined; in 4 cases (Samples *a*, *d*, *e*, *f*,) the ratio $AlBr_3$: 3Ag was ascertained. Sample *c* was accidently contaminated after opening by a piece of broken glass rod, which could not be separated from the fragments of the bulb. The analysis of this sample was therefore not finished. The complete weighings of a single analysis follow.

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[1] T. W. Richards, THIS JOURNAL, 31, 1146 (1909).

Analysis of Bulb No. 1.

	G.	G.
Bulb No. 1 in air	7.79985	
Correction for vacuum (Sp. gr. 2.215)	0.00312	
Bulb No. 1 *in vacuo*	7.80297	7.80297
Glass of bulb No. 1 in air	2.76411	
Corr. for vac. (Sp. gr. 2.6)	0.00088	
Glass *in vacuo*	2.76499	2.76499
Aluminum bromide (in vac.)		5.03798
Silver in air	6.11310	
Corr. for vac.	0.00019	
Silver *in vacuo*	6.11291	
Silver added in titration	0.00033	
Total amount of Ag (in vac.)	6.11324	6.11324

All weighings were thus corrected for vacuum by the application of the following corrections per gram: Silver, —0.000031; silver bromide, +0.000043; glass, +0.00032. The atomic weight of bromine was taken as 79.916, that of silver as 107.88.

In the following tables the results are summarized.

TABLE I.
Preliminary Analysis.
The Ratio of Aluminum and Silver Bromides.
Weights in Grams.

Sample.	Wt. of $AlBr_3$ in vac.	Wt. of AgBr in vac. before fusing.	Wt. of AgBr in vac. after fusing.	Corrections applied for AgBr dissolved.	Total amount AgBr.	$AlBr_3$:3AgBr.	Atomic weight of aluminum.
2	3.23784	6.84028	6.8397	0.00026	6.83996	0.47337	26.944

TABLE II.
The Ratio of Aluminum Bromide to Metallic Silver.

Sample.	Sample Ag.	Weight of $AlBr_3$ *in vacuo*. G.	Weight of Ag *in vacuo*. G.	$AlBr_3$:3Ag.	Atomic weight of aluminum.
1	B	5.03798	6.11324	0.824110	26.967
4	A	5.40576	6.55955	0.824105	26.965
5	B	3.41815	4.14786	0.824076	26.956
6	A	1.98012	2.40285	0.824071	26.954
			Average	0.824090	26.960
Total		15.84201	19.22350	....	26.963

The last figure, 26.963, which weights the analyses according to the mass of material employed, is probably the most acceptable outcome of this work. This value is about 0.5% lower than the usually accepted value 27.1. The probable error of the result is very small. Whether or not there may be a constant error from some entirely unknown cause lurking in the procedure, it is, of course, impossible to say. But there can be no doubt that the outcome is more to be depended upon than Mallet's for the reasons already specified. Moreover, the single preliminary analysis of Table I (in which silver bromide was weighed) not only served as a guide to the amount of silver to be used in the following titrations, but also confirms the others in proving that no important amount of impurity existed either in the silver or bromine—at least as far as a single determination can carry any weight. The fused silver bromide was a clear pale greenish-yellow. The close agreement of all the analyses of the final series shows that the samples used for analysis were chemically identical. The small variations are to be ascribed to the inevitable small errors of experiment.

The value 26.963 indicated by the present research agrees fairly well with Thomsen's 26.99, which also seems to have been more carefully carried out than Mallet's work involving the same process. Accordingly modern evidence seems to show that the atomic weight of aluminum is really less, not more, than 27. Theorists interested in the underlying determining factors of atomic weights and those concerned with the structure of the atom will note with interest that the new value is distinctly nearer a whole number than the old one and that, as just stated, it is rather less than more than this whole number.

We take pleasure in acknowledging our indebtedness to the Carnegie Institution of Washington for financial support in this investigation.

Summary.

This paper records the synthesis and analysis of pure aluminum bromide. The substance was prepared from very pure bromine and the purest obtainable aluminum. It was digested 3 times in nitrogen at different temperatures and fractionated by distillation twice in nitrogen and twice *in vacuo*. The residue was in each case discarded, as were 2 of the portions first volatilized.

The close agreement of all the 5 analyses shows that the material used for analysis was very nearly, if not quite, homogenous. In the 4 final analyses 15.84201 g. of aluminum bromide required 19.22350 g. of silver for complete combustion, corresponding to an atomic weight for aluminum of 26.963, if silver is taken as 107.88, the current international value.

CAMBRIDGE, MASS.

HYDROGEN OVERVOLTAGE.

A Reply to Edgar Newbery.

BY DUNCAN A. MACINNES.

Received October 11, 1920.

In a recent article, Newbery[1] has criticized the papers published, on hydrogen overvoltage, by MacInnes, Adler, and Contieri. The lack of agreement between this author and ourselves is, among other things, due to a difference in the use of the term "overvoltage." According to Newbery's implied definition the expression should be reserved for potentials determined by a commutator device, which periodically opens the exciting current at the electrode under examination and closes the potentiometer circuit connecting this electrode and a reference electrode. In the work of MacInnes and Adler,[2] and of practically every worker in this field, the exciting current remains flowing while the potentiometer measurements are made. Aside from the undoubted privilege of an author to define a term, within its range of meaning, in the sense most suitable for his purpose, I can find no precedents in the chemical literature for Newbery's objection to our use of the word.[3] In fact Newbery appears to be nearly, if not quite, alone in thus restricting the meaning of the term.

I will, therefore, use the term "overvoltage" in what follows as "the difference of potential that exists between a reversible hydrogen electrode and an electrode, in the same solution, at which hydrogen, H_2, is being formed from hydrogen ions."[4] The expression, "counter electromotive force" will be, in the lack of a better term, used for the potential obtained by a commutator device. The difference between overvoltage and counter electromotive force, in the senses just described, is Newbery's "transfer resistance."

My interpretation of Newbery's criticism is this, that the counter e. m. f. is more important and fundamental than the overvoltage since the latter is a combination of the counter e. m. f. and the "transfer resistance," the "transfer resistance" being, in turn, dependent upon the current density, the resistance of the electrolyte, the external pressure, etc. This is, of course, a criticism of all work on overvoltage not carried out with a commutator device. It is evident that the concept of "transfer resistance" should receive careful consideration.

The measurements by MacInnes and Adler were made with an apparatus shown diagrammatically in Fig. 1. Vessel C_1 held a rod of zinc, C_2 the

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[1] THIS JOURNAL, 42, 2007 (1920).

[2] *Ibid.*, 41, 194 (1919).

[3] See, for instance, Caspari, *Z. physik. Chem.*, 30, 89 (1899); Tafel, *ibid.*, 50, 641 (1904); Lewis and Jackson, *ibid.*, 56, 193 (1906); Thiel and Breuning, *Z. anorg. Chem.*, 83, 329 (1913); Coehn and Dannenburg, *ibid.*, 38, 609 (1901); Mott, *Trans. Am. Electrochem. Soc.*, 15, 569 (1909); Rideal, THIS JOURNAL, 42, 94 (1920).

[4] MacInnes and Adler, *loc. cit.*

electrode under observation, and C_3 the reference hydrogen electrodes. Between the electrodes in C_1 and C_2 was placed an adjustable source of potential opposite to, and slightly lower, than that naturally present between the electrodes. Between the electrodes in C_2 and C_3 a potentiometer was connected as shown. Newbery contends that a film of gas forms over the electrode in C_2 producing an electrical "transfer resistance" at the surface. Our experiments have shown, however, that gas does not cover more than a very small part of the electrode surface at the current densities of our experiments. Gas evolution took place from one or two favored spots, apparently holding nuclei of the gas phase. In the absence of these nuclei, gas evolution did not occur even at considerably higher voltages (see MacInnes and Adler, p. 200). In fact, the continued evolution of bubbles appears to be a sensitive test for the presence of gas phase on an electrode surface. This is precisely analogous to the gas evolution from a surface immersed in a supersaturated gas solution or in a superheated liquid. The presence of a *gas* film covering any large portion of the electrode surface and of an ohmic "transfer" resistance due to such a film are, at least, open to serious question.[1]

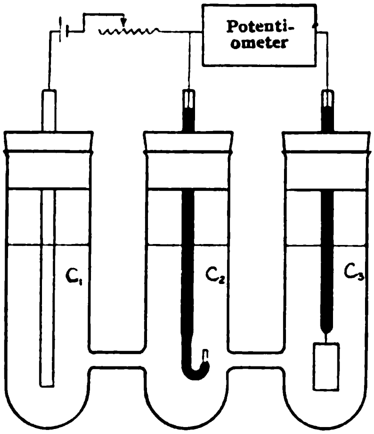

Fig. 1.

Further, Newbery himself points out quite logically, in a paper referred to in his criticism,[2] that the existence of "transfer resistances" at the surfaces of electrodes means that all conductance measurements are in error since, if the supposed resistance exists only during the time that the current is passing, the errors resulting would not be overcome by the usual artifice of using an alternating current. These transitory resistances are, according to this paper, of surprising magnitude, being as high as 1000 ohms for cells containing solutions whose resistances are of the order of 10 ohms. Also, he finds that the "transfer resistances" are greatest at low current densities! In one case mentioned 2 platinized electrodes,

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[1] An attempt was recently made in this laboratory, by Mr. W. R. Hainsworth, to determine whether the overvoltage readings of the apparatus represented in Fig. 1 are independent of the resistance of the circuit including the potentiometer and the electrodes in C_2 and C_3. Capillary tubing of different sizes was placed between the vessels, without changing the readings, and finally, a large wide tube filled with electrolyte connected Vessels C_1, C_2 and C_3, again without effect. In this apparatus the reference electrodes are apparently uninfluenced by the current passing between the electrodes in C_1 and C_2, at least for the current densities of our experiments.

[2] *Trans. Faraday Soc.*, 15, 126 (1919).

2 × 1 cm. and 2 cm. apart, dipping into *N* sulfuric acid an arrangement having a resistance of about 4 ohms by the usual methods, gave a "transfer resistance" of *180 ohms* at the lowest current density (2 milliamperes). In view of these figures it would appear, if they have any basis in reality, that all electrolytic conductance work is subject to large errors. However, the precision with which conductances can be measured and the agreement of the results of numerous workers using quite different potentials, current densities, and electrodes, is strong evidence against errors due to such a source, and against the presence of "transfer resistances" of any appreciable magnitude. Also, the same author has published[1] results of conductance measurements carried out by determining the potential drop between 2 reversible electrodes in, and the current passing through, a solution of an electrolyte. These measurements were independent of phenomena occurring at irreversible electrodes. His results are, with one exception, within a few tenths of a per cent. of the accepted values, and the deviations, which are both positive and negative, are readily explainable by the errors of the method. Since the experiments just referred to were apparently designed to demonstrate the existance of "transfer resistance" errors, it does not appear that the author has proved his point.

Further, Eastman,[2] in a recent, very careful, investigation finds that the difference between the conductances determined by direct and alternating current measurements (using nonpolarizing electrodes) is of the order of 0.02–0.03% and that both agree with the results of Kohlrausch with about the same accuracy. Newbery's contention, which seems to me to be quite unjustified on theoretical grounds, that the effects of his "transfer resistance" would disappear if a pure sine wave were used, is, at least, unnecessary, since Kohlrauchs's results with an unsymmetrical current from an induction coil, agree, with the accuracy just stated, with Eastman's values using direct current and symmetrical alternating current. Clearly, then, the evidence from conductance measurements is against the presence at electrodes of "transfer resistances" of any appreciable magnitude.

The solution of the whole difficulty lies, I am convinced, in the realization of the facts (*a*) that the overvoltage is larger than the counter e. m. f. and (*b*) that the difference between the quantities is a potential and not a resistance. Also, it appears to me, that all the phenomena so far observed in this field, including those brought to light by Newbery's experiments, can readily be explained by the theory as originally advanced by MacInnes and Adler. According to them, "Hydrogen overvoltage is due, primarily, to a layer of supersaturated dissolved hydrogen in the

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[1] *J. Chem. Soc.*, 113, 701 (1918).

[2] THIS JOURNAL, 42, 1648 (1920).

electrolyte surrounding an electrode."[1] Since the potential, in all probability, has its origin where the conductors change from ions to electrons, emphasis was placed upon the dissolved hydrogen in the electrolyte rather than that absorbed in the metal since in the latter the hydrogen is part of a metallic conductor. The gas phase can have only a secondary, though important, effect, being nonconducting. According to this hypothesis hydrogen overvoltage does not differ from concentration polarization. The magnitude of the effect lies, in all probability, in the fact that hydrogen, when dissolved, is not an electrolyte, and does not tend to migrate away from the electrode. Once formed it must be removed by diffusion, stirring, or by formation of the gas phase. The obvious difficulty with this hypothesis is that for the higher overvoltages the concentrations (or the pressures necessary to produce the concentrations) are inconceivably great if computed from the usual Nernst equation. However, we are dealing here, not with pressures in the usual sense, but with "fugacities."[2] The recent work on fugacities of ions shows that above moderate concentrations the ion fugacities increase much more rapidly than the ion concentrations.[3] An investigation is now in progress in this laboratory to determine whether, for high pressures of hydrogen, the fugacity differs markedly from the pressure. Until the results of this investigation are at hand this part of our explanation must be of the nature of a hypothesis. However, this hypothesis affords a ready explanation of all the phenomena in this field, as I hope to demonstrate below.

According to this theory *all* the overvoltage is due to a layer of supersaturated hydrogen solution, no part of the effect being assigned to resistance.

There remains an important question. Why does the overvoltage differ from the counter e. m. f.? According to Newbery the values of the counter e. m. f. are determined by the decomposition potentials of unstable hydrides formed on the surface of the electrodes. It is probable that this explanation is the correct one for a great number of cases. However, the fact must be recognized that the formation of these hydrides is a consequence of, and in no way an *explanation* of, overvoltage. In an exactly analogous manner the deposition of metals above hydrogen in the electromotive series results from, but does not explain, the failure of hydrogen to form gas at the reversible potential. According to the hypothesis advanced by MacInnes and Adler the deposition of metals high in the electromotive series and the formation of unstable hydrides are both due to the building up, during electrolysis, of a layer of dissolved hydrogen of high fugacity.

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[1] *Loc. cit.*, p. 207.

[2] Lewis, *Proc. Am. Acad. Sci.*, 43, 259 (1907).

[3] See the compilation by Noyes and MacInnes, THIS JOURNAL, 42, 243 (1920).

If the formation of hydrogen at an electrode is periodically interrupted by a commutator device, as in Newbery's work, this dissolved layer of hydrogen will begin to diffuse or be stirred away from the surface and the voltage will drop rapidly. However, if the electrode surface contains an unstable hydride this will act as a reservoir of hydrogen of high fugacity, keeping the voltage from falling below the decomposition potential of the hydride until the exciting current is again applied. The oscillograph work of Le Blanc[1] demonstrates that with an electrode at which gas is evolved, the potential drops rapidly, but by no means instantaneously, to a constant value of the counter e. m. f., after the exciting current is disconnected. This relatively slow decrease of potential indicates the presence of material capable of yielding higher potentials than those of the unstable hydrides just referred to.

If a metal has a potential higher than hydrogen in the electromotive series the diffusion or stirring away of dissolved hydrogen from the surface may cause the potential to drop, when the exciting current is interrupted, until the metal of the electrode can form ions, after which no further decrease can occur. For instance, when the exciting current is applied to an amalgamated zinc electrode in sulfuric acid the reactions occurring will be the deposition of nearby zinc ions (formed by "local action") and the discharge of hydrogen ions. The open circuit voltage would, therefore, be expected to be that of the zinc, in sulfuric acid containing few or no zinc ions. As a matter of fact, the potential of amalgamated zinc in fresh normal sulfuric acid against a hydrogen electrode in the same solution was found by the writer to be 0.84 volt, whereas Newbery's counter e. m. f. (or according to his definition "overvoltage") measurements yielded 0.88 to 0.70 volt.[2] Further, Newbery gives 0.16 to 0.29 and 0.27 to 0.23 volt for the counter e. m. f. measurements of nickel and cobalt, respectively, whereas the "normal potentials" against a hydrogen electrode are 0.22 and 0.29 volt. It seems nearly certain, therefore, that in these cases, and some others, the potentials that Newbery measured do not correspond to the decomposition of unstable hydrides, but are caused by the formation of ions by the metals themselves.

The considerations of the preceding paragraphs indicate clearly, I think, why the counter e. m. f. is nearly independent of the current density and the external pressure. It is also evident that nothing valuable with regard to the relation of counter e. m. f. to valence, passivity, etc., need be lost by adopting the theory advanced by MacInnes and Adler. Since, by our hypothesis, overvoltage is a concentration effect, it is equally obvious that the overvoltage should be dependent upon the current density.

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[1] "Abhandlungen der Deutchen Bunsen-Gesellschaft," No. 3.

[2] *Mem. Manchester Literary and Philosophical Soc.*, 61, (9) 3 (1917).

The influence of external pressure is more complicated, but, as is demonstrated in the earlier papers, follows directly from our theory.[1]

In conclusion, it is probable that I have not met, in detail, all of Newbery's objections to the theory proposed by MacInnes and Adler, and I am, naturally, in the dark as to the "many other" objections that he holds in reserve. However, enough is probably outlined above to indicate the fundamental difference of point of view upon which Newbery's aggressive criticism is based.

CAMBRIDGE 39, MASS.

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, UNITED STATES DEPARTMENT OF AGRICULTURE.]

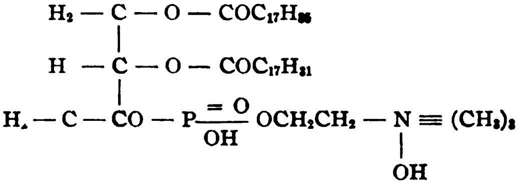
THE QUANTITATIVE ESTIMATION OF PHOSPHATIDES.

BY D. H. BRAUNS AND JOHN A. MACLAUGHLIN.

Received May 28, 1920.

The determination of phosphatides is often required in the analysis of foods and drugs. In the case of foods, phosphatides frequently serve as an index to the quantity of egg yolk in the food under examination. In the analysis of drugs, it is often necessary to determine phosphatides in order to establish whether or not statements made concerning the lecithin content of the preparation are warranted. Experience has shown that none of the methods hitherto proposed for the separation of phosphatides from such products is wholly satisfactory, for one reason or another. The investigation herein presented was undertaken for the purpose of devising a method which would be satisfactory. Since Maclean's[2] recent book, renders the publication of a bibliography superfluous, the references given in the present work have been limited to publications that offer suggestions of value for our particular purposes.

For the estimation of phosphatides we have considered 2 different phosphatides, first, lecithin, which is generally agreed to be a combination of glycerophosphoric acid, choline, oleic acid and stearic acid, and to have the formula $C_{44}H_{86}NPO_9$ or



$$\begin{array}{l}
H_2 - C - O - COC_{17}H_{35} \\
\qquad | \\
H\; - C - O - COC_{17}H_{31} \\
\qquad | \\
H_2 - C - CO - P\overset{=O}{\underset{OH}{\overline{\quad}}}OCH_2CH_2 - \underset{\underset{OH}{|}}{N} \equiv (CH_3)_3
\end{array}$$

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[1] A forthcoming paper from this laboratory will deal with the question of the relation of overvoltage to pressure. For the present purpose it is sufficient to say that the results of Goodwin and Wilson, mentioned in our first paper, have been confirmed as to the direction of the effect. The excess pressure in small bubbles has been considered and must be taken into account for higher overvoltages. However, this extra pressure is very small for the comparatively large bubbles from platinized platinum electrodes, and it does not sensibly affect the computations published.

[2] H. Maclean, "Lecithin and Allied Substances, the Lipins," Longmans, Green & Co., London, 1918.

and, second, kephalin, which is known to contain glycero-phosphoric acid, amino ethyl alcohol, stearic acid and an unsaturated acid, and to contain 4.17% of phosphorus.[1] Since choline and amino ethyl alcohol are the characteristic cleavage products which distinguish phosphatides from similar biological substances, especially the fats, a method for the estimation of phosphatides based upon the determination of these characteristic constituents should yield satisfactory results and should be successful in excluding phosphorus-containing compounds other than phosphatides from the estimation. The method may properly be applied as Maclean[2] has shown that most phosphatides in tissues consist of $^3/_4$ lecithin and $^1/_4$ kephalin, and the necessity for its use is demonstrated by Wintgen and Keller,[3] who have proved that a simple nitrogen determination is not reliable as a measure of the nitrogen content of phosphatides.

For this reason the method for the estimation of phosphatides which we propose involves several processes, namely, the separation of the phosphatides from the other substances in the material to be analyzed and the determination of phosphorus, of choline and of amino nitrogen in the mixed phosphatides after they have been obtained free from adventitious matter.

Separation of Phosphatides—Recognized Methods.

Beyer[4] first observed that seeds extracted with ether yield a certain per cent. of organic phosphorus-containing substances and that a subsequent extract obtained with warm alcohol yields to ether more of the organic phosphorus-containing substance, observations which were subsequently confirmed by Jacobson.[5] The same phenomenon was also observed when egg yolk and animal tissues were treated with ether and alcohol. Hoppe-Seyler[6] suggested that lecithin may be present in egg yolk partly in the free from and partly bound to vitellin. The combination is decomposed by alcohol but not by ether. Schulze and Steiger,[7] found this suggestion correct in the case of plant and animal tissues. Schulze[8] based a method for the quantitative estimation of phosphatides on these results. His original procedure was extraction of the finely pulverized material with anhydrous ether followed by extraction with boiling absolute alcohol, the phosphatides being determined in the combined extracts. He also suggested a modification in which the residue obtained

[1] P. A. Levene and C. J. West, *J. Biol. Chem.*, **33**, 11 (1918).

[2] H. Maclean, *Biochem. J.*, **9**, 351 (1915).

[3] Wintgen and Keller, *Archiv. Pharm.*, **244**, 3 (1906).

[4] Ad. Beyer, *Landw. Ver. Sta.*, **14**, 161 (1871).

[5] H. Jacobson, *Z. physiol. Chem.*, **13**, 38 (1889).

[6] F. Hoppe-Seyler, *Handbuch physiol. Chem.*, **1877**, p. 781.

[7] E. Schulze and E. Steiger, *Z. physiol. Chem.*, **13**, 365 (1889).

[8] E. Schulze, *ibid.*, **20**, 225 (1895); *Chem. Ztg.*, **28**, 751 (1914).

on evaporation of the combined ether and alcohol extracts is extracted with ether (secondary ether extract) in order to insure the absence of all compounds other than phosphatides. As early as 1884 Thudichum[1] proposed a complicated method, not merely for the separation of phosphatides from other components of tissues, but also from one another. In 1900, Juckenack[2] proposed the substitution of warm alcohol for ether in the extraction of phosphatides because not all the free lecithin in yolk of egg is dissolved by ether. Evaporation of the alcohol solution should be performed at a temperature not exceeding 60°, the boiling with alcohol being reduced to the time required for decomposing the protein compound of lecithin.

Fendler[3] found that some trade lecithins are soluble in alcohol and some are soluble in ether, while others require both for complete solution. He therefore extracted first with absolute alcohol and then with ether, determining the phosphorus in the combined extracts.

Erlandsen,[4] who found all phosphatides which he separated to be ether-soluble after extraction with alcohol, has shown that further purification of the phosphatide solution by precipitation with acetone or cadmium chloride is not advisable since these precipitations are not quantitative in all cases.

A special extraction apparatus was used by Koch and Woods[5] in a method which is a simplification of Thudichum's and depends upon the difference in solubility of the lead salts of the various phosphatides.

In washing the ethereal solution of phosphatide, several authors advise that the acidity be low so that hydrolysis may be avoided. Koch[6] has shown that the danger of hydrolyzing lecithin is rather slight, and his conclusions have been confirmed by Coriat.[7]

The method of Koch and Woods is objected to by Erlandsen[8] on the ground that a loss of phosphatides occurs during washing.

Bloor[9] devised a method for the determination of lecithin in small amounts of blood by running the blood into a mixture of alcohol and ether and determining the phosphorus content in an aliquot of the alcohol-ether solution. Moreover he found that inorganic phosphates added to the blood can be easily removed by shaking the alcohol-ether solution

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[1] J. L. W. Thudichum, "The Chemical Constitution of the Brain," London, 1884.

[2] A. Juckenack, *Z. Nahr. Genussm.*, 3, 12 (1900).

[3] G. Fendler, *Apoth. Ztg.*, 20, 22 and 488 (1905).

[4] A. Erlandsen, *Z. physiol. Chem.*, 51, 94, 151 (1907).

[5] W. Koch and H. S. Woods, *J. Biol. Chem.*, 1, 203 (1905); W. Koch, *ibid.*, 3, 160 (1907).

[6] W. Koch, *Am. J. Physiol.*, 11, 318 (1904).

[7] I. H. Coriat, *ibid.*, 12, 361 (1905).

[8] A. Erlandsen, *Z. physiol. Chem.*, 51, 96 note (1907).

[9] W. R. Bloor, *J. Biol. Chem.*, 22, 133, 1916 (1915); 24, 452 (1915).

with saturated ammonium sulfate solution. It is clear, however, that the ammonium sulfate interferes with the determination of nitrogen and choline, but Bloor's use of this reagent suggested to us the use of saturated sodium chloride solution in our work.

Koch and Woods[1] washed the secondary ether extract with acid chloroform water and obtained a high percentage of extract phosphorus[2] in the wash water. Collison[3] found that by excluding moisture in the alcohol-ether extraction the acid washing of Koch and Woods is superfluous. Koch and Woods[4] themselves state that Schulze was dealing with relatively dry plant tissues and not with moist animal tissues and that, therefore, his findings as to the solubility of inorganic phosphates in absolute alcohol and anhydrous ether are not valid. Later a convenient method was devised for reducing animal tissues to finely divided dry powder and it was found that by employing this procedure the washing with acid chloroform-water which had been recommended by Koch and Woods might be omitted. The method was recommended by Leathes[5] and a modification was made and used by Robertson[6] for preparing his tethelin. Robertson's method is as follows.

> Animal tissues are ground in a mortar with 3 times their weight of a mixture of equal parts by weight of anhydrous sodium and calcium sulfates and the mixture dried over a water-bath, stirring occasionally to prevent caking. Under these conditions drying is extremely rapid and involves a minimum exposure of the tissue to heated air. In an hour, a mixture of 60 g. of tissue with 180 g. of sodium and calcium sulfates becomes white and easily powdered. This dried mixture is returned to the mortar, finely pulverized and extracted with absolute alcohol at a temperature as near as possible to that of boiling alcohol.

For this purpose Robertson employed a modified Bailey-Walker extraction apparatus with alundum thimbles, the process being continued for 48 hours to complete extraction.

The method of Bordas and de Raczkowski[7] has found wide approval for the estimation of lecithin in milk. In common with other research workers in this field, they caution that it is advisable to avoid unnecessarily high temperature, lecithin being gradually destroyed by heat.

Study of the methods cited leads to the conclusion that extraction with ether and warm alcohol removes all phosphatides. The residue obtained on evaporation of the extract may be re-extracted with ether for purifica-

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[1] W. Koch and H. S. Woods, *loc. cit.*

[2] Koch and Woods classify phosphorus under 3 headings: (1) Inorganic phosphorus. (2) extract phosphorus, that contained in organic phosphorus-containing substances which are not phosphatides. (3) phosphatide phosphorus.

[3] R. C. Collison, *J. Biol. Chem.*, 11, 217 (1912).

[4] W. Koch and H. S. Woods, *idem.*, 206.

[5] J. B. Leathes, "The Fats," Longmans, Green & Co., London, 1910, p. 53.

[6] T. B. Robertson, *J. Biol. Chem.*, 24, 409 (1916).

[7] F. Bordas and de Raczkowski, *Compt. rend.*, 134, 1592 (1902).

tion and to exclude inorganic phosphates. Only the results of Juckenack indicate any objection to extracting with ether the residue from extraction with warm alcohol, and the results of Erlandsen,[1] which are quoted on p. 2240 are sufficient to overcome this objection.

Proposed Method for Separating Phosphatides.

If enough material is available, an extraction yielding about 0.300 g. of phosphatides should be made. This is sufficient for the determination of phosphorus in duplicate and of choline and amino alcohol. If great accuracy is unnecessary, the amount of phosphatides may be as small as 0.200 g. If the weight of phosphatides available is less than 0.200 g. the quantitative determination of phosphorus only is made and the presence of choline is indicated by qualitative tests, indentification being effected by the periodide or the mercuric iodide salt.

Animal or vegetable tissues which cannot be reduced to powder or solutions in volatile liquids are dried with anhydrous sodium and calcium sulfates, according to the method of Robertson.[2] Solutions of non-volatile liquids such as glycerol are boiled under a reflux condenser with absolute alcohol for an hour, the excess of alcohol evaporated on the steam-bath with occasional stirring, an equal volume of saturated-sodium chloride solution added to the residue and the mixture shaken out with ether. Upon addition of the solution (about 35%) of pure phosphorus-free sodium chloride the phosphatides separate as a brown layer on top of the liquid. By adding ether and gently rotating the separatory funnel, the phosphatides are dissolved. The mixture of glycerol and sodium chloride is transferred to another separatory funnel and the process of shaking out with ether is repeated several times. Extraction is completed by allowing the glycerol-salt solution to stand overnight in contact with ether. The solubility of phosphatides in glycerol is such that the addition of sodium-chloride solution is essential for separation. The ether solution of phosphatides is collected in a dry flask and allowed to stand for a few hours to effect separation of the last small amounts of glycerol-salt solution. The solution is filtered and distilled from a weighed flask.

Material which can be powdered without difficulty is dried *in vacuo* at the lowest possible temperature. Extraction of phosphatides from the dry material is made with absolute alcohol in an ordinary Soxhlet apparatus or in an extraction apparatus as described by Koch and Woods or by Robertson. By insulating the extraction thimble the temperature of the extraction liquid is maintained as nearly as possible at 50–60°.[3] Depending upon the material used, the extraction is completed in 10 to 48 hours. By changing the boiling flask the progress of extraction can be

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[1] A. Erlandsen, *loc. cit.*

[2] T. B. Robertson, *loc. cit.*

[3] A. Juckenack, *loc. cit.*

followed. Samples of the extract may be taken at intervals by using at the bottom of the thimble an outlet tube provided with a stopcock. In this way needless exposure of extracted phosphatide to heat is avoided and the completion of extraction observed. The incompletely exhausted residue is extracted in the same apparatus for 2 hours. The combined alcohol extracts are dried, mixed with sodium and calcium sulfates if necessary, and extracted with anhydrous ether. For small amounts it is sufficient to stir with a small pestle and to pour off the ether through a small filter, repeating the process to complete exhaustion; for larger amounts a Soxhlet apparatus should be used. The ether extract is reduced to 30–40 cc., then shaken with 15 cc. of saturated sodium chloride solution. The salt solution is drawn off and washed with 10 cc. of ether. The ether solutions are combined, evaporated, dried and weighed. This gives the weight of impure ether-soluble phosphatides free from extract phosphorus.

Weighing need be accurate to centigrams only, the object being to ascertain whether more or less than 0.20 g. of phosphatides is present, this being the smallest amount sufficient for the quantitative determination of phosphorus, choline and amino nitrogen.

Existing Methods for the Determination of Phosphorus.

Phosphorus is best determined according to the method of Neumann.[1] Koch and Woods[2] and Greenwald[3] have suggested modifications of the method for precipitating the ammonium phosphomolybdate, but all agree on the manner of destruction for organic matter. The colorimetric method, depending on the reduction of ammonium phosphomolybdate, makes possible the accurate determination of amounts of phosphorus weighing not less than 0.5 mg., requiring 0.010 g. of phosphatide. Taylor and Miller[4] used a centrifuge to separate the ammonium phosphomolybdate, made the reduction with hydrazine chloride and compared the color with a standard prepared with standard phosphate solution under similar conditions in a Duboscq colorimeter. Riegler[5] reduced with hydrazine sulfate, using a procedure similar to that of Taylor and Miller. Van Eck,[6] working under war conditions, used stannous chloride as the reducing agent and obtained satisfactory results by comparing the colored solutions in Nessler tubes. A further increase in delicacy has been obtained by Kober and Egerer[7] by using strychnine phosphomolybdate for the nephelo-

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[1] Albert Neumann, *Z. physiol. Chem.*, 37, 130 (1902).

[2] W. Koch and H. S. Woods, *loc. cit.*

[3] I. Greenwald, *J. Biol. Chem.*, 14, 369 (1913).

[4] A. E. Taylor and C. W. Miller, *ibid.*, 18, 220 (1914).

[5] E. Riegler, *Bull. sec. sci. acad. roumaine*, 2, 272 (1913–14).

[6] P. N. Van Eck, *Pharm. Weekblad.*, 55, 1037 (1918).

[7] P. A. Kober, and G. Egerer THIS JOURNAL, 37, 2373 (1915).

metric estimation. By this method 0.005 mg. of phosphorus, requiring 0.0001 g. of phosphatide, may be accurately determined.

Method Adopted for Phosphorus Determination.

The destruction of organic matter was effected according to the method of Neumann, adopting the minor modifications proposed by Bloor; and the phosphorus determination was made by the colorimetric method with ammonium phosphomolybdate following the procedure of Van Eck. The entire procedure is described, as we have found that it is necessary to follow it closely to obtain the best results.

The weighed residue of ether-soluble phosphatide is dissolved with alcohol, rinsed into a volumetric flask of suitable content (100 cc. for 0.300 g. of residue) and the flask filled to the mark. Five cc. of solution, representing 0.015 g. of residue, is pipetted into a large (200 mm. × 24 mm.) test-tube of resistant glass, 2 or 3 glass beads of 3 mm. diameter are added, and the solution is evaporated to dryness by immersing the tube in a water-bath. It should be watched and shaken frequently until boiling begins, after which the evaporation will generally proceed to dryness without requiring further attention. Since alcohol interferes with subsequent oxidation, the material in the tube is dried on the water-bath for 15 minutes to remove traces of this reagent. Four cc. of a 1 : 1 mixture of conc. nitric and sulfuric acids is added and the mixture is digested by heating with a microburner in the hood or with a Folin draught apparatus.[1] The heating is done in 2 stages with the tube inclined at an angle of about 30° to prevent spattering. During the first, the mixture is boiled gently over a low flame until red fumes cease to come off. This should require about 5 minutes. The heat is then gradually increased until the nitric acid is completely expelled, after which the sulfuric acid is boiled for 8–10 minutes. If charring occurs a small amount of strong nitric acid should be added and the process repeated. The mixture is cooled somewhat and 2 drops of a 0.25% cane sugar solution is added to remove traces of nitric acid which may prevent complete precipitation of phosphoric acid, After heating for one minute the solution is cooled and 5 cc. of water is added. The liquid is rinsed quantitatively into a porcelain dish with 5 to 10 cc. of water, 10 cc. of 30% ammonium nitrate solution added, and the whole carefully heated nearly to boiling. There is now added 4 cc. of 10% ammonium molybdate solution, made by dissolving the salt in cold water and filtering. The solution and precipitate should be heated for a short time. If care is taken not to heat the dish above the level of the liquid, the precipitate settles without adhering to the sides of the dish. Filtering is best done through a plug of asbestos fiber in a small funnel and the precipitate is washed several times with ammonium nitrate solution. The funnel is inverted over a beaker and

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[1] O. Folin and W. Denis, *J. Biol. Chem.*, 9, 503 (1911).

dil. sulfuric acid (1 to 10) is poured into the stem of the funnel to rinse the plug and precipitate into the beaker. 0.5 g. of stannous chloride is added and the solution allowed to stand for half an hour. If any precipitate adheres to the sides of the dish, it may be rinsed into the beaker with the dil acid. The blue liquid is filtered through a small plug of asbestos into a 100-cc. volumetric flask and made up to volume with the dil. sulfuric acid. The color is best washed from the plug by treating it in a dish with excess of sulfuric acid and filtering through another plug.

The blue color is compared with a standard made by adding to 10 cc. of a solution containing 0.05 mg. of phosphorus per cc. in a porcelain dish 2 cc. of conc. sulfuric acid and cc. of 30% ammonium nitrate solution, proceeding thereafter as directed. The standard is sufficiently stable to allow of making the comparisons.

Ten cc. of the standard blue liquid is put in a Nessler tube. So much of the blue liquid to be investigated is placed in another Nessler tube that the colors are roughly estimated to be the same. Usually 10 cc. is required if a 0.010 g. sample of phosphatide is used. Both tubes are filled to 100 cc. with the dil. sulfuric acid. Sulfuric acid must be used for the reason that the turbidity caused by separation of the tin salt on addition of water interferes with the determination. If the colors are not exactly the same, enough liquid is poured from one tube into a graduate to make the 2 colors identical in shade. Since the colors are not comparable if the dilutions differ by more than a very small amount, the more dilute being more green, this procedure must be strictly followed. If the liquid becomes turbid upon dilution it will clear after standing for an hour.

Consideration of Existing Methods for Determining Nitrogen and Amino Nitrogen.

For general work, the determination of nitrogen according to Dumas requires less substance than do other methods. Moreover, as the residue remaining from a Dumas nitrogen analysis contains the phosphorus as phosphoric acid, one sample would be sufficient for both determinations. However, the difficulty of transferring the residue from the tube quantitatively is so great that it is more advantageous to use a second sample for phosphorus.

Distearyl lecithin contains 1.74% of nitrogen and 3.84% of phosphorus. Other lecithins show a variation from these figures of only about 0.1% of their nitrogen and phosphorus content. 0.200 g. of phosphatide yields 3.04 cc. (0.0035 g.) of nitrogen at 20° and 760 mm., a quantity sufficient for accurate estimation. By the application of the micro-Dumas method as described by Fischer,[1] the weight of phosphatide required may be reduced to 0.010–0.020 g., yielding 0.0003 to 0.0007 g. of nitrogen.

The Dumas method is not so well adapted to making a series of deter-

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[1] H. Fischer, *Ber.*, 51, 1322 (1918).

minations as is that of Kjeldahl. In working with phosphatides it has been shown that the Gunning modification of the Kjeldahl procedure is the most satisfactory. A study of the relative accuracy of colorimetric and titrimetric procedures for determining nitrogen as ammonia has been made by Allen and Davisson,[1] who have shown that the use of 0.02 N solutions in conjunction with methyl red as indicator, as proposed by Mitscherlich and Herz,[2] yields an accuracy even greater than that of the colorimetric micro-Kjeldahl method as developed by Folin and Denis.[3] We use the latter method on account of the advantage of its brevity.

Amino nitrogen is determined by the method of Van Slyke.[4]

Methods Adopted for Determination of Choline and Amino Nitrogen.

We have adopted the method of acid hydrolysis of the phosphatides, because of its recognized superiority to alkaline hydrolysis and especially because Maclean[5] and Levene and Rolfe[6] have proved this beyond doubt, the latter investigators having found that on hydrolysis with barium hydroxide, barium salts of the fatty acids are obtained which can be freed from nitrogen only with the greatest difficulty.

A weighed amount (about 0.300 g.) of the ether-soluble phosphatides or an aliquot of the alcoholic solutions from which the alcohol is evaporated is boiled with about 30 cc. of 0.2 N sulfuric acid for 48 hours under a reflux condenser. A piece of tile and a small piece of paraffin may be added to prevent bumping and foaming. After cooling, the solution is filtered to separate the fatty acids. The filter with the fatty acids is boiled with 4 to 6 small portions of water and the cooled wash water added to the filtrate. The solution is then carefully neutralized with barium hydroxide solution, the precipitate collected on a filter and washed thoroughly with boiling water. The filtrate is acidified and evaporated to dryness. The residue is extracted with alcohol, the solution filtered through a small filter and the volume reduced to 10 cc. The alcoholic solution of choline must not be too highly concentrated since some of the amino ethyl alcohol platinum chloride, though soluble in alcohol, is carried down from concentrated solution by the precipitate of choline platinum chloride. Alcoholic solution of platinum chloride is added and the mixture allowed to stand until the precipitate settles. The precipitate is collected on a weighed filter, dried to constant weight at 105°, cooled and weighed. This is the weight of choline platinum chloride containing also some amino-ethyl alcohol platinum chloride. Upon multiplying the weight of the pure choline platinum chloride by 2.608, the weight of lecithin is obtained.

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[1] E. R. Allen and B. S. Davisson, *J. Biol. Chem.*, 40, 183 (1919).

[2] Mitscherlich and Herz, *Landw. Jahrb.*, 38, 279 (1909).

[3] O. Folin and W. Denis, *J. Biol. Chem.*, 11, 502 (1911).

[4] D. D. Van Slyke, *ibid.*, 12, 275 (1912).

[5] H. Maclean, *loc. cit.*

[6] P. A. Levene and Ida P. Rolfe, *J. Biol. Chem.*, 40, 1 (1919).

The filtrate, which is kept for the determination of amino nitrogen, is acidified with hydrochloric acid and carefully evaporated to dryness in a small evaporating dish. It is made slightly alkaline with sodium hydroxide, acidified with acetic acid and made up with water to a volume of 2.5 cc. in a small graduate. A Van Slyke's micro-amine nitrogen apparatus having been prepared, 2 cc. of the solution or suspension—corresponding to 0.240 g. of substance—is used for the determination of amino nitrogen.

A portion of the precipitate is used for the determination of amino nitrogen. The weight of amino-ethyl alcohol platinum chloride is obtained upon multiplying the weight of nitrogen by 19. The weight of the precipitate minus weight of amino-ethyl alcohol platinum chloride equals the weight of pure choline platinum chloride.

Amino nitrogen in the precipitate is added to that found in the filtrate and the total weight of nitrogen multiplied by 53.20 to obtain the total weight of kephalin.

Experimental Testing of the Combination of Methods Proposed.

For the purpose of testing the proposed combination of methods, a supply of lecithin was prepared by regenerating it from the cadmium compound of egg lecithin by treatment with ammonium carbonate as described by Bergell.[1] Although kept in a dark closet in a vacuum desiccator over calcium chloride, it was yellowish and gradually became dark brown.

For checking the Neumann method, about 4 g. of disodium phosphate was dissolved in about one liter of watr, 50 cc. of this solution was evaporated in a weighed porcelain dish and ignited, yielding 0.0987 g. of sodium pyrophosphate. This is equivalent to 0.0265 g. of phosphorus pentoxide per 25 cc. of solution. 25 cc. of the same solution treated according to Neumann's method required 20.2 cc. of 0.5 *N* alkali, corresponding to 0.0256 g. of phosphorus pentoxide, which is in fairly good agreement with the amount found on ignition.

The phosphorus and nitrogen determinations on lecithin gave the following results.

Substance. G.	Alkali required.	P. %.	N (by Kjeldahl). %.	Calc. for stearyl oleyl lecithin. % P.	% N.
0.2738	18.90 cc. 0.5 *N*	3.82	....	....	....
0.2568	17.77 cc. 0.5 *N*	3.83	....	3.86	....
0.7273	10.81 cc. 0.1 *N*	....	2.08	....	1.74

Although our results for phosphorus agree very well with the theoretical it will be noted that the nitrogen is high. This is often the case with lecithin preparations.

On account of the changes that take place on aging, the ordinary leci-

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[1] P. Bergell, *Ber.*, 33, 2584 (1900).

thins are not satisfactory as standards; and for this reason "hydrolecithin"[1] was used. A few grams were prepared from egg lecithin according to the method of Ritter.[2] Analysis did not yield very concordant results, but this may have been due to the small amount of substance, as the method of recrystallization recommended was not entirely satisfactory. Although the product was white when dry, it always produced colored solutions.

Subs., 0.1903, 0.1996: CO_2, 0.4527, 0.4746; H_2O, 0.1736, 0.1898.

Calc. for $C_{44}H_{90}NPO_9$: C, 65.37; H, 11.23. Found: C, 64.89, 64.80; H, 10.20, 10.60.

A standard solution for the colorimetric estimation was made by dissolving 0.200 g. of sodium phosphate in 200 cc. of water. 50 cc. of this solution was evaporated in a weighed porcelain dish, ignited, and weighed, yielding 0.0967 g. of sodium pyrophosphate, or 0.0113 g. of phosphorus per 25 cc. of solution.

Twenty-five cc. of the same solution treated according to Neumann's method required 21.17 cc. of 0.5 *N* alkali, equivalent to 0.0117 g. of phosphorus. For the standard, 50 cc. of the former solution was diluted to 500 cc., so that 10 cc. of this solution contained 0.00046 g. of phosphorus.

Colorimetric determination yielded results as follows:

Hydrolecithin. G.	Poured out from hydrolecithin tube to match standard. Cc.	P. Found. %.	P. Calc. %.
0.0015	17.0	3.70	3.84
0.0025	53.5	3.86	

The choline and amino nitrogen determinations were made with 0.260 g. of hydrolecithin and gave the following results:

Choline Platinum Chlorid 0.0751 g.

Precipitate used, 0.040 g. Calc. for whole precipitate: N, 0.000338 g. Found: 0.31 cc. or 0.00018 g.

0.000338 × 19 = 0.0064 g. of amino-ethyl alcohol platinum chloride.

0.0751 g. — 0.0064 g. = 0.0687 g. of pure choline platinum chloride.

0.0687 g. × 2.608 = 0.1792 g. of lecithin.

Filtrate.

4/5 of filtrate taken: 1.90 cc. of amino nitrogen obtained; whole filtrate would yield 2.37 cc. or 0.00138 g. of N; filtrate + ppts. 0.00138 g. + 0.000338 g. = 0.00172 g.

0.00172 × 53.20 = 0.0915 g. of kephalin. Therefore, 0.260 g. of phosphatides yielded

Lecithin		Kephalin		Phosphatides
0.1792 g.	+	0.0915 g.	=	0.271 g.

	M. P.	
ppts.	240°	with foaming.
Pure choline platinum chloride	224°	

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[1] Hydrolecithin, a crystalline phosphatide, was first prepared by Ritter, using Paal's colloidal palladium as a catalyzer for the reduction of egg lecithin by hydrogen. Ritter pointed out that this hydrolecithin may occur in addition to other lecithins in egg yolk. It contains 2 stearyl groups in its molecule instead of one stearyl and one oleyl group.

[2] R. Ritter, *Ber.*, 47, 530 (1914).

The water-alcohol solution of the platinum chloride precipitate yielded on evaporation the yellow octahedrons which were also produced by the platinum double salt made from pure choline hydrochloride, closely resembling platinum chloride crystals except that the choline double salt is easily soluble in water.

The proposed method was further tested on a sample of lecithin prepared from vitellin lecithin.

2.400 g. of this lecithin was dissolved in absolute alcohol and filtered into a 200-cc. volumetric flask. Only traces of insoluble matter were left on the filter. 25 cc. of the solution was made up to 100 cc. in a volumetric flask and 5 cc. of the latter solution was used for a phosphorus determination according to the colorimetric method. The water-alcohol solution of the choline precipitate produced the characteristic crystals whose melting-point was 230°. Colorimetric determination:

Phosphatides: 0.015 g. Calc.: P, 3.86; Found: 3.70.

Precipitation of choline platinum chloride and determination of amino nitrogen showed,

Phosphatides: 0.285 g. Found: Lecithin, 0.264 g.; kephalin, 0.0579; phosphatides (total), 0.3219.

Another test was made with a commercial preparation, "Glycerole Lecithin." It was stated on the label of the bottle that each teaspoonful contains one grain of pure lecithin. If we figure that one teaspoonful—4 cc.— of the liquid, consisting mainly of glycerol, weighs about 5 g. (200 cc. was found to weigh 245 g.), then 100 g. should contain 20 grains of lecithin or 0.052 g. of phosphorus = 0.05%. A colorimetric phosphorus determination showed 0.05% phosphorus to be present.

Two and a half g. of the preparation was mixed with an equal amount of saturated sodium chloride solution, shaken with ether, and treated as directed in the proposed method for the separation of phosphatides. The weight of the separated impure phosphatide was about 8 g., and contained, according to the phosphorus determination, about 3. g. of lecithin. The whole residue was dissolved in absolute alcohol, filtered into a 200-cc. volumetric flask and made up to volume. 25 cc. was diluted to 100 cc. with absolute alcohol and 5 cc. of the latter solution was taken for the phosphorus determination, which gave 0.045% of phosphorus. No phosphorus could be detected in the liquid which had been exhausted with ether, and only traces were found in the residue left on the filter when the alcoholic solution was filtered. Therefore, all of the phosphorus was present as phosphatides. The washing of the ether solution with saturated sodium chloride solution is here performed at the same time as the extraction. Upon multiplying the per cent. of phosphorus by the factor 25.4, based upon Maclean's[1] findings that phosphatides consist of $^3/_4$ lecithin and $^1/_4$

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[1] H. Maclean, *loc. cit.*

kephalin and the figures for nitrogen content of these substances as determined by Levene and West,[1] the phosphatide content is obtained; thus, 0.045 × 25.4 = 1.1%. According to the statement on the label, one teaspoonful—5 g.—contains 1 grain or 0.065 g. of lecithin, or 1.3%. In the 95 cc. remaining from the phosphorus determination, choline and amino nitrogen were determined. These 95 cc. correspond to $^{245}/_{8} \times {}^{95}/_{100}$ = 29.1 g. of "Glycerole Lecithin" and this weight contains, according to the phosphorus determination, 0.011 × 29.1 = 0.3201 g. of phosphatide. According to the statement on the label, this would be 0.013 × 29.1 = 0.3783 g. of phosphatide. Analysis showed 0.3038 g. of lecithin + 0.0636 g. of kephalin = 0.3674 g. of phosphatide.

The choline platinum chloride precipitate showed a melting point of 240°, and the characteristic crystals were observed when the water-alcohol solution of the precipitate was evaporated.

Summary.

1. A general method for the separation of phosphatides to be used in the quantitative estimation of these substances has been described and tested and has been found suitable for the analysis of proprietary pharmaceutical preparations as well as for quantitative estimation of phosphatides occurring in food products.

2. It has been shown that the method of drying with mixed sodium and calcium sulfates is very satisfactory for volatile liquids which contain galenical extracts that are hygroscopic. Further, it has been demonstrated that the proposed method of washing the ether extract with saturated sodium chloride solution to separate inorganic phosphates and extract phosphorus is effective.

3. It has been shown that the colorimetric method for the determination of phosphorus in the separated phosphatides is adapted to purposes of food and drug analysis. About 0.010 g. of material is required and from the phosphorus content the per cent. of phosphatide is calculated.

4. The determinations of choline and amino nitrogen serve as a check on that of phosphorus in the phosphatides, to exclude other phosphorus compounds from the estimation and establish the ratio of lecithin to kephalin.

WASHINGTON, D. C.

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[1] P. A. Levene and C. J. West, *loc. cit.*

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY.]

THE PREPARATION OF DICHLORO-ACETIC ACID FROM CHLORAL.

BY GEORGE W. PUCHER.

Received June 26, 1920.

The work described in this paper was undertaken at the suggestion of Professor Treat B. Johnson, and represents a part of a prolonged research dealing with the development of new methods of synthesizing organic combinations which possess both biochemical and therapeutical interest.

The fact that chloral can be converted into dichloro-acetic acid has been known since 1873, when Wallach[1] discovered that this change could be brought about by the action of potassium cyanide, or potassium ferrocyanide, on the aldehyde in aqueous solution. The transformation

$$Cl_3.C.CHO + H_2O \longrightarrow Cl_2CH.COOH + HCl$$

is one of both theoretical and practical interest, and the fact that it can be accomplished by the action of cyanides of alkali metals in aqueous solution is unique, in view of the fact that the action of even weak alkaline reagents, such as magnesium hydroxide,[2] cause chloral to decompose readily into chloroform and formic acid.

$$Cl_3C.CHO + H_2O \longrightarrow H.COOH + CH.Cl_3.$$

Different theories have been advanced to explain the mechanism of this interesting reaction. Wallach[2] first interpreted the change as one involving the formation of potassium chloride and prussic acid by the combined action of potassium cyanide and water on chloral. He assumed an intermediate unsaturated halogen derivative (I), which reacted with a hydroxyl group to form dichloro-acetic acid. According to this explanation, the hydroxyl group of the water by dissociation functions in a double capacity, namely, as an oxidizing and a reducing agent according to the following equation:

$$Cl_3C.CHO + KCN + H_2O \longrightarrow KCl + HCN \longrightarrow$$
$$\underset{\text{(I).}}{Cl_2C : CHO} + —OH \longrightarrow Cl_2CH.COOH.$$

The next interpretation proposed by Wallach[3] was one involving a direct dissociation of chloral into hydrochloric acid and dichloroketene (II), under the influence of potassium cyanide as a catalytic agent. Then hydrochloric acid

$$Cl_3C.CHO \longrightarrow \underset{\text{(II).}}{Cl_2C : CO} + HCl$$

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[1] Wallach, *Ann.*, 173, 288 (1874).

[2] Wallach, *Ber.*, 10, 1526 (1877).

[3] *Loc. cit.*

interacts with the alkali cyanide to produce prussic acid which adds to the ketene (II) to form dichloro-acetyl cyanide (III). This substance, in turn is transformed by hydrolysis into dichloro-acetic and prussic acids.

$$\underset{\text{(II).}}{Cl_2C:CO} + HCN \longrightarrow \underset{\text{(III).}}{Cl_2CH.CO.CN} \longrightarrow Cl_2CH.COOH + HCN.$$

That such an interpretation is not applicable to this reaction can be concluded from the work on ketene $CH_2:CO$, and its derivatives carried on by Staudinger and his co-workers. These investigators were unable to prepare dichloro-ketene (II)[1] on account of its great tendency to polymerize. Furthermore, if it were formed from chloral in aqueous solution it would undoubtedly add water in preference to prussic acid in accordance with the well known behavior of ketene towards this acid. Deakin and Wilsmore,[2] as well as Chick and Mortimer[3] have shown that prussic acid does not add to ketene to form acetyl cyanide (IV).

$$CH_2:CO + HCN \longrightarrow \underset{\text{(IV).}}{CH_3.COCN.}$$

The correct interpretation of the mechanism of this change, and the one which finds further confirmation experimentally in our work, is that recently proposed by Kötz.[4] He has proven conclusively that a cyanogen radical and water are essential factors in this reaction, and also that chloral-cyanohydrin (V) is formed as an intermediate product. The latter (V), when heated with water or amines in aqueous solution is converted into dichloro-acetyl cyanide which immediately undergoes hydrolysis with water to give dichloro-acetic and prussic acids. The complete transformation is expressed by the following formulas:

$$Cl_3C.CHO + HCN \longrightarrow \underset{\text{(V).}}{Cl_3C.CH(OH)(CN)} \xrightarrow{HCl} Cl_2CH.COCN \xrightarrow{H_2O}$$

$$\underset{\text{(III).}}{Cl_2CH.COOH + HCN.}$$

Therefore, chloral-cyanohydrin (V), by the action of water, undergoes a decomposition similar to that which is produced when tetrachloroethyl ether (VI) is treated with alkali.[5] The primary product of dissociation in both cases is the corresponding unsaturated ethylene derivative represented by Formulas VII and VIII, respectively. While the unsaturated ether (VII) is a stable derivative, Compound VIII, on the other hand, contains a mobile hydrogen atom which causes it to rearrange at once to give the corresponding acyl cyanide (III), a substance unstable in the presence of water.

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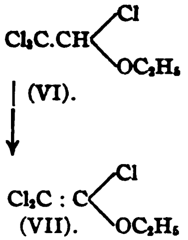
[1] Staudinger, *Ann.*, 256, 53 (1907).

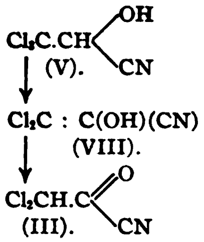
[2] Deakin and Wilsmore, *Proc. Chem. Soc.* (*London*), 97, 1968 (1911).

[3] Chick and Mortimer, *ibid.* 24, 77 (1908).

[4] Kötz, *J. prakt. Chem.*, 88, 531 (1914).

[5] Henry. *Ber.*, 12, 1839 (1879).





New facts supporting this mechanism of the reaction are presented in the experimental part of this paper.

The applications of dichloro-acetic acid for synthetical purposes have been very limited. It has been necessary for us to prepare the reagent in large quantities for our researches. This we have accomplished without the use of potassium salts. We find that a good yield of chloro-acetic acid can be produced by the interaction of chloral with an aqueous solution of commercial sodium cyanide. This simple method of making the reagent in any quantity desired is described in the experimental part of this article.

Experimental Part.

Procedure Employed for the Preparation of Dichloro-acetic Acid in Small Units.

The apparatus used for our preliminary experiments, that is, during the study of the chloral method of synthesis, consisted of a 500-cc. flask connected by a rubber stopper with a return condenser and a dropping funnel, and a stirring device which operated through a mercury seal. Chloral hydrate was first introduced into the flask in aqueous solution; then the solution of sodium cyanide was added at such a rate that the temperature of the mixture did not rise above 50°. The solution was stirred constantly during this operation and the reaction was complete after about 2 hours. This solution was evaporated to dryness on a water bath, and the dry residue of crude sodium dichloro-acetate and sodium chloride was suspended in anhydrous benzene. By saturation of this mixture with hydrochloric acid, the free acid was obtained. It was separated from the benzene by fractional distillation. Finally, it was purified by distillation under diminished pressure.

Action of Sodium Cyanide on Chloral Hydrate.

In order to determine what effect the substitution of commercial sodium cyanide for potassium cyanide would have in the preparation of dichloro-acetic acid according to Wallach's method a series of experiments was made as described above but with varying proportions of sodium cyanide. The amount of cyanide employed was calculated on the basis of the actual cyanogen content of the commercial product and the chloral used was always dissolved in a definite amount of water. The results obtained in a series of 5 experiments are recorded in Table I.

TABLE I.

50 G. of Chloral Hydrate Dissolved in 150 Cc. of Water.

Expt.	Sodium cyanide dissolved in 60 cc. of water. G.	Yield of $Cl_2CH.COOH$. %.
1	7	36
2	12	53
3	15	55
4	20	67
5	25	61.5

These results show very conclusively that sodium cyanide can be substituted in this reaction for potassium cyanide. A theoretical proportion of sodium cyanide is productive of a 55% yield of the acid, but this yield diminishes decidedly when less than a molecular proportion of cyanide is used. An increase of about 20% over the calculated amount gives the maximum yield of the dichloro-acetic acid. These results are represented graphically in Fig. 1.

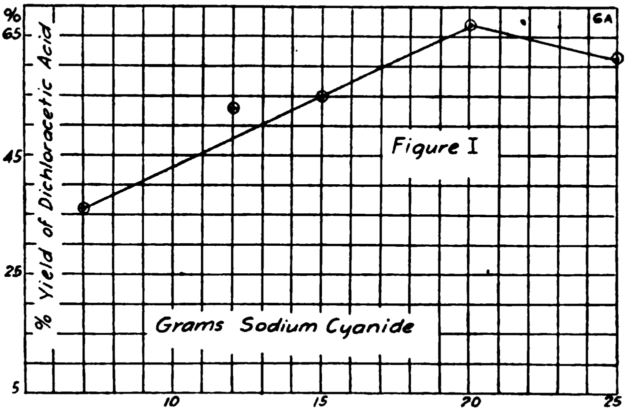


Fig. 1.

The Effect of Dilution on the Yield of Dichloro-acetic Acid.

In order to determine the best concentration for producing a maximum yield of dichloro-acetic acid, a series of experiments was performed in which the proportion of water was varied within wide limits, but the proportion of sodium cyanide was kept constant. A definite quantity of chloral hydrate was taken in each case and the series was operated at the beginning with water just sufficient to dissolve the sodium cyanide. The results of these experiments are recorded in Table II and represented graphically in Fig. 2.

TABLE II.

20 G. of NaOH in 60 Cc. of H_2O and 50 G. of Chloral Hydrate.

Expt.	Water added to chloral. Cc.	Yield of $Cl_2CH.COOH$. %.
1	0	12
2	50	46
3	100	59
4	150	67
5	200	66

It was observed that this reaction is very violent and almost uncontrollable when molten chloral is used, and is productive of a very low yield of the acid. Dilution of the solution with water leads to an increase in the yield which reaches its maximum when about 150 cc. of water is used for every 50 g. of chloral hydrate.

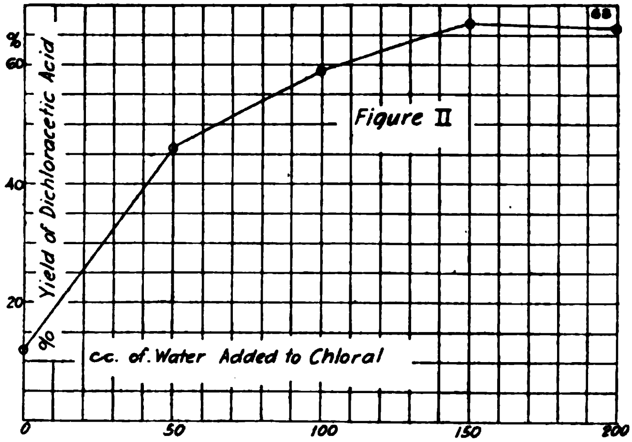


Fig. 2.

Effect of Substituting Certain Salts in Place of Sodium Cyanide.

In order to determine whether the cyanide radical is a necessary factor in this transformation of chloral hydrate into dichloro-acetic acid, a series of experiments was run in which various salts were incorporated. The salts investigated were sodium carbonate, sodium sulfite, sodium hydrogen sulfite and sodium acetate, and the operation was carried out in a manner similar to that employed when sodium cyanide was used. No dichloro-acetic acid was formed; in all cases chloroform was the normal product of reaction. On the other hand, when some sodium cyanide was introduced with any one of these salts, dichloro-acetic acid was formed immediately. These results are in accord with the original assumption made by Wallach,[1] namely, that the cyanide radical functions in this reaction, and that the reaction cannot be brought about in its absence. The results of our experiments are recorded in Table III.

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[1] Wallach, *Ann.*, 173, 288 (1874).

TABLE III.

Fifty G. of Chloral Hydrate Dissolved in 150 Cc. of Water.

Salt (sodium).	Weight used; dissolved in 45 cc. of water. G.	Sodium cyanide dissolved in 15 cc. of water. G.	Yield of $Cl_2CH\ COOH$. %.
Acetate	40	..	0
Carbonate	16	..	0
Hydrogen sulfite	32	..	0
Sulfite	19	..	0
Acetate	40	7	55
Carbonate	16	7	53
Hydrogen sulfite	32	7	38
Sulfite	19	7	51

In the application of this reaction, dichloro-acetic acid is always obtained in the form of its sodium salt by evaporation of the solution. To prepare the free acid from this salt, our first procedure was to dry the latter and then treat it with a slight excess of hydrochloric acid; finally, the liberated acid was extracted with benzene. This method of operation was never productive of yields over 50%. In the next modification of the procedure the aqueous solution was acidified with hydrochloric acid after completion of the reaction and then evaporated to dryness under diminished pressure. The dichloro-acetic acid was removed from the solid residue by extraction with benzene. This method of operation proved unsatisfactory, because a large amount of tar was always formed and, furthermore, the quality of the dichloro-acetic acid obtained was very poor. The use of sodium hydrogen sulfate to liberate the dichloro-acetic acid was not successful. The method finally chosen was that originally employed by Johnson and Cretcher[1] which involves the suspension of the crude sodium salt of dichloro-acetic acid in dry benzene and subsequent decomposition of it by hydrogen chloride passed through the benzene. Dichloro-acetic acid is purified best by distillation under diminished pressure. During the purification, a small amount of tarry residue is always obtained which is decomposed violently by treatment with nitric acid. This reaction is productive of a substance having the odor of chloropicrin which indicates that, very probably, some unaltered chloral-cyanohydrin is present in the dichloro-acetic acid before distillation.

The following procedure, based on the results of many preliminary experiments and already employed by us with success, is recommended for the preparation of pure dichloro-acetic acid in kilogram quantities.

One thousand g. of chloral hydrate is dissolved in 3000 cc. of water and the solution is heated to 40° in a large enameled pail, or stock pot. A stirrer is introduced before beginning the next operation. When the temperature reaches 40°, the flame is removed, the stirrer started, and a solution of 400 g. of commercial sodium cyanide dissolved in 1100 cc. of

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[1] Johnson and Cretcher, THIS JOURNAL, 37, 2149 (1915).

water is added to the solution. This solution should be added through a separatory funnel just rapidly enough to prevent the temperature of the mixture from rising above 50°. No application of heat is necessary since the heat of reaction is sufficient to maintain this temperature. After all of the cyanide is added the mixture is kept at 50° for an hour. At this stage the clear yellow solution is transferred to a large porcelain evaporating dish and the water evaporated over a steam-bath until a viscous, pasty mass is obtained. This crude mass of salt is then transferred to a saponification vessel where it is suspended in 2.5 liters of commercial benzene. The vessel used by us for this operation was an ordinary 4-liter wide-mouth bottle, which was equipped with a cork containing a stirrer operated through a mercury seal, as well as inlet and exit tubes for the passage of hydrogen chloride. While the hydrogen chloride is bubbled through the benzene the bottle is surrounded with ice water and the stirrer is run continually. The reaction is generally complete at the end of 4–5 hours, when the benzene solution is filtered and dried over sodium sulfate, and the solvent finally recovered by distillation from an oil-bath heated at 160°. The recovered solvent can be used for the next preparation. The dichloro-acetic acid is obtained as a heavy liquid which is purified by distillation under diminished pressure. It boiled, practically constant, at 102° (uncorr.) at 20 mm. On account of the large quantities of prussic acid evolved, special precautions must be taken to carry out the entire operation in a well-ventilated hood. The method of procedure requires only ordinary laboratory apparatus, and, in a few days, several kilograms of the acid can be prepared with a yield of 60–65% of the calculated amount.

Reversal of the order of addition, namely, chloral hydrate to the sodium cyanide solution, did not lead to an improvement in the yield of dichloroacetic acid. When sodium cyanide is added to the chloral solution the reaction proceeds very smoothly and a gradual rise in temperature is observed. At first the mixture is almost neutral to litmus, but finally becomes strongly acid during the addition of the cyanide, and at the close of the reaction, the solution is colored slightly yellow. No odor of chloroform is detected during this operation. On the other hand, when the chloral hydrate is added to the sodium cyanide solution, there is no apparent reaction until about half of the chloral has been added, when the temperature rises suddenly to 60° and in a short time the entire mixture assumes a dark red color. Chloroform was produced, and the basicity of the original cyanide solution gradually decreased until about two-thirds of the chloral had been added, when it became distinctly acid. After evaporation of the solution a residue was formed which was black and gummy in appearance. This material gave a yield of dichloroacetic acid amounting to only 45% of that calculated.

Corrosion Tests with Dichloro-acetic Acid.

In order to determine whether other vessels besides those constructed of glass could be used in reactions where dichloro-acetic acid is employed, the corrosive effect of this reagent on different metals was studied. Weighed strips of the different metals were immersed completely in acid of different concentrations and the loss by corrosion at different temperatures was determined quantitatively. The results obtained are recorded in Table IV where the losses in weight are expressed in terms of percentage of the original weight of metal taken. At 20°, the 4 metals investigated are not readily attacked by the acid, while the corrosion increased with dilution and with rise in temperature. Aluminum appears to be the most resistant to the action of the pure acid at high temperature, while the diluted acid fails to attack copper and lead appreciably.

TABLE IV.

Action of Dichloro-acetic Acid on Metals. Time of Action, 48 Hours.

Metal.	Temp. ° C.	Loss in weight in pure acid. %.	Loss in weight in 10% aqueous acid. %.	Loss in 10% benzene sat. with HCl dichloro-acetic acid. %.
Iron	20	0.55	3.5	2.53
Iron	90	2.78	..	..
Copper	20	0.00	1.1	0.02
Copper	90	4.85	..	..
Aluminum	20	0.14	17.7	0.19
Aluminum	90	0.66	..	..
Lead	20	1.51	1.5	..
Lead	90	9.30	..	..
Aluminum	190	0.31	..	..

Methyl Diethoxy Acetate, $(C_2H_5O)_2CHCOOCH_3$.

This ester can be prepared by the action of dimethyl sulfate on the sodium salt of diethoxy-acetic acid. Thirty g. of metallic sodium is dissolved in 400 cc. of absolute alcohol. If a molecular proportion (50 g.) of dichloro-acetic acid is added to this solution slowly the corresponding sodium salt of diethoxy-acetate is formed. The reaction is completed by heating the mixture on the steam-bath for 2 hours. At this stage the solution is cooled and filtered to remove sodium chloride. After the excess of alcohol is removed by distillation under diminished pressure the residue is mixed with 75 g. of dimethyl sulfate and the mixture heated on the water bath for 3 hours to complete the esterification. To isolate the ester the product is poured into water and extracted with ether. After removal of the ether, the ester was obtained in about 44% yield as a colorless oil with an agreeable odor. It boiled at 184–5°.

Calc. for $C_7H_{14}O_4$: C, 51.8; H, 8.7. Found: C, 51.7; H, 8.8.

Molecular weight (ebullioscopic method, benzene as solvent). Calc. value: 162. Found: 158.

The ester does not solidify at —81°; d^{25}. is 1.0049.

In a second experiment, the sodium salt of diethoxy-acetate, dissolved in methyl alcohol, was heated with dimethyl sulfate. The yield of ester, however, was less than that obtained by the former procedure, since it amounted to only 20% of the calculated value. The low yield here is accounted for by the fact that dimethyl sulfate was partially destroyed by the action of methyl alcohol with formation of dimethyl ether and methyl sulfuric acid. Baulin and Simon[1] showed that this is the case.

$$SO_2(OCH_3)_2 + CH_3OH \longrightarrow SO_2(OH)(OCH_3) + CH_3.O.CH_3.$$

It was shown that unaltered sodium salt of diethoxy-acetic acid was present in the aqueous solution in both of the above experiments. After extraction of methyl diethoxy-acetate with ether, barium hydroxide was added to remove sulfates. After the excess of barium had been removed as carbonate by saturating the solution with carbon dioxide, silver nitrate was added to precipitate the silver salt of diethoxy-acetate. This salt dried and subjected to the action of ethyl iodide in ether solution gave ethyl diethoxy-acetate.[2] From the aqueous solution which remained in Expt. 1 we recovered 15 g. of this ester and in Expt. 2, 25 g. These results show conclusively that only a part of the sodium salt of diethoxy-acetic acid interacted with dimethyl sulfate during esterification. Dimethyl sulfate does not interact with the copper salt of diethoxy-acetate.

NEW HAVEN, CONN.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

A STUDY OF THE POSSIBLE ASYMMETRY OF THE ALIPHATIC DIAZO COMPOUNDS.[3]

BY C. S. MARVEL WITH W. A. NOYES.

Received June 28, 1920.

During the last 20 years a large number of papers on the electron theory of valence have appeared in the literature. Most of the papers are of a speculative nature and the applications of the theory have been developed farther than the experimental evidence seems to justify. For some time one of us has been attempting to isolate some of the isomers which, according to this theory, should logically exist and, in that way, to obtain evidence to substantiate the theory.

A study of the aliphatic diazo compounds has been undertaken, since in these compounds, according to the structure usually accepted, 2 nitrogen atoms are combined with one carbon atom. The method of preparation of this class of compounds is such that one of the nitrogen atoms comes

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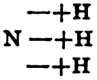
[1] Baulin and Simon, *Compt. rend.*, 170, 392 (1920).

[2] Johnson and Cretcher, *J. Biol. Chem.*, 26, 99 (1916).

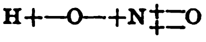
[3] An abstract of a thesis submitted by C. S. Marvel in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the University of Illinois.

from ammonia, while the other comes from nitrous acid. These compounds have the following electronic formulas



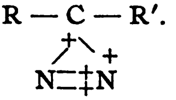
$$N\begin{matrix}-+H\\-+H\\-+H\end{matrix}$$

Ammonia.

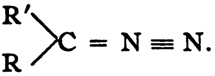


$$H+\!-O-\!+N\overset{+}{\underset{+}{\ }}\!=\!O$$

Nitrous Acid.

The electronic formula for an aliphatic diazo compound could then be written  $R - \underset{\overset{+\diagup\quad\diagdown+}{N=N}}{C} - R'$. It is readily seen that such a molecule would be asymmetric and optical isomers would be expected to exist.

The aliphatic diazo compounds were discovered by Curtius.[1] Diazoacetic ethyl ester, $N_2CHCOOC_2H_5$, the first of the series to be prepared, was obtained by the action of nitrous acid on glycocoll ester hydrochloride. The reaction has been extended to cover other α-amino esters and also similar compounds, as α-amino cyanides, α-amino ketones, and α-amino imides.

Curtius[2] assigned to the diazo compounds the structure  $R - \underset{\overset{\diagup\ \diagdown}{N=N}}{C} - R'$, after a thorough study of their reactions. This structure was accepted for about 20 years until Angeli[3] suggested that the structure might be  $\begin{matrix}R'\\R\end{matrix}\!\!>\!C = N \equiv N$. After Staudinger[4] showed that the diazo compounds could be obtained by the oxidation of hydrazones, Thiele[5] again brought forward the open-chain structure as more logical for these compounds. Hantzsch[6] from a study of the absorption spectra of diazomethane supported the Curtius structure. Darapsky and Prabhakar[7] studied the reduction of diazoacetic ethyl ester and from their results concluded that the Thiele-Angeli structure was correct. Forster and Cardwell[8] studied the action of the Grignard reagent on diazo compounds and stated that their results could best be explained on the Thiele-Angeli structure. Staudinger[9] with his co-workers carried out a very thorough investigation of the reactions of the aliphatic diazo compounds. He attempted without success to isolate isomeric diazo compounds one of which he expected to

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[1] Curtius, *Ber.*, 16, 2230 (1883).

[2] Curtius, *J. prakt. Chem.*, [2] 38, 394 (1888).

[3] Angeli, *Atti accad. Lincei*, 16, II, 790 (1907); 20, I, 626 foot note (1911).

[4] Staudinger, *Ber.*, 44, 2198 (1911).

[5] Thiele, *ibid.*, 44, 2522 (1911).

[6] Hantzsch, *ibid.*, 45, 3022 (1912).

[7] Darapsky and Prabhakar, *ibid.*, 45, 1657 (1912).

[8] Forster and Cardwell, *J. Chem. Soc.*, 103, 867 (1913).

[9] Staudinger, *Ber.*, 49, 1884–1974 (1916).

have the Curtius formula and the other the Thiele-Angeli formula. Recently Langmuir[1] has assigned to diazomethane an open chain structure based on Lewis' octet theory.

From the above it would seem that the true structure of the aliphatic diazo compounds is not definitely determined. The reactions which they undergo can be explained equally well by means of either the Curtius or the Thiele-Angeli formula. The formula originally proposed by Curtius is perhaps more generally accepted.

Levene[2] has suggested the possibility of electromers in aliphatic diazo compounds. He has presented as evidence for their existence, the conversion of certain hexosaminic acids into the corresponding anhydrosugar acids without racemization of the carbon atom bearing the amino group. In a previous paper[3] it had been shown that the benzal derivative of the ethyl ester of one of the hexosaminic acids gave a diazo compound on treatment with nitrous acid. This fact has apparently been considered as evidence that in replacement of an aliphatic amino group by an hydroxyl group the diazo compound is an intermediate product. Walden,[4] Fischer,[5] and others had shown previously that almost any optically active amino acid gave an active hydroxy acid on treatment with nitrous acid. However, no one has ever been able to obtain a diazo compound from an α-amino acid although such compounds can be obtained in a more or less pure condition from almost any of the α-amino esters. These facts make it appear doubtful that the diazo compound is an intermediate in the replacement of an amino group by a hydroxyl group when the free amino acid is treated with nitrous acid.

Another objection may be made against Levene's evidence for the existence of electromers in the aliphatic diazo series. The hexosaminic acids contain 4 asymmetric carbon atoms. Even if one of these carbon atoms does pass through a symmetrical structure in the replacement of the amino group, the final product would probably consist mainly of one of the 2 possible isomeric hydroxy acids, on account of the influence of the 3 other asymmetric carbon atoms present in the molecule.[6]

There are 3 general methods available for the preparation of aliphatic diazo compounds: (1) the method of Curtius,[7] by the action of nitrous acid on α-amino esters; (2) the method of v. Pechmann[8] by the decom-

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[1] Langmuir, THIS JOURNAL, 41, 1546 (1919).

[2] Levene, *J. Biol. Chem.*, 36, 89 (1918).

[3] *Ibid.*, 21, 348 (1915).

[4] Walden, *ibid.*, 28, 2772 (1895).

[5] Fischer, *ibid.*, 41, 2897 (1908); 45, 2448 (1912).

[6] Fischer, *Ann.*, 270, 64 (1892).

[7] Curtius, *Ber.*, 16, 2230 (1883).

[8] von Pechmann, *ibid.*, 27, 1889 (1894); 28, 855 (1895).

position of nitroso-imides with alkali; and (3) the method of Staudinger[1] by the oxidation of hydrazones with mercuric oxide.

The method of Staudinger is not applicable to the production of an optically active diazo compound since the hydrazones are symmetrical in structure. The method of v. Pechmann could not be used on account of the difficulties met in attempting to prepare the necessary nitroso-imides.

The diazo compounds studied were prepared by Curtius' method. The purification of the impure diazo compounds offered considerable difficulty. Curtius recommends steam distillation of small quantities as the best method of purification, although this method destroys a large part of the diazo compound. In working with ethyl α-diazo-caproate, $CH_3CH_2CH_2CH_2CN_2COOC_2H_5$, it was found that no purification was obtained by steam distillation and that approximately $^2/_3$ of the diazo compound was destroyed. This ester was found to be easily purified by vacuum distillation of the impure ester and yields as high as 30% of the calculated amount were obtained. Diazo esters were prepared from phenylamino-acetic acid, and α-amino-caprylic acid. These could not be obtained pure by vacuum distillation since on distillation they decomposed into the corresponding hydroxy esters. This result agrees with Curtius' earlier work with the diazo ester from phenylalanine.[2]

After having established the best method for obtaining the pure diazo ester from optically inactive amino-caproic acid, samples of ester were prepared from the *d*- and *l*-isomers. These samples were found to be inactive when examined in the polariscope. Since the difference between a positive and a negative nitrogen atom might not cause rotation the diazo esters were hydrolyzed with dil. sulfuric acid. If the diazo esters were asymmetric, on hydrolysis the positive nitrogen should have been replaced by a hydrogen atom and the negative nitrogen by an hydroxyl group. However, the products obtained on hydrolysis of the samples of ester from the active amino acid were found to be inactive.

In order to show that the hydrolysis with dilute acids actually produced an hydroxy ester from ethyl α-diazo-caproate, a larger sample was treated for some time with dil. acetic acid. The products obtained consisted of approximately equal parts of ethyl α-hydroxy-caproate, $CH_3CH_2CH_2CH_2CHOHCOOC_2H_5$, and ethyl Δ¹-hexenoate, $CH_3CH_2CH_2CH : CHCOOC_2H_5$. The result was unexpected, since text-books usually state that dilute acids decompose diazo esters quantitatively to the corresponding hydroxy esters. The acetic acid used was so dilute (10%) that it hardly seems probable that it could dehydrate the hydroxy ester after it had been formed. Curtius[3] has obtained fumaric ester from diazo-

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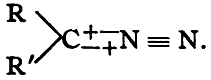
[1] Staudinger, *Ber.*, 44, 2198 (1911).

[2] Curtius, *ibid.*, 37, 1270 (1904).

[3] Curtius, *J. prakt. Chem.*, [2] 38, 477 (1888).

succinic ester by boiling it with water. This would be expected, as it is fairly easy to dehydrate malic ester, which may be regarded as a β-hydroxy ester.

The fact that inactive diazo compounds were obtained by the treatment of active amino esters with nitrous acid may be explained in 3 ways: (1) the 2 nitrogen atoms may be alike; (2) the nitrogen atoms may be different but the compounds racemize during the reactions; or (3) the Curtius formula may not be the correct expression for the structure of the diazo compounds. There is, however, a possibility of asymmetry even in the Thiele-Angeli formula, as the structure may be

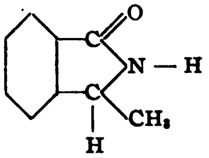


$$\genfrac{}{}{0pt}{}{R}{R'}\!\!>C\underset{-}{\overset{+}{\ }}\underset{+}{\overset{-}{\ }}N \equiv N.$$

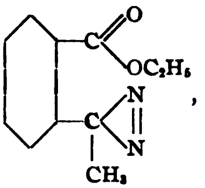
It is impossible to say which of these explanations is correct.

Curtius[1] prepared crystalline diazo compounds from the ester hydrochlorides of glycylglycine, diglycylglycine, and triglycylglycine by treatment with nitrous acid in the presence of sodium acetate. These diazo compounds were high-melting substances and quite stable. The reaction does not seem general for dipeptide esters, since it was found in this investigation that the ester hydrochloride of α-amino-*n*-caproylglycine on treatment with nitrous acid did not give a stable diazo compound but the hydroxy ester was isolated.

On account of the difficulty of obtaining pure diazo compounds by the Curtius method of preparation, it was decided to try out v. Pechmann's method or a modification of it as applied by Oppe[2] to the preparation of *o*-carboxyethyl-phenyl-diazomethane. Methyl phthalimidine



was prepared according to Gabriel's method.[3] The nitroso derivative was easily formed by treatment with nitrous acid in water solution. The diazo compound,



was obtained as a red, oily product but was never obtained pure. No

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[1] Curtius, *Ber.*, 37, 1295 (1904); 39, 1373, 1379 (1906).

[2] Oppe, *ibid.*, 46, 1095 (1913).

[3] Gabriel, *ibid.*, 26, 706 (1893).

further work was carried out on this compound since it was not possible to obtain crystalline salts of methyl phthalimidine to be used for its resolution into *d*- and *l*-forms.

An unsuccessful attempt was made to prepare nitroso *secondary*-butylurethane to use for the preparation of methylethyl-diazomethane by v. Pechmann's method.

The only evidence, which may be considered as pointing to the existence of asymmetric diazo compounds, was obtained by treatment of the optically active amino ester hydrochlorides with nitrous acid under special conditions which favored the production of hydroxy esters. The hydroxy esters obtained had a small rotation showing that the racemization was not complete. In carrying out these reactions the yellow color of the diazo compound was noticed indicating that it was formed as an intermediate product. The evidence, however, is not at all conclusive, since there is no evidence that the reaction must go entirely through the diazo stage.

In the attempt to obtain certain of the diazo compounds several new compounds were prepared and the methods of preparation of some known compounds were improved. These methods have been included in this paper.

EXPERIMENTAL.

1. Derivatives of Phenylamino-acetic Acid.

Phenylamino-acetic Acid.—The method used was similar to that described by Zelinsky and Stadinoff[1] but was slightly changed to make it applicable to the production of larger amounts of material.

One hundred g. of sodium cyanide was dissolved in 400 cc. of water and to this solution 106 g. of ammonium chloride was added. When all had dissolved there was added a solution of 212 g. of benzaldehyde in 400 cc. of methyl alcohol. The mixture was shaken thoroughly and then allowed to stand for 1 to 1$^1/_2$ hours. The reaction began very quickly and the flask became quite warm. After the reaction was completed, a liter of water was added to throw the oily amino cyanide out of solution. This was collected in a liter of benzene, and the benzene solution was separated and washed thoroughly with water. The benzene also extracted some unchanged benzaldehyde and some condensation products.

The amino cyanide was extracted from the benzene solution by shaking it twice with 600 cc. of hydrochloric acid (1 volume of hydrochloric acid, sp. gr. 1.19, to one volume of water). To hydrolyze the amino cyanide, the hydrochloric acid solution was refluxed for 2 hours. The solution was cooled and filtered from some tarry material and the free amino acid precipitated with ammonium hydroxide. The amino acid was filtered off with suction, washed with water and alcohol to remove the color and

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[1] Zelinsky and Stadinoff, *Ber.*, 39, 1725 (1906).

dried. The yield varied from 105 to 110 g. (34–36% of the calculated amount).

A purer product was obtained by recrystallizing from hot water. This was rather tedious on account of the limited solubility of the amino acid in hot water. Larger runs were made with practically the same percentage yields. Longer standing of the first solution did not increase the yield. The yield was not improved by longer hydrolysis.

***dl*-Ethyl Phenylamino-acetate.**—This ester has previously been prepared by Kossel.[1]

Two hundred g. of phenylamino-acetic acid was suspended in one liter of absolute alcohol and 70 to 80 g. of hydrogen chloride was passed in. The acid dissolved completely. The solution was refluxed on the water-bath for 3 hours and then the alcohol was distilled under reduced pressure. The residue was dissolved in a little water, the solution covered with benzene and the free ester liberated with ammonium hydroxide. The benzene layer was separated, dried over anhydrous sodium sulfate and distilled. After the benzene was removed, the amino ester was distilled under reduced pressure. The yield varied from 142 to 153 g. (60 to 65% of the calculated amount) in different runs. The product boiled at 114–115° at 5 mm.; n_D at 25° is 1.500.

To obtain pure ester hydrochloride, the free ester was dissolved in 5 volumes of dry benzene and dry hydrogen chloride was passed into the solution. The product was filtered with suction and dried in a vacuum desiccator over solid sodium hydroxide. The yield was practically theoretical. M. p. 200°.

Acetyl *dl*-Ethyl Phenylamino-acetate.—Ten cc. of acetic anhydride was added to 11.5 g. of the free ester in a small flask. The solution was allowed to stand for about 2 hours and was then heated for one hour on the water-bath. The excess of acetic anhydride was destroyed with alcohol and the reaction mixture warmed to drive off the ethyl acetate and acetic acid. An oily product was left which crystallized when treated with ligroin and stirred. The crystals were filtered off and dried on a clay plate. The yield was 11 g., m. p. 65–66°.

Subs., 0.3961: 21.9 cc. N at 23° and 748.5 mm.
Calc. for $C_{12}H_{15}O_3N$: N, 6.33. Found: 6.30.

Carbethoxy *dl*-Ethyl Phenylamino-acetate.—Eighteen g. (2 mols.) of the free amino ester was dissolved in 50 cc. of dry ether, and 5.5 g. (one mol) of ethyl chlorocarbonate was slowly added. After one hour the ester hydrochloride was filtered off with suction (11 g. was obtained) and the benzene evaporated. The residue was crystallized from ligroin. The yield was 7 g. M. p. 57°.

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[1] Kossel, *Ber.*, 24, 4145 (1891).

Subs., 0.4233: 21.9 cc. N at 25° and 740 mm.
Calc. for $C_{13}H_{17}O_4N$: N, 5.58. Found: 5.80.

Acetyl ethyl phenylamino-acetate and carbethoxy ethyl phenylamino-acetate did not yield nitroso compounds when treated with nitrous oxides in dry ether, with sodium nitrite in glacial acetic acid solution, or with sodium nitrite in hydrochloric acid solution.

Attempts to Prepare Ethyl Phenyl-diazoacetate.—Curtius[1] and Kossel[2] have tried without success to prepare this diazo compound. By using essentially the same method that Curtius employed we have obtained 0.1 g. of diazo ester (12.3% N; calculated 14.7%) from 46 g. of ethyl phenylamino-acetate hydrochloride. By the use of Kossel's method a crude diazo ester was obtained by the action of silver nitrite on ethyl phenylamino-acetate in dry ether. The product could not be purified. Neither of these methods is of any practical use for preparing this compound. By the action of sodium nitrite and acetic acid on ethyl phenylamino-acetate hydrochloride in sodium acetate solution, the impure diazo ester may be prepared in fairly good yields. The details of this preparation are identical with those given later for the preparation of ethyl diazocaproate. However, on attempting to distil the impure ethyl diazophenylacetate it decomposed giving ethyl mandelate which was identified by its boiling-point and its melting-point.

Resolution of Phenylamino-acetic Acid.—This amino acid has been resolved by Betti and Mayer[3] by means of *d*-camphor-sulfonic acid. This method is easy to carry out and a pure *l*-acid is easy to obtain. The *d*-acid is obtained in purity of about 90–95%.

One hundred and fifty-one g. of phenylamino-acetic acid and 232 g. of *d*-camphor-sulfonic acid (Reychler) were dissolved in 750 cc. of boiling water. The solution was allowed to cool overnight. The first crop of crystals was filtered with suction. The yield of *l*-salt was 153–167 g. and the specific rotation was —37° to —40°. The pure *l*-salt has a rotation of —44°. By concentrating the mother liquors to $^1/_2$ volume, a second crop of crystals weighing 10–20 g. was obtained. The specific rotation was —25° to —26°. The mother liquors were saved for the preparation of the *d*-amino acid.

The first crop of crystals was recrystallized from 500 cc. of boiling water. The yield of pure *l*-salt was 107–114 g. (54–58%) with specific rotation of —43.5° to —44°. The yield may be increased somewhat by working up the mother liquors.

From the original mother liquor after filtering off the second crop of *l*-salt the *d*-amino acid was obtained by adding a slight excess of ammonium

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[1] Curtius, *Ber.*, **37**, 1266 (1904).
[2] Kossel, *ibid.*, **24**, 4155 (1891).
[3] Betti and Mayer, *ibid.*, **41**, 2071 (1908).

hydroxide. Sixty-five to 70 g. of the *d*-acid (with rotation of +127° to +146° was obtained from 151 g. of inactive acid.

The *l*-acid was prepared by dissolving the *l*-salt in hot water and adding the theoretical quantity of sodium hydroxide. From 206 g. of *l*-salt, 80 g. of pure *l*-acid were obtained.

***l*-Ethyl Phenylamino-acetate Hydrochloride.**—The *l*-ester hydrochloride was prepared according to the directions used in preparing the inactive ester. The free ester was not distilled, as distillation of one run caused racemization. The pure ester hydrochloride is obtained by drying the benzene solution of the free ester thoroughly and then passing in dry hydrogen chloride. From 81 g. of *l*-acid there was obtained 83 g. *l*-ester hydrochloride with specific rotation of —84.6°. Fischer and Weichbold[1] give the rotation as —88.95°. It seems probable that their ester hydrochloride was less pure and contained some of the amino acid hydrochloride, since they took no precautions to remove this impurity.

Acetyl *l*-Ethyl Phenylamino-acetate.—4.3 g. of *l*-ester hydrochloride was dissolved in 10 cc. of water. The free ester was liberated with ammonium hydroxide and taken up in benzene. The benzene solution was dried and treated with 2.5 g. of acetic anhydride. The reaction mixture was refluxed for 1 to 2 hours, the benzene and excess acetic anhydride distilled off and the residue crystallized from ligroin. Only about one g. of product was obtained. M. p. 69–70°.

Subs., 0.3965 in 19.3006 g. abs. alcohol gave rotation of —4.37° in a 2-dcm. tube for sodium light. $[\alpha]_D$ = —138.7°.

Attempts to Prepare an Optically Active Diazo Compound from the *l*-ester Hydrochloride.—*A. Curtius Method.*—21.5 g. of the *l*-ester hydrochloride was diazotized as described under the inactive compound. The crude ether solution after concentration to 20 cc. gave a rotation of —1° in a 2-dcm. tube. After steam distillation twice the oil was taken up in ether and the rotation observed was —0.1°. There was only 0.0087 g. material obtained on evaporating the ether and this was too small an amount to analyze. Other runs were made with less favorable results.

B. Kossel Method.—Ten g. of the *l*-ester hydrochloride was treated in dry ether with 8 g. of silver nitrite. After 10 days the solution was filtered from the silver chloride. On concentrating the ether about 2 g. of the nitrite of the ester was obtained. After filtering off the solid ester nitrite the ether solution was washed thoroughly with cold water to remove any of the ester nitrite which had remained in solution. The ether solution was then dried and made up to 25 cc. The solution had a deep yellow color. In a 2-dcm. tube the rotation was —4.21°.

Five cc. of this ether solution was titrated with iodine solution. 3.5

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[1] Fischer and Weichbold, *Ber.*, 41, 1292 (1908).

cc. of 0.1 N iodine solution was used up, showing that the 5 cc. of solution contained 0.033 g. of diazo ester.

Fifteen cc. of the ether solution was shaken up with 20% sulfuric acid until the yellow color was destroyed, the ether dried over sodium sulfate, and the solution again made up to 15 cc. In a 2-dcm. tube the rotation was —0.96°.

This experiment may indicate the existence of an optically active diazo ester which on hydrolysis gives an active hydroxy ester. It has been found, however, that 20% sulfuric acid will cause racemization of active ethyl mandelate. This is shown by the following experiment.

l-Ethyl mandelate was prepared as described in the following experiment. The rotation of a sample was taken in a one-dcm. tube and found to be —2.02°. The ester was then shaken with 20% sulfuric acid for 15 minutes, taken up in ether, dried, and after the ether had been removed, again examined in the polariscope. The rotation in a one-dcm. tube was only —1.6°.

This evidence makes it seem probable that the rotation observed in the diazo ester solution was due to the presence of *l*-ethyl mandelate and that the treatment with sulfuric acid caused racemization of this ester.

Attempts to Prepare *l*-Ethyl Mandelate.—Fischer and Weichbold[1] have found that treatment of *d*-ethyl phenylamino-acetate in dil. sulfuric acid solutions with sodium nitrite gave ethyl mandelate with slightly negative rotation.

21.5 g. of the *l*-ester hydrochloride was dissolved in 130 cc. of N sulfuric acid and the solution cooled to 0°. A solution of 6.4 g. of sodium nitrite in 10 cc. of water was added slowly and with stirring. A yellow oil soon began to separate from the solution. After all of the nitrite was added, the solution was kept at 0° for one hour and then gradually allowed to warm up to room temperature. After about 2 hours the evolution of gas had stopped and the oily layer was collected in ether, the ether solution dried and distilled under reduced pressure. 7.5 g. of mandelic ester boiling at 130–135° at 13 mm. was obtained. The rotation was taken in a one-dcm. tube and was found to be —5.25°. The ester was then crystallized from petroleum ether, and was found to melt at about 30°. The result confirms the previous work in that most of the ester was racemized. In this experiment, however, the mandelic ester obtained rotates in the same direction as the amino ester from which it was prepared.

Action of Acetic Anhydride on the Nitrite of *l*-Ethyl Phenylamino-acetate.—1.6 g. of the *l*-ester nitrite obtained by the action of silver nitrite on an *l*-ester hydrochloride in dry ether[2] was dissolved in 20 cc. of dry ether and treated with 2 g. of acetic anhydride. The solution warmed

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[1] Fischer and Weichbold, *Ber.*, 41, 1294 (1908).

[2] Kossel, *ibid.*, 24, 4155 (1891).

up slightly. After 2 days the solution was concentrated under reduced pressure over solid sodium hydroxide. After several days crystals separated. These were dried on a clay plate. They melted at 68–70°. A mixed melting-point with the acetyl derivative of *l*-ethyl phenylaminoacetate showed that the 2 compounds were identical.

2. Derivatives of Methyl Phthalimidine.

Methyl Phthalimidine.—The compound was prepared according to Gabriel's directions through phthalyl-acetic acid. Phthalyl-acetic acid[1] was obtained in 48% yield when the directions in the literature were followed. When this compound is treated with alkali and then with acid and hydrazine sulfate methyl phthalazone was obtained in 67% yields.[2] Gabriel's directions for the reduction of methyl phthalazone[3] are not very definite and the directions used for this step are given here.

Eighty g. of methyl phthalazone was dissolved in 400 cc. of hydrochloric acid (sp. gr. 1.19). To this solution 150 g. of granulated zinc was added in portions. After about 2 hours the zinc had dissolved and the solution was treated with an excess of sodium hydroxide solution. The methyl phthalimidine was obtained by extracting this solution 15 to 20 times with 100-cc. portions of ether. The methyl phthalimidine is not very soluble in ether and therefore the extraction is slow.

After evaporating the ether 30 g. of crude methyl phthalimidine was obtained. The product was purified by vacuum distillation. The yield was 25 g. The substance boiled at 180° at 10 mm. and melted at 100°. The material crystallizes very slowly. It oxidizes in the air to give a reddish colored substance.

Nitroso Methyl Phthalimidine.—Twenty g. of methyl phthalimidine was dissolved in 200 cc. of hydrochloric acid (one volume of acid of sp. gr. 1.19 to one volume of water) and the solution cooled to 0°. While the solution was cooled 10 g. of sodium nitrite in 20 cc. of water was added slowly. The nitroso compound first separated as an oil but soon solidified. After one hour the crystals were filtered off and recrystallized from 50% alcohol, with a yield of 20 g. (83% of the calculated amount).

For analysis the product was again recrystallized from 50% alcohol. The purified product melts at 86.5–87°.

Subs., 0.1104: 16 cc. N at 744 mm. and 26°.
Calc. for $C_9H_8O_2N$: N, 15.9. Found: 16.2.

Attempt to Prepare *o*-Carboxethyl Phenyl Methyl Diazomethane.—3.5 g. of nitroso methyl phthalimidine was dissolved in 300 cc. of dry ether. The solution was cooled to —10° and a solution of one g. of sodium in 10 cc. of absolute alcohol was added in portions. After about

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[1] Gabriel, *Ber.*, **26**, 952 (1893).

[2] *Ibid.*, **26**, 706 (1893).

[3] *Loc. cit.*

$^1/_2$ hour carbon dioxide was passed into the solution to react with the sodium ethylate. The ether solution became deep red in color. The sodium carbonate was filtered off and washed with dry ether, and the ether was removed under reduced pressure. A reddish oil remained. On standing for sometime this oil gradually changed to a yellow solid which melted at 195–200°. This was recrystallized from alcohol and melted at 220°. The amount obtained was too small for satisfactory analysis.

Attempts to Resolve Methyl Phthalimidine.—The resolution was attempted with *d*-camphor-sulfonic acid and *d*-bromocamphor-sulfonic acid. Neither of these acids gave a crystalline salt with the base. The methyl phthalimidine was then boiled with a solution of sodium hydroxide the excess of sodium hydroxide was neutralized with nitric acid and the *o*-α-aminoethyl-benzoic acid precipitated as the silver salt. The silver salt was boiled with ethyl iodide in dry ether, the silver iodide removed and the ether evaporated. An oily substance was obtained. Its properties corresponded to those of an amino ester. It did not give crystalline salts with *d*-camphor-sulfonic acid or *d*-bromocamphor-sulfonic acid.

Since it was not possible to resolve the methyl phthalimidine, the work on this series was abandoned.

3. Derivatives of α-Amino-*n*-caproic Acid.

The amino acid was prepared from the bromo acid according to the method described in the literature.[1] The amino acid was resolved through the formyl derivative.[2] α-Amino-*n*-caproic ethyl ester was prepared according to the method of Fischer.[3] Thirty g. of amino acid gave 29 g. of ester, boiling at 82–83° at 9 mm. The ester hydrochloride was prepared from this by dissolving the ester in dry ether and passing hydrogen chloride into the solution. The yield was 33 g.

Ethyl α-Diazo-*n*-caproate.—Fifty g. of the ester hydrochloride (free from excess of hydrochloric acid) was dissolved in 150 cc. of water, and the solution was cooled to —10°. To this solution 60 g. sodium acetate and 60 g. sodium nitrite were added. Then, during one hour, 75 cc. of glacial acetic acid was added. Very little evolution of nitrogen occurred. The solution was kept at —5° to —10° for $3^1/_2$ hours. The ether became deeply colored, due to the formation of the diazo ester.

After the reaction was practically complete, the ether layer was separated, washed 2 or 3 times with water, 2 or 3 times with sodium hydrogen carbonate solution and then allowed to stand over solid barium hydroxide to remove all of the acetic and nitrous acids. This was found to be very necessary as any trace of acid caused decomposition later on in the preparation. The ether solution was then thoroughly dried over calcium

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[1] *Z. physiol. Chem.*, **86**, 454 (1913); THIS JOURNAL, **42**, 320 (1920).

[2] *Ann.*, **362**, 333 (1908).

[3] Fischer, *Ber.*, **34**, 433 (1901).

chloride. The ether was removed in a vacuum desiccator over solid sodium hydroxide and the residue distilled under reduced pressure. About 2 g. of low-boiling material came over and then the diazo ester boiled between 75 and 78° at 10 mm. The yield was 15 g. The ester was redistilled and 13 g. (30% of the calculated amount) was obtained; the variation in boiling-point was less than 1°.

Steam distillation did not purify this diazo ester, as was shown by the following experiment. 1.4 g. of diazo ester (N = 11.7%) was distilled with 25 cc. of water and 5 g. of barium hydroxide. From the distillate 0.5 g. diazo ester (N = 11.6%) was recovered. Approximately $^2/_3$ of the ester was destroyed and no purification was obtained.

The ester was analyzed by the sulfuric acid method.[1]

Subs., 0.1414, 0.1730, 0.1614: 19.0 cc. N at 25° and 749 mm., 23.0 cc. N at 26° and 745 mm., 23.2 cc. N at 25° and 745 mm.

Calc. for $C_8H_{14}O_2N_2$: N, 16.47. Found:. 15.2, 15., 16.2.

The ester is lemon-yellow in color; crystallizes when cooled in mixtures of carbon dioxide-snow and ether; it is lighter than water; n_D at 26° = 1.453.

Decomposition of Ethyl *α*-Diazo-*n*-caproate with Dilute Acetic Acid.—Ten g. of the diazo ester was refluxed for one hour with 50 cc. of 10% acetic acid. The ester loses its yellow color. The reaction mixture was cooled and the ester taken up in ether. The ether solution was dried and distilled under reduced pressure. The following fractions were obtained: I, 2.5 g. boiling at 67–72° at 10 mm.; II, 1.5 g. boiling at 72–85° at 10 mm.; III, 3 g. boiling at 85–90° at 10 mm. Fraction I decolorized a solution of bromine in carbon tetrachloride and reacted with dil. potassium permanganate solution. On saponification with potassium hydroxide solution and acidification, an acid was obtained which was volatile with steam. The acid was distilled with steam to separate it from any non-volatile hydroxy acid. The volatile acid was taken up in ether and dried and the ether evaporated. One g. of the acid in 5 cc. of carbon disulfide was treated with 1.6 g. of bromine and the solution allowed to stand overnight. Most of the bromine color disappeared. On spontaneous evaporation an oily dibromo acid was obtained but it could not be obtained in crystalline condition.

Subs., (dibromo acid) 0.7165: 25.7 cc. of 0.101 *N* NaOH.

Neutral equivalent calc. for $C_6H_{10}O_2Br_2$: 274. Found: 276.

Fittig[2] has prepared Δ^1-hexenoic acid and gives its melting-point as 30–32°. He also describes the α-β-dibromo-hexoic acid and gives its melting-point at 71°. Although in this work these acids were not obtained in crystalline condition, there is little doubt that both were prepared.

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[1] Curtius, *J. prakt. Chem.*, [2] 38, 418 (1888).

[2] *Ann.*, 283, 118 (1894).

Fraction III was saponified with potassium hydroxide solution. The solution was made acid and distilled with steam to remove the small amount of unsaturated acid. The solution was then extracted with ether to obtain the hydroxy acid. The hydroxy acid from the ether layer was obtained as an oil. By crystallizing from petroleum ether it was obtained in white crystals melting at 58°. Abderhalden[1] gives the melting-point of α-hydroxy-caproic acid at 60°. The copper salt was prepared as described by Abderhalden. The analysis and decomposition temperature of the copper salt confirmed the conclusion that the acid was α-hydroxy-caproic acid.

Copper salt decomposed at 270°.

Subs. (Cu salt), 0.1727: CuO, 0.0416.
Calc. for $(C_4H_9CHOHCO_2)_2Cu$: Cu, 19.54. Found: 19.50.

***l*-Ethyl α-Amino-*n*-caproate.**—Thirteen g. of *l*-amino acid [$(\alpha)_D$ —22°] was esterified in the usual manner. The yield of free ester was 11.5 g. (72% of that calculated) boiling at 86–87° at 12 mm. The rotation in a one-dcm. tube was —11.65°. The hydrochloride was prepared as described before. The yield was 14 g.

1.7582 g. of the hydrochloride in 13.4371 g. of water gave a rotation of —1.7° in a 2-dcm. tube in sodium light; $(\alpha)_D$ = —7.25°.

***d*-Ethyl α-Amino-*n*-caproate.**—Thirteen g. of *d*-amino acid [$(\alpha)_D$ = +17°] gave 11 g. ester boiling at 85° at 10 mm. The rotation in a one-dcm. tube was +6.15°. The ester gave 13 g. of the hydrochloride. The rotation of the salt was not taken.

Attempts to Prepare Optically Active Diazo Compounds from the *d*- and *l*-ester Hydrochlorides.—Fourteen g. of *l*-ester hydrochloride was dissolved in 50 cc. of water and diazotized as described under the preparation of ethyl diazo-caproate. 20 g. of sodium acetate, 20 g. of sodium nitrite and 25 cc. of glacial acetic acid were used. The yield of diazo ester was 1.5 g., boiling at 70–71° at 7 mm.

Subs., 0.2817: 35.8 cc. N at 23° and 743 mm.
Calc. for $C_8H_{14}O_2N_2$: N, 16.47. Found: 14.45.

The ether solution first separated from the diazotization reaction mixture, was examined in the polariscope and seemed to show a possible rotation of about —0.03°. After distillation the ester was inactive.

0.626 g. of diazo ester in 10.24 g. dry ether was examined in a 2-dcm. tube. There was no rotation. The ether solution was shaken with dil. sulfuric acid until it became colorless, dried and the solution again examined in the polariscope. It was inactive.

Twelve g. of *d*-ester hydrochloride was diazotized and 2 g. of diazo ester boiling at 72–73° at 8 mm. was obtained. The nitrogen content was

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[1] Abderhalden, *Z. physiol. Chem.*, 84, 39 (1913).

14.6%. Neither the crude ether solution nor the purified ester dissolved in dry ether showed any signs of optical activity.

Attempt to Prepare *l*-Ethyl α-Hydroxy-*n*-caproate.—Thirteen g. of *d*-ethyl α-amino-caproate hydrochloride (from free ester with rotation of only +2.15°) was dissolved in 130 cc. of *N* sulfuric acid. The solution was cooled to 0° and diazotized with a solution of 7 g. of sodium nitrite in 10 cc. of water. A yellow oil soon began to separate. After standing for about one hour at 0° the solution was removed from the ice-bath and gradually warmed to about 40°. The oily product was collected in ether, dried and distilled under reduced pressure. The total distillate weighed 4 g. It boiled partly at 65–70° and partly at 87–90° at 10 mm. 2 g. of dry ether was added and the rotation taken in a one-dcm. tube. The rotation was +0.7°. The free ester decolorized bromine and reacted with permanganate solution, showing the presence of Δ^1-hexenoic ester. The product was not investigated further to show the relative proportions of unsaturated ester and hydroxy-ester. As nearly as could be determined by the boiling-point they were present in almost equal amounts.

α-Bromo-*n*-caproyl Chloride.—Fifty g. of α-bromo-caproic acid was heated with 28 g. of thionyl chloride under a reflux condenser until no more sulfur dioxide was evolved. The residue was distilled under diminished pressure. A very little low-boiling material was obtained and then the acid chloride came over. There was considerable residue of high-boiling material, doubtless unchanged acid. The yield was 37 g. (67% of the amount calculated) boiling at 102–105° at 30 mm.

Subs., 0.2144: 19.42 cc. of 0.1 *N* $AgNO_3$ (method of Stepanow).
Calc.: 20.08 cc.

α-Bromo-*n*-caproyl-glycine.—This compound was prepared according to the directions which Fischer[1] gives for α-bromo-*iso*-caproyl-glycine.

22.5 g. of glycocoll was dissolved in 300 cc. of *N* sodium hydroxide solution. The solution was cooled to 0° and in alternate portions 65 g. of α-bromo-caproyl chloride and 350 cc. of *N* sodium hydroxide solution were added. The temperature was kept below 10°. The mixture was shaken vigorously during the reaction. When the odor of the acid chloride had disappeared, 75 cc. of 5 *N* hydrochloric acid was added. The bromo-caproyl-glycine separated as an oil and was taken up immediately in ether. The ether solution was separated and the bromo-caproyl-glycine precipitated by means of an equal volume of petroleum ether. The product separated in white crystals. Yield 58 g. (76% of the amount calculated); m. p. 114–115°.

Subs., 0.4993, 0.4994: 20.2 cc., 20.2 cc.; 0.101 *N* NaOH.
Neutral equivalent calc. for $C_8H_{14}O_3NBr$: 252. Found: 244.8; 244.7.

α-Amino-*n*-caproyl-glycine.—Thirty g. of α-bromo-*n*-caproyl-glycine

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[1] Fischer, *Ann.*, 340, 142 (1905).

was dissolved in 150 cc. of ammonium hydroxide (sp. gr. 0.9). The solution was allowed to stand for 4 days at room temperature and then was evaporated to dryness on the water-bath. The ammonium bromide was removed by 3 extractions with 75 to 100 cc. of boiling alcohol. The yield was 19 g. (85% of the calculated amount).

To obtain a pure sample for analysis, 3 g. was dissolved in 60 cc. of hot water, and to the solution 120 cc. of alcohol was added. The dipeptide was filtered with suction. Yield 2.8 g.; m. p. 226°. The compound melted sharply and then decomposition occurred. The dipeptide burns with difficulty when the Dumas method is employed for determination of nitrogen.

Dumas Method.

Subs., 0.1858: 23.0 cc. N at 24° and 738 mm.

Calc. for $C_8H_{16}O_3N_2$: N, 14.89. Found: 14.85.

Kjeldahl Method.

Subs., 0.2000, 0.2000: 21.36 cc., 21.31 cc. 0.1 *N* H_2SO_4.

Calc. for $C_8H_{16}O_3N_2$: N, 14.89. Found: 14.95, 14.91.

Ethyl Ester Hydrochloride of α-Amino-*n*-caproyl-glycine.—Ten g. of dipeptide was suspended in 100 cc. of absolute alcohol. The solution was saturated with dry hydrogen chloride which caused all of the dipeptide to dissolve. The solution was then refluxed for 15 minutes on the water-bath and cooled. Many of the dipeptide ester hydrochlorides will crystallize from the alcohol. In this case the compound did not crystallize when the solution was cooled in an ice-bath for several hours. Ether would not cause the ester to separate from solution. When the solution was concentrated *in vacuo*, a gum-like mass remained. Finally after standing for over a week *in vacuo* over sodium hydroxide a little free hydrochloric acid could be detected but the compound did not crystallize. The yield of crude product was 14.5 g.

Subs., 0.411: 17.27 cc. 0.01022 *N* $AgNO_3$.

Calc. for $C_{10}H_{20}O_3NCl$: Cl, 14.05. Found: 15.12.

That the compound really was the ester hydrochloride was shown by the fact that it gave the corresponding hydroxy ester on treatment with nitrous acid.

Ethyl Ester of α-hydroxy-*n*-caproyl-glycine.—Fourteen g. of the crude ester hydrochloride prepared in the above experiment was dissolved in 50 cc. of water, 10 g. of sodium acetate was added and the solution was cooled to 0°. Then 5 g. of sodium nitrite was added, and after it had dissolved 6 cc. of glacial acetic acid was gradually added. Nitrogen gas was evolved and an oily substance separated. This soon changed to a white solid. After sometime the solid was filtered off. A little yellow oil came through with the water. This oil is not diazo ester, as it does not decolorize iodine solution and does not give gas when treated with sulfuric acid. The solid hydroxy ester was purified by dissolving it in a little ether and adding petroleum ether to the solution. Yield 3–4 g. M. p. 90–91°.

Subs., 0.2308: (Kjeldahl), 10.75 cc. 0.1 *N* H_2SO_4.
Calc. for $C_{10}H_{19}O_4N$: N, 6.45. Found: 6.52.

4. Derivatives of α-Amino-caprylic Acid.

α-Amino-caprylic Acid.—This compound has been prepared in 35% yields by treating the ammonium addition compound of heptaldehyde with aqueous hydrocyanic acid followed by hydrolysis.[1] Fifty-five g. of sodium cyanide was dissolved in 100 cc. of water and to the solution 57 g. of ammonium chloride was added. To this solution was then added a solution of 114 g. of heptaldehyde in 100 cc. of methyl alcohol. The solution became warm and after about a half hour a layer of the amino cyanide began to separate. The reaction mixture was allowed to stand overnight. The amino cyanide was taken up in ether and the ether distilled off. To accomplish the hydrolysis, 500 cc. of hydrochloric acid (350 cc. of acid sp. gr. 1.19, and 150 cc. of water) was added and the solution was refluxed for $2^1/_2$ hours. It was cooled and filtered to remove most of the oily impurity which had separated. The amino acid was precipitated from the filtrate by adding ammonium hydroxide. The product obtained was quite dark in color. For purification it was dissolved in dilute solution of sodium hydroxide and boiled with bone black. The solution was filtered and the amino acid precipitated by means of a saturated solution of ammonium chloride. The product was filtered with suction and washed with water and dried on filter paper. The yield was 70–75 g. (43–47% of the calculated amount). The amino acid may be crystallized from water, but it is not very soluble even in boiling water.

Ethyl α-Amino-caprylate Hydrochloride.—Fifty g. of the amino acid was esterified as described under the corresponding caproic acid derivatives. The yield of ester was 40 g. It boiled at 110° under 10 mm. pressure; n_D at 21° is 1.436.

The amino ester was converted to the hydrochloride in the usual way. The yield was nearly quantitative, m. p. 76–77°.

Subs., 0.4980, 0.4971: 21.55 cc., 21.49 cc. 0.1022 *N* $AgNO_3$ (Volhard).
Calc. for $C_{10}H_{22}O_2NCl$: Cl, 15.88. Found: 15.66, 15.67.

Attempt to Prepare Ethyl α-Diazo-caprylate.—The ester hydrochloride was diazotized according to the directions followed in the preparation of the ethyl α-diazo-caproate. Twenty-three g. of the ester hydrochloride gave 2 g. of yellow oil boiling at 102–107° at 11 mm. Analysis by the sulfuric acid method showed only 5% of nitrogen. A second run decomposed during distillation after the product was distilling at 90° at 6 mm., and 2.5 g. of ethyl α-hydroxy-caprylate boiling at 80–85° at 7 mm. was obtained. This was identified only by the saponification number.

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[1] Erlenmeyer and Sigel, *Ann.*, 176, 344 (1875).

Subs., 1.452: 8.16 cc. 0.9782 *N* NaOH.
Saponification number: Calc. from $C_6H_{13}CHOHCO_2C_2H_5$: 188. Found: 182.

Another experiment was carried out in which the free ester was diazotized in acetic acid solution. The results were not much better.

18.7 g. of ethyl amino-caprylate was dissolved in 50 cc. of water and 6 cc. of glacial acetic acid. The solution was cooled below 0° and 20 g. of sodium acetate and 15 g. of sodium nitrite were added. The solution was covered with ether and 20 cc. of glacial acetic acid slowly added. After standing at 0° for 4 hours the ether layer was separated and worked up according to the usual method. Nine g. of product boiling at 105–110° at 10 mm. was obtained. This product contained only 8.15% of nitrogen. The product was then refractionated at 6 mm. and divided into 3 portions.

Fraction 1. 4 g. boiling below 90°: N = 4.6%.
Fraction 2. 3 g. boiling below 90–95°: N = 9.2%.
Residue. 2 g. not analyzed.

The percentage of nitrogen should be 14.14%. Therefore, the diazo compound was about 65% pure.

5. Derivatives of Secondary Butylamine.

Ethylmethyl-ketoxime.[1]—250 g. of hydroxylamine sulfate (90% pure) was dissolved in 1500 cc. of water. To the solution were added 216 g. of ethylmethyl-ketone and 160 g. of sodium carbonate. The solution was allowed to stand for 24 hours. The oxime was taken up in ether, dried over calcium chloride and distilled. The yield was 203 g. (85% of that calculated); b. p. 150–155°.

Secondary **Butylamine.**—Ninety g. of methylethyl-ketoxime was dissolved in one liter of absolute alcohol. To the solution 150 g. sodium was added in portions, within one hour. The solution was boiled and more absolute alcohol was added from time to time until all the sodium had reacted. About 300 cc. of absolute alcohol was added. When all the sodium was in solution, the amine and alcohol were distilled with steam. To the distillate a slight excess of hydrochloric acid (sp. gr. 1.19) was added and the solution evaporated to dryness on the water-bath. The amine hydrochloride was placed in a flask attached to a condenser and the free amine liberated with a very concentrated solution of sodium hydroxide. The free amine was separated and dried over solid sodium hydroxide and distilled. Yield 40 g. (53% of the amount calculated), boiling at 66–70°.

Secondary **Butyl Urethane,**

$$\begin{matrix}CH_3\\C_2H_5\end{matrix}\!\!>\!CHNHCOOC_2H_5$$

[2]—Forty g. of *secondary* butylamine was dissolved in 100 cc. of dry ether and to the

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[1] Janny, *Ber.*, 15, 2779 (1882).
[2] *Rec. trav. chim.*, 14, 19 (1895).

cold solution was added a solution of 30 g. of ethyl chlorocarbonate in an equal volume of dry ether. The reaction was very vigorous. After the reaction was complete the amine hydrochloride was filtered off and 28.5 g. was obtained. The ether was evaporated and the urethane distilled under reduced pressure. Yield 30 g. (75% of the calculated amount); b. p. 87–88° at 14 mm.

Attempts to Prepare the Nitroso Derivative of *Secondary* Butyl Urethane.—The urethane was dissolved in glacial acetic acid and treated with sodium nitrite but was recovered unchanged. The solution in 30% acetic acid did not give better results. The urethane was treated in dry ether with amyl nitrite and dry hydrogen chloride but was recovered unchanged from the reaction mixture.

Summary.

1. Ethyl α-diazo-*n*-caproate was prepared in 30% yields from the corresponding amino ester hydrochloride by a slight modification of Curtius' method of preparing diazo esters.

2. Samples of this diazo ester prepared from the *d*- and *l*-forms of the amino ester hydrochloride were found to be optically inactive. They were decomposed by dil. sulfuric acid and the resulting compounds were also optically inactive.

3. Ethyl α-diazo-*n*-caproate was decomposed by dil. acids and the products formed were ethyl α-hydroxy-*n*-caproate and ethyl Δ^1 hexenoate.

4. Impure diazo esters were prepared from phenylamino-acetic acid and α-amino-caprylic acid. These esters decomposed on attempting to purify them by vacuum distillation and the corresponding hydroxy esters were obtained.

5. The treatment of optically active amino ester hydrochlorides with nitrous acid under certain conditions gave optically active hydroxy esters. If the diazo ester is an intermediate product this is evidence for the existence of an asymmetric diazo compound.

6. Improved methods for the preparation of *dl*-phenylamino-acetic acid, *dl*-ethyl phenylamino-acetate, *l*-phenylamino-acetic acid, *l*-ethyl phenylamino-acetate hydrochloride, methyl phthalimidine, α-amino-caprylic acid, *secondary* butyl amine and *secondary* butyl urethane were devised.

7. The following new compounds were prepared:

dl-Acetyl-ethyl phenylamino-acetate, $C_{12}H_{15}O_3N$, m. p. 65–66°.

dl-Carboethoxy ethyl phenylamino-acetate, $C_{13}H_{17}O_4N$, m. p. 57°.

l-Acetyl ethyl phenylamino-acetate, $C_{12}H_{15}O_3N$, m. p. 69–70°, $[\alpha]_D = -138.7°$.

Nitroso methyl phthalimidine, $C_9H_8O_2N_2$, m. p. 86.5–87°.

Ethyl α-diazo-*n*-caproate, $C_8H_{14}O_2N_2$, b. p. 75–76° at 10 mm.

l-Ethyl α-amino-*n*-caproate, $C_8H_{17}O_2N$, b. p. 86–87° at 12 mm., $[\alpha]_D = -11.65°$ in a one-dcm. tube

l-Ethyl α-amino-*n*-caproate hydrochloride, $C_8H_{18}O_2NCl$, $[\alpha]_D = -7.25°$.

α-Bromo-*n*-caproyl chloride $C_6H_{10}OClBr$, b. p. 102–105° at 30 mm.

α-Bromo-*n*-caproyl-glycine, $C_8H_{14}O_3NBr$, m. p. 114–115°.

α-Amino-*n*-caproyl-glycine, $C_8H_{16}O_3N_2$, m. p. 226°.

Ethyl ester of α-oxy-*n*-caproyl-glycine, $C_{10}H_{19}O_4N$, m. p. 90–91°.

Ethyl α-amino-caprylate, $C_{10}H_{21}O_2N$, b. p. 110° at 10 mm.

Ethyl α-amino-caprylate hydrochloride, $C_{10}H_{22}O_2NCl$, m. p. 76–77°.

URBANA, ILL.

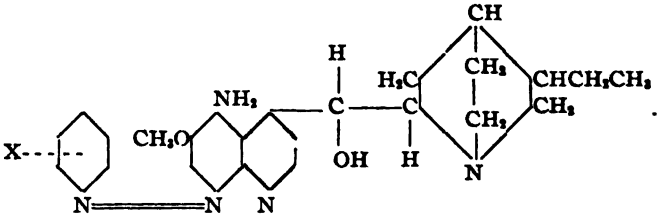
[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH.]

SYNTHESES IN THE CINCHONA SERIES. VI. AMINOAZO AND HYDROXYAZO DYES DERIVED FROM CERTAIN 5-AMINO CINCHONA ALKALOIDS AND THEIR QUINOLINE ANALOGS.

BY WALTER A. JACOBS AND MICHAEL HEIDELBERGER.

Received June 29, 1920.

In our study of 5-amino-dihydroquinine[1] it was found to couple smoothly in dil. acetic acid solution with diazo compounds to form aminoazo dyes in which we assume the azo group to enter Position 8 in the quinoline portion of the molecule



This assumption seems justified since, on the one hand, Position 8 is the only one which satisfies the usual laws of substitution for a 5-amino-6-methoxyquinoline (analogous to α-amino-β-methoxynaphthalene), and finally, since 5-aminoquinoline was also found to yield aminoazo dyes which could be reduced to 5,8-diamino-quinoline.

Of the dyes from 5-amino-dihydroquinine the phenylazo-, *p*-sulfophenylazo-, and the *p*-methoxy- and *p*-ethoxy-phenylazo-compounds were prepared and studied. 5-Amino-dihydroquinidine and 5-amino-ethyldihydrocupreine also readily yielded phenylazo compounds. These substances are usually red, well defined, crystalline compounds, forming orange-red solutions in neutral solvents and deep purple solutions in

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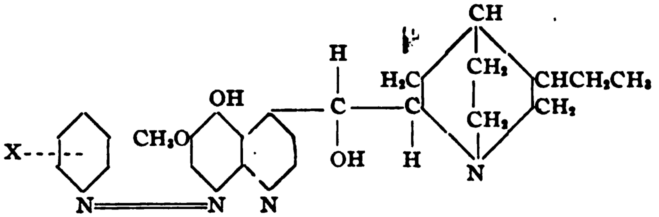
[1] THIS JOURNAL, 42, 1485 (1920).

dilute mineral acids, except in the case of the *p*-methoxy- and ethoxy-dyes, the salts of which are a pronounced violet-blue.

If the solution of one of the amino dyes in mineral acid is boiled, a very rapid color change from a purplish-red to a brown-red is to be noted, due to the replacement of the amino group by hydroxyl, with elimination of ammonia which is readily detected on rendering alkaline. By this reaction it has been possible to prepare from the 5-amino-8-azo-cinchona dyes the corresponding 5-hydroxy compounds



The lability of the amino group in the 5-amino compounds is surprisingly great, since boiling on the water-bath in a mixture of equal parts of 1 : 1 hydrochloric acid and alcohol suffices in all instances to cause complete cleavage in from 5 to 15 minutes, the alcohol being added to increase the solubility of the dye salts. Although the replacement of an amino group by hydroxyl in acid solution has been previously noted and used for preparative purposes in a number of instances, as in the preparation of α-naphthol from α-naphthylamine[1] and the dihydroxybenzenes from the phenylenediamines,[2] as a rule high temperatures have been found essential. The ease of replacement of amino by hydroxyl in our compounds more closely resembles that occurring in salts of *sym.*-triaminobenzene and its derivatives, permitting their ready and complete conversion into phloroglucinol and its derivatives at the temperature of the water bath.[3]

It was of interest to determine whether the lability of the amino group in our compounds was due to the influence of the cinchona molecule as a whole, or whether analogous dyes obtained from 5-aminoquinoline would behave in the same way. As a matter of fact, phenylazo-5-aminoquinoline yielded phenylazo-5-hydroxyquinoline, but it required a definitely longer period of heating to bring about complete cleavage. On the other hand, the dyes from 5-amino-6-methoxyquinoline, which afforded a closer parallel to the 5-amino-dihydroquinine dyes, were found to be as easily converted into the hydroxy dyes as the alkaloidal derivatives themselves. It would seem, therefore, that the methoxy or ethoxy group in Position 6 contributes markedly to the lability of the amino groups in these compounds.

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[1] Ger. Pat. 102,358.

[2] *Ber.*, 30, 2569 (1897).

[3] *Monatsh.*, 18, 755 (1897); 19, 223, 236, 249 (1898); 21, 39 (1900).

The hydroxyazo dyes are also substances with excellent properties and crystallize very readily. In spite of the hydroxyl group they do not dissolve in dil. alkali, but after making an alcoholic solution alkaline it may be diluted freely without precipitating the dye, subsequent addition of ammonium chloride being, however, sufficient to cause precipitation.

On reduction the new cinchona and quinoline dyes yield amino compounds in which interesting relationships have been observed in the replacement of the amino group by hydroxyl. These studies are still in progress, and we shall describe them in a subsequent communication.

I.

5-Amino-8-phenylazo-dihydroquinine.—One g. of aniline dissolved in 30 cc. of normal hydrochloric acid was diazotized with 10 cc. of normal sodium nitrite, with chilling. A solution of 3.4 g. of 5-amino-dihydroquinine[1] in 20 cc. of normal acetic acid was diluted to 200 cc., treated with 20 cc. of saturated sodium acetate solution, chilled to about 10°, and slowly treated, with turbining, with the diazo solution. The original orange-red solution rapidly changed to a deep red, and after 15 minutes the dye was precipitated as deep red flocks by the addition of an excess of ammonia, filtered off, and washed with water. On taking up the moist dye in hot alcohol it dissolved partially but almost immediately crystallized. Recrystallized from 95% alcohol, the dye gradually separated as glistening, red needles containing approximately one molecule of water of crystallization when air-dried. The yield was 2.2 g. The air-dry substance melts at 155–7° with preliminary darkening and sintering. It dissolves sparingly in the cold in methyl and ethyl alcohols, benzene, and chloroform, but readily on warming, forming red solutions. It is sparingly soluble in acetone and ether. Solutions in dilute acids are reddish-purple, and in conc. sulfuric acid an intense purple. After dissolving the dye in 10% hydrochloric acid the hydrochloride deposits on rubbing as deep brown, microscopic needles.

Subs. (air-dry), 0.4760: loss, 0.0227 *in vacuo* at 80° over H_2SO_4.
Calc. for $C_{26}H_{31}O_2N_5.H_2O$: H_2O, 3.89. Found: 4.77.
Subs., anhydrous, 0.1109: 15.0 cc. N (24.0°, 772 mm.).
Calc. for $C_{26}H_{31}O_2N_5$: N, 15.72. Found: 15.79.

5-Hydroxy-8-phenylazo-dihydroquinine.—5 g. of the preceding aminoazo dye were treated with a hot mixture of 25 cc. of alcohol and 25 cc. of 1 : 1 hydrochloric acid and the resulting deep purple solution heated on the water-bath. The mixture rapidly changed to a dark brown and set to a jelly which slowly changed to long, brown needles of the hydrochloride of the hydroxyazo dye. After 15 minutes the mass was diluted with water, chilled, and treated with an excess of ammonia, yielding a purple mass of the free base. After filtering and washing with water,

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[1] *Loc. cit.*

the dye was taken up in hot alcohol, quickly separating as brownish yellow, microscopic leaflets in a yield of 4.2 g. On dissolving in hot water with the aid of dil. sulfuric acid, filtering, adding an equal volume of alcohol, and then treating hot with a slight excess of ammonia, the dye quickly crystallized as lustrous, orange-brown platelets which, when rapidly heated to 140° and then slowly, gradually sinter together and effervesce at 145–8°. When air-dry it contains one molecule of water of crystallization which requires heating at 100° *in vacuo* for its complete removal. The dye is readily soluble in hot benzene and chloroform, less readily in hot methyl and ethyl alcohols, and very sparingly in hot acetone, forming orange-red solutions, and is almost insoluble in ether. It dissolves in dil. sulfuric acid with an orange-red color, and in the conc. acid with a cherry-red shade, appearing purple in thin layers. In dil. hydrochloric acid it forms an insoluble, gelatinous salt.

Subs. (air-dry), 0.2940: loss, 0.0122 *in vacuo* at 100° over H_2SO_4.
Calc. for $C_{26}H_{30}O_3N_4.H_2O$: H_2O, 3.88. Found: 4.15.
Subs., anhydrous, 0.1296: 14.2 cc. N (25.5°, 754 mm.).
Calc. for $C_{26}H_{30}O_3N_4$: N, 12.55. Found: 12.43.

5-Amino-8-(*p*-sulfophenylazo)-dihydroquinine.—A solution of diazotized sulfanilic acid was rapidly added to 3.4 g. of amino-dihydroquinine under the same conditions as previously given. A dark red-brown, amorphous precipitate of the dye formed at once, and was filtered off and washed with water. On treating with hot alcohol it dissolved partially, but almost immediately changed to orange, microscopic needles. The yield was 4 g. after washing with acetone. On recrystallizing from 50% alcohol it formed delicate, minute, orange needles containing about 0.5 molecule of water of crystallization. In working with large quantities of the dye it was found more convenient to dissolve it in the minimum amount of dil. alkali, add an equal volume of alcohol, warm, and reacidify with an equivalent amount of acetic acid. The air-dry substance darkens above 180°, decomposes at about 245°, and is practically insoluble in the usual neutral solvents. In dil. mineral acids it gives a deep cherry-red solution, appearing purple in thin layers, and when not too dilute sulfuric or hydrochloric acid is used the difficultly soluble salt separates as a dark-colored, crystalline powder. In conc. sulfuric acid the solution is bright red, appearing purple in thin layers. The solution in 50% acetic acid is quickly reduced by stannous chloride to diamino-dihydroquinine, which will be described in a later communication.

Subs. (air-dry), 0.5041: loss, 0.0114 *in vacuo* at 80° over H_2SO_4.
Calc. for $C_{26}H_{31}O_5N_5S.0.5H_2O$: H_2O, 1.68. Found: 2.26.
Subs. (anhydrous), 0.1188: 13.4 cc. N (23.5°, 772 mm.).
Calc. for $C_{26}H_{31}O_5N_5S$: N, 13.32. Found: 13.18.

5-Hydroxy-8-(*p*-sulfophenylazo)-dihydroquinine. — Two g. of the amino-azo dye were treated with a hot mixture of 20 cc. of alcohol and 20 cc. of 10% hydrochloric acid and boiled on the water-bath. The solution almost immediately set to a jelly which soon began to change to the crystalline salt of the new dye. After 5–10 minutes the mixture was made alkaline with dil. sodium hydroxide, a strong odor of ammonia being at once noticeable. The deep purple solution was treated with an excess of acetic acid, yielding 1.8 g. of glistening, salmon-colored needles on diluting and rubbing. Recrystallized from 50% alcohol it separated as delicate, lustrous, scarlet needles containing approximately one molecule of water of crystallization. The dye decomposes at 275° with preliminary darkening, and is fairly readily soluble in hot 50% alcohol and methyl alcohol, sparingly in hot water and hot alcohol, and practically insoluble in the usual neutral solvents. With dil. hydrochloric and sulfuric acid it forms brown-orange salts and dissolves in conc. sulfuric acid with a deep scarlet color, appearing violet in thin layers and changing to orange on dilution with water. In alkali the color is purplish red.

Subs. (air-dry), 0.4260: loss, 0.0164 *in vacuo* at 100° over H_2SO_4.
Calc. for $C_{26}H_{30}O_6N_4S.H_2O$: H_2O, 3.31. Found: 3.85.
Subs. (anhydrous), 0.1358: 12.8 cc. N (24.5°, 750 mm.).
Calc. for $C_{26}H_{30}O_6N_4S$: N, 10.63. Found: 10.67.

5-Amino-8-(*p*-methoxyphenylazo)-dihydroquinine.—Although diazotized *p*-anisidine failed to yield a dye in dil. acetic acid as in previous cases, the following conditions were successfully employed. 1.23 g. of *p*-anisidine in 15 cc. of 2 *N* hydrochloric acid were diazotized at 0° with 2 cc. of 5 *N* sodium nitrite. 3.4 g. of amino-dihydroquinine in 10 cc. of *N* acetic acid were then added and the mixture immediately treated with sufficient saturated sodium acetate solution to bind the free hydrochloric acid. After 2 hours the mixture, from which an almost black tar had separated, was diluted with enough alcohol to form a homogeneous solution, warmed, and made alkaline with ammonia. The dye gradually separated on rubbing, and after filtering and washing with cold alcohol the yield was 2.8 g. Recrystallized twice from 95% alcohol it forms red, microscopic needles and platelets which melt slowly at 150–3°. It dissolves readily with an orange-red color in cold chloroform, on boiling in methyl or ethyl alcohol, acetone, or benzene, and but sparingly in ether. In strong mineral acid it gives a deep violet-blue color which changes to brownish-red on dilution, a phenomenon apparently due to hydrolysis of the polyacid salts originally formed. In conc. sulfuric acid the color is deep red, appearing violet in thin layers. As in the case of the other amino cinchona dyes, the deep violet-blue color in acid changes to a purplish-red on boiling, with simultaneous cleavage of ammonia.

Subs., 0.1440: 18.6 cc. N (25.0°, 765 mm.).
Calc. for $C_{27}H_{33}O_3N_5$: N, 14.72. Found: 14.90.

5-Amino-8-(*p*-ethoxyphenylazo)-dihydroquinine.—Under the conditions used with *p*-anisidine 1.75 g. of *p*-phenetidine hydrochloride also yielded a dark brown tar. After decanting the supernatant liquid the dye was dissolved in alcohol and treated with ammonia. On rubbing, the base crystallized and was filtered off and washed with 85% alcohol. The yield was 2.6 g. Recrystallized first from a relatively large volume of 95% alcohol, then by dissolving in warm chloroform and adding a little ligroin, it was gradually deposited as long, thin, narrow, orange platelets, often grouped in rosets. It apparently contains solvent of crystallization which is slowly lost on exposure to the air or on drying *in vacuo* at 100°. The dye decomposes at 202–3° with preliminary darkening, and dissolves readily in warm chloroform, much less easily in boiling methyl and ethyl alcohols, and quite sparingly in hot benzene. It is very difficultly soluble in acetone and ether and insoluble in water and ligroin. The solution in dil. mineral acids is blue-violet, changing on dilution to a dark wine-red, owing to hydrolysis of the polyacid salts. Conc. sulfuric acid gives a deep purple color. In boiling dilute acids it also yields an hydroxyazo dye, which was not studied. For analysis the substance was heated *in vacuo* at 80° over sulfuric acid.

Subs., 0.1224: 15.8 cc. N (22.0°, 746 mm.).
Calc. for $C_{28}H_{35}O_3N_5$: N, 14.30. Found: 14.67.

5-Amino-8-phenylazo-dihydroquinidine.—This substance was prepared exactly as was the isomeric dihydroquinine dye. The amorphous product, taken up in hot, dry acetone, crystallized on cooling and rubbing, the mother liquor yielding additional amounts on dilution with water to incipient turbidity. The total yield was 2.7 g. Recrystallized from 85% alcohol the base separates as rosets of orange-red leaflets when deposited rapidly, or as a dark red crust when allowed to crystallize slowly. The air-dry compound contains 1.5 molecules of water of crystallization and melts and intumesces at 135° with preliminary sintering. It turns dark brown on dehydrating, and then melts to a tar at about 140–5°, intumescing at about 155°. It is readily soluble in absolute alcohol, chloroform, warm benzene, and warm acetone, forming deep red solutions. The dye dissolves in 10% hydrochloric acid with a deep purplish-red color, the hydrochloride separating on rubbing as brown, hair-like needles with a greenish luster. The solution in conc. sulfuric acid is an intense violet.

Subs. (air-dry), 0.4887: loss, 0.0276 *in vacuo* at 80° over H_2SO_4.
Calc. for $C_{26}H_{31}O_2N_5.1.5H_2O$: H_2O, 5.72. Found: 5.65.
Subs. (anhydrous), 0.1232: 16.6 cc. N (23.5°, 771 mm.).
Calc. for $C_{26}H_{31}O_2N_5$: N, 15.73. Found: 15.74.

5-Amino-8-phenylazo-ethyldihydrocupreine.—Treated as in the case of amino-dihydroquinine, 3.55 g. of amino-optochin[1] yielded 3 g. of the

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[1] This Journal, 42, 1486 (1920).

aminoazo dye. The base separates from 95% alcohol as red, glistening needles containing one molecule of water of crystallization. It starts to sinter at 145° and shrinks together and melts at 150–5°. It is sparingly soluble in cold methyl and ethyl alcohols, benzene, and chloroform, but readily on warming, forming deep reddish-orange solutions. It is difficultly soluble in acetone and very sparingly in ether. The solutions in dilute acids are deep reddish-purple in color and purple in conc. sulfuric acid.

Subs. (air-dry), 0.4098: loss, 0.0155 *in vacuo* at 100° over H_2SO_4.
Calc. for $C_{27}H_{33}O_2N_5.H_2O$: H_2O, 3.77. Found: 3.78.
Subs. (anhydrous), 0.1333: 17.25 cc. N (21.5°, 768 mm.).
Calc. for $C_{27}H_{33}O_2N_5$: N, 15.23. Found: 15.17.

5-Hydroxy-8-phenylazo-ethyldihydrocupreine.—The deep purple solution in hot aqueous-alcoholic hydrochloric acid rapidly changed to deep red. On dilution with alcohol, adding ammonia, and finally water until turbid, the crystalline base was readily obtained. Recrystallized twice from 85% alcohol the dye forms lustrous, red needles containing 3.5 molecules of water of crystallization. It starts to sinter at 85°, shrinks together and melts at 90.5°, and is soluble in alcohol, acetone, ether, and hot benzene, forming red solutions. It dissolves in 10% sulfuric acid with a deep brown-red color, and in the conc. acid with a deep purple color. The anhydrous dye softens above 100°, sinters to a tar at 110–20°, and melts completely, with decomposition, at about 200°.

Subs. (air-dry), 0.6035: loss, 0.0715 *in vacuo* at 80° over H_2SO_4.
Calc. for $C_{27}H_{32}O_3N_4.3.5H_2O$: H_2O, 12.03. Found: 11.84.
Subs. (anhydrous), 0.1181: 12.6 cc. N (26.5°, 761 mm.).
Calc. for $C_{27}H_{32}O_3N_4$: N, 12.17. Found: 12.18.

II.

5-Amino-8-phenylazoquinoline.—5-Aminoquinoline was coupled with diazotized aniline and the base isolated as in the case of the cinchona derivatives. The dye separates from 50% alcohol as arborescent masses of garnet-colored leaflets which melt at 209–11°. It is soluble in alcohol, acetone, chloroform, hot benzene, and less readily in ether. Its solution in dilute acid is deep red, appearing purple in thin layers and changing to orange on dilution. In conc. sulfuric acid the color is deep red.

Subs., 0.1224: 23.8 cc. N (22.5°, 767 mm.).
Calc. for $C_{15}H_{12}N_4$: N, 22.57. Found: 22.68.

On reduction with ammonium sulfide the analogous *p*-sulfophenyl-5-aminoquinoline, which was similarly prepared, yields 5,8–diaminoquinoline, melting at 161–3° ,and corresponding in its properties with those described by Claus and Kramer,[1] who give the uncorrected melting point of 156°.

5-Hdroxyy-8-phenylazoquinoline.—The aminoazo dye was boiled

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[1] Claus and Kramer, *Ber.*, 18, 1247 (1885).

with 100 parts of 10% hydrochloric acid, a portion of the amino hydrochloride separating at once The color of the deep purplish-red solution slowly changed, with deposition of the brown hydrochloride of the hydroxyazo dye. About one hour was required for the complete disappearance of the purple color. The collected salt was suspended in 50% alcohol and the base liberated with ammonia. After several recrystallizations from alcohol the dye forms slightly purplish-red, lustrous needles, which melt at 164–5° with preliminary sintering. It is easily soluble in chloroform, fairly readily in hot alcohol, benzene and acetone, and but sparingly in ether. It gives a scarlet solution in conc. sulfuric acid, appearing purple in thin layers and changing to orange on dilution.

Subs., 0.1191: 17.6 cc. N (25.0°, 758 mm.).
Calc. for $C_{15}H_{11}ON_3$: N, 16.86. Found: 16.88.

5-Amino-6-methoxyquinoline.—The 5-nitro-6-methoxyquinoline[1] used for this preparation was easily obtained in excellent yield by nitrating 6-methoxyquinoline with fuming nitric acid at 0°.

28 g. of the nitro compound were suspended in 200 cc. of 1 : 1 hydrochloric acid, treated with 125 g. of stannous chloride, and heated on the water-bath for one hour. A clear, deep red solution was soon obtained, and the free base was finally precipitated with excess alkali as a yellow oil which crystallized on cooling. Extraction of the mother liquor with ether yielded an additional quantity, the total amounting to 90% of that theoretically possible. Recrystallized first from benzene and then from ligroin, it forms yellow, arborescent platelets and needles which melt at 154–6° (corr.) with slight preliminary sintering. It has a faint odor, resembling that of anise, and dissolves readily in alcohol, acetone, chloroform, and hot benzene, but less easily in ether. Its solution in dilute acid is reddish-orange.

Subs., 0.1393: 19.2 cc. N (22.5°, 765 mm.).
Calc. for $C_{10}H_{10}ON_2$: N, 16.08. Found: 16.02.

5-Amino-6-methoxy-8-phenylazoquinoline.—Obtained in the usual way, the crude dye was precipitated by ammonia as red, amorphous flocks which soon crystallized on dissolving in a small volume of acetone. It separates slowly and incompletely from 85% alcohol as thin, deep red rods which exhibit a green reflex when dry, and melt at 163–4°. It dissolves, especially on warming, in the usual solvents, forming deep orange-red solutions. In dilute acids the color is purplish-red, and in conc. sulfuric acid a deep purple.

Subs., 0.1062: 18.6 cc. N (25.0°, 758 mm.).
Calc. for $C_{16}H_{14}ON_4$: N, 20.12. Found: 20.02.

5-Hydroxy-6-methoxy-8-phenylazoquinoline.—On treating the aminoazo dye with 30 parts of a mixture of equal amounts of alcohol and 1 : 1

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[1] Decker and Engler, *Ber.*, 42, 1739 (1909).

hydrochloric acid a deep purple mass of the salt separated and gradually dissolved when heated on the water-bath, the color of the solution changing to red, with subsequent deposition of the brown salt of the hydroxy dye. This was converted into the base as usual, and this recrystallized from alcohol, forming broad, scarlet, often curved needles which melt at 181–3°. It is readily soluble in chloroform and in the other usual solvents on warming. It is but sparingly soluble in cold dilute mineral acids, and on boiling forms deep red-orange solutions. The color in conc. sulfuric acid is wine-red, appearing purple in thin layers.

Subs., 0.1133: 15.0 cc. N (24.5°, 759 mm.).
Calc. for $C_{16}H_{13}O_2N_3$: N, 15.04. Found: 15.16.

Summary.

It is shown that 5-amino-dihydroquinine couples readily with diazotized aromatic amines to form crystalline azo dyes in which the amino group is remarkably labile, boiling for a few minutes with dil. mineral acid being sufficient to replace the amino group by the hydroxyl group, with elimination of ammonia. The resulting hydroxyazo dyes are also easily crystallizable substances. Similar results were obtained using 5-amino-dihydroquinidine and 5-amino-ethyldihydrocupreine (amino-optochin) as couplers. Since it was of interest to determine whether the observed phenomena were a function of the quinoline portion of the cinchona structure, parallel experiments were run with 5-aminoquinoline and 5-amino-6-methoxyquinoline. Both of these bases coupled as did the amino alkaloids, and the amino group of the resulting dyes was also readily eliminated and replaced by hydroxyl, the lability being greater in the case of the methoxy derivatives.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE OKLAHOMA AGRICULTURAL EXPERIMENT STATION.]

THE CARBOHYDRATES OF THE PECAN.

BY W. G. FRIEDEMANN.

Received July 7, 1920.

The pecan (*Carya olivaeformis*) is the most widely distributed and economic important nut-bearing tree in Oklahoma. Two references were found in the literature on the chemical composition of the pecan kernel. Deiler and Fraps[1] determined the characteristics of the pecan oil obtained from the kernel. A study of the proteins of pecans has been made by Dowell and Menaul.[2] This investigation was undertaken to determine the carbohydrates of the edible portion of the pecan.

[1] A. C. Deiler and G. S. Fraps, *Am. Chem. J.*, 43, 90 (1910).

[2] C. T. Dowell and P. L. Menaul. Unpublished report. Oklahoma Agr. Expt. Sta. Also E. H. Nollan, *J. Biol. Chem.*, 21, 614(1915).

Experimental.

A proximate analysis of the pecan kernels gave results as tabulated below:

	%.
Moisture	3.75
Ash	1.70
Crude protein	12.27
Crude fiber	1.71[a]
Nitrogen-free extract	10.81
Ether extract	69.76

[a] Protein-free. The crude fiber uncorrected was 1.90%. Protein in crude fiber was 10.19%.

The carbohydrates were determined in pecan flour obtained from the pecan kernels by completely removing the pecan oil by extraction with ether.

Sugars, pentoses, pentosans (araban), methylpentosans[1] and crude fiber were determined according to the A. O. A. C. methods.

No precipitate formed when the 5% sodium hydroxide extract of pecan flour was diluted with an equal volume of alcohol; therefore xylan[2] was absent.

Araban was considered present as other pentosans were not identified; a gum separated when the combined filtrates from the crude fiber determination were slightly acidified and evaporated to a volume of several cc. at room temperature.

Mannans[3] were not identified as no precipitate formed when the 3% sodium hydroxide extract of the sugar-free flour was heated on the water-bath with Fehling's solution.

Amyloid was identified by the blue coloration with iodine when added to the hot-water extract obtained according to Winterstein's[4] method. The amyloid was calculated from the mucic acid obtained by the A. O. A. C. method for galactan.

Starch was absent, as no blue color was noticed when an iodine solution was added to the flour. Also no more reducing sugars were found than were accountable from the pentosans when the sugar-free flour was subjected to the diastase method[5] for the determination of starch.

Tannins (a constituent of the nitrogen-free extract) were shown to be present by the bitter taste and the characteristic tests of the water extract of pecan flour. The difference between the combustible water-soluble solids and total sugars was considered as tannins. Only the thin, hard brown outer coating of the kernel was colored blue by neutral ferric chlo-

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[1] C. A. Browne, "Handbook of Sugar Analysis," 1912, p. 456.

[2] *Ibid.*, p. 553.

[3] *Ibid.*, p. 594.

[4] Winterstein, *Ber.*, 25, 1273 (1892).

[5] E. Abderhalden, "Biochemisches Handlexikon," Vol. II, 1911, p. 126.

ride solution when a cross-section was examined under the microscope, indicating tannins.

The hemicellulose, calculated by difference, was considered a dextran, as no other sugar than dextrose was formed when it was subjected to the action of dilute alkalies and acids. This dextran was also proven to be present by subtracting the carbohydrates identified from the total carbohydrates found in the combined filtrates from the crude fiber determination.

The percentage composition is as follows:

	Total carbohydrates.	Pecan kernel.[a]
Sucrose	9.03	1.18
Invert sugars	21.90	2.88
Pentoses	.....	....
Araban	14.82	1.95
Xylan	.....	....
Methylpentosans	1.68	0.22
Cellulose (crude fiber)	14.29	1.76
Mannans	.....	....
Amyloid	4.54	0.59
Starch	.....	....
Tannins	2.57[c]	0.33[c]
Hemicellulose (dextran), etc.[b]	31.17	4.09
	100.00	13.00

[a] Moisture-free basis.

[b] By difference in the nitrogen-free extract plus crude fiber.

[c] Same result by Proctor's modification of Lowenthal's method.

STILLWATER, OKLAHOMA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY.]

THE CONDENSATION OF FORMALDEHYDE WITH ORTHO-NITROPHENOL.[1]

BY JACOB B. FISHMAN.

Received July 9, 1920.

During the last 2 years the attention of pharmacologists has been directed to benzyl alcohol as a local anesthetic. The pharmacological action of this alcohol was first investigated by Macht[2] in 1918. He found it to be a powerful local anesthetic of very low toxicity as compared with cocaine and its substitutes. While it has been found to be active on mucous membranes as well as in subcutaneous injection, nevertheless the compound possesses several objectionable properties which prevent its wide application. Not only does it undergo slow oxidation

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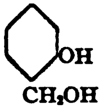
[1] Constructed from a dissertation presented to the Faculty of the Graduate School of Yale University in candidacy for the degree of Doctor of Philosophy, June 1920 (T. B. Johnson).

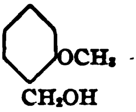
[2] Macht, *J. Pharmacol.*, 13, 263 (1918); 14, 323 (1919).

in solution,[1] but it is only sparingly soluble in water and its application produces smarting. Furthermore, its activity has a shorter duration than that of cocaine.

Hirschfelder, Lundhorn and Norrgaard[2] have recently reported that certain phenolic derivatives of benzyl alcohol possess marked anesthetic properties and among the compounds studied by them were saligenin (I), methyl saligenin (II), ethyl saligenin (III) and homosaligenin (IV).



(I).



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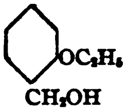

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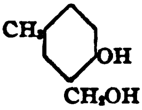

(IV).

Of these different alcohols saligenin I was reported as the most active.

These very desirable properties of benzyl alcohol and its derivatives served as an incentive to search further in this field for new combinations of pharmacological interest. Theoretically a combination of the greatest interest would be that having the constitution of 3,4-dihydroxy-benzyl alcohol on account of its close relationship to adrenaline. Here we have a constitution favorable for both anesthetic and vasoconstrictor action or, in other words, a drug which might be expected to exhibit the combined physiological effects of benzyl alcohol and catechol.[3] The purpose of this investigation was to develop the synthetical aspects of this work. The condensation reaction which we describe in this paper should be of especial interest as affording a convenient method of preparing new benzyl alcohol combinations whose study may contribute still further data of pharmacological interest.

The condensation of formaldehyde with *o*-nitrophenol is productive of combinations which have hitherto received very little attention. Stoermer and Behn[4] first investigated the mutual reactivity of these 2 reagents and found that they interacted in the presence of hydrochloric acid with production of 3-nitro-4-hydroxy-benzyl alcohol (V). Their yield of this compound was, however, very small, and the reaction was always productive of a large amount of other material. Stoermer and Behn separated their alcohol, melting at 97°, by repeated crystallization from hot water, and write that many times they obtained as reaction product material from which they could not isolate the benzyl-alcohol derivative. The structure of their alcohol was established by the fact that it gives a methyl ether (VI), which, on oxidation, is easily converted into nitroanisic acid (VII).[5]

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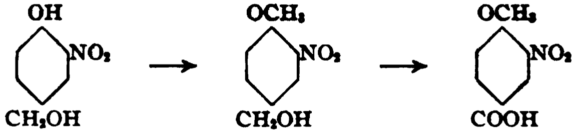
[1] Hjort and Eagan, *J. Pharmacol.*, 14, 211 (1919).

[2] Hirschfelder, Lundhorn and Norrgaard, *ibid.*, 15, 261 (1920).

[3] Fränkel, "Die Arzneimittel-Synthese," p. 428.

[4] Stoermer and Behn, *Ber.*, 34, 2459 (1901).

[5] Cahours and Salkowski, *Ann.*, 41, 71 (1842); 163, 6 (1872).

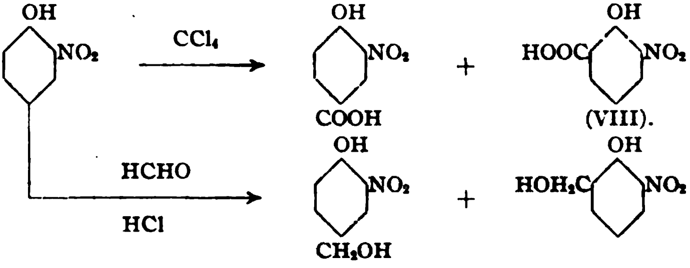


(V). (VI). (VII).

Another method for the preparation of this same alcohol was patented by Bayer and Co.[1] This is based upon the observation that 3-nitro-4-hydroxy-benzyl chloride is converted into the corresponding alcohol by hydrolysis with boiling water. Their method of synthesis is essentially an application of Stoermer and Behn's condensation reaction in the presence of very strong hydrochloric acid when the chloride is formed instead of its alcohol. Neither Stoermer and Behn nor the patentees make any references in their publications to the yields of pure alcohol obtained or the nature of the different by-products formed in the reaction.

We have now subjected their condensation reaction to a very careful study and have established the conditions favorable for the production of a maximum yield of the alcohol. The important factors governing the course of the reaction are concentration of hydrochloric acid, molecular proportion of formaldehyde and the time of heating. A full report of this phase of our research is given in the experimental part of this paper.

We now find that formaldehyde interacts with *o*-nitrophenol to form 2 isomeric alcohols, namely: The compound first identified by Stoermer and Behn, 3-nitro-4-hydroxy-benzyl alcohol (V), melting at 97° and a hitherto unknown isomeric compound having the structure of 3-nitro-2-hydroxy-benzyl alcohol (X). The latter melts at 75°. In other words, formaldehyde attacks the *o*-nitrophenol molecule in the same nuclear positions as carbon tetrachloride when the latter reagent condenses with this phenol.[2] These structural relationships are expressed by the following formulas:



(V). (X).

The structure of the new alcohol represented by Formula X was established by the fact that it underwent oxidation with potassium permanganate giving nitro-salicylic acid (VIII), the same as that obtained

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[1] Bayer and Co., *D. R. P.* 136,680 (1902); *D. R. P.* 132,475 (1902).

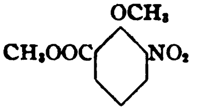
[2] Hasse, *Ber.*, 10, 2187 (1877).

by Deninger[1] by direct nitration of salicylic acid. By alkylation with methyl iodide in alkaline solution, the alcohol X is converted smoothly into its corresponding methyl ether XI. When this compound was subjected to oxidation with potassium permanganate the primary alcohol group was destroyed and the corresponding acid XII, melting at 191°, was formed.

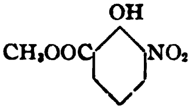
$$(NO_2)^3(OCH_3)^2.C_6H_3.CH_2OH \xrightarrow{O_2} (NO_2)^3(OCH_3)^2.C_6H_3.COOH.$$

(XI). (XII).

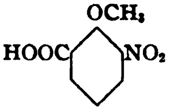
An aromatic acid having this same constitution has already been described by Keller.[2] He investigated the action of dimethyl sulfate on the potassium salt of nitrosalicylic acid, and states that the reaction is productive of 3 compounds melting at 110°, 125° and 220°, respectively. The substance melting at 220° was formed in very small amount and was not further investigated. Since his analyses and melting-points excluded from consideration the methyl ester of nitrosalicylic acid (XIV) and its corresponding methyl ether (XIII), Keller concluded that both of his compounds melting at 110° and 125°, respectively, must be methyl ethers of nitrosalicylic acid, corresponding to Formula XII. Obviously 2 ethers of this constitution are not possible. Furthermore, Keller states that his compound melting at 125° was unstable and was decomposed by heating in aqueous solution giving nitrosalicylic acid. It seems evident from Keller's description of his reaction products that he was dealing with a mixture of 2 or more compounds and did not succeed in isolating pure 3-nitro-2-methoxy-benzoic acid (XII).



(XIII).



(XIV).



(XII).

Experimental Part.

The Preparation of *o*-Nitrophenol.—All of the reagent used in this research was prepared by direct nitration of phenol according to the method outlined by Hart.[3] Operating with a unit of phenol corresponding to 1000 g., the following proportions of necessary reagents were used to accomplish the reaction. 1600 g. of sodium nitrate, 2000 g. of conc. sulfuric acid, 4000 g. of water and 100 g. of 95% alcohol. The method of operating was as follows: The sulfuric acid was added slowly with stirring and cooling to the aqueous solution of the sodium nitrate and into this acid mixture, which was kept at room temperature, the alcoholic solution of the phenol was dropped in slowly with constant and vigorous

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[1] Deninger, *J. prakt. Chem.*, [2] **42**, 551 (1890).

[2] Keller, *Arch. Pharm.*, **246**, 1 (1908).

[3] Hart, THIS JOURNAL, **32**, 1105 (1910),

stirring. After 4 hours the reaction mixture was poured into twice its volume of ice water, when the crude phenol separated and was purified by steam distillation. Our best yield was equivalent to 51% of the weight of phenol used for nitration.

The Interaction of Formaldehyde with *o*-Nitrophenol. 3-Nitro-4-hydroxy-benzyl Alcohol, $(NO_2)^3.(OH)^4.C_6H_3.CH_2OH$.—In order to obtain this aromatic alcohol the method described by Stoermer and Behn was first employed. Fifty g. of *o*-nitrophenol mixed with 125 g. of formaldehyde solution (39%) and 250 g. of hydrochloric acid (35.4%) were digested on a sand-bath for 6 hours. The reaction mixture was then cooled, the supernatent liquor poured off and the residual oily product distilled with steam to remove unchanged nitrophenol. The recovered *o*-nitrophenol weighed 12 g. The undistilled oily residue, which solidified on cooling, was filtered off, and after drying weighed 32 g. In order to purify this material it was extracted with boiling water until no more oil dissolved, and the aqueous solution allowed to cool, when golden-yellow crystals were obtained. These were further purified by crystallizing them several times from hot water, when pure prismatic crystals of 3-nitro-4-hydroxy-benzyl alcohol melting at 97° were obtained. Upon concentrating the aqueous filtrates, crystalline material varying in appearance and of indefinite melting-point was always obtained, but it was extremely difficult to purify it by crystallization. The material insoluble in water was amorphous and constituted more than $^1/_2$ of the weight of crude reaction product.

From the results of this preliminary experiment it was very apparent that the reaction was incomplete under the conditions employed, since unchanged nitrophenol was recovered, and furthermore, other products besides the desired alcohol were also formed by condensation with formaldehyde. In fact, the reaction was more complicated than we anticipated. In order to gain a better knowledge of the changes involved our work resolved itself into 2 definite phases: first, the investigation of the best conditions for controlling the reaction; and second, the purification and identification of the different products formed.

In order to determine the best conditions for bringing about a more complete condensation between the *o*-nitrophenol and formaldehyde, several series of experiments were conducted in each of which the effect of varying one of the following factors was studied, *viz.*, molecular concentration of hydrochloric acid, quantity of formaldehyde, length of time of heating, and use of condensing agents other than hydrochloric acid. It was found that the quantity of *o*-nitrophenol, which will interact with formaldehyde, varies according to the proportions of hydrochloric acid used as condensing agent, the yield of condensation product is increased and the quantity of unaltered nitrophenol is reduced by using a liberal excess of hydrochloric acid. When using 125 g. of formaldehyde the maximum yield of alcohol was obtained by condensing 50 g. of nitrophenol with the formaldehyde in the presence of 275 g. of conc. hydrochloric acid. Dilution of the hydrochloric acid leads to a poorer yield of the condensation product and consequently to an increase in the amount of nitrophenol which can be recovered.

The condensation of formaldehyde with *o*-nitrophenol is a change of slow velocity, and an extension of the time of digestion in presence of hydrochloric acid is productive of increased yields of reaction products. The yield of crude condensation product is not, however, any criterion of the success of the reaction. Three hours appears to be the most favorable time for heating in order to obtain the maximum yield of the benzyl alcohol. While much unaltered *o*-nitrophenol is recovered under these conditions, on the other hand, the condensation product is much purer. Longer time of digestion leads to the formation of increased quantities of secondary products which are difficult to separate.

Stoermer and Behn[1] recommend using 125 g. of formaldehyde for condensation with 50 g. of *o*-nitrophenol. This is an excess of 350% over the theoretical quantity and much more than is necessary. Fifty g. of formaldehyde is sufficient to produce almost as good a yield of the alcohol. Several experiments were conducted in order to ascertain the best proportions of this reagent to be used, and also the effect of changing the time of digestion when different quantities of the aldehyde were taken. It was found that an increase in the proportion of formaldehyde was favorable for the formation of secondary reaction products. The best yields of nitrobenzyl alcohol are obtained by using 60 g. of formaldehyde and 100 g. of *o*-nitrophenol and digesting with 500 g. of conc. hydrochloric acid for about 6 hours. The yield of crystallized alcohol under these conditions is about 50% of the calculated quantity. For example, a representative experiment gave 94 g. of total reaction product which yielded 54 g. of unaltered nitrophenol and 40 g. of crude condensation product. From the latter were isolated 24 g. of crystalline alcohol. No advantage is gained by extending the time of heating beyond 6 hours and almost as good yields of alcohol are obtained after 4 or 5 hours' digestion. In other words, one molecular proportion of formaldehyde can satisfy theoretically only one position in the *o*-nitrophenol nucleus, and the use of larger quantities leads to the formation of secondary products which contaminate the nitrobenzyl alcohol formed.

We also investigated the effect of different condensation agents on the course of the reaction. Several experiments were conducted in which sulfuric acid, dil. sodium carbonate solution, phosphoric acid and mag-

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[1] *Loc. cit.*

nesium chloride were each substituted for hydrochloric acid, but the results obtained were entirely unsatisfactory.

The following conclusions may be drawn from the results of our experiments: (1) a high concentration of hydrochloric acid is essential for maximum condensation of formaldehyde with *o*-nitrophenol; (2) in order to avoid side reactions leading to secondary products and to obtain the maximum yield of alcohol it is not advisable to use more than a theoretical quantity of formaldehyde for condensation; (3) working with molecular proportions of formaldehyde it is not advisable to continue the heating for a longer period than 6 hours in order to obtain a maximum yield of alcohol. This time should be reduced if an excess of formaldehyde is used in order to avoid formation of by-products.

The Separation of 3-Nitro-4-hydroxy-benzyl Alcohol from 3-Nitro-2-hydroxy-benzyl Alcohol.—Application of a formaldehyde *o*-nitrophenol condensation with 200 g. of formaldehyde solution (40%), 300 g. of *o*-nitrophenol and 1500 g. of conc. hydrochloric acid, by digestion for 6 hours is productive of 144 g. of unchanged *o*-nitrophenol and 63 g. of crystalline material containing the 2 isomeric benzyl alcohols. The remainder of the reaction product is an amorphous substance insoluble in hot water and not distillable with steam.

The yellow crystalline material (63 g.) was a mixture of 2 alcohols. Two distinct crystalline forms were apparent by examination under a microscope and the material melted at about 80°. Repeated fractional crystallizations from hot water enables one to isolate, in a pure condition, Stoermer and Behn's[1] 3-nitro-4-hydroxy-benzyl alcohol melting at 97°, but the yield is poor, and on concentrating the aqueous filtrates a crystalline product is obtained which cannot be purified by crystallization from the ordinary solvents. The separation of the 2 alcohols is, however, easily accomplished by digestion of the mixture in ethyl alcohol with potassium hydroxide. Stoermer and Behn's compound melting at 97° interacts with formation of a soluble potassium salt, while the isomeric alcohol gives a potassium salt which is insoluble in this solvent. Our method of operating was as follows.

Fifty g. of impure crystalline product melting at about 80° was dissolved in 30 cc. of 95% alcohol, and 18 g. of potassium hydroxide then dissolved in the solution by warming it on the steam-bath. A red precipitate was formed at once, and after boiling the mixture for about 20 minutes it was then cooled and the solution filtered by suction. The precipitate was washed with a little alcohol and saved. The filtrate, which contained the potassium salt of 3-nitro-4-hydroxy-benzyl alcohol, was heated in an open dish to remove alcohol, the potassium salt then dissolved in water and the solution acidified with hydrochloric acid. An

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[1] *Loc. cit.*

oil separated which dissolved in boiling water. Upon cooling this solution, yellow prisms of Stoermer and Behn's alcohol deposited, which melted sharply at 97°.

The potassium salt which separated from the alcohol was dissolved in water and the solution acidified with hydrochloric acid, when an oil separated at once. This dissolved in hot water and on cooling separated in the form of yellow needles. This substance melted at 75° and was not altered by further crystallization from hot water. Apparently it was a definite substance and its separation from Stoermer and Behn's alcohol was practically quantitative. From 50 g. of the condensation product about 35 g. of 3-nitro-4-hydroxy-benzyl alcohol and 12 g. of the isomeric compound melting at 75° was obtained. The proportion of these 2 compounds formed in the interaction of *o*-nitrophenol with formaldehyde is thus about 75% of the alcohol melting at 97° and 25% of the compound melting at 75°.

3-Nitro-2-hydroxy-benzyl Alcohol, $(NO_2)^3.(OH)^2.C_6H_3CH_2OH$.—This new alcohol formed as a secondary product in the condensation of *o*-nitrophenol with formaldehyde, crystallizes in the form of yellow needles melting at 75°. It is easily soluble in alcohol, ether and benzene and more easily soluble in cold water than its isomer, 3-nitro-4-hydroxy-benzyl alcohol. It forms a bright red potassium salt which is very difficultly soluble in alcohol. It may be further distinguished from its isomer by its behavior towards cold strong sulfuric acid. This acid dissolves it readily with a deep red color, while its isomer is only sparingly soluble.

Calc. for $C_7H_7O_4N$: N, 8.28.
Found: 8.09, 7.98 (Kjeldahl).

In order to establish the structure of this compound it was subjected to oxidation with potassium permanganate in alkaline solution. Five g. of the alcohol and 4 g. of potassium hydroxide were dissolved in about 100 cc. of water. The solution was then heated on the steam-bath while 5 g. of potassium permanganate was added in small portions, while the solution was shaken. After warming the mixture for about one hour, the manganese dioxide was filtered off and the clear red filtrate acidified with hydrochloric acid. A crystalline substance separated immediately. This was filtered off and purified by crystallization from hot water, when small yellow needles were obtained on cooling. This substance was an acid melting at 144° and was characterized by its easy solubility in alcohol and in boiling water and its property of forming red colored salts with alkalies. It also interacted to give a blood-red coloration with ferric chloride. Analysis, the melting point and properties of the compound established its identity with the known 3-nitrosalicylic acid, which has been prepared by Deninger[1] by the direct nitration of salicylic acid.

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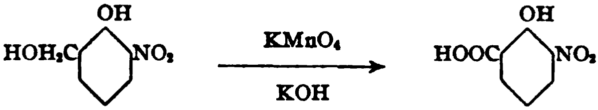
[1] *Loc. cit.*

Calc. for $C_7H_5O_5N$: N, 7.65. Found: 7.61, 7.44.

The constitution of 3-nitro-2-hydroxy-benzyl alcohol is, therefore, definitely established by its behavior on oxidation as is expressed by the following reaction.



3-Nitro-2-Methoxy-benzyl Alcohol, $(NO_2)^3(OCH_3)^2.C_6H_3.CH_2OH$.—Five g. of 3-nitro-2-hydroxy-benzyl alcohol was alkylated by digestion in 30 cc. of 60% methyl alcohol with 1.5 g. of sodium hydroxide and 6 g. of methyl iodide. To complete the reaction the solution was heated on the water-bath for 10 hours. The alcohol was then distilled and the oily reaction product extracted with ether. The ethereal solution, after having been washed several times with dil. sodium hydroxide solution to remove any unchanged nitro-hydroxy-benzyl alcohol, was dried over sodium sulfate and the ether removed by distillation, when the above alcohol was obtained. It crystallized from a mixture of petroleum ether and ordinary ether in colorless needles melting at 42°. The alcohol is sparingly soluble in hot water but extremely soluble in ether, benzene, alcohol, chloroform and acetic acid. The yield of the methoxy alcohol was about 60%.

Calc. for $C_8H_9O_4N$: N, 7.65. Found: 7.64, 7.38.

3-Nitro-2-methoxy-benzoic Acid, $(NO_2)^3(OCH_3)^2.C_6H_3.COOH$.—This acid was obtained by the oxidation of the nitro-alcohol described above. Potassium permanganate was used for this purpose and the operation was carried out in a manner similar to that used in the oxidation of 3-nitro-2-hydroxy-benzyl alcohol. The corresponding benzoic acid derivative was obtained in the form of colorless needles which were easily purified by crystallization from alcohol, and melted at 191–2°. This acid is moderately soluble in alcohol but difficultly soluble in water.

Calc. for $C_8H_7O_5N$: N, 7.11. Found: (Kjeldahl), 7.20, 7.00.

Keller[1] claims to have obtained an acid of this same constitution by the alkylation of 3-nitrosalicylic acid. He assigned a melting-point of 110° to his compound.

Summary.

1. A careful study has been made of the conditions governing the formation of 3-nitro-4-hydroxy-benzyl alcohol by the condensation of *o*-nitrophenol with formaldehyde in aqueous solution. The best results are obtained by applying the reaction in the presence of hydrochloric acid as a catalyst.

2. It has been found that formaldehyde can react with *o*-nitrophenol

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[1] Keller, *Arch. Pharm.*, **246**, 1–50 (1908).

to form 3-nitro-2-hydroxy-benzyl alcohol. This compound has been isolated and its constitution established.

3. The methoxy derivative of 3-nitro-2-hydroxy-benzyl alcohol has been prepared. Oxidation of this alcohol leads to the formation of 3-nitro-2-methoxy-benzoic acid. This is a new method of synthesizing this aromatic acid and its constitution is definitely established by the method of formation.

NEW HAVEN, CONN.

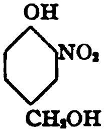
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY.]

SOME DERIVATIVES OF 3-NITRO-4-HYDROXY-BENZYL ALCOHOL.[1]

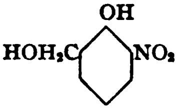
BY JACOB B. FISHMAN.

Received July 15, 1920.

In the preceding paper the writer has described the behavior of *o*-nitrophenol when heated with formaldehyde in the presence of hydrochloric acid. It was shown that this reaction is productive of the 2 isomeric alcohols (I) and (II), which result theoretically by addition of the aldehyde to the nitrophenol in Positions 4 and 6 of the benzene nucleus, respectively.



(I).



(II).

The isomer presented by Formula I is formed in the larger proportion in this reaction, and, since it accumulated in large amount as a result of our investigation, it seemed of especial interest to utilize the material for the preparation and study of new derivatives. The structure of the compound is favorable not only for the synthesis of new and important derivatives of benzyl alcohol possessing possible therapeutic interest, but also for the formation by oxidation of 3-nitro-4-hydroxy-benzaldehyde and the corresponding 3-nitro-4-hydroxy-benzoic acid which are products of pharmaceutical and biochemical interest.

Oxidation of the alcohol (I) with the required proportion of potassium permanganate resulted in the smooth formation of the corresponding aldehyde, $C_6H_3(\overset{1}{CHO})(\overset{3}{NO_2})(\overset{4}{OH})$, which has already been described by Paal.[2] If an excess of permanganate is used for oxidation, the aldehyde is converted into 3-nitro-4-hydroxy-benzoic acid almost quantita-

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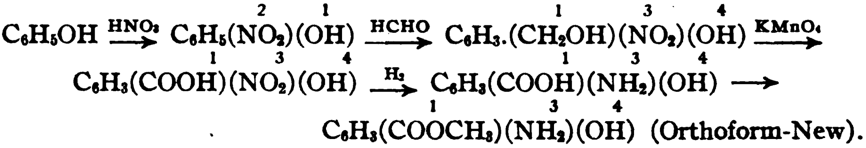
[1] Constructed from a dissertation presented to the Faculty of the Graduate School of Yale University in candidacy for the degree of Doctor of Philosophy, June 1920. (T. B. Johnson).

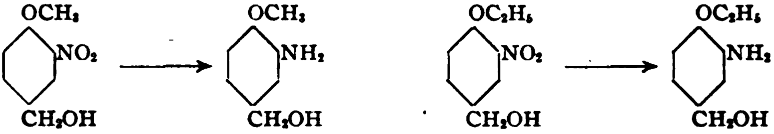
[2] Paal, *Ber.*, 28, 2413 (1895).

tively.[1] This behavior on oxidation not only establishes the constitution of the alcohol, but the reaction is also one of commercial interest, because it reveals a new method of synthesizing the basic intermediate required for the preparation of the local anesthetic methyl 3-amino-4-hydroxy-benzoate (Orthoform-New).[2] The complete synthesis of this local anesthetic from phenol is expressed below.



$$C_6H_5OH \xrightarrow{HNO_3} C_6H_5\overset{2}{(NO_2)}\overset{1}{(OH)} \xrightarrow{HCHO} C_6H_3.\overset{1}{(CH_2OH)}\overset{3}{(NO_2)}\overset{4}{(OH)} \xrightarrow{KMnO_4} C_6H_3\overset{1}{(COOH)}\overset{3}{(NO_2)}\overset{4}{(OH)} \xrightarrow{H_2} C_6H_3\overset{1}{(COOH)}\overset{3}{(NH_2)}\overset{4}{(OH)} \longrightarrow C_6H_3\overset{1}{(COOCH_3)}\overset{3}{(NH_2)}\overset{4}{(OH)}\ \text{(Orthoform-New).}$$

While 3-nitro-4-hydroxy-benzyl alcohol undergoes oxidation with formation of well-characterized compounds, it does not exhibit the same stability when subjected to the action of reducing agents. Attempts to prepare the corresponding hydroxy amine in pure condition by reduction were unsuccessful. By protection of the molecule, however, by alkylation of the phenolic hydroxyl group, Formulas IV and V, we were able to obtain easily the corresponding ether derivatives of this amine. The methyl and ethyl derivatives (V) and (VII) were prepared for our research and were isolated in the form of stable crystalline compounds. The methyl ether of 3-nitro-4-hydroxy-benzyl alcohol (IV) has been prepared previously by Stoermer and Behn[3] and Jacobs and Heidelberger.[4]



(IV). (V). (VI). (VII).

Especially interesting was the behavior of these 2 amines, (V) and (VII), towards nitrous acid in hydrochloric acid solution. Diazotization of these amines followed by warming of the diazonium salts in aqueous solution was not productive of the corresponding phenols. On the other hand, the diazonium chlorides were found to be stable combinations which did not decompose below 130° when heated in capillary tubes. These salts are not stable on exposure to light, but can be digested in aqueous solution for hours without destruction. In fact, their behavior is exceptional for this type of nitrogen compounds. We are apparently dealing here with a unique case in which an alkyl group exerts a stabilizing influence on the diazonium radical. Tassily[5] has recently called

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[1] Deninger, *J. prakt. Chem.*, [2] **42**, 552 (1890).

[2] "New and Nonofficial Remedies" (1916) p. 35; *D. R. P.* 97,333, 97,334, 111,932; U. S. P. 610,348 and 625,158. (Both of these patents have expired)

[3] Stoermer and Behn, *Ber.*, **34**, 2459 (1901.)

[4] Jacobs and Heidelberger, *J. Biol. Chem.*, **20**, 676 (1915.)

[5] Tassily, *Bull. soc. chim.*, **1920**, p. 30.

attention to a stability of the same order in the case of the diazonium salts of *ortho*- and *para*-anisidine. It is not exceptional to find such a pronounced stability of the diazonium radical in the benzene series, but it is generally revealed in those cases where strongly negative groups are substituted in the benzene nucleus.[1] While the diazonium group in these compounds is characterized by its unusual stability, it reacts normally, however, under conditions utilized for applying a Sandmeyer reaction. For example, the diazonium salt prepared from 3-amino-4-methoxy-benzyl alcohol is transformed smoothly into 3-cyano-4-methoxy-benzyl alcohol by warming its solution with cuprous cyanide.

Experimental Part.

The Behavior of 3-Nitro-4-hydroxy-benzyl Alcohol on Oxidation with Potassium Permanganate.

3-Nitro-4-hydroxy-benzaldehyde, $(NO_2)^3(OH)^4.C_6H_3.CHO$.—This aldehyde is easily obtained when the oxidation of the alcohol is carried out with the required amount of potassium permanganate. Favorable conditions for oxidation are to dissolve 5 g. of the alcohol and a molecular proportion of potassium hydroxide in about 100 cc. of water and heat the solution to 90–100°. While hot, 3 g. of potassium permanganate is then added in small portions. Oxidation is complete after 15 minutes. The precipitated manganese dioxide is then filtered off and the solution acidified with hydrochloric acid, when the aldehyde separates in crystalline condition. It crystallized from hot water in the form of needles and melted at 142°. The compound corresponded in all its properties with the aldehyde obtained by direct nitration of *p*-hydroxy-benzaldehyde.[2]

Calc. for $C_7H_5O_4N$: N, 8.38. Found: 8.30.

3-Nitro-4-hydroxy-benzoic Acid, $(NO_2)^3(OH)^4.C_6H_3.COOH$.—This acid is obtained in excellent yield when 3-nitro-4-hydroxy-benzyl alcohol is subjected to oxidation with an excess of potassium permanganate. Upon acidifying the alkaline solution with hydrochloric acid, the substance separated in the form of colorless prisms melting at 183–184°. The acid was identical with that formed by direct nitration of *p*-hydroxy-benzoic acid.[3]

Calc. for $C_7H_5O_5N$: N, 7.65. Found: 7.40.

Behavior of 3-Nitro-4-hydroxy-benzyl Alcohol on Reduction.

Several attempts were made to reduce the compound to the corresponding amine, but without success. According to a patent by Bayer and Co.,[4] this change is easily brought about by reducing the nitro-hydroxy-benzyl

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[1] Knoevenagel, *Ber.*, **28**, 2053 (1895); Hantzsch, *ibid.*, **28**, 680 (1895).

[2] Paal, *loc. cit.*

[3] Deninger, *ibid.*

[4] *D. R. P.* 148,977 (1901).

alcohol with zinc dust in alcoholic solution. This method was followed as closely as possible, but instead of obtaining a crystalline hydrochloride of the base, a resinous product insoluble in hydrochloric acid resulted; it could not be purified further. The alcohol was also subjected to reduction with stannous chloride and hydrochloric acid, and with ferrous sulfate and ammonia, but in no case did we succeed in isolating a definite crystalline substance.

3-Nitro-4-methoxy-benzyl Alcohol, $(NO_2)^3(OCH_3)^4.C_6H_3.CH_2OH$.—This methyl ether was prepared by warming 10 g. of 3-nitro-4-hydroxybenzyl alcohol in methyl alcohol solution with the theoretical amount of potassium hydroxide and 10 g. of methyl iodide. After the reaction was complete, the alcohol was removed by distillation, the reaction product dissolved in ether and the solution washed with sodium hydroxide to remove any unchanged alcohol. After evaporation of the ether, the alkyl derivative was obtained in the form of colorless needles which crystallized from hot water and melted at 69°. If the washing with sodium hydroxide is omitted, yellow instead of colorless crystals are obtained. The yield of methoxy derivative is about 70%.

This same methoxy compound has been prepared by Stoermer and Behn.[1] They described it as yellow needles melting at 69°. Jacobs and Heidelberger,[1] who applied Cannizzaro's reaction to 3-nitro-4-methoxy-benzaldehyde, state that the alcohol is formed in good yield by this method, but they assigned to the compound a melting-point of 59–60.5°. They undoubtedly were dealing with an impure product.

3-Nitro-4-ethoxybenzyl Alcohol, $(NO_2)^3(OC_2H_5)^4C_6H_3.CH_2OH$.—The procedure used for alkylation with ethyl iodide was similar to that employed in the preparation of the methyl derivative. Application of the reaction with 10 g. of the alcohol, 35 g. of potassium hydroxide and 8 g. of ethyl bromide in 65 cc. of 95% alcohol was productive of a yield of the ethyl ether corresponding to 60% of theoretical amount. The ether crystallizes from boiling water in colorless needles melting at 66°.

Calc. for $C_9H_{11}O_4N$: N, 7.11. Found: 7.13, 7.03.

3-Amino-4-methoxy-benzyl Alcohol, $(NH_2)^3(OCH_3)^4C_6H_3.CH_2OH$.—The reduction of 3-nitro-4-methoxy-benzyl alcohol to the corresponding amine was accomplished successfully by application of the method first utilized by Claisen and Shadwell[2] for the reduction of *o*-nitrobenzoyl formic acid, namely, by the action of ferrous sulfate in ammoniacal solution. Ten g. of the alcohol was dissolved in 25 cc. of ethyl alcohol; the solution was mixed with 200 cc. of conc. ammonia and then diluted with 100 cc. of water. To this mixture 100 g. of finely powdered ferrous sulfate was added in small portions and with constant shaking. The reduc-

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[1] *Loc. cit.*

[2] Claisen and Shadwell, *Ber.*, 12, 353 (1879).

tion was continued for about a half hour, when 160 g. of barium hydroxide in 300 cc. of hot water was added and the mixture then heated on the steam-bath for about a half hour longer to precipitate all sulfates and iron in solution. After removal of the barium by precipitation with carbon dioxide the solution was concentrated *in vacuo* and cooled, when the amine separated in crystalline condition. The substance was purified by crystallization from boiling benzene and, as the solution cooled, separated in the form of beautiful colorless crystals melting at 95°. The amine is slightly soluble in cold water, but very easily soluble in hot water, in hot benzene, in alcohol, in ether and in dil. acids. It is perfectly stable on exposure to air. The yield of pure amine is about 75%.

Calc. for $C_8H_{11}O_2N$: N, 9.15. Found: 9.21, 9.05.

3-Amino-4-ethoxy-benzyl Alcohol, $(NH_2)^3(OC_2H_5)^4C_6H_3.CH_2OH$.—The reduction of 3-nitro-4-ethoxy-benzyl alcohol to the corresponding amine was carried out in a manner similar to that used in the preparation of its lower homologue. The amine was obtained in the form of colorless flat prisms melting at 83°. It is easily soluble in hot water, in hot benzene, in alcohol and in ether.

Calc. for $C_9H_{13}O_2N$: N, 8.38. Found: 8.33, 8.51.

2-Methoxy-5-hydroxy-methyl-benzene Diazonium Chloride, $(OCH_3)^2(CH_2OH)^5C_6H_3.N : NCl$.—This very stable diazonium salt is obtained by diazotization of 3-amino-4-methoxy-benzyl alcohol under the following conditions. Five g. of the amine is dissolved in 12 cc. of conc. hydrochloric acid previously diluted with 75 cc. of water. Eight g. of sodium nitrite dissolved in 40 cc. of water is added slowly, while the temperature of the solution is kept below 10°. After the diazotized solution is allowed to stand for one hour, it is then warmed at 60° for 20 minutes and finally evaporated to dryness by heating it at 60° under diminished pressure. A crystalline residue is obtained composed of sodium chloride and the diazonium salt of the amine. The latter is easily extracted with hot absolute alcohol, from which it separates when a very concentrated solution is cooled, in the form of cream-colored plates. The compound is exceedingly soluble in alcohol, but can be precipitated from this solvent in crystalline condition by dilution with ether. The yield is practically quantitative. The diazonium chloride is extremely soluble in water, in alcohol, and in glacial acetic acid, but is insoluble or very difficultly soluble in ether, in benzene, in chloroform and in carbon tetrachloride. It decomposes without melting and with evolution of red fumes at 131°. The aqueous solution is neutral to litmus and no acid reaction is produced even after boiling. Conc. sulfuric acid decomposes the diazonium salt with evolution of nitrogen. The Kjeldahl method, therefore, could not be applied successfully for its analysis. Nitrogen was determined by the Dumas method.

Calc. for $C_8H_9O_2N_2Cl$: N, 13.95; Cl, 17.68. Found: N, 13.96; Cl, 17.74.

2-Ethoxy-5-hydroxy-methyl-benzene Diazonium Chloride, $(OC_2H_5)^2$-$(CH_2OH)^5C_6H_3$.N : NCl.—This compound was prepared in a manner similar to that used in the preparation of the methoxy homologue, *viz.*, by diazotization of the corresponding amine. The diazonium salt which resulted in an almost quantitative yield, possesses similar properties to the methoxy derivative, and the same crystalline form. It also decomposes at 131°.

Calc. for $C_9H_{11}O_2N_2Cl$: Cl, 16.53. Found: 16.45.

3-Cyano-4-methoxy-benzyl Alcohol, $(CN)^3(OCH_3)^4C_6H_3.CH_2OH$.—This nitrile is formed by first diazotizing 3-amino-4-methoxy-benzyl alcohol and then applying in the regular manner Sandmeyer's reaction with copper cyanide. Five g. of the amine was diazotized in the usual manner and the diazonium compound decomposed by adding the solution slowly to hot cuprous cyanide solution. This product was heated for about half an hour to complete the reaction. Extraction of this solution with ether removed all the nitrile. It was purified by crystallization from hot water and separated in the form of needles melting at 81°. The cyanide is very soluble in both ether and alcohol. The yield was about 50%.

Calc. for $C_9H_9O_2N$: N, 8.59. Found: 8.77, 8.60.

Summary.

1. 3-Nitro-4-hydroxy-benzyl alcohol has been subjected to direct oxidation with alkaline permanganate and the corresponding known aldehyde and acid have been obtained, thus contributing a new and convenient method for preparing these substances.

2. A new method for the preparation of the local anesthetic "orthoform-new" is suggested by our work.

3. The following new derivatives of 3-nitro-4-hydroxy-benzyl alcohol have been prepared: 3-nitro-4-ethoxy-benzyl alcohol, 3-amino-4-methoxy-benzyl alcohol, 3-amino-4-ethoxy-benzyl alcohol, 2-methoxy-5-hydroxy-methyl-benzene diazonium chloride, 2-ethoxy-5-hydroxy-methyl-benzene diazonium chloride, 4-methoxy-3-cyano-benzyl alcohol.

NEW HAVEN, CONN.

[Contribution from the Chemical Laboratory of the University of Kansas.]

THE ACTION OF AMMONIA AND AMINES ON THE SUBSTITUTED UREAS AND URETHANES.

II. ALLOPHANIC ESTER.

By F. B. Dains and E. Wertheim.

Received July 16, 1920.

In a previous paper[1] a study of the action of amines on carbonyl diurethan was presented. It seemed advisable later to follow this with an investigation of the action of amines on allophanic ester, which may be regarded as the mono-carbethoxy derivative of urea, while carbonyl-diurethane is di-carbethoxy urea. We wished not only to ascertain what differences there might be in the course of the reaction, but also to verify the experimental data in the literature which recorded only the formation of a substituted biuret and appeared unnecessarily incomplete.

It will be noted that allophanic ester, $\overset{1}{NH_2}\overset{2}{CO}\overset{3}{NH}\overset{4}{COOR}$, differs from the carbonyl-diurethane in having at Position 4 only one carboxy group that can enter into reaction; the other point of attack is the amine group at Position 1.

Thus, if the primary amine should react at Position 1, an aryl allophanic ester and ammonia could be obtained.

$$RNH_2 + NH_2CONHCOOC_2H_5 = RNHCONHCOOC_2H_5 + NH_3. \quad (I)$$

On the other hand, if 4 were the point of attack, the result might be a mono-aryl biuret and alcohol.

$$NH_2CONHCOOCH_3 + H_2NR = RNHCONHCONH_2 + C_2H_5OH. \quad (II)$$

As a matter of fact, all of the above products were isolated, which substantiates the validity of the assumptions of these reactions.

At higher temperatures mono- and di-substituted ureas are produced, doubtless because of the continued action of the amines on the biuret.

$$RNHCONHCONHR + RNH_2 = RNHCONH_2 + RNHCONHR. \quad (III)$$

Above 160°, Schiff[2] has found that the monophenyl urea decomposes yielding diphenyl urea, which would account for the relatively small amount of the monophenyl derivative found.

Experimental Part.

Preparation of Ethyl Allophanate.—The literature records many methods for the preparation of this ester, but most of them are unsatisfactory so far as yield is concerned.[3] The greater portion of the allo-

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[1] This Journal, 41, 1004 (1919).

[2] Schiff, *Ann.*, 352, 83 (1907).

[3] Amato, *Jahresber.* 749 (1873); Saytzeff, *Ann.*, 135, 230 (1865); Wilm, *ibid.*, 192, 243 (1878); Schroeter, *Ber.*, 26, 2172 (1893); Hlasiwetz, *Ann.*, 134, 116 (1865); *Ann. chim. phys.* [8] 22, 349, 358 (1911); This Journal, 41, 1005 (1919).

phanic ester used in the following experiments was made by the action of ethyl chloroformate on urea, a method probably first suggested by Wilm and Wischin.[1] Later Schiff repeated this work.[2] When he heated molar mixtures of urea and ethyl chloroformate, he obtained only cyanuric acid, ammonium chloride, ethyl carbonate and a trace of biuret. When the proportions were changed and 2 mols of the urea were used, Schiff obtained a 7.5% yield of the ester, together with cyanuric acid and a trace of biuret. Therefore he concluded that the method was not suitable for the preparation of the ethyl allophanate.

The following modification of the procedure gave good results. One mol. of ethyl chloroformate is poured over 2.1 mols of the urea in a flask connected with a reflux condenser. This mixture is now warmed on a water-bath for 2 or 3 hours, or at least for half an hour after drops cease to fall from the condenser. Water is added to the warm mass and it is filtered with suction and again washed with cold water. When dry it is ready for use. The melting point varies from 189° to 192°, depending upon the purity of the urea. The yield is from 62 to 65%. During the operation no hydrogen chloride was evolved, a fact also observed by Schiff. This explains the role of the second mol of urea, which evidently combines with the acid to form urea hydrochloride. Experiments showed that when pyridine or quinoline was used to take up the acid, there was a decrease in both the purity and the yield of the ester because of the partial decomposition of the ethyl chlorocarformate[3] by the tertiary amine. The method of Billmann,[4] in which urethane is heated with phosphorus pentoxide, is simple, but the yield is somewhat less.

I. Ethyl Allophanate and Amines.

Hofmann[5] found that this ester reacts with aqueous ammonia at 100° to give the biuret and alcohol. However, anhydrous liquid ammonia, or liquid ammonia containing 2% of water is without effect, since the ester can be recovered unchanged. This is in decided contrast to the ease with which carbonyl-diurethane reacts under like conditions.

1. Aniline and Ethyl Allophanate.—Hofmann also showed[5] that aniline at its boiling-point reacted with ethyl allophanate to give diphenyl biuret. He assumed, though without any evidence, that monophenyl biuret was first formed. On the contrary, the experimental results indicate that phenyl allophanic ester is the primary product.

After ethyl allophanate was heated with slightly more than one mol of aniline at 120–125° for one hour, the reaction product was extracted with

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[1] Wilm and Wischin, *Ann.*, 147, 155 (1868).

[2] Schiff, *ibid.*, 291, 372 (1896).

[3] Hopkins, *J. Chem. Soc.*, 117, 278 (1920).

[4] Billmann, *Ber.*, 50, 508 (1917).

[5] Hofmann, *ibid.*, 4, 265 (1871).

a cold dilute solution of sodium hydroxide. Ethyl-phenyl allophanate was precipitated (m. p. 105°) when the filtrate was acidified. Its identity was proven by comparison with a known sample of the ester, which had been made by the action of phenyl isocyanate on urethane.[1]

Diphenyl Biuret.—The allophanic ester (one mol) and aniline (2 mols) were heated at 125° for one hour. After the residue had been treated with dil. alkali to remove the soluble phenyl allophanic ester, it was crystallized repeatedly from alcohol, from which the biuret separated as a mass of white needles, with a silky luster. It melted at 209–10°.

Calc. for $C_{14}H_{13}O_2N_3$: N, 16.47. Found: 16.44, 16.63.

Monophenyl Urea and Diphenyl Urea.—When a mixture of the ester and aniline was heated at 160° to 170°, both monophenyl urea and diphenyl urea were formed. They were separated by the differences in their solubilities and were identified by analysis and by comparison with a known sample of each compound.

2. ***o*-Anisidine and Ethyl Allophanate.**—*o*-Anisyl-allophanic ethyl ester (*o*-$CH_3OC_6H_4NHCONHCOOC_2H_5$) was formed when the allophanic ester was heated with *o*-anisidine at 130° to 140° for 2 hours. It dissolved in a dilute solution of sodium hydroxide and crystallized from alcohol in fine needles, which melted at 125°. It is insoluble in water but very soluble in acetone and in benzene. The same compound was made by the action of ethyl chlorocarbonate on mono-*o*-anisyl urea.

Di-*o*-Anisyl Biuret, $NH(CONHC_6H_4OCH_3)_2$.—This was the main product isolated when 2 mols of the amine were used and the temperature varied from 130° to 140°. It crystallized from acetone or from alcohol in white needles which melted at 211–2° with partial sublimation.

Calc. for $C_{16}H_{17}O_4N_3$: N, 13.33. Found: 13.15.

Di-*o*-anisyl urea was the only product formed when the compounds were heated at 175° for 2 hours. Crystallized from alcohol, it melted at 182°.[2]

Calc. for $C_{15}H_{16}O_3N_2$: N, 10.29. Found: 10.24.

3. ***o*-Toluidine and Ethyl Allophanate.—Ethyl-*o*-tolyl-allophanate,** *o*-$C_7H_7NHCONHCOOC_2H_5$.—Equal mols of the ester and *o*-toluidine heated between 115° and 116° for 4 hours gave the substituted ester. It was soluble in dil. alkali, melted at 133° and was identical with the ester prepared from the *o*-tolyl urea and ethyl chlorocarbonate.[3] When 2 mols of *o*-toluidine were used at temperatures varying from 160–190° 3 compounds could be isolated: monotolyl urea (m. p. 189°); di-*o*-tolyl urea (m. p. 245–7°); and di-*o*-tolyl biuret, which formed white needles when crystallized from alcohol, and melted at 204–5°.

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[1] Dains, Greider, Kidwell, THIS JOURNAL, 41, 1008 (1919).

[2] Conrad and Limpach, *Ber.*, 21, 1654 (1888); Muhlhauser, *Ann.*, 207, 245 (1881).

[3] Piccard, *J. Chem. Soc.*, 81, 1571 (1902); THIS JOURNAL, 41, 1010 (1919).

Calc. for $C_{16}H_{17}O_2N_3$: N, 14.84. Found: 14.36.

The last 2 compounds were separated with difficulty by repeated fractional crystallization from alcohol.

4. ***m*-Toluidine and Ethyl Allophanate.**—No *m*-tolyl-allophanic ester could be found, when the same experimental conditions that were successful in the case of *o*-toluidine were used. Three products were isolated: *m*-tolyl urea (m. p. 143°); di-*m*-tolyl urea (m. p. 217°); and di-*m*-tolyl biuret. The last of the three is difficultly soluble in the usual organic solvents, but could be crystallized from alcohol from which it separated as a cotton-like mass of white needles, which melted at 179–9°.

Calc. for $C_{16}H_{17}O_2N_3$: N, 14.84. Found: 14.65, 14.75.

5. ***m*-Nitro-aniline and Ethyl Allophanate.**—Equal mols of the ester and *m*-nitro-aniline were dissolved in kerosene and heated for 2 hours at 125°. The residue was partly soluble in cold solution of sodium hydroxide from which acid precipitated ethyl *m*-nitrophenyl allophanate, the same as that which had been obtained previously by Piccard from *m*-nitrophenyl-hydroxy-oxamide.[1] This crystallized from alcohol in yellow needles which melted at 189–90°.

Calc. for $C_{10}H_{11}O_5N_3$: N, 16.60. Found: 16.71.

Di-*m*-nitrophenyl Biuret.—When heated at 145°, the same components gave the biuret in the form of yellow crystals difficultly soluble in alcohol; they melted at 215–16°.

Calc. for $C_{14}H_{11}O_6N_5$: N, 20.30. Found: 20.29.

At higher temperatures mononitro-phenyl urea was obtained as yellow crystals (m. p. 165°), soluble in hot water and di-*m*-nitro-diphenyl urea (m. p. 133–4°).

Calc. for $C_{13}H_{10}O_5N_4$: N, 18.54. Found: 18.30.

6. ***p*-Bromo-aniline and Ethyl Allophanate.**—The reaction followed in the main the lines suggested for aniline, although great difficulty was experienced in separating the products on account of their comparative insolubility in most organic solvents. Below 120°, no action seems to occur.

Di-*p*-bromo-diphenyl Biuret.—In one case, after the components had been heated for 2 hours at 120°, a product was obtained which was washed with hot water, hot alcohol and hot acetic acid. The residue, crystallized from boiling nitrobenzene, separated in small plates with a pearly luster, which began to decompose at 280°.

Calc. for $C_{14}H_{11}O_2N_3Br_2$: N, 10.26. Found: 10.20.

Heated at 140°, *p*-bromo-aniline and the ester gave mono-*p*-bromophenyl urea, difficultly soluble plates which decomposed above 270°.

Calc. for $BrC_6H_4NHCONH_2$: N, 13.03. Found: 13.00.

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[1] Piccard, *J. Chem. Soc.*, **81**, 1569 (1902).

At 150° the formation of di-*p*-bromo-diphenyl urea occurred.

Calc.: N, 7.57. Found: 7.46.

II. Methyl Allophanate and Aromatic Amines.

Preparation.—The methyl ester was made by the action of methyl chlorocarbonate (one mol) on urea (2 mols), according to the procedure used in the preparation of the ethyl derivative. The maximum yield obtained was 75%, but the product was of a high degree of purity. It is only slightly soluble in hot water, but can be readily recrystallized from dil. alcohol or from acetone.

1. **Aniline and Methyl Allophanate.**—While the action in the main is analogous to that of the ethyl ester, yet one interesting difference presented itself in that the methoxy-group showed less stability than the ethoxy toward the amine.

Although a great variety of temperatures were chosen, methylphenyl allophanate was not isolated in any experiment. This is singular, because the first product of the action of amines on the ethyl ester is the corresponding ethylaryl allophanate.

α-Phenyl Biuret, $C_6H_5NHCONHCONH_2$.—Molar quantities of the methyl ester and aniline were heated at 150° for 2 hours. The melt was extracted with a dilute solution of sodium hydroxide and the filtrate treated with dil. acid. The precipitated biuret can be crystallized from alcohol, acetone, or hot water, from which it separates in shining scales, which usually melt at 164°, 165° or 167°. However, after further recrystallization if the crystals are dried at 100° they melt and darken at 155°. Piccard and Carter[1] give the melting-point at 156°, as does also McKee,[2] who obtained it by the action of hydrogen chloride on methylphenyl-isobiuret. Schiff,[3] who prepared it from phenyl-hydroxy-oxamide, says that the true melting-point is 165°.

Calc. for $C_8H_9O_2N_3$: C, 53.62; H, 5.08; N, 23.46. Found: C, 46.18; H, 5.33; N, 23.58.

Molar weight (McCoy's method in absolute alcohol).

Calc.: 179. Found: 179.91, 187.

Heated with aniline the α-phenyl biuret gave ammonia and diphenyl biuret.

Other Products.—Diphenyl biuret was produced at all temperatures from 150° to 170°, while above this point diphenyl urea was the main product. Monophenyl urea was isolated in only one case. Evidently the amount formed with the methyl-ether is less than that produced with the ethyl ester.

2. **o-Toluidine and Methyl Allophanate. o-Tolyl Biuret,** C_7H_7-

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[1] Piccard and Carter, *J. Chem. Soc.*, **79**, 846 (1900); **81**, 1563 (1902).

[2] McKee, *Am. Chem. J.*, **26**, 254 (1901).

[3] Schiff, *Ann.*, **352**, 79 (1907).

$NHCONHCONH_2$. This was found in various amounts when temperatures ranging from 140–170° were employed. It was soluble in alkali and crystallized from dil. alcohol in fine white needles, which melted and sublimed at 179–180°. It corresponded in every way to the biuret obtained by Piccard and Carter[1] from *o*-tolyl-hydroxyl-oxamide. The other products isolated were di-*o*-tolyl biuret, *o*-tolyl urea and di-*o*-tolyl urea. No methyltolyl allophanate was found.

III. Aniline and Ethyl Benzoyl Allophanate, $C_6H_5CONHCONHCOOC_2H_5$.

For comparison, the action of aniline on an acyl derivative of allophanic ester was tried. Thus, benzoyl-allophanic ester and aniline when heated at 150° gave benzoyl-phenyl urea (m. p. 209°).

Calc., $C_{14}H_{12}O_2N_2$: N, 11.65. Found: 11.56.

This same urea had been obtained previously by the action of aniline on benzoyl urethane[2] and on ethyl-benzoyl-thioncarbamate,[3] $C_6H_5CONHCSOC_2H_5$.

Phenyl hydrazine and Ethyl Allophanate, 1-Phenyl-4-carbethoxy-semicarbazide, $C_6H_5NHNHCONHCOOC_2H_5$.—Below 140° there was no reaction between the components; at that temperature, however, the new ester was formed with the elimination of ammonia but no alcohol, and after repeated crystallization from alcohol, it was obtained in the form of small white scales, melting at 175–6°.

Calc. for $C_{10}H_{13}O_3N_3$: N, 18.93. Found: 19.18.

The compound is isomeric with the 1,1-phenyl-carbethoxy-semicarbazide, $C_6H_5N(COOC_2H_5)NHCONH_2$, which can be synthesized by the action of ethyl chlorocarbonate on the monophenyl-semicarbazide and which melts at 171–5°.[4] The mode of formation of the ester melting at 176°, shows conclusively that it must be an isomer and not identical with the 1,1-phenyl-carbethoxy-semicarbazide.

Heated above its melting-point the 1-4 ester lost alcohol, the ring closed and 1-phenyl-urazole was formed, while with ammonia it gave a compound melting at 195°, which is being investigated.

1-Phenyl-urazole, $C_6H_5N\text{-}NHCONHCO$ (m. p. 263–4°) is formed quantitatively whenever phenylhydrazine and the ester are heated above 140°. It was identified by comparison with a known sample of the urazole and by the synthesis of its acetyl derivative (m. p. 169°).

Phenyl Hydrazine and Methyl Allophanate.—The same interesting reactivity of the methoxy group was noted in the case of methyl ester. The intermediate 1,4-phenyl-carbomethoxy-semicarbazide could not be

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[1] Piccard and Carter, *J. Chem. Soc.*, 81, 1563 (1902).

[2] Wheeler and Johnson, *Am. Chem. J.*, 24, 208 (1900).

[3] Wheeler and Merriam, THIS JOURNAL, 23, 289 (1901).

[4] Wheeler and Beardsley, *Am. Chem. J.*, 27, 269 (1902); Acree, *Ber.*, 37, 618 (1904).

isolated. When the mixture was heated at 150° for a short time no change occurred, but longer heating at this temperature, or for a few minutes at 153°, gave the 1-phenyl-urazole as the sole product.

Summary.

(1) A study has been made of the progressive action of primary amines on methyl and ethyl allophanate which has resulted in the isolation of aryl allophanic esters, mono- and di-aryl biurets and mono- and di-substituted ureas.

(2) Phenylhydrazine has been found to give 1-phenyl-4-carbethoxy-semicarbazide and 1-phenyl-urazole. The investigation is being continued in this laboratory.

LAWRENCE, KANSAS.

[CONTRIBUTION FROM THE LABORATORY OF WERNER DRUG AND CHEMICAL CO.]

THE METHIODIDES OF THE CONDENSATION PRODUCTS OF SOME CYCLIC ALDEHYDES WITH QUINALDINE AND ALPHA PICOLINE, AND THEIR POSSIBLE VALUE AS INDICATORS IN ACIDIMETRY.

BY LOUIS F. WERNER.

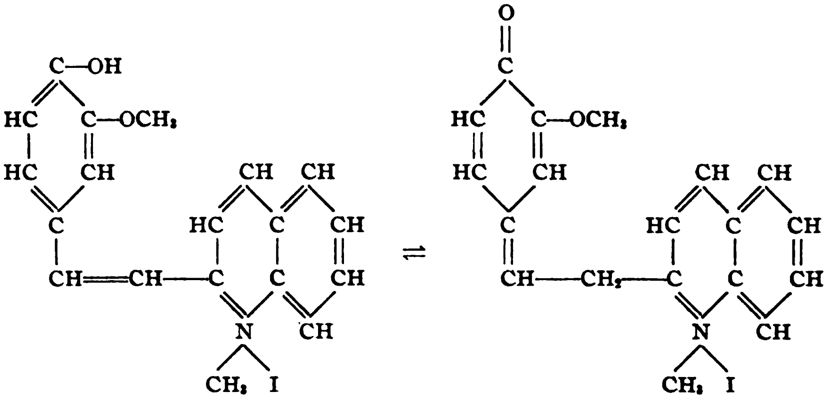
Received July 16, 1920.

The aqueous solution of the methiodide of 2(3-methoxy-4-hydroxy-styryl)quinoline when treated with sodium hydroxide solution was found to give a deep fuchsine-colored fluid, instead of the anticipated precipitate of the quaternary-ammonium hydroxide. As the hydrochloride of 2(3-methoxy-4-hydroxy-styryl)quinoline under like conditions gave but a milky emulsion of the free base, the color noted must be due to the auxochrome effect of the methyl group attached to nitrogen.

Following up these results, the methiodides of the condensation products of various cyclic aldehydes with quinaldine were prepared, and their behavior with sodium hydroxide determined. The methiodides of the condensation products of quinaldine with benzaldehyde, furfural, *o*-hydroxy-benzaldehyde, *p*-hydroxy-benzaldehyde, protocatechuic aldehyde, and also the condensation product of piperonal with *α*-picoline, were prepared and studied.

The results secured showed that in order that the methiodides of compounds of this type have the properties of an indicator, that there be a phenolic hydroxyl group attached to the neucleus of the aldehyde used in its preparation. Thus in the case of the methiodides of 2-styryl-quinoline, 2(*β*-furfuryl-vinyl)quinoline, 2(4,3-methylene-dioxyl)pyridine, the yellow-aqueous solutions of these salts were rendered colorless upon the addition of sodium hydroxide solution, but the methiodides of 2(2-hydroxy-styryl)quinoline and of 2(4-hydroxy-styryl)quinoline gave a blood-red coloration, and the methiodide of 2(3-methoxy-4-hydroxy-styryl)quinoline gave a fuchsine-red colored solution, and the methiodide of 2(3,4-dihydroxy-styryl)quinoline gave a grape-colored solution.

The probable effect of the alkali upon those compounds which show this color change is to cause a molecular rearrangement, to give a quinone,



A few preliminary tests carried out to determine the possibility of using these compounds as indicators, indicated that they may be used as such, provided that the hydriodic acid first formed by their hydrolysis in water be neutralized with alkali.

Experimental.

2(β-Furfuryl-vinyl)quinoline, $C_4H_3O.C_2H_2.C_9H_6N$.—Quinaldin, 9 g., and furfural, 6 g., were heated in the presence of 2 g. of anhydrous zinc chloride upon the boiling water-bath for 5 hours. Water, and then a slight excess of hydrochloric acid was added, and steam passed into the mixture until all but tar was dissolved. The solution was filtered hot through a wetted filter, and conc. hydrochloric acid added to the cooled filtrate. The precipitated hydrochloride was filtered out as an orange-colored powder, dissolved in water, filtered, and reprecipitated with hydrochloric acid. The free base was finally secured by dissolving the hydrochloride in water and carefully adding ammonium hydroxide, filtering from the tarry impurities which precipitate first. The free base is recrystallized from ligroin. M. p. (corr.) 56°. The base is soluble in all the ordinary organic solvents.

Subs., 0.3823: 23.4 cc. N (over 30% KOH at 27° and 749 mm.).
Clac. for $C_{15}H_{11}ON$: N, 6.33. Found: 6.69.

2(β-Furfuryl-vinyl)quinoline methiodide, $C_4H_3O.C_2H_2.C_{10}H_9NI$.—This substance was prepared by heating 3 g. of 2(β-furfuryl-vinyl)quinoline with an excess of methyl iodide in a sealed tube in the dark, at a temperature of 140°. It was necessary to heat for 4 to 5 hours, an oil-bath being used. The contents of the tube were then recrystallized from water, and the salt was secured as orange colored needles, having a steel-blue iridescence when viewed in natural light. The substance is soluble in hot alcohol and hot water, but is practically insoluble in the usual organic solvents. M. p. (corr.) 226.2°.

An aqueous solution of this salt is lemon-yellow in color under neutral or acid conditions, and colorless in the presence of alkalies, but the change in color is so slight as to give it no value as an indicator.

Subs., 0.5878: 22.4 cc. N (over 30% KOH at 27° and 746 mm.).
Calc. for $C_{16}H_{14}ONI$: N, 3.86. Found: 4.15.

2(3,4-Methylene-dioxy-styryl)pyridine methiodide, $C_7H_5O_2.C_2H_2.C_6H_8$-NI.—2(3,4-Methylene-dioxy-styryl)pyridine[1] and an excess of methyl iodide were heated in a boiling water-bath in the dark for 4 hours. The contents of the bomb tube were then recrystallized from water, the salt being secured as a lemon-colored microcrystalline powder. It is soluble in hot water, alcohol, and acetone, but is but slightly soluble in the usual organic solvents. M. p. (corr.) 276°.

An aqueous solution of this salt is yellow in aqueous acid or neutral solution and colorless in alkaline solution, but the substance has no value as an indicator.

Subs., 0.5029: 19.2 cc. N (over 30% KOH at 27° and 732 mm.).
Calc. for $C_{15}H_{14}O_2NI$: N, 3.82. Found: 4.08.

2-Styryl quinoline methiodide, $C_6H_5.C_2H_2.C_{10}U_9NI$.—2-Styryl-quinoine[2] and an excess of methyl iodide were heated in a sealed tube in the dark for 4 hours in a boiling water-bath. The contents of tube were recrystallized from water, and the salt was secured as acicular bright orange-colored crystals. It is soluble in hot water and alcohol, but only slightly soluble in the common organic solvents. M. p. (corr.) 235.2° with decomposition.

A solution of this substance in neutral or acid aqueous solution is a faint yellow, but is rendered colorless by adding alkali. It is of no service as an indicator.

Subs., 0.5881: 21.4 cc. N (over 30% KOH at 27° and 735 mm.).
Calc. for $C_{18}H_{16}NI$: N, 3.75. Found: 3.91.

2(2-Hydroxy-styryl)quinoline methiodide, $C_6H_5O.C_2H_2.C_{10}H_9NI$.—2(2-Hydroxy-styryl)quinoline[3] and an excess of methyl iodide were heated in a sealed tube in the dark at 135° to 140°. The contents of the tube were recrystallized from water, and it was thus secured as a bright orange-colored crystalline powder. It is soluble in hot water and hot alcohol, slightly soluble in other organic solvents. M. p. (corr.) 236°.

One cc. of a 0.1% solution in 250 cc. of water was turned to a blood-red

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[1] Thiemich, *Ber.*, 30, 1578 (1897).

[2] Wallach and Wuesten, *ibid.*, 16, 2008 (1883).

[3] Dzierzgowski, *ibid.*, 27, 1980 (1894).

color upon the addition of a drop of 0.1 *N* sodium hydroxide solution but the color reverted to pale lemon upon standing, for a few seconds. Not until 0.4 cc. of the alkali had been added was the blood-red color permanent. This behavior is due undoubtedly to the fact that a certain amount of alkali is needed to neutralize the hydriodic acid formed by the hydrolysis of the salt.[1] It was found that the blood-red color was discharged by 0.12 cc. of 0.1 *N* hydrochloric acid, but it returned upon adding again 0.1 cc. of 0.1 *N* sodium hydroxide solution. To use this substance as an indicator, it would be necessary therefore, to "sensitize" the solution by the addition of the proper amount of sodium hydroxide to overcome this acidity, analogous to the addition of hydrochloric acid to the sodium salt of helianthin (methyl orange).

Subs., 0.6100: 21.1 cc. N (over 30% KOH at 25° and 745 mm.).
Calc. for $C_{18}H_{10}ONI$: N, 3.60. Found: 3.81.

2(4-Hydroxy-styryl)quinoline methiodide, $C_6H_5O.C_2H_2.C_{10}H_9NI$.—Methyl iodide in excess was heated with 2(4-hydroxy-styryl)quinoline[2] in an oil-bath at 140° in the dark. Recrystallized from water, the substance is secured as a bright orange-colored crystalline powder. It is soluble in hot alcohol and hot water, but is only slightly soluble in other solvents. M. p. (corr.) 250.8° with decomposition.

Tested as the preceding compound as to its value as an indicator, it gave similar results, it giving a lemon-yellow solution in presence of acids and in neutral solutions, and a blood-red solution in the presence of alkalies.

Subs., 0.6181: 20.2 cc. N (over 30% KOH at 26° and 743 mm.).
Calc. for $C_{18}H_{16}ONI$: N, 3.60. Found: 3.52.

2(4-Hydroxy-3-methoxy-styryl)quinoline methiodide, 4,3-$OH.OCH_3.C_6H_3.C_2H_2.C_{10}H_9NI$.—This substance was prepared by heating 2(4-hydry-3-methoxy-styryl)quinoline[3] with an excess of methyl iodide in the dark in a boiling water-bath. The product is a brick-red crystalline powder, slightly soluble in hot water and alcohol, practically insoluble in other solvents. It was powdered and purified by extracting 3 times with boiling 95% alcohol to remove tar and any unchanged base. M. p. 267° (corr.) with decomposition.

Upon determining the sensitivity of this compound to acids and bases, it was found that 0.4 cc. of 0.1 *N* sodium hydroxide solution was required to secure a permanent fuchsine-red colored solution, using a mixture of one cc. of 0.1% solution to 250 cc. of water, but only 0.1 cc. of 0.1 *N*

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[1] Compounds of this type, despite the common conception that quaternary ammonium compounds are all strong bases, are on the contrary very weak bases, and those containing no phenolic group are readily precipitated from their strong aqueous solutions of their salts by ammonium hydroxide.

[2] Wallach and Wuesten, *Ber.*, 16, 2009 (1883).

[3] Nencki, *ibid.*, 27, 1974 (1894).

hydrochloric acid was required to turn it to the neutral lemon-yellow color. This dye also would require sensitizing with sodium hydroxide solution before it would serve as an indicator.

Subs., 0.6041: 19.70 cc. N (over 30% KOH at 26° and 749 mm.).
Calc. for $C_{19}H_{18}O_2NI$: N, 3.34. Found: 3.59.

2(3,4-Dihydroxy-styryl) quinoline, $4,3(OH)_2.C_6H_3.C_2H_2.C_9H_6N$.—This was prepared by heating 4.6 g. of protocatechuic aldehyde, 4.8 g. of quinaldin and 2 g. of zinc chloride upon a boiling water-bath until the mass was nearly solid. The paste was then dissolved in water and a little hydrochloric acid, and filtered hot. The hydrochloride was then precipitated by adding an excess of hydrochloric acid, and cooling, and was recrystallized in this manner several times, and the free base secured in a pure condition by adding 5 cc. of glacial acetic acid to the solution, and then carefully adding ammonium hydroxide solution to the appearance of the first permanent turbidity. Upon cooling and agitating well, the tarry impurities were precipitated, and filtered out. The brilliant clear solution was then treated with steam, resulting in the hydrolysis of the acetate, and the precipitation of the free base. This is a very pretty example of progressive hydrolysis, as the bright red color of the acetate rapidly fades as the temperature rises, and is followed by the precipitation of the free base. This last operation is repeated, thus securing the compound in a pure condition. M. p. 244.6° (corr.). The base is slightly soluble in alcohol, acetone and benzol, but not sufficiently to be purified by recrystallization.

Subs., 0.3390: 15.4 cc. N (over 30% KOH at 21° and 746 mm.).
Calc. for $C_{17}H_{13}O_2N$: N, 5.32. Found: 5.32.

2(3,4-Dihydroxy-styryl)quinoline methiodide, $4,3\text{-}(OH)_2.C_6H_3.C_{10}H_9NI$.—This was prepared by heating 2(3,4-dihydroxy-styryl-quinoline in a sealed tube with an excess of methyl iodide at 140° in an oil-bath for 5 hours, protected from the light. The salt was recrystallized from water as a brownish-orange powder, soluble in hot water and alcohol, slightly soluble in cold alcohol and water, and other usual solvents. M. p. 266.8° (corr.) with decomposition.

Upon testing the approximate sensitivity of this salt to alkalies and acids, it was found that to secure a permanent grape-colored solution, 0.4 cc. of 0.1 *N* sodium hydroxide solution was required in a mixture of one cc. of a 0.15% solution in 250 cc. of water, which was converted to the original lemon-yellow colored solution by the addition of 0.1 cc. of 0.1 *N* hydrochloric acid. This indicator would also require sensitizing to fit it for practical use.

Subs., 0.6069: 19.0 cc. N (over 30% KOH at 27° and 749 mm.).
Calc. for $C_{18}H_{16}O_2NI$: N, 3.46. Found: 3.43.

Summary.

The work showed that the addition of a methyl group to the nitrogen atom of the condensation products of the *ortho-* and *para-*hydroxy aromatic aldehydes with quinaldin gave these compounds the properties of indicators, but that compounds not possessing these *ortho-* or *para-*phenol groups did not acquire this property. A little preliminary work was done to determine the suitability of these compounds to serve as indicators in volumetric analysis.

CINCINNATI, O.

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO.]

THE C_4-SACCHARINIC ACIDS. I. THE RESOLUTION OF *dl*-2,3-DIOXYBUTYRIC ACID INTO THE OPTICALLY-ACTIVE COMPONENTS. THE DERIVATIVES OF THESE ACIDS.

BY J. W. E. GLATTFELD AND GEORGE E. MILLER.[1]

Received July 19, 1920.

The saccharinic acids are acids which would result from the oxidation of the $\mathrm{H-\underset{|}{C}=O}$ group of an aldo-monosaccharide of the formula $C_nH_{2n}O_n$ to the $\mathrm{O=\underset{|}{C}-OH}$ group at the expense of one of the $\mathrm{H-\overset{|}{\underset{|}{C}}-OH}$ groups which would be reduced to the $\mathrm{H-\overset{|}{\underset{|}{C}}-H}$ group. These acids have the same molecular formula as the corresponding aldo-monosaccharides and may thus be looked upon as the results of an internal oxidation-reduction reaction. The saccharinic acids formed from some of the pentoses and hexoses have been the direct subject of study[2] by Nef and his students at various times, and have also entered into consideration in connection with all the sugar-oxidation experiments conducted in this laboratory in recent years. These oxidations were carried out in alkaline solution, under which conditions the production of saccharinic acids was a possibility. In a recent paper from this laboratory[3] there was reported, in the oxidation of maltose in alkaline solution, the production of an acid, the phenylhydrazid of which gave a perfect analysis for that of a 4-carbon-atom saccharinic acid. The properties of the free acid furthermore were those which would be expected of one of these acids. Its configuration could not be reported because of lack of

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[1] The dissertation of which this paper is a condensation was presented by George E. Miller as part fulfilment of the requirements for the degree of Doctor of Philosophy in the University of Chicago. The original dissertation is on file in the University library.

[2] Nef, *Ann.*, **376**, 1–120 (1910).

[3] THIS JOURNAL, **40**, 973 (1918).

data as to the properties and constants of the 4-carbon-atom saccharinic acids.

Nef has referred[1] to the handicap which this lack of data has imposed on the work with sugars in alkaline solution. In order to supply some of this deficiency we have attempted the preparation of the saccharinic acids in a systematic way and have started with the C_4-saccharinic acids to throw light on the first question of interest in this connection, namely, which of the possible optically-active C_4-saccharinic acids is formed in the oxidation of maltose in alkaline solution. The present paper is a report on the preparation of the first pair of saccharinic acids, the 2,3-dioxy-butyric acids. Work on the preparation of the other 8 active acids is now in progress.

The *dl*-2,3-dioxy-butyric acid has been prepared by Hanriot.[2] The synthesis was repeated by Nef[3] who studied the acid in somewhat more detail and reported a few of its properties as well as those of the phenylhydrazid and brucine salt. The constitution of the *dl*-acid was proved by Nef[2] by the method of synthesis and by oxidation to malic acid. We prepared our acid in accordance with the procedure of these investigators. The analysis of the vacuum-dried barium salt showed the substance to be pure. The acid was finally obtained by precipitating the barium from an aqueous solution of the salt quantitatively by means of sulfuric acid. The solution of the acid was subjected to complete distillation *in vacuo* and the acid was then obtained as a slightly yellow oil. It was freed from inorganic salt by repeated solution in ethyl acetate, and was then used in the resolution described below.

The phenylhydrazid was made according to Nef's directions.[3] After many recrystallizations it was found to melt at 100–101° instead of at 99° as reported by Nef.

In order to prove that the acid was actually *dl*-2,3-dioxy-butyric acid it was prepared also from vinylacetic acid $CH_2 : CHCH_2COOH$ by oxidation with permanganate. The vinylacetic acid was prepared according to the directions of Hauber[4] and oxidized according to the directions of Penschuk.[5] The acid so prepared gave a phenylhydrazid which melted at 100–101°. A mixed melting-point determination of this phenylhydrazid with the one from the *dl*-acid above, showed them to be identical.

Fichter and Sonneborn[6] also prepared the 2,3-dioxy acid from vinylacetic acid by the above method and state that the acid is identical with that made by Hanriot from the α-chlorohydrine. As they base their

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[1] Nef, *Ann.*, 376, 9 (1910).

[2] Hanriot, *Ann. chim. phys.* [5] 17, 62 (1879).

[3] Nef, *Ann.*, 376, 35 (1910).

[4] Hauber, *Ber.*, 36, 2897 (1903).

[5] Penschuk, *Ann.*, 283, 109 (1894).

[6] Fichter and Sonneborn, *Ber.*, 35, 942 (1902).

statement only on the analysis of the barium salt for barium oxide, which would obviously be the same for the barium salts of all dioxy-butyric acids, they cannot be said to have proved the identity of the acids from the two sources. It was, therefore, considered necessary to make the proof of the identity absolute by preparing the phenylhydrazids and proving them identical before proceeding with further studies of the acid.

The Resolution of the *dl*-2,3 Dioxy-butyric Acid into the Active Components.

Brucine, cinchonine, quinine and strychnine were tried and brucine found to be best for the resolution. The brucine salt was made in the usual way[1] by adding a slight excess of the alkaloid to an aqueous solution of the acid and heating the mixture on the water-bath. The use of an electrically-driven mechanical stirrer greatly hastened the solution of the alkaloid.

Eighty-three g. of the *dl*-acid and 305 g. of brucine were heated in about 2 liters of water on the boiling water-bath until the solution reacted alkaline to litmus. Three g. of brucine did not go into solution. After extraction with benzol and subjection of the extracted solution to complete vacuum distillation, 337 g. of crude brucine salt was obtained. This was treated with 750 cc. of boiling absolute alcohol. Fifteen g. of flocculent material remained undissolved. This material was separated by hot filtration. The clear filtrate was allowed to stand overnight and deposited crystals which weighed 58.4 g. The mother liquor was subjected to complete vacuum distillation at 60°. The residue, weighing 257.5 g., was dissolved in 300 cc. of boiling absolute alcohol. This solution deposited crystals which weighed 13.55 g. The mother liquor from the second crop was subjected to complete vacuum distillation at 70°. The residue weighed 204 g. This was treated with 140 cc. of boiling alcohol. This solution deposited a third crop of crystals which weighed 54.8 g. A fourth crop of crystals which weighed 17 g. was obtained in the same way by treating the residue, which weighed 141 g., with 72 cc. of hot absolute alcohol. The mother liquor from the fourth crop was subjected to complete vacuum distillation. The residue weighed 130 g. No more crystals could be obtained.

The rotations of these 4 crops of brucine salts were taken in exactly 4% aqueous solution. The density of the solution was considered to be 1.011. The following results were obtained.

Crop.	$[\alpha]_D^{20}$.	α in one dcm. tube.
I	—29.42	—1.19
II	—27.95	—1.12
III	—27.95	—1.12
IV	—26.95	—1.09

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[1] THIS JOURNAL, 40, 976 (1918). Footnote.

The rotation of the successive crops of brucine salts convinced us that a partial separation of the *dl*-acid into its optical components had been effected. Our next effort was, therefore, to obtain the less soluble brucine salt in its purest form. Another quantity of crude brucine salt was prepared and recrystallized as above. Again the specific rotation of the first crop was —29.42°. The successive crops had approximately the same rotations as the corresponding ones in the first experiment. The salt with the specific rotation of —29.42° was now dissolved in the smallest possible quantity of hot absolute alcohol. The solution deposited a crop of crystals whose specific rotation was taken. This crop was again dissolved in the smallest possible quantity of absolute alcohol and allowed to stand overnight during which time it deposited a crop of crystals, which was separated by filtration and dried to constant weight *in vacuo* over sulfuric acid. The rotation of this crop was taken. This process was repeated 7 times. The rotations of the successive crops were invariably between —29.18° and —29.42°. It was, therefore, concluded that the *pure* brucine salt of one of the optical isomers had the specific rotation of approximately —29.42°.

The Free Acid from the Brucine Salt, $[\alpha]_D^{20}$, —29.42°.—One hundred and thirty-seven g. of the brucine salt, $[\alpha]_D^{20}$ —29.42°, was dissolved in about 4 liters of hot water and treated with a hot solution of 118 g. of crystallized barium hydroxide in the usual way[1] to remove brucine from its salts. After the removal of brucine by filtration and extraction of the filtrate with benzol, the barium was removed with sulfuric acid and the filtrate from the barium sulfate was subjected to complete vacuum distillation. The residue was taken up in absolute alcohol and the solution was filtered to remove any inorganic salts present. The alcohol was completely removed by distillation *in vacuo* finally at 100°, and the acid was left as a clear yellow and very mobile oil.

The rotation of a portion of this acid was then taken and another portion was titrated. Other portions were converted into the barium and calcium salts and the phenylhydrazid.

Rotation.—The specific rotation of the acid in approximately 4% solution was found to be —8.29°, *i. e.*, 2.32 g. acid dissolved in 45.78 g. water gave α in a one dcm. tube —0.40°. The density of the solution was assumed to be 1.00 and the temperature was approximately 20°.

Titration.—The titration showed that the acid was present largely as lactone. The amounts of free acid and lactone were determined[2] and the following results obtained.

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[1] This Journal, 40, 981 (1918), footnote 2.

[2] The method of determining the free acid and lactone in a mixture of the two is as follows. The weighed sample is dissolved as rapidly as possible in cold water and immediately titrated to pink with 0.1 *N* sodium hydroxide solution, using phenolphthalein as indicator. A quantity of 0.1 *N* sodium hydroxide solution in excess of

	Weight of sample. G.	0.1 *N* NaOH for free acid. Cc.	0.1 *N* NaOH for lactone. Cc.	Total NaOH used. Cc.	Calc. for C_4 saccharinic acid.[a] Cc.
I........	0.4765	5.72	39.75	45.47	45.70
II.......	0.4843	5.83	40.76	46.59	46.47

[a] In calculating the theoretical cc. account must, of course, be taken of the amounts of free acid and lactone present in the samples as indicated by the titration figures.

These titrations show that about 14.4% of the sample in water solution exists as free acid and the rest as lactone. This agrees with Nef's observations.[1]

The Barium Salt.—A mixture of one g. of acid. 3 g. of barium carbonate and 75 cc. of water was heated to make this salt. The salt was gummy and could not be made to crystallize except by triturating with absolute alcohol. There was obtained 0.4 g. of the vacuum-dried salt; $[\alpha]_D^{20}$ +1.48°, *i. e.*, 0.4 g. salt in 9.6 g. water gave α +0.03° in a half-decimeter tube.

The Calcium Salt.—A mixture of 1.2 g. of acid, 3 g. of calcium carbonate and 75 cc. of water was heated to make this salt. It became crystalline only when triturated with absolute alcohol. There was obtained 0.4 g. of vacuum-dried salt; rotation, $[\alpha]_D^{20}$ +2.47°, *i. e.*, 0.4 g. of salt in 9.6 g. water gave α +0.05° in a half-decimeter tube.

The Phenylhydrazid.—A mixture of 1.75 g. of acid, 2 cc. of phenylhydrazine and 2 cc. of ethyl acetate gave, in the usual way 3.15 g. of the crude phenylhydrazid. This was recrystallized from 18 cc. of ethyl acetate and gave one g. of phenylhydrazid with the melting point of 102–103°. This was recrystallized from 3.7 cc. of ethyl acetate and gave 0.75 g. of crystals with a melting point of 102–103°. The specific rotation of this compound was found to be +1.71°, *i. e.*, 0.54 g. in 12.06 g. of water gave α +0.07° in a one dcm. tube.

The Free Acid from the Non-crystallizable Brucine Salt.—The mother liquor from the 4 crops of crystalline brucine salts was subjected to complete vacuum distillation at 60° and gave a residue which weighed 130 g. as mentioned above. The brucine was set free in the usual way and 15.25 g. of a light brown ether-soluble oil was obtained. The specific rotation of this acid was determined as +7.18°, *i. e.*, 1.65 g. of acid in 39.6 g. of water gave α +0.287° in a one dcm. tube. As the specific rotation of the optical isomer of the acid from the brucine salt rotating —29.42° should be +8.29°, the acid now under consideration was evi-

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the calculated amount is then added and the mixture heated on the boiling water-bath for 15 minutes. It is then cooled and a measured quantity of 0.1 *N* hydrochloric acid is added to acid reaction and the mixture boiled to expel carbon dioxide. It is again cooled and the excess hydrochloric acid is determined with 0.1 *N* sodium hydroxide. solution. The quantity of sodium hydroxide solution added at first in the cold determines the amount of free acid present and the remainder added determines the quantity of lactone.

[1] *Ann.*, 376, 35 (1910).

dently still contaminated with some of the racemic acid. It was, therefore, converted into the barium salt. The 15.25 g. of acid yielded 14.8 g. of the vacuum-dried barium salt. This salt had a specific rotation of —1.48°, *i. e.*, one g. of salt in 24 g. of water gave α —0.03°. This indicates that the salt was pure, as this rotation is equal and opposite to that of the barium salt from the crystalline brucine salt. The gum was set free from this salt and purified in the usual way. The weight of free acid was 6 g. It was a light yellow mobile oil.

The rotation of a portion of this acid was taken, another portion was titrated and another portion was converted into the phenylhydrazid with the following results.

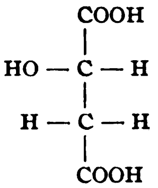
The Rotation.—The specific rotation of the acid was found to be +8.00°, *i. e.*, 0.83 g. of acid dissolved in 19.92 g. of water gave α +0.32° in a one dcm. tube.

The Titration.—A titration of another portion of the acid gave the following results. Only one titration was made because of the small amount of acid available.

Weight of sample. G.	0.1 *N* NaOH for free acid. Cc.	0.1 *N* NaOH for lactone. Cc.	Total. Cc.	Calc. for C_4 saccharinic acid. Cc.
0.4014	6.18	31.93	38.11	38.18

The Phenylhydrazid.—This compound was obtained only as a gum, very soluble in ethyl acetate.

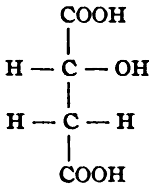
Determination of the Configuration of the Two Optical Isomers.—The foregoing data prove that the *dl*-2,3-dioxy-butyric acid had been separated into the pure dextro- and levo-rotating components. The next step in the problem was to assign the proper configuration to each of the new acids. It was shown that the dioxy acid which rotated —8.29° could be oxidized to natural, levo-rotating, malic acid. The malic acids were shown by Fischer[1] to have the configurations



$$\begin{array}{c} COOH \\ | \\ HO-C-H \\ | \\ H-C-H \\ | \\ COOH \end{array}$$

l-malic or natural malic acid.

and



$$\begin{array}{c} COOH \\ | \\ H-C-OH \\ | \\ H-C-H \\ | \\ COOH \end{array}$$

d-malic acid.

Of the two 2,3-dioxy-butyric acids under consideration only one could give *l*-malic acid by oxidation, namely the one with the configuration I (see below). The acid which rotates —8.29° then must have this configuration as it gives *l*-malic acid and must, therefore, be called *l*-2,3-dioxy-butyric acid while the acid which rotates +8.00° must have the configuration II (see below) and must be called *d*-2,3-dioxy-butyric acid.

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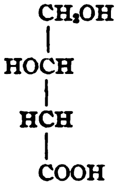
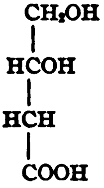
[1] *Ber.*, 29, 1378 (1896).



$$\begin{array}{c} CH_2OH \\ | \\ HOCH \\ | \\ HCH \\ | \\ COOH \end{array}$$

(I).



$$\begin{array}{c} CH_2OH \\ | \\ HCOH \\ | \\ HCH \\ | \\ COOH \end{array}$$

(II).

The experimental evidence for these conclusions follows.

Nef[1] has reported on the oxidation of *dl*-2,3-dioxy-butyric acid to *dl*-malic acid. We repeated Nef's work. As our procedure differed somewhat from Nef's it is given below.

The *dl*-dioxy-butyric acid is treated with 10 times its weight of nitric acid of sp. gr. 1.305 and heated for 2 hours at 65° in a water-bath. The reaction mixture is subjected to complete vacuum distillation at a temperature not exceeding 65°. The residue—a yellow gum—is dissolved in 10 to 12 times its weight of cold water. This solution is treated with an excess of calcium carbonate and this mixture shaken for 10 to 15 minutes. The excess of calcium carbonate is then removed by suction filtration. The filtrate is now concentrated by boiling to about $^1/_2$ its volume during which process the normal calcium malate separates.[2] To obtain the free *dl*-malic acid the vacuum-dried salt is suspended in a large volume of hot water and the necessary quantity of oxalic acid, calculated on the basis of an analysis of the vacuum-dried salt, is added in hot solution. The mixture is kept on the boiling water-bath for 3 hours and frequently shaken. It is then cooled and the calcium oxalate is separated by filtration. The filtrate is subjected to complete vacuum distillation finally at 100°. The residue is extracted 3 times with boiling ether. The combined filtered ether solution is completely evaporated, finally on the water-bath. The residue is placed *in vacuo* over sulfuric acid until the weight is constant when the malic acid remains as white scales. It was proved by experiment that malic acid itself is not appreciably oxidized under the above procedure.

Five and two-tenths g. of the 2,3-dioxy-butyric acid $[\alpha]_D^{20}$ —8.29, was now oxidized, following the above procedure in every detail, and a total of 2.15 g. of insoluble calcium salt was obtained. Part of this insoluble calcium salt was used for analysis for calcium oxide (see below) and the acid was obtained from the rest. The weight of acid obtained was 0.5127 g. This will be referred to hereafter as "free acid."

The proof of the identity of this insoluble salt with the calcium salt of pure natural malic acid and of the identity of the "free acid" with pure natural malic acid was brought by comparing the analyses of the 2 corre-

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[1] *Ann.*, 376, 36 (1910).

[2] *Ibid.*, 233, 168 (1886).

sponding vacuum-dried calcium salts, and the melting points, the specific rotations and the titration of the 2 corresponding acids. The natural malic acid was recrystallized from ether. Part of it was then dried *in vacuo* over sulfuric acid and part was converted into the normal calcium salt by the procedure described above.

Analysis of the Calcium Salts.—The first 2 analyses were of the salt obtained by oxidizing the 2,3-dioxy-butyric acid, the last 2 of the salt of pure natural malic acid.

Subs., 0.2025, 0.2197, 0.2070, 0.1639: CaO, 0.661, 0.0712, 0.0670, 0.0530.
Calc. for $C_4H_4O_5Ca$: CaO, 32.56. Found: 32.65, 32.40, 32.36, 32.28.

Melting Points.—The melting points of the "free acid," the pure natural malic acid, and a mixture of the two are as follows: Melting point "free acid," 96°; natural malic acid, 95°; mixture, 95–96°.

The Rotations.—The specific rotations of the "free acid" and of the natural malic acid were taken with the following results.

0.5117 g. of "free acid" in 12.3931 g. water gave α —0.13° in a one dcm. tube.

0.6588 g. of natural malic acid in 15.8939 g. water gave α —0.126 in a one dcm. tube.

$[\alpha]_D^{20}$ of "free acid."	$[\alpha]_D^{20}$ of natural acid.
—3.46°	—3.18°

The Titrations.—Samples of the "free acid" and of the natural acid were titrated with the following results.

	Weight of sample. G.	0.1 *N* NaOH for neutralization. Found. Cc.	Calc. Cc.
I	0.1533	22.91	22.83
II	0.1177	17.38	17.57
III	0.1671	24.77	24.94

The first and second titrations were made with the "free acid" and the third titration was made with the natural acid.

Summary.

dl-2,3-Dioxy-butyric acid from glycerol-α-monochloro-hydrine has been prepared. Proof of the structure of *dl*-2,3-dioxy-butyric acid is given by its preparation from vinyl-acetic acid, $CH_2 : CH.CH_2COOH$. The resolution of the *dl*-acid into the optical components by the use of brucine is reported. Configurations are assigned to the 2 forms of the acid and proofs of the correctness of these configurations given. The following specific rotations for the *d*- and *l*-forms of the acid and some of the derivatives are given.

	Free acid.	Barium salt.	Calcium salt.	Phenylhydrazid.
d-form	+8.00°	—1.48°	....	....
l-form	—8.29°	+1.48°	+2.47°	+1.71°

CHICAGO, ILLINOIS.

[Contribution from the Kent Chemical Laboratory, University of Chicago.]

THE PREPARATION OF OPTICALLY ACTIVE HYDRAZINES. I. THE PREPARATION OF *dl-p*-TRIMETHYLETHYL-PHENYLHYDRAZINE. THE ISOLATION OF PURE *d-p*-TRIMETHYLETHYL-ANILINE.

By J. W. E. Glattfeld and C. H. Milligan.[1]

Received July 19, 1920.

In connection with the preparation of the optically-active C_4-saccharinic acids undertaken in this laboratory it was found that success depended in each case on the ability to resolve the *dl*-acid into the components by means of optically-active alkaloids. Such separations are usually very tedious, require many recrystallizations, and sometimes leave one in doubt as to whether a complete separation has actually been effected. It has seemed highly desirable, therefore, to make available other reagents than the alkaloids for such work.

Phenylhydrazine is known to form with many oxy acids easily crystallizable compounds, the phenylhydrazids. Some of the homologs such as tolyl-hydrazine form at times even more easily crystallizable compounds. It was thought, therefore, that an optically-active phenylhydrazine might be a possible substitute for the alkaloids when the latter do not give good results or when there is any doubt as to the completeness of the resolutions.

A search in the literature of optically-active hydrazines disclosed the fact that only 3 such compounds have been prepared, namely, *d*-α-optically-active amyl-phenylhydrazine;[2] *l*-α-ethyl-menthylhydrazine,[3] and *l*-menthylhydrazine.[4] The few known derivatives of these substances indicated that they might be very helpful in work with the oxyacids.

None of the hydrazines mentioned above was available, however, and it was decided to attempt the preparation of a number of racemic phenylhydrazines, and the resolution of these into active isomers in the hope that in this work some fairly easily-prepared active hydrazine would be discovered which could be used as a reagent in the separation of the saccharinic acids to supplement the alkaloids.

The present paper is the report of an attempt to prepare the first pair of these hydrazines decided upon, namely, the active trimethylethylphenylhydrazines. The hydrazine in its *dl* form was prepared, but all

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[1] The dissertation of which this paper is a condensation was presented by C. H. Milligan as part fulfilment of the requirements for the degree of Doctor of Philosophy in the University of Chicago. The original dissertation is on file in the University library.

[2] *Ber.*, 38, 867 (1905).

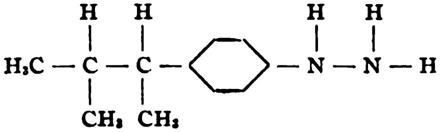
[3] *J. Russ. Phys. Chem. Soc.*, 27, 534 (1896).

[4] *J. prakt. Chem.*, II, 52, 425 (1895).

attempts to resolve it into the components failed, due largely, we think, to the instability of the free hydrazine in the air under ordinary conditions. The instability of the *dl* form suggested that the active components would also be very unstable and thus be useless as reagents. On the other hand, some of the derivatives of the *dl* form (see below) are perfectly stable compounds, and it was thought possible that the derivatives of the active forms would also be stable. We therefore decided to proceed with attempts to obtain the active forms. After much experimentation one of the amines, *d*-*p*-trimethylethyl-aniline, was obtained in the pure condition. It was intended to prepare from this the corresponding active phenylhydrazine by diazotization and reduction but time was lacking to complete this. This work will be continued, however, as soon as opportunity offers and attempts will be made to prepare other active phenylhydrazines.

Experimental Part.

This paper is a report on the preparation of *dl*-*p*-trimethylethyl-phenylhydrazine.



In order to prepare this substance, it was necessary first to prepare, in turn, the following corresponding compounds: (1)trimethylphenyl-ethylene; (2) trimethylethyl-benzene; (3) *p*-trimethylethyl-nitrobenzene; (4)*p*-trimethylethyl-aniline.

Only the second of these compounds is mentioned in the literature, under the name of *secondary*-amyl-benzene.[1] It seems probable in the light of our experiments, however, that the compound there discussed was *tertiary*-amyl-benzene.

For purposes of report, the work done and results obtained, will possibly be most easily followed if we discuss, in the order in which they are listed above, the preparation of the necessary compounds.

1. **Trimethylphenyl-ethylene.**—This compound was prepared from magnesium *iso*-propyl iodide and acetophenone by a modification of the method used by Klages[2] devised by Grignard.[3] The magnesium *iso*-propyl iodide was made in the usual way with all ordinary precautions by carefully dropping *iso*-propyl iodide into ether containing magnesium turnings. The ether was stirred constantly by a mechanical stirrer and kept cold. At the end of the reaction the solution was allowed to come to the temperature of the room and was then forced away from the re-

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[1] *Ann. Chim. phys.*, [6] 1, 434 (1884); *Monatsh.*, 9, 622 (1888).

[2] Klages, *Ber.*, 35, 2641 (1902); 33, 439 (1900).

[3] Grignard, *Compt. rend.*, 130, 1322 (1900).

maining magnesium turnings and into another flask properly fitted up and protected against moisture, etc.

Acetophenone was then carefully dropped into the solution with stirring. The end of the reaction was reached when the heat of reaction was not sufficient to keep the solution boiling. We found this condition to prevail after about $^1/_2$ the theoretical amount of acetophenone had been added. It had been found in preliminary experiments that further addition of acetophenone did not increase the yield and could be recovered unchanged. The mixture was then kept at the boiling temperature, with stirrer operating, for from 2 to 3 hours. The ether was then distilled off, after which the thick pasty residue was heated on the boiling water-bath for from 4 to 6 hours. The mass was then allowed to cool, the stirrer started and water carefully added from the dropping funnel. When all the mass had been completely hydrolyzed, the mixture was extracted 3 or 4 times with ether. The ether solution was dried with sodium sulfate and fractionated. The part which boiled between 175–200° was collected. This fraction weighed 125 g. when 100 g. of acetophenone was used.

In order to isolate the hydrocarbon in a pure state, this fraction (175–200°) was refractionated and the part which boiled at 187–188° collected. This fraction, in alcohol, was treated with phenylhydrazine, and the hydrazone of acetophenone, formed on standing, was removed by filtration. The filtrate was fractionated at 18 mm. pressure and the fraction of boiling range 75–95° was dissolved in a little dry ether and treated with dry hydrogen chloride to remove phenylhydrazine. The filtrate from the phenylhydrazine hydrochloride was subjected to repeated fractionation and gave finally 5.6 g. of a colorless liquid which boiled at 187–188°. The analysis of samples of this liquid showed that the compound thus prepared was not methyl-*iso*-propyl-phenyl-carbinol, but trimethyl-phenyl-ethylene.

Subs., 0.1167, 0.1217: CO_2, 0.3871, 0.3982; H_2O, 0.0989, 0.1032.

Calc. for $C_{11}H_{14}$: C, 90.35; H, 9.65. Found: C, 90.60, 90.70; H, 9.40, 9.44.

2. **Trimethylethyl-benzene.**—The next step was to reduce the unsaturated hydrocarbon to the saturated one. One hundred and twenty-five g. of the crude trimethyl-phenyl-ethylene (boiling range 175–200°) was treated, in a flask fitted with a wide reflux condenser, with 30 g. of red phosphorus and 50 cc. of a saturated solution of hydrogen iodide. The reaction mixture was heated to boiling and iodine added carefully in small portions through the condenser until fumes due to escaping hydrogen iodide were visible at the top of the condenser. The mixture was kept boiling until the color due to iodine in the hydrocarbon disappeared. The reaction mixture was now subjected to distillation. The distillate formed 2 layers of almost equal volume of which the lower was hydriodic acid, the upper almost pure hydrocarbon. The layers were separated, the hydriodic acid

returned to the reaction flask, and again distilled. This process was repeated as long as any hydrocarbon separated in the distillate.

The hydrocarbon was then washed with water and dil. sodium hydroxide solution and dried first by calcium chloride and finally over melted sodium which removed also the last trace of iodine, and then fractionated. That portion (40 g.) boiling at 180–190° was used for the subsequent preparations, a part being refractionated a number of times in order to get a pure product. The fraction boiling at 186–188° was considered pure.

Analysis of a sample of this product (186–188°) gave the following results:

Subs., 0.1688: CO_2, 0.5503; H_2O, 0.1602.

Calc. for $C_{11}H_{16}$: C, 89.12; H, 10.88. Found: C, 88.9; H, 10.69.

3. ***p*-Trimethylethyl-nitrobenzene.**—Forty g. of trimethylethyl-benzene boiling at 180–190° was dissolved in 24 g. of glacial acetic acid and added dropwise to a constantly stirred mixture of 40 g. of glacial acetic acid[1] and 88 g. of fuming nitric acid kept at 35–40°. After the addition, the contents of the flask were kept at 50° for 3 hours, cooled and poured into twice the volume of cold water. The nitro compound thus obtained was extracted with low-boiling ligroin, and the ligroin extract repeatedly shaken with water and finally with a small amount of sodium carbonate solution and then dried over sodium sulfate and fractionated. A yield of 46 g. of nitro compound, boiling range 140–155° at 20 mm. pressure, was obtained.[2] After a number of fractionations, this gave 30 g. boiling at 152–154° under 20 mm. pressure. This fraction was considered pure substance and was used for analysis and for the determination of the position of the nitro group.

Subs., 0.2147: CO_2, 0.5423; H_2O, 0.1508.

Subs., 0.2557, 0.2835: N_2, 18.2 cc. (29° and 737.4 mm.), 19.1 cc. (25° and 736.9 mm.).

Calc. for $C_{11}H_{15}NO_2$: C, 68.38; H, 7.80; N, 7.29. Found: C, 68.37; H, 7.8; N, 7.51, 7.44.

Position of the Nitro Group.—One g. of the compound was treated in the usual way[3] with 10 g. of chromic acid dissolved in 25 cc. of 5 *N* acetic acid. This mixture was allowed to stand for 24 hours on a steam-bath, and gave, after filtration, solution in sodium hydroxide and reprecipitation with hydrochloric acid, 0.7 g. of crude substance with melting range 228–230°. After recrystallization from water, the crystals had a

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[1] *Ann.*, 327, 224 (1903).

[2] From the fraction which had the boiling range 130–132° there was obtained a small amount of white crystalline solid which had a melting point of 114–115°. In repetitions of the nitration crystals of the same melting point were usually obtained from this fraction. The almost invariable production of this compound led to the conclusion that it was the *o*-nitro-compound,

[3] Weyl, "Die Methoden der Organischen Chemie," 1909, Vol. I, 518.

sharp melting point of 236°. A sample of *p*-nitrobenzoic acid at hand melted sharply at 236°. Furthermore a mixed melting-point determination proved the two to be identical. The compound oxidized, therefore, had the nitro group in the *para* position to the trimethylethyl group.

4. ***p*-Trimethylethyl-aniline.**—A mixture of 23 g. of the nitro compound, 36 g. of tin and 75 cc. of conc. hydrochloric acid was warmed to 100°, kept near this temperature, and very frequently shaken until the odor of the nitro compound had almost entirely disappeared. The remaining nitro compound was removed by steam distillation. The residue was made alkaline with sodium hydroxide, although a large excess of alkali is to be avoided. The aniline was extracted with low-boiling ligroin, dried over anhydrous sodium carbonate, and fractionated repeatedly at 18 mm. pressure. There was obtained finally 16 g. of a colorless oil of boiling range 129–131° at 18 mm. pressure.

That the substance was the pure aniline was proved by the analysis of samples for nitrogen.

Subs., 0.1853, 0.2225 g.: N_2, 14.5 cc. (22° and 736.6 mm.), 17.46 cc. (19° and 731.3 mm.).

Calc. for $C_{11}H_{17}N$: N, 8.57. Found: 8.76, 8.75.

5. ***dl-p*-Trimethylethyl-phenylhydrazine.**—This compound was made by a modification of the method of Fischer.[1] Fifteen g. of the aniline was diazotized, forming a gelatinous mass which was added in small amounts to a cold solution of sodium sulfite. A light yellow crystalline solid was obtained. The cold reaction mixture was treated with zinc dust and acetic acid until the yellow color had disappeared. The sulfonate thus obtained was filtered off, together with the excess of zinc dust, etc., and purified by crystallization from hot water, giving 19 g. of white plates which decomposed when heated to 190°.

The hydrochloride of the hydrazine was prepared by dissolving the sulfonate in a small amount of boiling water and passing hydrogen chloride into this hot solution. As the solution cooled, the hydrochloride crystallized out in rosets of fine white needles which were perfectly stable when dry.

The hydrochloride was dissolved in water and treated with sodium hydroxide. The solution was extracted with ether and the ether removed by distillation. The hydrazine separated out in fine needles as the residue cooled. This residue was subjected to distillation at 9 mm. pressure in an atmosphere of hydrogen. There was thus obtained 9 g. of a slightly yellow compound of boiling range 147–150° at 9 mm. which soon entirely solidified. The solid had a melting point of about 60°, and was soluble in alcohol, ligroin, benzene but less soluble in ether than in any of these. In contact with the air a part of this solid soon turned red and in the

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[1] *Ann.*, 190, 78 (1877).

course of a few hours liquefied. When this substance is kept in an atmosphere of hydrogen, decomposition takes place very slowly, if at all.

Samples of this solid were quickly weighed and analyzed, with the following results:

Subs., 0.2085, 0.0698 g.: N_2, 28 cc. (19° and 735.2 mm.), 14.9 cc. (28° and 730.25 mm.).

Calc. for $C_{11}H_{18}N_2$: N, 15.78. Found: 15.62, 15.66.

As stated above, it was found impossible to resolve the hydrazine into the optical components. Several attempts were made to do this and some data have been accumulated. It was shown, for instance, that the hydrazine reacts with the sugars to form hydrazones or osazones and that it reacts with oxyacids such as *l*-erythronic, *d*-mannonic and *d*-gluconic acids. From the study of these derivatives, however, it did not seem likely that the racemic hydrazine could be resolved completely by the use of such compounds although some evidence of resolution was obtained. The hydrazine forms a particularly stable and well-crystallizing compound, m. p. 160–163°, presumably the hydrazid, with *d*-galactonic lactone.

The Resolution of *dl*-*p*-Trimethylethyl-aniline.

The resolution was finally accomplished by the use of *d*-oxymethylene camphor[1] according to the method of Pope and Read,[2] as follows.

Sixteen and five-tenths g. of the aniline was dissolved in 25 cc. of 30% acetic acid and added slowly and with shaking to a solution of 17.5 g. of *d*-oxymethylene camphor in 70 cc. of methyl alcohol. The yellow oil which separated out as a lower layer was shaken a number of times with water, then dissolved in as small a quantity of boiling alcohol as possible and reprecipitated from the cold solution with water. The liquid was decanted after the pasty mass had settled out completely. The latter was stirred thoroughly with dil. sodium hydroxide solution then with water and finally taken up in a little alcohol, and placed in a vacuum desiccator over sulfuric acid. After having stood for 2 days, the residue was a semicrystalline mass weighing 30.9 g. The specific rotation of this—presumably a mixture of equal parts of the isomers—was found to be +257.5°.

Subs., 0.6922 in 15.68 g. of 95% alcohol gave in a 2 dcm. tube α +17.82.

The mass was now treated with ligroin until most of the gummy material was removed and there remained a slightly yellow solid, which, after having been thoroughly air-dried, weighed 18.9 g. and which had a melting range of 156–158°. This product was twice recrystallized from boiling alcohol, and was then perfectly white. It weighed 8.2 g. A portion of it was dissolved in 95% alcohol. The specific rotation of this solution was determined as +300°.

Subs., 0.6540 in 20 cc. of 95% alcohol gave in a 2 dcm. tube α +19.69° at 25–26°.

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[1] *Ann.*, **281**, 333 (1894).

[2] Pope and Read, *J. Chem. Soc.*, **95**, 171 (1909).

This product was recrystallized 3 times from alcohol. The specific rotation was taken after each recrystallization and always found to be +300°, indicating that the compound was pure. The product now melted sharply at 168°.

Pure *d*-*p*-Trimethylethyl-aniline.—Forty g. of the product obtained as indicated above was heated at boiling for 30 hours with 225 cc. of conc. hydrochloric acid and then cooled. The liquid was decanted from the solid and evaporated to dryness on a steam-bath. The total solid thus obtained was treated with 200 cc. of strong sodium hydroxide solution and subjected to steam distillation as long as any oil came over. The distillate was made acid and evaporated on the steam-bath, the aniline set free again and distilled with steam, this process being repeated several times in order to purify the aniline. There was finally obtained 11.6 g. of the hydrochloride. This was treated with an excess of sodium hydroxide solution, the aniline thoroughly extracted with low-boiling ligroin and the ligroin solution dried with sodium carbonate. The ligroin was removed by distillation and the residue distilled at 24 mm. pressure. The distillate had a boiling range of 139–140° and weighed 8.6 g. When placed in a one dcm. tube, this oil gave α +0.96°. The hydrochloride was prepared by dissolving the aniline in ligroin and passing in hydrogen chloride. An air-dry sample of the hydrochloride thus prepared had a specific rotation of +0.974.

Subs., 1.0294 in 20 cc. of water containing 3 drops of conc. hydrochloric acid, gave in a 2 dcm. tube α + 0.10.

l-*p*-Trimethylethyl-aniline.—We were unable to obtain the more soluble derivatives of the aniline with *d*-oxymethylene camphor in the crystalline condition. When the filtrates from the crystalline derivative were evaporated to dryness and dried over sulfuric acid *in vacuo*, a few more crystals of the less soluble isomer separated. These were removed by treatment of the mass with ligroin, in which the crystals did not dissolve. A gum was finally obtained which did not deposit crystals on standing in a vacuum over sulfuric acid for 10 days, $[\alpha]_D^{20}$ +229, in 95% alcohol. The aniline from this, obtained as above, boiled at 139–140° and gave α +0.76 when placed in a one dcm. tube. The hydrochloride gave $[\alpha]_D^{20}$ +0.565. These figures show that the aniline was not perfectly pure.

Summary.

dl-*p*-Trimethylethyl-phenylhydrazine, and *dl*-*p*-trimethylethyl-aniline have been prepared, some of their properties determined and the latter partly resolved into the two optical isomers. The hydrazine was prepared from acetophenone and magnesium-isopropyl-iodide and making, successively, trimethyl-phenyl-ethylene, trimethylethyl-benzene, *p*-trimethylethyl-nitrobenzene, *p*-trimethylethyl-aniline.

CHICAGO, ILLINOIS.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.]

THE CONDENSATION OF BENZOYL CHLORIDE WITH ETHYLENE IN THE PRESENCE OF ALUMINUM CHLORIDE.

BY JAMES F. NORRIS AND HENRY B. COUCH.

Received July 19, 1920.

In an endeavor to correlate the chemical reactions of hydrocarbons and to determine the factors which influence the activity of hydrogen atoms in organic compounds, the conclusion was drawn that unsaturated radicals and aryl radicals have approximately the same activating influence on certain hydrogen atoms in compounds containing these groups. The ability of a hydrogen atom joined to a carbon atom to enter into a condensation of a definite type is dependent on the nature of the groups with which the carbon atom is linked. These groups differ in weight, negativity, unsaturation, and form as represented by the stereo-chemical effect and chain or ring structure; and they differ, no doubt, in other respects not understood at present. It is highly probable that what is commonly called negativity is a factor of the greatest importance. A study of the effect of the change in the negativity of the substituting radicals in compounds of a definite type on the activity of the carbon-hydrogen bond has led to interesting results, and has suggested subjects for research which will throw additional light on the influence of structure on the chemical behavior of organic compounds.

The work described below was undertaken as a result of the fact that the vinyl and phenyl groups produce in compounds of different types the same general effect on the activity of certain atoms in these compounds. At present the best quantitative means of comparing the negativity of radicals is the ionization-constants of acids which contain these groups. The ionization-constant of benzoic acid is 6.6×10^{-5} and that of acrylic acid is 5.6×10^{-5}. These figures indicate that when the hydrogen atom in formic acid is replaced by a phenyl or a vinyl radical acids are obtained which differ but slightly in activity as measured by their ionization in water. If such activity is traceable to negativity the 2 radicals differ but slightly in this quality. A comparison of the reactions of a number of compounds containing a phenyl radical and analogous compounds containing a vinyl radical brought out the fact that the effect of these 2 groups was markedly similar. For example, vinyl bromide and phenyl bromide in many reactions behave alike. In both cases the halogen is relatively inactive towards reagents with which ethyl bromide and other saturated alkyl halides react. Again, the activity of the hydroxyl group in benzyl alcohol and that of the same group in allyl alcohol are strikingly alike in many respects. While methyl alcohol is not converted into methyl chloride in an open vessel by aqueous hydrochloric acid, benzyl alcohol,

$C_6H_5.CH_2OH$, and allyl alcohol, $CH_2 = CH.CH_2OH$, yield the chloride under these conditions. The activation produced by the 2 radicals, phenyl and vinyl, appear in this case to be similar.

From the above it appeared possible that a hydrogen atom in ethylene and one in benzene might show similar reactivity since in the first case the atom is linked to vinyl and in the second to phenyl. It seemed worth while to test this view. The most characteristic reaction of aromatic hydrocarbons is perhaps their ability to condense with acyl or alkyl halides in the presence of aluminum chloride. The Friedel-Crafts reaction has been applied almost exclusively to aromatic hydrocarbons and their derivatives. Accordingly, an attempt was made to condense benzoyl chloride with ethylene in the presence of aluminum chloride. Benzoyl chloride was chosen as it enters smoothly into condensations of the type to be studied and the compound expected, phenylvinyl ketone, had been previously prepared by other methods and its properties were known.

The condensation did take place and the product obtained had the properties of phenylvinyl ketone described by Tollens.

A search of the literature was made to determine if any reactions analogous to the above had been studied. A paper by Krapivin[1] was found in which a similar condensation between acetyl halides and unsaturated hydrocarbons was described. The reactions studied were those between acetyl bromide and propylene and trimethylene, and between acetyl chloride and *iso*-butylene, trimethylene, hexylene, heptylene, and octylene. In all cases one of the hydrogen atoms of the hydrocarbons was replaced by the acyl radical.

It seems highly probable from these results that unsaturated compounds containing a double bond can replace aryl hydrocarbons in the Friedel-Crafts synthesis. This preliminary paper is published now as the authors cannot continue the work in common. The study of the reaction will be continued, as it opens up a new synthetic method which will prove of great value in the preparation of unsaturated compounds. It can also be applied to the synthesis of saturated hydrocarbons and their derivatives on account of the fact that the double bond can be readily reduced by the methods now available. It appears possible to make by this synthetic method compounds the preparation of which was difficult or impossible by the methods now in use. The behavior of alkyl halides, acyl halides, and polyhalogen derivatives will be studied with unsaturated hydrocarbons, including those containing aryl radicals.

Other reactions more or less characteristic of aromatic hydrocarbons will be studied to determine whether ethylene and its derivatives show a

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[1] Krapivin, *Bull. soc. imp. nat. Moscou*, 1, 176 (1908); *Chem. Zentr.*, 1910, I, 335; *C. A.*, 5, 1281.

behavior analogous to such hydrocarbons. It is an interesting fact in this connection that phenyl ethylene yields a nitro compound of the structure $C_6H_5CH_2 = CHNO_2$ when treated with nitric acid. In this case the nitration takes place in the side-chain. The work which is being done is part of an investigation which has as its aim the determination of the factors which influence the activity of the carbon-hydrogen bond in organic compounds.

Experimental.

The condensation of ethylene with benzoyl chloride was effected by first preparing the compound of the latter with aluminum chloride in the presence of carbon disulfide, and passing the gas at room temperature slowly through the mass of crystals covered with the liquid.

A mixture of 25 g. of benzoyl chloride, 24 g. of anhydrous aluminum chloride, and 600 cc. of carbon disulfide was heated to boiling for 2 hours in a flask provided with a reflux condenser. On cooling, a mass of nearly colorless crystals separated. Ethylene dried by bubbling through conc. sulfuric acid was next passed to the bottom of the flask containing the carbon disulfide and the crystals of the molecular compound. The gas was absorbed very slowly. When 10 liters, which is about 2.5 molecules of ethylene to one of benzoyl chloride, had been passed through the mixture, the crystals had become covered with a dark, viscous liquid which interfered seriously with their coming into contact with the gas. The flask was then opened and the crystals crushed with a flattened glass rod. Ethylene was again passed through the mixture. Finally the reaction was stopped and the mixture poured onto ice. When the intermediate compound had decomposed the carbon disulfide was separated, poured through a dry filter-paper, and distilled. The residue was distilled with steam when an oil of characteristic sharp odor passed over along with some benzoic acid. On cooling the contents of the flask a large amount of benzoic acid crystallized out. This fact indicated that the reaction had not been complete. The oil volatile with steam was shaken with a dilute solution of sodium hydroxide and taken up with ether. On the evaporation of the solvent a pungent oil was obtained.

Moureau[1] describes a compound as phenylvinyl ketone which he obtained by condensing the chloride of acrylic acid with benzene in the presence of aluminum chloride. The compound is slightly soluble in water from which it crystallizes at 4° to 5° in needles which melt at 42°, and forms a phenylhydrazone which melts at 130°.

Later Van Marle and Tollens[2] and Schafer and Tollens[3] describe as phenylvinyl ketone a compound which possessed properties different

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[1] Moreau, *Ann. chim. phys.*, [7] 2, 199 (1894).

[2] Van Marle and Tollens, *Ber.*, 36, 1355 (1903).

[3] Schafer and Tollens, *ibid.*, 39, 2187 (1906).

from those of the compound isolated by Moureau. According to Tollens the ketone is a yellow oil, which could not be obtained as crystals. It had a characteristic, pungent odor and polymerized rapidly to a very viscous resin. The phenyl-hydrazone prepared from the oil was obtained in well-defined yellow crystals, which melted at 152–153° and gave a greenish blue fluorescent solution in alcohol.

The compound prepared by us possessed all the properties described by Tollens. The phenylhydrazone was prepared as follows. About 1.5 cc. of the oil was dissolved in 7 cc. of alcohol and treated with 2 cc. of freshly distilled phenylhydrazine. The mixture was heated on the steam-bath for half an hour. The crystals which separated were recrystallized from boiling alcohol. The compound, which was obtained in long, fine needles of a canary-yellow color, melted at 151° (uncorr.). The alcoholic solution of the phenylhydrazone showed a beautiful greenish blue fluorescence at the surface of the liquid.

A solution of the oil in carbon tetrachloride decolorized bromine rapidly; in a short time hydrobromic acid was evolved. The oil slowly changed to a wax-like mass; this occurred more rapidly when it was allowed to stand overnight in the presence of water.

The yield of the ketone obtained was about 25%; but it is highly probable that this could be markedly increased under better experimental conditions. There did not appear to be side reactions taking place in appreciable amounts, although a small quantity of a product insoluble in carbon disulfide was obtained. The main difficulties to overcome are to increase the rate of the absorption of the gas and to prevent the enclosure of the crystals of the addition-product of benzoyl chloride and aluminum chloride by the viscous reaction-product. The condensation will be studied more fully.

Summary.

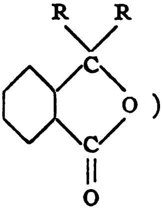
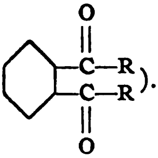
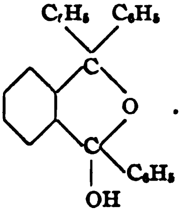
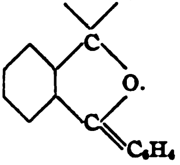
On account of the similarity in the chemical behavior of elements joined to the vinyl and to the phenyl radicals an attempt was made to condense ethylene with benzoyl chloride by means of aluminum chloride. Phenylvinyl ketone was prepared in the same way.

[Contribution from the Chemical Laboratory of The Rice Institute.]

THE REACTION BETWEEN PHENYL-MAGNESIUM BROMIDE AND THE ESTERS OR ANHYDRIDE OF PHTHALIC ACID.

By Lloyd B. Howell.

Received July 26, 1920.

It is the commonly accepted fact that the so-called Grignard reagents, R–Mg–X, react with esters to give tertiary alcohols. But an examination of the literature concerning the condensation between the Grignard reagents and certain derivatives of phthalic acid, *viz.*, the methyl and ethyl esters and the anhydride, shows some discrepancies. All workers agree that the product of the reaction of 2 moles of a magnesium alkyl, or aryl, halide and phthalic anhydride, or phthalic esters, is a mixture[1] of a phthalide (general formula, ) and an *ortho* diketone (general formula, ). The reaction of Grignard reagents in yet higher molecular quantities, however, has been variously reported. In 1905 and 1906, Guyot and Catel[2] showed that phenyl-magnesium bromide in excess (over 3 moles) acted normally upon dimethyl phthalate, or phthalic anhydride, to give the tertiary alcohol triphenyl-hydroxy-α,α'-benzo-β,β'-dihydro-furfurane, . But in 1909 Shibata[3] reported that excess of the same Grignard reagent, reacting with diethyl phthalate, produced a phthalan derivative of the structure,  Shibata

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[1] *Ber.*, 38, 240 (1905).

[2] Guyot and Catel, *Compt. rend.*, 140, 254 (1905); *Bull. soc. chim.*, [3] 35, 554 (1906).

[3] Shibata, *J. Chem. Soc.*, 95, 1449 (1909).

for some reason failed to give any recognition to the previous work of Guyot and Catel and made the statement that no tertiary alcohol was formed, but instead, the dehydration product shown above. Both the French and Japanese workers claimed that a large excess of phenyl-magnesium bromide must be employed, and the latter claimed that it was this excess which brought about the dehydration of the expected product.

It has been found that the differences in the results obtained were due to the various methods of isolation employed. Guyot and Catel, after making the condensation between dimethyl phthalate and phenyl-magnesium bromide and hydrolyzing the product in the usual manner, crystallized their product from the ether or benzene solution. The solid obtained melted at 118°. Shibata made the condensation with the diethyl ester in practically the same manner, but found it necessary to isolate the product by distillation under diminished pressure after impurities had been expelled by distillation with steam. His product had a melting point of 194°.

The preparation of triphenyl-hydroxy-α,α'-benzo-β,β'-dihydro-furfurane from either dimethyl or diethyl phthalate has been found possible. It can be made also from phthalic anhydride, although with more difficulty. Furthermore, it has been shown that the compound of Shibata can be prepared from either the dimethyl or the diethyl ester. Moreover, it is found that if the tertiary alcohol obtained by Guyot and Catel be heated to a temperature required for distillation under diminished pressure (280° to 300°) it is dehydrated and yields the compound which was obtained by Shibata.

In the isolation of the triphenyl-hydroxy-α,α'-benzo-β,β'-dihydro-furfurane much difficulty is commonly experienced. Even if crystallization is attempted after driving off such volatile impurities as benzene, bromobenzene or diphenyl, an amorphous jelly or a glass-like mass is apt to be the only result. This was found to be true in many trials. In one case crystals failed to form in the viscous mother liquor until it had stood for over 2 years, notwithstanding the use of all ordinary means of starting such processes. When a few crystals have been obtained and purified, the process of "seeding out" is very advantageous. It was no doubt because of such discouraging results, not mentioned by Guyot and Catel, that Shibata had recourse to distillation.[1]

Experimental Part.

1. **Preparation of Triphenyl-hydroxy-α,α'-benzo-β,β'-dihydro-furfurane from Diethyl Phthalate.**—In a 1000-cc. round-bottom flask provided with an efficient reflux condenser, 19.2 g. (8 moles) of dry magnesium turnings, covered by a large excess of anhydrous and alcohol-free ether, was slowly treated with 125.6 g. (8 moles) of dry monobromo-

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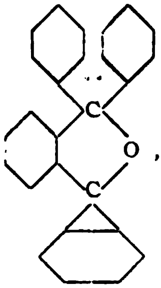
[1] Professor Roger Adams, of the University of Illinois, has called the attention of

benzene. After the resulting "Grignard" solution had been refluxed for $^1/_2$ hour it was cooled and 23 g. (one mole) of freshly prepared diethyl phthalate in 50 cc. of anhydrous and alcohol-free ether was added very slowly from a separatory funnel (total time, one hour) while the mixture was shaken constantly and the flask was cooled by ice-water. Each addition caused a yellow solid to form, but this dissolved instantly in the ether. The solution gradually darkened from yellow to brown.

When the condensation was complete, the magnesium-ether complex was hydrolyzed as usual, by pouring it into slightly more than the calculated amount of hydrochloric acid dissolved in a large volume of well iced water while the solution was stirred. The ether was then removed, dried over anhydrous sodium sulfate for a few hours, then decanted and allowed to evaporate spontaneously in a loosely covered dish. The ether solution thus obtained passed through a remarkable series of color changes. At first it was light orange in color and fluorescent. Then it changed in 12 hours to a deep purple hue and finally, after 24 hours, the color faded to reddish-purple with a remarkable green fluorescence.

When practically all of the ether had evaporated, the resulting viscous yellow oil was allowed to stand for several weeks. After about a month, slow crystallization commenced. From time to time the crude crystals were separated from the semi-fluid, jelly-like mass, washed with a trace of ether on a porous plate and allowed to stand overnight in a thin layer. When, subsequently, they were recrystallized twice from a mixture of equal volumes of toluene and chloroform, they gave a sharp melting point of 118° (corr.). From nearly all other common solvents, such as ether, alcohol, acetone and benzene, the material failed to emerge in crystalline condition but reverted to the original jell or amorphous glassy mass.

2. Preparation of a Compound ($C_{26}H_{18}O$ m. p. 192-3°) from Dimethyl Phthalate.—The Grignard reagent (slightly more than 5 moles) was

the writer to the fact that the structure, , assumed for the product by Shibata, involves the peculiarity of a 3-membered ring and a 6-membered (aromatic) ring with one side in common. Such a structure is entirely unprecedented elsewhere in the literature, and work undertaken at both the University of Illinois and The Rice Institute, indicates the possibility of an entirely different structure for the dehydration product of triphenyl-hydroxy-α,α'-benzo-β,β'-dihydro-furfurane.

prepared as described above with 12.8 g. of magnesium turnings and 83.7 g. of monobromo-benzene. This product was condensed with 18 g. (one mole) of freshly prepared dimethyl phthalate in a manner similar to that used with the diethyl ester.

To isolate the product after hydrolysis, the oil obtained from the ether was transferred at once to a large flask and distilled in a slow current of steam until about 5 liters of distillate (water, some bromo-benzene, benzene and diphenyl) had passed over. The deep yellow oil, after it cooled, set to a dark and brittle cake. It was broken up and subjected to distillation under 26 mm. pressure in a 50-cc. Claisen flask. The dark oil "bumped" badly, and distilled, with violent foaming, between 290° and 300°. The distillate showed little tendency to crystallize when cold, but it was found that the addition of a little ether was very effective in causing crystallization to start.

After the crude light-brown product was crushed and "worked" with a little ether on a porous plate, it was recrystallized 3 times from toluene. The crystals were nearly white (slightly grayish) and melted sharply at 192–193° (stem immersed).

This compound was identified as that prepared by Shibata, by a mixed m. p. determination with analyzed material made from diethyl phthalate according to his procedure.

3. Dehydration of Triphenyl-hydroxy-α,α'-benzo-β,β'-dihydro-furfurane upon Heating.—A few g. of recrystallized triphenyl-hydroxy-α,α'-benzo-β,β'-dihydro-furfurane was slowly heated under reduced pressure (26 mm.) in a Wood's metal bath. The crystals melted to yield a colorless oil at 119°. This oil slowly darkened to a yellow color at 160°, to deep yellow with a green fluorescence at about 170°, to red-brown at 200° and to dark amber, with fluorescence persisting, above 350° (temperature of bath). The bath was then heated slowly to nearly 400°, while the behavior of the oil was closely watched. When the temperature of the vapor had reached 280° (uncorr.), a very noticeable condensation of moisture occurred in the cool parts of the apparatus. No moisture had previously been evident in the apparatus. At 295°, distillation of a pale greenish-yellow fluorescent liquid began.

At this stage, the heating was discontinued, the residue in the flask was cooled and removed as a coarse dark-brown crystalline powder. It was dissolved in toluene and crystallized. The crude product thus obtained was freed from oily impurities by pressing it on a clay plate and then recrystallized twice from toluene and dried at 130° for 2 hours. The crystals were nearly pure white, and melted at 192–193°.

Subs., 0.1618: CO_2, 0.5305; H_2O, 0.0781.

Calc. for $C_{26}H_{18}O$: C, 90.17; H, 5.24. Found: C, 89.36; H, 5.36.

Summary.

1. The reaction of an excess of phenyl-magnesium bromide upon the methyl or ethyl ester of phthalic acid gives a mono-hydric tertiary alcohol which is a derivative of furfurane.

2. If the product of the reaction of an excess of phenyl-magnesium bromide upon the esters of phthalic acid is heated to about 300°, it loses a molecule of water and gives the compound $C_{26}H_{18}O$ of m. p. 192–193° which Shibata[1] claimed to be a derivative of phthalan and the direct product of the original condensation.

HOUSTON, TEX.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY.]

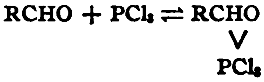
ADDITION REACTIONS OF PHOSPHORUS HALIDES. I. THE MECHANISM OF THE REACTION OF THE TRICHLORIDE WITH BENZALDEHYDE.

BY JAMES B. CONANT AND ALEXANDER D. MACDONALD.

Received August 11, 1920.

I. Introduction.

It has been shown in a previous paper[2] that phosphorus trichloride adds to the ends of the conjugated system of certain unsaturated ketones. This addition takes place with an increase in valence of the phosphorus atom from 3 to 5. The chlorine atoms in the addition product are very active and are readily replaced by hydroxyl or oxygen when the reaction mixture is treated with acetic acid or acetic anhydride. The product thus formed is a phosphonic acid or an intermediate cyclic compound. An exactly similar reaction takes place when simple aldehydes or ketones are treated with phosphorus trichloride. In this case, however, the primary addition product is formed by the 1,2-addition of the phosphorus atom.



$$\mathrm{RCHO} + \mathrm{PCl_3} \rightleftharpoons \underset{\substack{\vee \\ \mathrm{PCl_3}}}{\mathrm{RCHO}}$$

(I).

Benzaldehyde was chosen as a suitable aldehyde for studying the mechanism of this reaction and only the results obtained with this substance are presented here. The reaction, however, takes place readily with most aldehydes and ketones and the limits of the reaction will be discussed in a subsequent paper.

The Primary Reversible Reaction.

When benzaldehyde and phosphorus trichloride are brought together considerable heat is evolved and the addition reaction (Equation I) proceeds to a definite equilibrium. If equimolecular amounts of the 2 sub-

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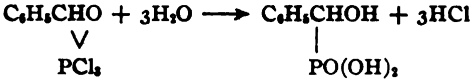
[1] *Loc. cit.*

[2] THIS JOURNAL, 42, 830 (1920).

stances are employed, only about 30% of the addition product is formed On treating such a reaction mixture with water both the unused trichloride and the addition product react vigorously. The former produces phosphorous acid, the latter an α-hydroxy-phosphonic acid as the final product.



$$\underset{\underset{PCl_3}{\vee}}{C_6H_5CHO} + 3H_2O \longrightarrow \underset{\underset{PO(OH)_2}{|}}{C_6H_5CHOH} + 3HCl$$

The amount of phosphorous acid thus formed can be determined by cautiously oxidizing it to phosphoric acid and precipitating it in the usual manner with magnesia mixture. The hydroxy phosphonic acid does not produce a precipitate under the same conditions. The amount of trichloride in the equilibrium mixture can thus be easily ascertained.

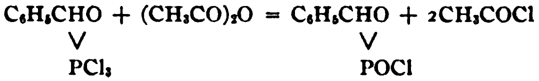
Quantitative experiments of this sort were performed with varying ratios of the 2 substances and also with varying amounts of an inert solvent (benzene). The equilibrium constant

$$K = \frac{[C_6H_5CHO][PCl_3]}{V[C_6H_5CHOPCl_3]}$$

could thus be calculated from the concentration as determined in each experiment. Samples taken from time to time showed that a condition of equilibrium was usually reached in the course of 28 hours. The values of K for 7 different experiments varied from 6.9 to 8.3; the average was 7.4. The initial concentrations of the reacting substances were varied over wide limits in the different experiments. The values for K are constant within the experimental errors of the method. They clearly show that *the primary addition reaction is reversible* and can be expressed in terms of the usual law of mass action.

Intermediate Products Containing a Phosphorus Oxygen Ring.

The addition product reacts with acetic anhydride and, as in the case of the unsaturated ketones,[1] the products are acetyl chloride and a mixture of an acid chloride (I) and an anhydride (II). Phosphorus trichloride reacts very slowly with acetic anhydride below 50°, the primary addition compound reacts rapidly. The equilibrium of the initial addition reaction is thus upset by the removal of the product and the entire set of reactions proceed to completion. When a large excess of acetic anhydride is used, most of the acid chloride first formed is converted into the acid anhydride. These reactions are represented by the following equations.



$$\underset{\underset{PCl_3}{\vee}}{C_6H_5CHO} + (CH_3CO)_2O = \underset{\underset{POCl}{\vee}}{C_6H_5CHO} + 2CH_3COCl$$

(I).

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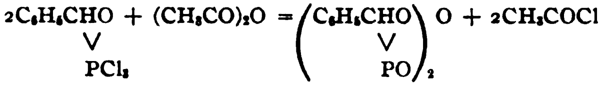
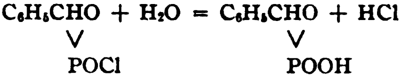
[1] *Loc. cit.*



$$2\underset{\underset{\textstyle PCl_3}{\vee}}{C_6H_5CHO} + (CH_3CO)_2O = \left(\underset{\underset{\textstyle PO}{\vee}}{C_6H_5CHO}\right)_2 O + 2CH_3COCl$$

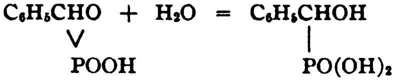
(II).

The mixture of the acid chloride and anhydride is left as a gum after the evaporation of the acetyl chloride and the excess of acetic anhydride. This gum, when treated with water, yields hydrochloric acid and a monobasic acid containing a phosphorus oxygen ring. The amount of chloride ion thus formed is a measure of the relative amount of acid chloride (I) in the mixture.



$$\underset{\underset{\textstyle POCl}{\vee}}{C_6H_5CHO} + H_2O = \underset{\underset{\textstyle POOH}{\vee}}{C_6H_5CHO} + HCl$$

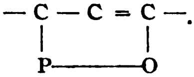
This ring acid was isolated in the form of an insoluble barium salt. Its structure follows from the fact that it is a monobasic acid which, on boiling with water, is converted into the hydroxy-phosphonic acid.



$$\underset{\underset{\textstyle POOH}{\vee}}{C_6H_5CHO} + H_2O = \underset{\underset{\textstyle PO(OH)_2}{|}}{C_6H_5CHOH}$$

It reduces potassium permanganate solution slowly, whereas the hydroxyphosphonic acid is oxidized immediately by the same reagent. This difference would, of course, be expected from the structure of the 2 compounds. The isolation of this acid proves that the fundamental process in the interaction of benzaldehyde and phosphorus trichloride is *the 1,2-addition of the phosphorus atom to the carbonyl group.*

Hitherto no acid containing a phosphorus oxygen ring has been reported. It is suggested that the name "phostonic" be applied to the general class of such acids from their obvious similarity to lactonic acids. The individual substances are named in this article, however, as inner esters by prefixing anhydro-; the acid in question is thus anhydro-α-hydroxybenzylphosphoric acid.

It is interesting to compare the stability of the phosphorus oxygen ring in this acid with the stability of the ring in the intermediate products obtained from unsaturated ketones. In the case of the unsaturated ketones it was shown that the intermediate products contained the 5-membered unsaturated ring:  $-\underset{\underset{\textstyle P}{|}}{C}-C=\underset{\underset{\textstyle O}{|}}{C}-$. This ring was so easily opened by water and acid that only the anhydride and acid chloride could be obtained. The phostonic acid, however, is only slowly converted into the hydroxyphosphonic acid by boiling with pure water. The reaction is accelerated in aqueous solution by mineral acids. In acetic acid the ring is opened rather slowly by hydrogen chloride. The difference between these 2 rings is thus very great and is an exception to the usual belief in regard to the greater stability of 5-membered rings. This may be due, of course, to the fact that one ring contains an ethylene linkage and the other does not.

The Reaction in Glacial Acetic Acid.

Fossek[1] prepared a number of hydroxy-phosphonic acids by treating phosphorus trichloride with a large excess of an aldehyde or ketone and decomposing the resulting oil with water. He suggested no mechanism for the reaction[2] but clearly showed that his products were α-hydroxy-phosphonic acids. The necessity of employing a large excess of one of the substances is now obvious. Since water was used to decompose the reaction mixture there was obtained only an amount of phosphonic acid corresponding to the equilibrium of the initial reaction; by the use of the large excess of aldehyde, the reaction was forced as far to the right as possible. It is possible to complete the reaction with equimolecular amounts by the use of acetic anhydride for the reasons given above. To obtain the hydroxy-phosphonic acid, the product, of course, must be boiled with water to decompose the intermediate phostonic acid.

Glacial acetic acid also reacts more rapidly with the addition product than with the trichloride. However, since the trichloride reacts rapidly with acetic acid on warming, it is necessary to work below 35° and it is best to allow the 2 compounds to react and then add the acid. Here also the phostonic acid is formed as in the case of acetic anhydride. If the reaction mixture is allowed to stand for several days this is slowly converted into the hydroxy-phosphonic acid. Saturation of the mixture with hydrogen chloride hastens the process. This reaction proceeds probably through the formation of the acid chloride of the hydroxy-phosphonic acid, which then reacts with the acetic acid.

$$\begin{array}{c} C_6H_5CHO \\ \vee \\ POOH \end{array} + HCl \longrightarrow \begin{array}{c} C_6H_5CHOH \\ | \\ POCl(OH) \end{array} \longrightarrow \begin{array}{c} C_6H_5CHOH \\ | \\ PO(OH)_2 \end{array}$$

If the mixture is poured into water and the solution evaporated to dryness the conversion is rapid and complete. This is the most satisfactory method of preparing the hydroxy-phosphonic acid. Good yields can be obtained without using an excess of either of the 2 substances. As the hydroxy-phosphonic acid is very soluble in water it is somewhat hard to isolate in a pure condition. It was found that an aniline salt of the acid could be readily prepared in ether solution and was easily recrystallized from alcohol. By the use of this salt the acid can be quickly and conveniently isolated.

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[1] Fossek, *Monatsh.*, 5, 120, 627 (1884); 7, 121 (1886).

[2] Michaelis, *Ber.*, 18, 899 (1895); *ibid.*, 3, 1297 (1901), referring to Fossek's work suggested that an intermediate ring compound is first formed in this and similar cases.

II. Experimental.

Equilibrium Measurements.

A mixture of 5.0 g. of benzaldehyde (4.78 cc.) and 6.48 g. of phosphorus trichloride (4.06 cc.) was placed in a tightly stoppered Erlenmeyer flask and allowed to stand at room temperature (25°). One-cc. samples were removed by a pipet at intervals and introduced into 50 cc. of distilled water; the whole was then shaken vigorously. The aqueous solution was extracted with two 20-cc. portions of benzene to remove unchanged benzaldehyde and then heated on the steam-bath for a few minutes to remove any traces of benzene. Bromine water was added a little at a time to the solution after it had been cooled to room temperature. The phosphorous acid formed by the interaction of the trichloride and water was thus oxidized to phosphoric acid; the addition or bromine water was continued until a permanent color was produced. Magnesia mixture was now added and the magnesium ammonium phosphate allowed to precipitate in the usual way. The precipitate was filtered, washed, and ignited to constant weight. Parallel experiments with pure hydroxybenzyl phosphonic acid showed that it did not produce a precipitate under these conditions. Similar experiments were performed with various proportions of the 2 substances and also with the reaction mixture diluted with anhydrous benzene to 25 cc., 50 cc., 75 cc., and 100 cc., respectively.

TABLE I.—VALUES OF *K* FROM THE FINAL MEASUREMENTS.

Expt.	Mols. of C_6H_5CHO. *a*.	Mols. of PCl_3. *b*.	$Mg_2P_2O_7$ equiv. to PCl_3 in 1 cc. G.	Actual wt. $Mg_2P_2O_7$ at equil. G.	Fract. of PCl_3 reacted. *y*.	*V* in Liters.	*K*.
1.........	0.0472	0.0472	0.595	0.412	0.308	0.00884	8.3
2.........	0.0472	0.0944	0.817	0.646	0.209	0.0129	8.0
3.........	0.0944	0.0472	0.387	0.221	0.429	0.0136	7.3
4.........	0.0944	0.0944	0.422	0.305	0.277	0.025	7.1
5.........	0.0944	0.0944	0.211	0.173	0.182	0.050	6.9
6.........	0.0944	0.0944	0.141	0.123	0.129	0.075	7.4
7.........	0.0944	0.0944	0.1055	0.094	0.109	0.100	6.9
						Average,	7.4

TABLE II.—COURSE OF THE REACTION.

Expt.	$Mg_2P_2O_7$ equiv. to PCl_3 in 1 cc.	Weights of $Mg_2P_2O_7$ (*W*) formed and fract. of PCl_3 reacted (*y*). *W*.	*y*.	*W*.	*y*.	*W*.	*y*.
		3 hours.		28 hours.			
1.....	0.595	0.433	0.272	0.412	0.308		
2.....	0.817	0.670	0.180	0.646	0.209		
3.....	0.387	0.279	0.279	0.221	0.429		
		47 hours.		71 hours.		122 hours.	
4.....	0.422	0.338	0.199	0.318	0.246	0.305	0.277
5.....	0.211	0.179	0.151	0.176	0.166	0.173	0.182
6.....	0.141	0.123	0.129	0.120	0.147	0.123	0.129
7.....	0.106	0.097	0.076	0.094	0.109	0.094	0.109

The results obtained are summarized in Tables I and II. Table I shows the values for K calculated from the final measurements; Table II, the course of the reaction to the final equilibrium. The amount of magnesium pyrophosphate equivalent to the trichloride initially present in one-cc. of the reaction mixture could be calculated from the quantity of materials used and the total volume. The difference between this value and the magnesium pyrophosphate actually weighed represents the amount of trichloride which had formed the addition product. The ratio of this difference to the initial amount is obviously the fraction of the trichloride reacted. If we represent this fraction by y, and the initial quantities (in mols.) of C_6H_5CHO by a and of trichloride by b, the quantity of the addition product is yb. The equation for K can then be written as follows, where V equals the volume in liters of the reaction mixture.

$$K = \frac{(a - yb)(b - yb)}{Vyb}.$$

This method of determining K is obviously not very accurate and the values obtained vary considerably. Nevertheless they are sufficiently constant to indicate the fundamental fact, namely, that the reaction under investigation comes to a definite equilibrium which is determined by the factors expressed in the usual law of mass action. Similar results were obtained earlier in the research by a different method. The re-reaction mixture was decomposed with water and the amount of unchanged benzaldehyde was determined by measuring its volume in a specially constructed pipet somewhat similar to that used in the Babcock method for determining fat in milk. These approximate values showed that the reaction came to an equilibrium in 2 to 3 hours (no solvent was employed, so that the experiments were parallel to No. 1 in the tables). The fraction of benzaldehyde which reacted was 0.35 as compared with 0.30 determined by weighing the magnesium pyrophosphate.

Reaction in Acetic Anhydride.

A mixture of the acid chloride and anhydride of the phostonic acid was prepared bv the interaction of phosphorus trichloride, benzaldehyde, and acetic anhydride. A typical experiment follows. 10 g. of benzaldehyde (0.094 mol.), 13 g. of trichloride (0.094 mol.), and 20 g. of acetic anhydride (0.20 mol.) were mixed in a 150-cc. distilling flask provided with a calcium chloride tube. The color of the mixture became pink and the temperature rose somewhat, but was kept below 40°, by cooling the flask with water. The mixture was allowed to stand overnight at room temperature. The contents of the flask were evaporated at a pressure of 50–60 mm. at 50° for 2 hours. A viscous resin weighing 22 g. was left. This resin was soluble in chloroform, but no crystalline solid could be obtained from it. By making the chloroform solution of a known volume and taking definite amounts of it for various experiments, all the results could be calculated on the basis of the entire weight of materials employed.

Five such experiments were performed with various amounts of acetic anhydride. The proportion of acid chloride in the resulting mixture was determined in a typical experiment as follows. Two cc. of the chloroform solution of the resin (total vol. =48 cc.) was evaporated to dryness and the residue dissolved in water. This solution was then acidified with nitric acid and titrated against 0.2 *N* silver nitrate according to Volhard's method. Equivalent of chloride ion found = 0.000234, calculated for the acid chloride = 0.00391; therefore, the resin is 6% acid chloride. The experiments may be summarized as follows. Equimolecular amounts of benzaldehyde and trichloride were used in each experiment.

TABLE III.

Mols. of acetic anhydride per mol. of benzaldehyde.	Acid chloride in resin. %.
1.0	45
1.0	39
1.5	28
1.5	26
2.0	6

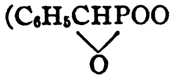
Increasing the amount of acetic anhydride decreases the amount of acid chloride; this latter substance evidently reacts with the acetic anhydride to form acetyl chloride and the anhydride of the phostonic acid.

Aniline Salt of Hydroxybenzyl Phosphonic Acid, $C_6H_5CHOHPO(OH)ONH_3C_6H_5$.—A portion of the resin obtained in each of the 5 experiments just mentioned was converted into the aniline salt of hydroxy benzylphosphonic acid. For example, 5 cc. of the chloroform solution (total vol. = 48 cc.) was evaporated and the residue boiled with water for several hours and evaporated to dryness. The somewhat gummy residue of hydroxy-phosphonic acid was dissolved in a little alcohol and the solution diluted with 3 times its volume of ether. A slight excess of an ethereal solution of aniline was added. A voluminous white precipitate formed at once and was filtered off, washed with a mixture of ether and alcohol and dried. Weight 2.3 g., which is equivalent to 22.1 g. for the entire mixture, or 84.5% of the calculated yield from 0.094 mol. of aldehyde, which is 26.4 g. Similar yields were obtained in the other 4 experiments. The resin was thus shown to be an intermediate stage in the formation of the hydroxy-phosphonic acid.

The aniline salt of hydroxybenzyl phosphonic acid could be recrystallized from alcohol. It melted with decomposition at 201–202°.

Calc. for $C_{13}H_{16}O_4NP$: N, 5.0. Found: 5.1.

The pure acid could be obtained from the salt as follows. Five g. was decomposed with 150 cc. of 5% solution of sodium hydroxide and the mixture distilled with steam until no more aniline came over. The residual solution was cooled, neutralized with acetic acid, and an excess of lead acetate added. A heavy white precipitate of the lead salt formed; this was filtered, washed with water, suspended in 200 cc. of water and decomposed with hydrogen sulfide. The lead sulfide was filtered off and the filtrate evaporated to dryness. 2.9 g. of hydroxybenzyl phosphonic acid, m. p. 170–172°, was thus obtained. This acid was identical with material obtained from the reaction in acetic acid (see below) and recrystallized from dil. hydrochloric acid. It is identical in its properties with the substance prepared by Fossek.[1]



Barium Salt of Anhydro-α-hydroxy-benzyl Phosphonic Acid, $(C_6H_5\underset{\diagdown O \diagup}{CHP}OO)_2Ba$.—20 g. of benzaldehyde, 26 g. of phosphorus trichloride, and 29 g. of acetic anhydride were mixed in a 150 cc. distilling flask and allowed to react as described in the previous experiments. After standing for 2 days at room temperature the mixture was evaporated under diminished pressure at a temperature of 40–45°. Forty g. of resin was thus obtained. Twenty-seven g. of this resin was dissolved in 250 cc. of water by very gentle warming and stirring. The cooled solution was treated with the calculated quantity of barium hydroxide (20 g.) dissolved in 250 cc. of water. A white precipitate was formed. The solution was now made barely alkaline to litmus with ammonium hydroxide; the precipitate increased in amount. The solution was filtered and the precipitate washed with water and dried. The yield was 18.8 g., which is 63% of the amount theoretically possible calculated from the amount of resin taken and the benzaldehyde initially employed.

Samples of barium salt thus prepared were dried to constant weight at 110° and analyzed for barium and phosphorus. They were found, however, to be contaminated with barium phosphate. The phosphoric acid was undoubtedly produced by a side reaction between the trichloride and the acetic anhydride. The amount of phosphate present was determined and the analyses corrected for it. A sample of the salt was heated with dil. hydrochloric acid on the steam-bath until a clear solution was obtained. Magnesia mixture was added to the cooled solution and the magnesium ammonium phosphate precipitated by making the solution alkaline with ammonia in the usual way. The precipitate was contaminated with barium and was redissolved in nitric acid and the phosphate precipitated with ammonium molybdate. The ammonium phosphomolybdate was filtered, redissolved, and the phosphate precipitated as

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[1] *Loc. cit.*

magnesium ammonium phosphate and ignited and weighed as the pyrophosphate.

Subs. (I), 0.3807, 0.3011: $BaSO_4$, 0.2064, 0.1633; $Mg_2P_2O_7$, 0.1611, 0.1238.
Subs., 0.3400, analyzed as above for phosphate: $Mg_2P_2O_7$, 0.0111.
Subs. (II), 0.3427, 0.3437: $BaSO_4$, 0.1910, 0.1922; $Mg_2P_2O_7$, 0.1453, 0.1489.
Subs., 0.3253, analyzed for phosphate: $Mg_2P_2O_7$, 0.0120.

%.	Calc. for $C_{14}H_{12}O_6BaP$.	Found: Uncorrected.				Corrected for phosphate.			
		I.		II.		I.		II.	
Ba	28.9	31.9	31.9	32.8	32.9	28.7	28.7	29.2	29.4
P	13.0	11.8	11.9	11.8	12.1	12.1	12.1	12.1	12.4

The barium salt of anhydro-α-hydroxy-benzyl phostonic acid is a white powder only slightly soluble in water, but readily soluble in dilute acids. It could not be recrystallized successfully. As would be expected from its structure, the salt is only very slowly oxidized by potassium permanganate solution. A comparison of the rate of oxidation of this compound and the neutral barium salt of hydroxy-phenyl phosphonic acid was made by shaking 0.1 g. of the solids with 10 cc. of a very dilute pernamganate solution made slightly acid with sulfuric acid. The permanaganate color disappeared in 5 minutes in the case of the hydroxy-phenyl phosphonic salt, but faded only at the end of an hour with the phostonic acid salt.

Anhydro-α-hydroxy-benzyl Phosphonic Acid.—This acid was obtained as a gum contaminated with barium salts by acidifying the barium salt. Seven g. of barium salt was placed in a mortar and ground with 50 cc. of 6 *N* hydrochloric acid. The mixture became pasty, and a white sticky gum separated on the sides of the mortar and on the pestle. The aqueous solution was poured off and the gum ground with 3 portions of cold water. It was then spread on a porous plate and dried in a desiccator over sulfuric acid. 2.6 g. of dried material was thus obtained. When dissolved in alcohol it left a small amount of insoluble barium salt and the alcoholic solution on evaporation yielded a somewhat purer resin. However, all the barium compounds could not be removed by this treatment. An analysis showed that it still contained about 10% of barium, presumably as the unchanged barium salt. The resin dissolved in sodium hydrogen carbonate with evolution of carbon dioxide.

The acid could be obtained only in this impure condition. However, the titration with sodium hydroxide, oxidation with permanganate, reaction with aniline, and hydrolysis to hydroxy-benzyl phosphonic acid, showed that the material at hand was the phostonic acid.

Subs., 0.211: 4.73 cc. of 0.2 *N* NaOH (using phenolphthalein).
Calc. for phostonic acid, 6.2 cc.; allowing for 10% of barium as barium salt, 4.3 cc.

The acid decolorized permanganate solution only $^1/_7$ as fast as a sample of hydroxy-phosphonic acid. It did not form a crystalline aniline salt when treated with aniline in ether solution, a reaction very characteristic of the hydroxy-benzyl phosphonic acid. Only a non-crystalline material was obtained which yielded no solid in alcohol or ether solution when seeded with the aniline salt of hydroxy-benzyl phosphonic acid.

Conversion of the Phostonic Acid into the Hydroxy Phosphonic Acid.

Two g. of the impure phostonic acid described above was warmed on the steam-bath with 75 cc. of conc. hydrochloric acid until a clear solution was obtained. The solution was filtered to remove a slight amount of insoluble material. The filtrate was treated with dil. sulfuric acid until no further precipitate of barium sulfate formed. The mixture was filtered and evaporated to dryness. The crude hydroxy-benzyl phosphonic acid thus obtained was changed into its aniline salt as previously described. 2.2 g. of pure salt, m. p. 200° to 201°, was thus obtained; this was 67% of the theoretical amount. Three g. of a sample of the barium salt of the phostonic acid was similarly treated and yielded 2.6 g. of aniline salt, which was 96%.

This hydrolysis of the phostonic acid to the hydroxy-phosphonic acid could be followed by determining the increase in acidity of a solution of the barium salt on boiling with water. 0.194 g. of the salt (neutral to phenolphthalein) was boiled with 55 cc. of water under a return condenser. At the end of $3^1/_2$ hours the solution required 0.00029 equivalent of sodium hydroxide for neutralization; the hydrolysis was thus 36% complete. In similar experiments dil. hydrochloric acid was substituted for water and the net gain in acidity determined. With a total acid concentration of 0.033 N, the hydrolysis was 49% complete in 3 hours, and 67% in 16 hours. With an acid concentration of 0.1 N, in 1 hour 45% was converted; in 8 hours, 66%. The reaction is evidently accelerated by the presence of the hydrogen ion.

Reaction in Glacial Acetic Acid.

In the first experiments with glacial acetic acid as a medium the aldehyde and acid were mixed together and the trichloride run in slowly from a dropping funnel. The reaction mixture was then allowed to stand at a definite temperature. Test samples were withdrawn from time to time and added to water. The amount of unreacted benzaldehyde was determined in the specially constructed pipet previously referred to. It was found that at temperatures below 25° the reaction proceeded very slowly; at temperatures above 40°, on the other hand, the reaction seemed to proceed rapidly, but never more than 70% of the aldehyde was used up. This was undoubtedly due to the rapid reaction of the trichloride directly with the acetic acid at this temperature. The most favorable temperature was 30° to 35°. Even under these conditions, however, about 15% of the benzaldehyde was recovered unchanged.

The best results were obtained by first cautiously mixing the aldehyde and trichloride at 20° to 40°, allowing the mixture to stand for one or two hours and then adding glacial acetic acid. The mixture was then kept between 30° and 35° and allowed to stand for one or two hours longer. At the end of this time the reaction was complete and all the aldehyde had reacted as shown by the absence of any oil when the mixture was poured into water. In all these experiments a 10% excess of trichloride was used and an amount of acetic acid equivalent to 3 or 4 mols. per mol. of aldehyde.

In the preparation of hydroxy-benzyl phosphonic acid by this method the reaction mixture is poured into water and evaporated to dryness. The syrup which is left deposits crystals of the acid on cooling. These may be freed from adhering syrup on a porous plate and recrystallized from dil. hydrochloric acid. However, the yield is low by this procedure because of the difficulty of handling the easily soluble phosphonic acid in the presence of a little phosphoric acid formed by a side reaction. The acid may be more conveniently isolated as the aniline salt.

A typical preparation of the hydroxy-benzyl phosphonic acid by this procedure follows. Ten g. of benzaldehyde (one mol.) and 14 g. of phosphorus trichloride (one mol. + 10% excess) were cautiously mixed in a flask fitted with a calcium chloride drying tube. After standing for one hour, 18 g. (3 mol.) of glacial acetic acid was added and the mixture allowed to stand for 3 hours. The temperature was kept between 25° and 35° during the entire experiment. The mixture was then poured into 200 cc. of water and evaporated to dryness on the steam-bath. The crude acid was dissolved in a little alcohol and the solution diluted with 100 cc. of ether. 10 g. of aniline dissolved in 10 cc. of ether was then added and the precipitate of the aniline salt filtered off. Yield, 18 g., or 72%. The isolation of the free acid from this salt has already been described.

The phostonic acid is formed directly in the reaction in glacial acetic acid but is slowly changed into the hydroxy-phosphonic acid on standing. The following experiments illustrate this. Ten g. of aldehyde, 13 g. of trichloride, and 17 g. of acetic acid were allowed to react as just described. The reaction mixture was then evaporated under diminished pressure at 50° for 2 hours. A colorless gum was left. This gum was dissolved in a little water and treated with the calculated amount of a solution of barium hydroxide. The solution was made barely alkaline with ammonia and the white precipitate filtered, washed, and dried; yield, 9.5 g., or 43%. Tests on the salt showed that it was the barium salt of the phostonic acid. A similar experiment was carried out and the reaction mixture allowed to stand for 7 days before evaporation. Three g. of the barium salt was obtained which is only a 13% yield. Hydrogen chloride accelerates this conversion of the phostonic acid into the hydroxy-phosphonic acid in acetic acid solution. A reaction was carried out in the usual way with acetic acid and the mixture then saturated with dry hydrogen chloride and allowed to stand overnight. The amount of barium salt obtained corresponded to only 16%.

The mixture of acid chloride and anhydride obtained in the experiments with acetic anhydride was dissolved in acetic acid and the solution saturated with dry hydrogen chloride. After standing overnight, 53% of barium salt was obtained by the usual procedure. In similar experiments only 30% of salt was obtained after 3 days standing and only 22% after 11 days. A sample of the original mixture of acid chloride and anhydride yielded 63% of the barium salt when treated directly with water and barium hydroxide. It is evident that in glacial acetic acid the phosphorus oxygen ring is slowly opened by hydrogen chloride.

Summary.

1. Phosphorus trichloride forms an addition compound with benzaldehyde. The reaction is reversible and quantitative experiments show that the factors governing the equilibrium can be expressed in terms of the law of mass action.

2. The values obtained for the equilibrium constant vary from 6.9 to 8.3 the average is 7.4.

3. The addition compound reacts with acetic anhydride forming acetyl chloride and a mixture of an acid anhydride and an acid chloride.

4. The structures of the anhydride and the chloride, and in turn that of the addition product, follow from their transformation by water into the monobasic acid. This acid can be hydrolyzed to hydroxy-benzyl-phosphonic acid. It therefore, contains a 3-membered carbon oxygen phosphorus ring; it is suggested that acids of this type be called phostonic acids.

5. Benzaldehyde, phosphorus trichloride and glacial acetic acid react to form acetyl chloride and the phostonic acid together with some hydroxy-phosphonic acid. Dilution with water and subsequent evaporation of the solution to dryness converts the phostonic acid into the hydroxy-phosphonic acid. The latter acid can be conveniently isolated in the form of an aniline salt.

CAMBRIDGE, MASS.

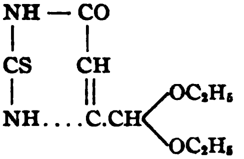
[Contribution from the Department of Chemistry, Yale University.]

RESEARCHES ON PYRIMIDINES. LXXXIX. THE CONDENSATION OF BENZAMIDINE WITH ETHYL γ-DIETHOXY-ACETO-ACETATE.

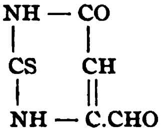
By Treat B. Johnson and Louis A. Mikeska.

Received August 11, 1920.

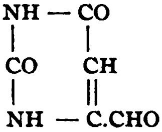
It has been shown in a previous paper from the Sheffield Laboratory[1] that ethyl γ-diethoxy-aceto-acetate condenses smoothly with thio-urea in the presence of sodium ethylate to give the thiopyrimidine (I), containing an acetal grouping in the 4-position of the pyrimidine ring. This acetal group is very susceptible to hydrolysis in acid solution, and, by digestion of the pyrimidine (I) with hydrochloric acid, is easily destroyed in this case with formation of the corresponding aldehyde group as is represented in Formula II. In fact, this is the only synthetical method that has yet been developed for the introduction of an aldehyde group into the pyrimidine ring, and is apparently a reaction of general application in the uracil series. Desulfurization of the thiopyrimidine (II) leads to the production of the corresponding oxygen derivative, uracil-aldehyde (III), a pyrimidine combination of biochemical interest, and one whose value for synthetical work in this series has not yet been realized.



(I).



(II).



(III).

It became of special interest to us in the development of different phases of our researches on amines to extend the application of our method of synthesizing cyclic aldehydes in the pyrimidine series. We have, therefore, turned our attention to an investigation of the behavior of ethyl γ-diethoxy-aceto-acetate towards amidine combinations. Theoretically this ester should interact with amidines in a manner similar to that of ethyl aceto-acetate to give representatives of a new class of pyrimidine acetals which, on hydrolysis, should undergo conversion into their corresponding aldehydes. The successful application of this synthesis with amidines would make possible the preparation of representatives of a new type of cyclic amine compounds which give promise of having considerable interest from a pharmacological standpoint. With the exception of the work that has been contributed dealing with the chemistry of diethylbarbituric acid (IV) and related compounds, practically no attention has been paid to the pharmacology of pyrimidine compounds. The unsaturated or simplest forms of pyrimidine compounds contain the characteristic

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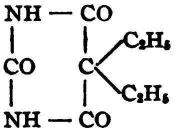
[1] Johnson and Cretcher, This Journal, 37, 2144 (1915).

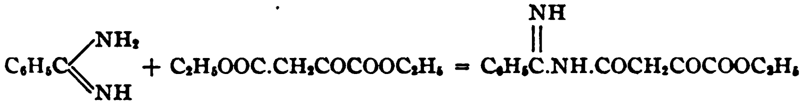


(IV).

nitrogen carbon linking ...N = CR — NH..., which is known to exhibit, in other cyclic series, marked physiological properties. It is not improbable, therefore, that a careful pharmacological and physiological study of pyrimidines containing this amidine grouping will reveal to us other combinations which may prove to be as important medicinally as the hypnotics discovered in the barbituric acid series. With a reactive aldehyde group present in such combinations we would have at our command means of introducing synthetically into the cycle a great variety of side groups through application of reactions characteristic of this unsaturated grouping.

The work which we now describe in this paper is of a preliminary nature and deals only with a study of the behavior of ethyl γ-diethoxy-aceto-acetate towards benzamidine. We find that these reagents have a very pronounced affinity for each other, and, by interaction, lead to a variety of condensation products depending upon the experimental conditions employed.

Benzamidine reacts with ethyl γ-diethoxy-aceto-acetate to form 3 different compounds, 2 of which are acyclic and one cyclic in nature. If the amidine is allowed to interact with the β-ketone ester in molecular proportions, and in the absence of free alkali, they combine smoothly with loss of alcohol giving an acyclic combination to which we have assigned the constitution expressed in Formula VIII. The reaction takes place at ordinary temperature, and this compound (VIII) is apparently the only product formed under such conditions. The evidence which has led us to assign to this condensation product this constitution and not that of an acrylic acid (IX), or a cyclic salt (X), are the facts that (1) it is not stable in the presence of alkali, and (2) it undergoes a smooth rearrangement by such treatment, or when heated above its melting point, to give the normal pyrimidine (VI). In other words, benzamidine reacts with this ketone ester in a manner similar to diethyl oxalyl-acetate which Pinner observed to condense with benzamidine as shown below.[1]



$$C_6H_5C\begin{cases}NH_2\\NH\end{cases} + C_2H_5OOC.CH_2COCOOC_2H_5 = C_6H_5\overset{\overset{NH}{\|}}{C}.NH.COCH_2COCOOC_2H_5$$

Condensation of benzamidine with the β-ketone ester in aqueous solution and in the presence of a molecular proportion of alkali leads to an

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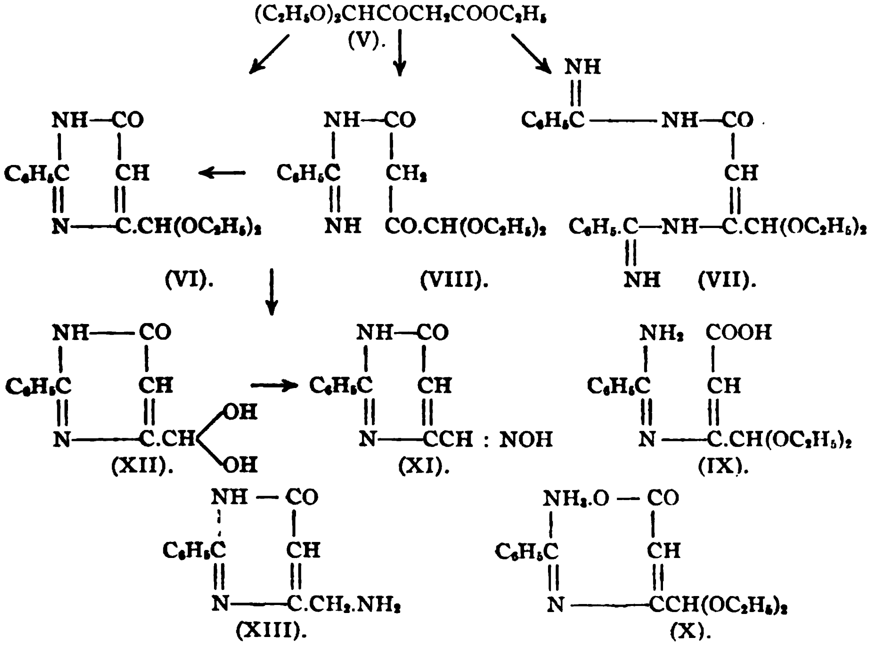
[1] "Imidoaether," pp. 255–6. Gustave Schmidt, Berlin (1892).

entirely different result. Here we obtained no evidence of the formation of the compound represented by Formula VIII. The chief product of reaction was the normal pyrimidine acetal (VI). Along with this, a secondary product was formed to which we assigned the constitution of a crotonic acid derivative represented by Formula VII. This substance very probably results from the action of benzamidine on the acylbenzamidine (VIII). We were not able to submit this substance to a careful investigation on account of the small amount of material available.

2-Phenyl-6-oxy-4-aldehydo-pyrimidine (XII) is formed almost quantitatively by acid hydrolysis of its corresponding acetal (VI). While this pyrimidine-aldehyde gives all the reactions characteristic of its class, we have not represented it structurally as containing a free aldehyde group. The compound contains a molecule of water which is so firmly bound that we have represented it structurally as water of constitution instead of water of crystallization. In other words, the pyrimidine (XII) bears the same relationship to its corresponding aldehyde as chloralhydrate does to chloral. The aldehyde hydrate interacts with hydroxylamine, as might be expected, to form the oxime of the aldehyde (XI). On reduction with stannous chloride the latter is transformed smoothly into the amine (XIII). This is the first amine, containing the amino group in an aliphatic side chain of the pyrimidine, to be synthesized in this series. These various transformations are expressed by the following formulas.



Further work dealing with a study of the reactions of pyrimidine aldehydes is in progress. The amine combinations, which we propose to synthesize and of which the pyrimidine (XIII) is our first representative, will be subject to a pharmacological research in order to determine whether they possess any specific therapeutic value. It is our intention to prepare also the higher homologues of pyrimidines corresponding to Formula XIII and related compounds in which the amino group is linked to carbons in the β and γ positions, respectively, with respect to the pyrimidine cycle.

Experimental Part.

Ethyl γ-Diethoxy-aceto-acetate, $(C_2H_5O)_2CH.CO.CH_2COOC_2H_5$.—This ester was prepared by condensing ethyl diethoxy-acetate with ethyl acetate according to the procedure described in a previous paper from this laboratory.[1]

The Condensation of Ethyl γ-Diethoxy-aceto-acetate with Benzamidine: γ-Diethoxy-β-benzamidino-crotonyl-benzamidine. Formula VII.—Benzamidine and ethyl diethoxy-aceto-acetate (V) interact at ordinary temperature and if the operation is conducted according to the following procedure it is possible to isolate and identify 2 definite products of reaction. Ten g. of the ketone ester is dissolved in sufficient 10% sodium hydroxide solution to form the sodium salt of the ester. A molecular proportion (7.15 g.) of the hydrochloride of benzamidine is also dissolved in the same amount of 10% sodium hydroxide solution to liberate the free benzamidine base. Then these two akaline solutions are mixed, and the resulting solution allowed to stand at ordinary temperature. The slight evolution of heat which occurs when the 2 solutions are mixed indicates immediate reaction. After this mixture has stood for about 24 hours, a crystalline substance begins to deposit; when the reaction has proceeded for 2 days, this solid is separated by filtration and the aqueous filtrate saved (see below). The weight of this insoluble product is generally about 3.0 g. It was colorless and crystalline and was purified by crystallization from hot alcohol in which solvent it is quite soluble. It crystallized in prismatic crystals and exhibited the characteristic property of possessing a double melting point. The compound first melts at 106° to an oil, then solidifies in the capillary tube; on further heating, it melts at 136° to a clear oil with slight effervescence. The compound is insoluble in alkali and soluble in acids.

Calc. for $C_{22}H_{28}O_3N$: N, 14.2. Found: 13.96.

The alkaline filtrate saved above was exactly neutralized by addition of the required amount of hydrochloric acid, whereupon a crystalline product immediately separated in the form of a voluminous colorless precipitate. The compound is soluble in an excess of hydrochloric acid. It

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[1] Johnson and Cretcher, *loc. cit*

was purified without difficulty by crystallization from boiling 95% alcohol from which is separated, as the solution cooled, in the form of slender needles. These melted at 175°. A complete analysis of this substance indicated that we were dealing with a true pyrimidine combination, namely, *2-phenyl-4-diethoxymethyl-6-oxypyrimidine*, Formula VI.

Calc. for $C_{15}H_{18}O_3N_2$: C, 65.6; H, 6.57; N, 10.2. Found: C, 65.4; H, 6.50; N, 10.1.

2-Phenyl-6-oxy-4-aldehydo-pyrimidine. Formula XII.—This new pyrimidine aldehyde is easily obtained by digesting its acetal, described above, with dil. hydrochloric acid. On evaporating the solution to dryness the pyrimidine is obtained in a crystalline condition and is easily purified by crystallization from water or 95% alcohol. The aldehyde is quite soluble in this solvent. It melts at 205°. The results obtained by analysis showed that we are dealing here with a compound containing a molecule of water. It is bound, however, very firmly in the pyrimidine molecule, and the fact that it cannot be expelled by heating at 135° indicates that it is not linked as water of crystallization but as water of constitution as in chloral hydrate.

Calc. for $C_{11}H_{10}O_3N_2$: N, 12.8. Found: 12.63.

Condensation of Benzamidine with the β-Ketone Ester in Neutral Solution.—The 2 compounds described above and represented in the introduction of this paper by Formulas VII and VI are products of the condensation reaction between the β-ketone ester and benzamidine when applied in the presence of 2 molecular proportions of sodium hydroxide. An entirely different result is obtained if the β-ketone ester (V) is added directly to an aqueous solution of the free amidine in the absence of alkali. A molecular proportion of the amidine hydrochloride (7.15 g.) was first dissolved in a 10% alkaline solution containing in solution 1.83 g. of sodium hydroxide. To this solution the β-ketone ester was added when there was an immediate reaction with evolution of heat. A yellow oil began to separate immediately and within a few minutes, if it was stirred, it solidified completely. After the reaction mixture had stood at ordinary temperature for about 48 hours, the reaction was considered complete and the crystalline product then separated by filtration. It was purified by crystallization from 95% alcohol and separated from the solution as it cooled, in the form of colorless crystals which melted constant at 145° with slight evolution of gas. This decomposition involves a profound change which is a very characteristic property of this substance. If the temperature of the sulfuric acid bath is held at the temperature of decomposition, namely, 145°, this solid melts completely; then the oil solidifies entirely and the new substance does not melt until it is heated to 174°. (This change will be discussed below.) The compound melting at 145° did not lose water at 100°, and was extremely soluble in sodium hydroxide solution. The properties of the substance and the results obtained by complete analysis proved that we were not dealing here with a pyrimidine combination, but with one of 3 cyclic derivatives, namely, γ-diethoxy-β-benzamidino-crotonic acid (IX), a salt (X), or an acyl derivative of benzamidine, represented structurally by Formula VIII. The chemical properties of the compound and the conditions under which it is formed have led us to assign to it provisionally the constitution of *γ-diethoxy-acetoacetyl-benzamidine*, Formula VIII.

Calc. for $C_{15}H_{20}O_4N_2$: C, 61.64; H, 6.86; N, 9.59. Found: C, 61.74; H, 7.2; N, 9.8.

Rearrangement of γ-Diethoxy-acetoacetyl-benzamidine (VIII) into 2-Phenyl-4-diethoxy-methyl-6-oxypyrimidine (VII).—As stated above, the substance melting at 145° undergoes a rearrangement at this temperature, being transformed into a product melting at 174°. This latter compound proved to be identical with 2-phenyl-4-diethoxy-methyl-6-oxypyrimidine, VI. It crystallized from boiling 95% alcohol in the form of needles, and when mixed with the acetal the melting point was not altered. This acyclic compound (VIII) is also rearranged into the pyrimidine (VI) by the action of alkali. About 0.8 g. of the compound was dissolved in 7 cc. of a 10% aqueous solution of sodium hydroxide and the solution allowed to stand at ordinary temperature for 12 hours. On acidifying with hydrochloric acid the pyrimidine melting at 172–3° separated at once. The same transformation could also be brought about within a few minutes by simply heating the alkaline solution of the acyclic compound.

The Oxime of 2-Phenyl-6-oxy-4-aldehydo-pyrimidine, $C_{11}H_9O_2N_3$. Formula XI.—This compound can be prepared by dissolving the pyrimidine aldehyde (XII) (0.97 g.) in 10 cc. of water containing in solution 0.5 g. of sodium hydroxide or slightly more than 2 molecular proportions of alkali, and then adding to this solution a molecular proportion of hydroxylamine hydrochloride. The mixture is then allowed to stand at ordinary temperature for 6 to 8 hours and the alkaline condition finally neutralized with dil. acetic acid. The oxime separates at once upon neutralization and can be purified by crystallization from alcohol. It melts with decomposition at about 268°. This method of operating does not always lead, however, to a pure sample of the oxime. Oftentimes the oxime is accompanied by a powder which is insoluble in alcohol and contains sodium. In fact, it is extremely difficult to remove this element, when present, by treatment with acids. In order to obtain the oxime quantitatively and free from sodium the following procedure is recommended: dissolve the aldehyde in boiling water and add to the aqueous solution a concentrated aqueous solution containing a molecular proportion of hydroxylamine hydrochloride. The oxime will separate instantaneously and the yield is practically quantitative.

Calc. for $C_{11}H_9O_2N_3$: N, 19.5. Found: 19.33, 19.4.

Reduction of the Oxime $C_{11}H_9O_2N_3$, Formula XI, to the Corresponding Amine 2-Phenyl-4-Aminomethyl-6-oxypyrimidine $C_{11}H_{11}ON_3$. Formula XIII.—The reduction of the oxime is easily brought about by the action of tin chloride in hydrochloric acid solution. For 2 g. of the oxime we used 6 g. of the tin salt. The reaction is allowed to proceed at ordinary temperature for about 24 hours and finally at 45–50° for 2 hours. The tin is then removed in the usual manner by precipitation as sulfide, and the aqueous solution evaporated to dryness *in vacuo*. The pyrimidine base is obtained in the form of a stable, crystalline hydrochloride, which is easily purified by crystallization from 95% alcohol. This salt is colorless and melts with decomposition at 263–5°.

Subs., dried at 100°.
Calc. for $C_{11}H_{11}ON_3.HCl$: N, 17.72. Found: 17.6.

Summary.

1. Benzamidine condenses with ethyl γ-diethoxy-aceto-acetate in the presence of alkali to give the pyrimidine, 2-phenyl-4-diethoxy-methyl-6-oxypyrimidine (VI).

2. Hydrolysis of this pyrimidine (VI) leads to the formation of the corresponding pyrimidine aldehyde which exists in the form of a stable hydrate (XII).

3. The pyrimidine aldehyde-2-phenyl-6-oxy-4-aldehydo-pyrimidine (XII) interacts normally with hydroxylamine to give an oxime, which is converted by reduction into 2-phenyl-4-aminomethyl-6-oxypyrimidine (XIII).

4. Benzamidine and ethyl γ-diethoxy-aceto-acetate interact in neutral solution with formation of diethoxy-acetoacetyl-benzamidine (VIII).

NEW HAVEN, CONN.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JAMES BUCHANAN BRADY UROLOGICAL INSTITUTE, JOHNS HOPKINS HOSPITAL.]

MERCURY DERIVATIVES OF PHTHALEINS.[1]

BY EDWIN C. WHITE.

Received August 11, 1920.

During the past 3 years the writer and collaborators have been engaged on studies of organic mercury compounds, particularly with reference to their use, both internally and locally, in the treatment of genito-urinary infections and of syphilis. The results obtained in the laboratory and the clinic with some of these compounds[2] have been of sufficient value to

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[1] This work was carried out with the aid of funds granted by the United States Interdepartmental Social Hygiene Board for Research in the prevention and treatment of venereal diseases.

[2] E. G. Davis, E. C. White and R. Rosen, "Urinary Antisepsis," *J. Urology*, 2, 277 (1918); J. E. Burns, E. C. White and J. G. Cheetham, "Experimental Nephropathy Produced by a Mercury Derivative of Phenolsulphonphthalein," *ibid.*, 3, 1 (1919); H. H. Young, E. C. White and E. O. Swartz, "A New Germicide for Use in the Genito-Urinary Tract—Mercurochrome-220," *J. Am. Med. Assn.*, 73, 1483 (1919).

warrant a description of the preparation and properties of these substances, particularly because little of a chemical nature has heretofore appeared in regard to mercurated phthaleins and because the methods used by the writer differ from the method described in the meager literature available.

This literature consists solely of 2 German patents. Pauly and Traumann[1] prepared derivatives containing as many as 4 "or more" atoms of mercury by the action of mercuric chloride on the sodium salt of fluorescein or halogenated fluorescein. Their statement that the latter is used instead of "phthalsäure fluorescein" indicates that the halogen was in the phthalic acid residue, not in the phenolic part of the molecule. The process was as follows. The nearly neutral solution of the phthalein (*i. e.*, one containing about 2 molecules of sodium hydroxide to one molecule of phthalein) was boiled with the desired amount of mercuric chloride, the precipitate first formed was dissolved by treatment with sodium carbonate and the solution was evaporated to dryness. No analysis or evidence of structure is given in the patent, nor is there any indication of the nature of the inorganic group held by the second bond of the mercury atom, a most important consideration when substances of this kind are to be used for pharmacological purposes.

Fahlberg, List and Co.[2] extend the process of the earlier patent to include a number of other phthaleins and succineins. The materials covered by these patents were studied pharmacologically by Klages and Schreiber,[3] Titze and Wedemann,[4] and Hahn and Kostenbader.[5] The mercury content of these compounds as given in the last article indicates that many of them were not single, definite compounds, but were probably mixtures. In only a few cases is the inorganic group held by the mercury indicated, so that the nature of the substances worked with is not fully shown.

Of the compounds described in the present paper, only one, a derivative of phenolphthalein, is crystalline. The others are amorphous and their chemical identification depends on a knowledge of the parent phthalein, determination of mercury content, and in some cases, of the second group attached to the mercury atom. Melting points, which in the case of the crystalline mercury derivatives of certain phenols and amines afford, in connection with analytical data, a means of rigidly establishing chemical and physico-chemical identity, are not shown by any of the mercurated phthaleins. In other words, the chemical data on these compounds can establish only identity of composition as between 2 substances of this

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[1] Pauly and Trauman, *D. R. P.*, 201,903.

[2] Fahlberg, List & Co., *D. R. P.*, 308, 335; *C. A.*, 13, 1621 (1919).

[3] Klages and Schreiber, *17th Internat. Cong. Med.*, 1913. Report of Section of Therapeutics, p. 95.

[4] Titze and Wedemann, *Centr. Bakteriol.*, 57, (I), Referate 179 (1913).

[5] Hahn and Kostenbader, *Z. Chemotherapie*, Originalabhandlungen, 2, (I), 71(1912).

class, and cannot show possible differences such as isomerism or variation in the state of molecular aggregation. Differences of this kind have a fundamental bearing on the biological behavior of dyes, as is shown, for example, in the work of Schuleman[1] on vital staining. It should be remembered that salts of acids of high molecular weight, such as we have in most dyes, show in solution more or less pronounced colloidal properties. The physico-chemical characteristics of a dye are, therefore, almost as important as the purely chemical ones when the dye is to be used for pharmacological study or for clinical administration. Identity of composition may or may not mean identity of biological behavior, and for this reason in our work we have adopted the safe course of considering as different individuals any 2 substances which, though of the same composition, are not made by precisely the same procedure. In at least one case we have found that 2 presumably identical samples made by different methods showed a marked difference in toxicity.

In order to distinguish the substances described in this paper as well as other mercurated dyes to be reported later, the generic name "Mercurochrome" has been coined, the individual member of the group being indicated by suffixing the laboratory number. The purpose of this nomenclature is practical rather than scientific, since one member of the group—dibromo-hydroxymercury-fluorescein, number 220—has come into considerable clinical use as a local urinary disinfectant[2] and the chemical name is too unwieldy for the clinician.

The position of the mercury in these compounds has not been rigidly demonstrated, but there is strong presumptive evidence that the metal enters the phenolic residues, in position *ortho* to the hydroxyl or the quinone oxygen. Mercuration in general is a process quite analogous to halogenation, nitration and sulfonation; and since none of these processes leads to substitution in the phthalic acid residue of phthaleins, but goes only as far as tetra substitution in the phenolic residues it is to be presumed that mercury also enters these residues. Moreover, if the 4 *ortho* positions mentioned above are occupied, as in the case of eosin, mercury cannot be substituted in the molecule by any method tried in this work. The method used in the German patents, the second of which makes a claim for a mercury derivative of tetrabromo-fluorescein was also tried several times with eosin, and although mercuric chloride was used in one case and mercuric acetate in another, in both experiments a mercury salt of the dye, as indicated by its insolubility in alkali, was the only product obtained. (Possibly the tetrabromo-fluorescein of the patent was the derivative of tetrabromo-phthalic acid.) If, on the other hand, 2 of the *ortho* positions are occupied, as in the dibromo-fluorescein or *o*-

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[1] Schuleman, *Biochem. Z.*, 80, 1 (1917).

[2] Young, White and Swartz, *loc. cit.*

cresol-phthalein, exhaustive mercuration leads to a product containing no more than 2 atoms of mercury, corresponding to the 2 unoccupied positions. Finally, if the phthalein contains no substituent groups in the *ortho* positions, as in fluorescein or phenolsulfon-phthalein, 4 atoms of mercury, and no more, can be made to enter the molecule by the methods used in this work. The behavior of phenolphthalein is rather peculiar, as the product of exhaustive mercuration in this case seems to contain only 3 atoms of the metal.

The effect produced on color by the introduction of mercury into the phthalein appears to be qualitatively the same as that produced by halogens, but is much less intense. It it is considerable only in compounds containing at least 2 mercury atoms. Thus, the tetramercury derivative of fluorescein with alkali gives a notably redder tint than fluorescein itself produces, but far less red than is that of eosin. The monomercury derivative of fluorescein, on the other hand, appears to the eye to have practically the same color as fluorescein, though it is possible the spectroscope might show some difference. The same is true in the case of phenolphthalein, whose trimercury derivative gives an intense bluish-purple salt, whereas the monomercury derivative gives a salt of the same pink color as is given by the parent substance. The dimercury derivative of *o*-cresol-phthalein, which represents the maximum degree of mercuration, likewise gives an intense bluish-purple color with alkali. The monomercury derivative of phenolsulfon-phthalein shows the same color and about the same range of color change on the hydrogen-ion scale as does phenolsulfon-phthalein, but the salt of the tetramercury derivative shows a much bluer nuance, the difference being most marked as the solution is diluted. The last-named compound is interesting, also, because it shows the effect of organically-bound mercury in decreasing solubility. Although phenolsulfon-phthalein is fairly soluble in water, to form a yellow solution, the tetramercury derivative is entirely insoluble. It can be boiled for hours without imparting the slightest trace of color to the water, even though the filtrate is made alkaline.

The readiness with which phthaleins undergo substitution by mercury is shown by the variety of conditions under which the reaction will proceed. The dye may be in solution, either in alcohol as the free acid or in water as the salt, or it may be used in a state of suspension in water. The mercury may be used in an insoluble form, as the oxide, or in solution, preferably the acetate. The nature of the product and maximum degree of substitution attainable will vary with the conditions chosen. Two general reactions were used, the action of yellow mercuric oxide on a solution of a phthalein salt and the action of mercuric acetate on the free phthalein. The first of these reactions appears to proceed as far as the substitution of 3 atoms of mercury in phenolsulfon-phthalein, but does not go beyond the second stage of substitution in fluorescein. In phenolphthalein the substitution of even the first atom of mercury takes place with some difficulty, and in dibromo-fluorescein and eosin no substitution at all occurs by this method.

The second reaction will lead to the maximum degree of substitution permitted by the free *ortho*-positions, with the exception, already noted, of phenolphthalein. The phthalein may be used in alcoholic solution, or if it is insoluble in alcohol, it may be suspended in water. In the former case, an *acetoxy-mercury* derivative, $RHgOOCCH_3$ is formed, but in the latter case the acetic acid is partially removed by hydrolysis and there results a mixture of acetoxy-mercury and hydroxymercury derivatives. In the case of the monomercury derivative prepared in this way from dibromo-fluorescein—"Mercurochrome-220"—the hydrolysis is practically complete.

Method of Analysis.—When the mercury is bound to acetic acid the latter is determined by distillation with steam in the presence of phosphoric acid, a method used by Brieger and Schuleman,[1] who, however, give no details. The following procedure was found satisfactory About 0.5 g. of the substance is weighed into a 300-cc. Claisen flask, 10 to 15 cc. of syrupy phosphoric acid is added, then about 100 cc. of water. The steam-delivery tube passes through the long neck of the flask, the short neck being closed by a rubber stopper. By bending slightly the delivery tube leading to the condenser the flask is tilted towards the steam generator, the short neck thus serving as an excellent trap to catch any spray containing phosphoric acid. The steam distillation is continued until no more acetic acid comes over, as indicated by titration of the distillate with 0.1 *N* alkali. If the steam current is vigorous, usually the process is complete when about 300 cc. of distillate has been collected.

In the determination of mercury, the organic matter is destroyed by permanganate and sulfuric acid. About 0.2 g. of the substance is weighed into an 800-cc. Pyrex Kjeldahl flask and 10 cc. of conc. sulfuric acid is added to the flask which is tilted to allow the acid to run along the neck slowly, so as to wash down any adherent particles. To mix the materials the flask is shaken gently and heated until the acid begins to fume moderately. This treatment should yield a clear solution or an even suspension. The mixing must be continued until no lumps are left. *Finely powdered* potassium permanganate is now added little by little; each time as much as can be held on the end of a pen-knife blade is used, and the materials are thoroughly mixed after each addition. The slight flash which sometimes occurs is of no danger. The addition of permanganate is continued until a considerable excess of the brown oxide is present, which may be recognized by the development of a green color (manganate) on further application of heat. From one to 1.5 grams of permanganate is required. The

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[1] Brieger and Schuleman, *J. prakt. Chem.* (2) 89, 97 (1914).

heating must be regulated so that the bottom of the neck of the flask does not become hot to the touch; there is then no danger of loss of mercury by volatilization. When the mixture has cooled to room temperature it is diluted with about 100 cc. of water and powdered oxalic acid is added until a clear solution is obtained. This is transferred to a beaker, and filtered, if necessary, to remove any undissolved particles of oxide. The volume is made up to about 200 cc. with the rinsings, and when the solution is cool, the mercury is precipitated by hydrogen sulfide and weighed. The Gooch crucible is preferably prepared with a disc of filter paper under the asbestos; the mercury sulfide can then be filtered with the greatest ease. Controls run by this method, with various phthaleins and known amounts of mercuric chloride, showed that 98–99% of the mercury is recovered.

A similar method was used by Rupp and Kropat,[1] who, however, carried out the oxidation in alkaline solution. In either method, if halogens are absent, the mercury may be determined volumetrically with potassium thiocyanate.

Experimental.

Action of Mercuric Oxide on Phenolphthalein.—Three g. of phenolphthalein was dissolved in 25 cc. of *N* sodium hydroxide solution, the solution was made up to about 150 cc. with water and boiled with 3 grams of yellow oxide of mercury for 3 hours. Some reduction of the oxide or decomposition of the mercuration product took place; this was indicated by the formation of a small amount of very fine gray precipitate which appeared to be mercury or perhaps mercurous oxide. This material, which occurs to some extent in every case of the action of mercuric oxide on a phthalein salt, could not be removed by filtration. It was, therefore, allowed to settle in a tall cylinder for several days, the clear supernatant liquid was poured off, and centrifuged to remove remaining traces of the gray substance. The mercurated phthalein, precipitated by carbon dioxide, settles out as a slightly purplish, milky precipitate. It was separated and washed by centrifuging, dried on the water-bath, then washed with alcohol, and dried at 110°.

Subs., 0.2000: HgS, 0.0820.
Calc. for $C_{20}H_{13}O_4(HgOH)$: Hg, 37.3. Found: 35.3.

The substance was insoluble in all the usual solvents except glacial acetic acid, in which it gave a turbid solution. It could not be crystallized. Its color with alkali is the same as that of phenolphthalein. The analysis indicates a monomercurated derivative containing a small amount of unchanged phenolphthalein.

Action of Mercuric Oxide on Fluorescein.—Two hundred cc. of 0.1 N sodium hydroxide solution was saturated with about 3.5 g. of fluorescein

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[1] Rupp and Kropat, *Apotheker Ztg.*, **1912**, p. 377.

and without filtering off the excess of fluorescein, 5 g. of mercuric oxide was added. The mixture was boiled for 4 hours, while water was added to replace that lost by evaporation. After it was clarified by centrifuging and evaporated to dryness on the steam-bath, it gave an iridescent green scaly product.

Subs., 1.5278: Loss, 0.1215 at 115°.
Subs., 0.2000: HgS, 0.1068.
Calc. for $C_{20}H_8O_5Na(HgOH)_2$: Hg, 49.6. Found: Hg (calc. to dry basis) 49.9; H_2O, 7.9.

This experiment was repeated with 10 g. of mercuric oxide. When the mixture was boiled for 9 hours, it gave a solution which contained some of the oxide in colloidal suspension. It could not be completely clarified by centrifuging or by adsorbents, so it was evaporated to dryness after removing as much as possible by means of the centrifuge. Even with the extra mercury thus contained, the amount was less than that required for a trisubstitution product, which showed that the substitution of mercury by this reaction does not proceed beyond the second stage. Of course, if only one equivalent of mercuric oxide is used, mono-hydroxymercury-fluorescein can be prepared. By treatment of the solution of the salt with dil. hydrochloric acid, if it is stirred thoroughly and an excess of acid is avoided, chloromercury-fluorescein is precipitated as a caseous mass. After washing the material until it is free of chlorides by centrifuging, a sample was dried and analyzed for chlorine by the lime method. In this way all the mercury is removed by volatilization, so that no mercury is left to interfere with the precipitation of silver halide.

Subs., 0.1110: AgCl, 0.0282.
Calc. for $C_{20}H_{11}O_5(HgCl)$: Cl, 6.26. Found: 6.28.

If it is desired to isolate the free hydroxymercury-fluorescein, very dil. sulfuric acid is used instead of hydrochloric acid; the precipitate is of the same pasty nature in both cases. The salt of dihydroxymercury-fluorescein shows a rather pronounced eosin-like color, though the red is not nearly so intense as that of eosin.

Action of Mercuric Oxide on Phenolsulfon-phthalein.—Five cc. of *N* sodium hydroxide solution was diluted to about 150 cc. and the solution was saturated with phenolsulfon-phthalein—about 2 g.—so as to insure the absence of any dibasic salt. Without filtering the excess, 6 g. of mercuric oxide was added and the mixture was boiled for 4 hours. The purplish solution was centrifuged and evaporated to dryness on the water-bath; the residue was powdered and dried at 110°. The material formed a purple powder with a bronze luster.

Subs., 0.2000: HgS, 0.1333.
Calc. for $C_{19}H_{10}O_5SNa(HgOH)_3$: Hg, 58.7. Found: 57.4.

The use of the disodium salt instead of the monosodium salt seems to interfere with the reaction. This is shown by the following experiment: 3.5 g. of phenolsulfon-phthalein, 20 cc. of sodium hydroxide solution, 250 cc. of water and 5 g. of mercuric oxide were boiled for 9 hours. After clarification of the solution by centrifuging, the dye was precipitated by dil. sulfuric acid and the precipitate was washed free from sulfate by centrifuging, and then dried.

Subs., 0.2000: HgS, 0.1028.
Calc. for $C_{19}H_{12}O_5S(HgOH)_2$: Hg, 50.9. Found: 44.3.

In this case, even long boiling with an excess of the oxide did not cause the reaction to proceed completely to the second stage, although it passed the first stage, which requires a mercury content of 35.1%.

Action of Mercuric Acetate on Phenolphthalein.—Three g. of the phthalein was dissolved in 50 cc. of alcohol and mixed with a filtered solution of 25 g. (8 mols) of mercuric acetate in 50 cc. of water and 50 cc. of glacial acetic acid. At room temperature overnight no reaction occurred beyond the formation of a small amount of mercurous acetate. The color of a sample when heated with alkali was that of the unchanged phthalein. The mercurous acetate was removed and the filtrate heated on the steam-bath. In about 2 hours rosets of stout bladed crystals began to form rapidly. The heating was continued for one hour longer and the mixture was allowed to stand overnight. The crystal paste was filtered, washed with alcohol to remove unchanged phenolphthalein, then with water acidulated with acetic acid and finally with water to remove the excess of mercury salt. The crystals were dried in the air for several days and at 100° for one hour. The analysis indicates tri-acetoxy-mercury-phenolphthalein

Subs., 0.2000: HgS, 0.1292.
Distn. with H_3PO_4: Subs., 0.5000: 14.4 cc. 0.1 *N* NaOH.
Subs., 0.8648: Loss 0.0420, dried to constant weight at 120°.
Calc. for $C_{20}H_{11}O_4(HgOOCCH_3)_3$: Hg, 55.0; CH_3COOH, 16.4; loss at 120, 5.4.
Found: Hg, 55.6; CH_3COOH, 17.1; loss, 4.8.

In view of the slightly high value found for acetic acid and the loss at 120°, it was thought that the substance in hand might possibly be a tetramercury derivative containing acetic acid of crystallization. It was found, however, that these values do not agree nearly so well with the formula for any such substance as they do with that of the trimercury derivative given above, which contains no solvent of crystallization. The loss at 120° is to be ascribed to the elimination of one molecule of acetic acid, formed by one of the acetate groups and the hydrogen of an hydroxyl, thus:[1]

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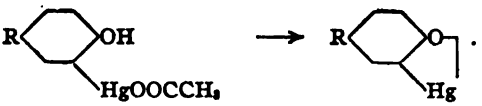
[1] In unpublished work, the writer has noticed a similar elimination of acetic acid in the case of mercury derivatives of certain simpler phenols.



Tri-acetoxy-mercury-phenolphthalein is insoluble in all the usual solvents, but is readily and completely soluble in a solution of sodium hydroxide with the production of a deep purple color. This shows that the bladed crystals are not mercurous acetate and do not contain any appreciable amount of it. The alkaline solution is decolorized by carbon dioxide, and solutions of the salt on standing some time deposit a small amount of gray substance, probably metallic mercury.

A product which gives the same analysis and shows the same properties, but consists of minute granules, is obtained if only 4 equivalents of mercuric acetate are used. This material is easily soluble in hot glacial acetic acid, from a mixture of which, with water and alcohol, it can be crystallized, in the form of bladed crystals, which are almost insoluble in acetic acid.

Action of Mercuric Acetate on Fluorescein.—Three and three-tenths g. of fluorescein was dissolved in 200 cc. of 0.1 *N* sodium hydroxide solution and acidified with 5 cc. of glacial acetic acid. To this was added the filtered solution of 25 g. (about 8 mols) of mercuric acetate in 200 cc. of water slightly acidulated with acetic acid to prevent hydrolysis. The mixture was boiled for 10 hours, while water was added to keep the volume about constant, washed free from mercury by the centrifuge and dried. There was some mechanical loss by the washing, as a portion formed a fine suspension which could not be clarified. The yield of product was about 10 g.

Subs., 0.2000, 0.2000: HgS, 0.1450, 0.1447.

Distn. with H_3PO_4: Subs., 0.5000: 5.5 cc. 0.1 *N* NaOH.

	Hg.	CH_3COOH.
Calc. for $C_{20}H_9O_5(HgOH)_3$	61.3	0
$C_{20}H_8O_5(HgOH)_4$	66.9	0
$C_{20}H_9O_5(HgOOCCH_3)_3$	54.3	16.2
$C_{20}H_8O_5(HgOOCCH_3)_4$	58.7	17.5
Found	62.5, 62.3	6.6

These figures indicate that the product is a mixture of tetra-hydroxy-mercury-fluorescein and tetra-acetoxymercury-fluorescein, the former predominating and probably being formed from the latter by hydrolysis. Calculation indicates that the latter is present to the extent of 6.6/17.5, or 37.7%. If the remainder, or 62.2%, is the tetrahydroxy derivative, the mercury content of the mixture should be:

$$\frac{37.7 \times 58.7 + 62.2 \times 66.9}{100}, \text{ or } 63.7\%.$$

The calculated value is so close to that found that the composition of the mixture seems fairly exactly fixed.

The substance is insoluble in the usual solvents, soluble in alkali with a color similar to that of dihydroxy-mercury-fluorescein. On treatment of the alkaline solution with iodine the brilliant color of erythrosin is produced, and the product stains the skin a bright rose color, whereas the mercury compound has only feeble staining power.

Action of Mercuric Acetate on *o*-Cresol-phthalein.—Three g. of the phthalein in 50 cc. of alcohol was treated with 25. of mercuric acetate in 50 cc. water and 50 cc. glacial acetic acid. Since no precipitate formed when this mixture was heated for 2 hours on the steam-bath, the heating was continued overnight. A pasty precipitate, representing most of the material, was produced. It contained much mercurous acetate, in addition to the mercuration product, and could not be purified. Alcohol added to the solution precipitated a further small amount of mercurous acetate in fine crystals. After filtering these off, the filtrate was diluted with a large amount of water and after standing for some time the yellowish granular material was filtered off. To remove any unchanged cresolphthalein it was ground up and washed thoroughly with alcohol, in which it was only slightly soluble. The residue was dissolved in hot 50% acetic acid, from which on standing a slightly yellow, granular precipitate settled. It could not be crystallized; so it was pressed between paper, dried at 105° and analyzed. The yield was very small.

Subs., 0.1000: HgS, 0.0550.

Calc. for $C_{22}H_{16}O_4(HgOOCCH_3)_2$: Hg, 46.6. Found: 47.4.

This substance dissolves in alkali with a brilliant purple color. The shade is much deeper, *i. e.*, bluer, than that of the analogous derivative of phenolphthalein.

Action of Mercuric Acetate on Dibromo-fluorescein.—Forty-nine g. of dibromo-fluorescein was dissolved in 8 g. of sodium hydroxide in 50 cc. of water, and diluted to 200 cc. This solution was stirred and treated with 12.5 cc. of glacial acetic acid. An even, pasty precipitate was formed if the stirring was vigorous. A solution of 22.5 g.[1] of mercuric oxide in 25 cc. of glacial acetic acid and 50 cc. of water, diluted after solution to 100 cc., previously prepared and filtered, was added to the dye suspension and the whole was diluted to a volume of about 500 cc. The mixture was boiled until a portion of filtered solution when treated with ammonium sulfide gave no test for mercury. In various preparations the time required was 4.5 to 6 hours. As the solution boiled, the precipitate became darker in color and somewhat more granular. The filtration, however, was difficult, so the material was washed by centrifuging to remove acetic acid and sodium acetate, and dried at 110°. The yield was almost quantitative.

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[1] The theoretical amount for one equivalent is 21.7 g. The excess used takes care of the amount lost as mercurous acetate, which is always formed in small amount when commercial yellow oxide of mercury is dissolved in acetic acid.

Subs., 0.2000: HgS, 0.0657.

Distn. with H_3PO_4: Subs., 0.5000: 0.5 cc. 0.1 *N* NaOH.

Calc. for $C_{20}H_9O_5Br_2(HgOOCCH_3)$: Hg, 26.8; CH_3COOH, 8.0. Calc. for $C_{20}H_9O_5Br_2(HgOH)$: Hg, 28.4; CH_3COOH, 0.0. Found: Hg, 28.3; CH_3COOH, 0.6.

These results indicate that the product is dibromo-hydroxymercury-fluorescein. The hydrolysis of the acetoxy-mercury compound, which is probably formed as an intermediate step, appears to be almost if not quite complete. It is possible that the small titration value found for the distillate from the phosphoric acid is due to a small amount of sodium acetate that was not removed in the washing.

Dibromo-hydroxymercury-fluorescein is a red powder which, when ground up, shows marked electric properties; it sticks to glass or paper even when perfectly dry. It is insoluble in the usual solvents, but dissolves in 2 equivalents of sodium hydroxide, to give a deep cherry-red solution. This solution is fairly stable, but on long standing a small amount of metallic mercury or mercurous oxide may settle out. This decomposition seems to be retarded if the solution is kept in dark bottles. The free acid is also completely soluble in ammonium sulfide; from this solution mercuric sulfide is precipitated only slowly.[1]

Action of Mercuric Acetate on Phenolsulfon-phthalein. — Three and a half g. of the dye was dissolved in 200 cc. of 0.1 *N* solution of sodium hydroxide, acidified with 10 cc. of glacial acetic acid, which did not re-precipitate the phthalein, and treated with the filtered solution of 15 g. of mercuric acetate in 100 cc. of water. The solution was boiled for 3 hours, at the end of which time a somewhat crusty precipitate had formed. The precipitate was washed free of salts by centrifuging and dried. It formed a dark brown powder, insoluble in the usual solvents except methyl alcohol, with which it gave a slight color, and boiling glacial acetic acid, with which it gave an intense purple-red solution. This, however, contained only a small amount of dissolved material, and a crystalline product was not obtained. The substance dissolved in a dilute solution of sodium hydroxide with a bluish-purple color, much deeper than that of the parent substance.

Subs., 0.2000: HgS, 0.1442.

Distn. with H_3PO_4: Subs., 0.5000: 5.2 cc. 0.1 *N* NaOH.

Calc. for $C_{19}H_{10}O_5S(HgOH)_4$: Hg, 65.8; CH_3COOH, 0. Calc. for $C_{19}H_{10}O_5S(HgOOC\ CH_3)_4$: Hg, 57.8; CH_3COOH, 17.2. Found: Hg, 62.1; CH_3COOH, 6.2.

These figures indicate that a mixture of the hydroxymercury- and acetoxymercury-derivatives was formed, as in the case of fluorescein. If the

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[1] The disodium salt of dibromo-hydroxymercury-fluorescein, "Mercurochrome-220," has found some use as therapeutic agent and is being prepared on a commercial scale. The product has been found to contain about 23% of mercury and about 8% of moisture. The mercury content calculated to a dry basis varies from 24 to 25% instead of the theoretical value of 26.8% for a pure salt. Probably the difference is due to the presence of a small amount of sodium acetate.

content of acetoxymercury-derivative is 6.2/17.2 or 36.0%, the mercury content of the mixture should be $\frac{36.0 \times 57.8 + 64.0 \times 65.8}{100}$, or 63.0%, a figure in close agreement with that found.

Some of the product was boiled a long time with a large amount of water in an attempt to complete the hydrolysis. No change in the material appeared to take place and the mercury content was not increased, as would have been the case had further hydrolysis taken place. An attempt was made to secure a product free from combined acetic acid by dissolving the material in a 10% solution of sodium hydroxide and precipitating it with sulfuric acid, but this led to considerable decomposition.

Summary.

Two processes of mercuration are described which are applicable to phthaleins. The substitution of mercury is analogous to sulfonation, halogenation or nitration, and the metal enters the phenolic group of the phthalein molecule, in the *ortho* position to the hydroxyl or the quinone oxygen. The number of atoms of mercury entering the molecule is limited by the number of such free *ortho* positions, and if all 4 are occupied no substitution of mercury takes place.

Mercury derivatives containing from one to 4 atoms of the metal have been prepared from the following phthaleins; phenolphthalein, *o*-cresolphthalein, fluorescein, di-bromo-fluorescein and phenolsulfon-phthalein. The methods of substitution differ from those used in the earlier literature on mercurated phthaleins.

It is pointed out that chemical composition alone does not fix the identity of biological behavior or therapeutic effect of compounds of this class, and that samples cannot be considered identical unless they are made in precisely the same way and have the same composition.

BALTIMORE, MD.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF CORNELL UNIVERSITY.]

TETRACHLORO-PHENOLPHTHALEIN.

BY E. T. WHITING.

Received August 13, 1920.

As this derivative of phenolphthalein had never been made and as it was desirable to measure its ultra-violet and visible absorption,[1] its preparation was undertaken by the author at the suggestion of Professor W. R. Orndorff and under the direction of Dr. S. A. Mahood.

Numerous attempts to chlorinate phenolphthalein in alkaline solution and in carbon tetrachloride resulted in failure. Tetrachloro-phenolphthalein was finally made by the following method. 50 g. of *pure* phenol-

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[1] See *Phys. Rev.* N. S., 10, 779 (1917) for the absorption curves.

phthalein (m. p. 253°) was suspended in 500 cc. of *pure* glacial acetic acid and 62 g. of chlorine dissolved in 975 cc. of glacial acetic acid was slowly added, the mixture being stirred vigorously with a mechanical stirrer. The phenolphthalein dissolved completely within $^3/_4$ hour, and on standing overnight some of the tetrachloro product crystallized out. This was filtered off and the solution concentrated by distilling off a large portion of the solvent when most of the material in solution crystallized out in colorless crystals. 45 g. of the *pure* tetrachloro-phenolphthalein, melting at 215°, was obtained. Some of this was recrystallized twice from benzene and found to have the same melting point. The crystals from glacial acetic acid and from benzene contained no solvent of crystallization, as was shown by the very slight loss in weight they sustained when heated to 200°. Analyses for chlorine were made on both products, after heating to constant weight at 150°, by the lime method.[1]

Subs. (from benzene) (I), 0.3040; (II) (0.4290 from glacial acetic acid); (III) 0.1896; (IV) 0.2840: (I) 0.1 *N* $AgNO_3$, 26.59; (II) 37.67; (III) 16.66; (IV) 24.86.

Calc. for $C_{20}H_{10}O_4Cl_4$: Cl, 31.11. Found: (I) 31.01; (II) 31.13; (III) 31.15; (IV) 31.04; average, 31.08.

It will be seen from these analyses that the product was very pure This was the material used in measuring the absorption spectra by Professor R. C. Gibbs and Drs. H. E. Howe and E. P. T. Tyndall, of the Department of Physics, Cornell University.

Tetrachloro-phenolphthalein is soluble in methyl and in ethyl alcohols, in acetone and in ethyl acetate. It is not very soluble in benzene in the cold, but dissolves readily in boiling benzene and crystallizes out on cooling in well-formed colorless crystals. It is also soluble in glacial acetic acid and crystallizes well from this solvent. It is insoluble in petroleum ether and in water. In dil. caustic alkalies, provided they are not used in excess, it dissolves with a violet color, and acids precipitate the phthalein from this solution in colorless, amorphous flocks. Ether shaken with this mixture dissolves the precipitate. In excess of caustic alkalies the phthalein dissolves forming a colorless solution of the salt of the carbinol carboxylic acid, which crystallizes out of the solution in colorless needles when alcohol is added and the mixture allowed to stand for a few days. A *very slight* excess of alkali decolorizes the violet-colored solution of the phthalein in dil. alkali. When heated this colorless solution does not become violet. Alcohol also decolorizes the violet solution of the phthalein in dil. alkalies, and the colorless solution becomes violet when heated. On cooling it again becomes colorless. It dissolves in a 10% solution of sodium carbonate with the same violet color, but the solution is not completely decolorized by an excess of the solvent, although the color becomes much fainter. On warming this solution the color

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[1] *Am. Chem. J.*, 41, 397 (1909).

deepens. In a cold 10% sodium hydrogen carbonate solution the phthalein is almost insoluble, imparting only a faint violet tint to the solution on standing. In excess of a strong solution of ammonia in water it dissolves with a violet color. On boiling the ammonia from this solution the colorless phthalein separates in crystalline form. On shaking the violet-colored sodium carbonate solution several times with ether the color is completely removed, all the phthalein going into the ether. On the other hand, all the phthalein can be removed from an ether solution by shaking it a number of times with sodium carbonate solution. The phthalein dissolves in conc. sulfuric acid with a bright red color, probably forming an oxonium sulfate of the quinoid modification. Water precipitates the unchanged phthalein from this solution in the amorphous condition readily soluble in ether.

The phthalein dissolves in *colorless* nitrobenzene on warming and the solution has no color.

As the tetrachloro-phenolphthalein resembles the tetrabromo-phenolphthalein so closely, both in its chemical and its physical properties, and is made in the same way, it is highly probable that it contains 2 chlorine atoms in each ring *ortho* to the hydroxyl group, a structure analogous to that deduced by Baeyer for the tetrabromo-phenolphthalein.[1]

Tetrachloro-phenolphthalein Diacetate.—This product was made by heating the phthalein with pure acetic anhydride for an hour, cooling and adding absolute ethyl alcohol to remove the excess of acetic anhydride and precipitating with water. It melted sharply at 117°. After drying to constant weight in the water oven it was analyzed for chlorine by the lime method.

Subs., 0.3088, 0.2295: 0.1 N $AgNO_3$, 22.80, 16.86.
Calc. for the diacetate: Cl, 26.26. Found: 26.17, 26.04.

The diacetate is soluble in acetic anhydride, ethyl acetate, alcohol and glacial acetic acid. It is insoluble in caustic alkalies and in the alkaline carbonates. It is saponified on boiling with caustic alkalies, more rapidly and completely with an alcoholic solution of the alkalies. It dissolves in conc. sulfuric acid with a bright red color, exactly like that given by the phthalein itself, and evidently undergoes hydrolysis to the phthalein in this solvent.

ITHACA, N. Y.

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[1] *Ann.*, **202**, 168 (1880).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

THE ACTION OF THE GRIGNARD REAGENT ON THIOCYANATES.

BY ROGER ADAMS, H. B. BRAMLET, AND F. H. TENDICK.

Received August 16, 1920.

In a previous paper, a review was given of the various reactions between the Grignard reagent and those organic compounds which contain a cyan radical. In addition, it was shown that cyanamides were readily converted into amidines[1] by the action of the Grignard reagent. In this communication the action of the Grignard reagent on alkyl thiocyanates is described. Two main reactions have been shown to take place according to the following equations.

$$RSCN + RMgBr \longrightarrow RSR + MgBrCN$$

$$RSCN + RMgBr \longrightarrow \underset{\displaystyle \begin{array}{c}\downarrow\\ RSH\end{array}}{RSMgBr} + RCN$$

Excess (3 moles) of Grignard reagent was always used. It has been found that with aliphatic thiocyanates and the Grignard reagent, a mixture of thio-ether and mercaptan is produced. By the usual method of addition, namely, of the thiocyanate to the Grignard reagent, the yield of mercaptan is higher than when the Grignard reagent is added to the thiocyanate. In the same way, the yield of thio-ether is lower in the former and higher in the latter case. If, after the Grignard reagent and thiocyanate are mixed, the solid and the ether solution are worked up separately, as would be expected, the ether solution yields chiefly thio-ether and the solid material yields chiefly mercaptan.

If an aromatic Grignard mixture is used with the thiocyanates, the second reaction is the principal one almost to the exclusion of the first.

It might be expected that the RCN produced in the second equation would react with the excess of Grignard reagent to give an addition compound that on subsequent decomposition would yield a ketone.

$$RCN + RMgBr \longrightarrow RC(NMgBr)R \longrightarrow RCOR.$$

Such a reaction was shown to take place when phenyl magnesium bromide was employed. Upon decomposition of the reaction mixture with hydrochloric acid, a solid, the hydrochloride of benzophenone-imide, separated, insoluble both in the ether and in the hydrochloric acid layers. Moreover, in the ether layer, a certain amount of benzophenone was obtained. With an aliphatic Grignard mixture, the cyanides produced would be converted into unstable imide hydrochlorides which would yield volatile ketones that could not be separated from the large amount of ether used as a solvent. None of these ketones was isolated when aliphatic Grignard reagent was used.

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[1] THIS JOURNAL, 38, 2768 (1916).

The yields of thio-ethers and mercaptans are small when the Grignard reagent and thiocyanate are of low molecular weight, due to the fact that the products are volatile with the ether which is used as a solvent and thus easily lost. However, as the molecular weights of the Grignard reagent and the thiocyanate increase, the yields of the thio-ethers and mercaptans become better. The use of this reaction for the preparation of either thio-ethers or mercaptans can hardly be recommended because mixtures are always obtained and the separation of the 2 products by fractionation is necessary.

The action of phenyl-magnesium bromide on benzoyl cyanide was studied. Several reactions took place simultaneously with the production of triphenyl-carbinol, triphenyl-methane and benzoic acid. The formation of the triphenyl-carbinol may be easily explained by the following equations.

$$C_6H_5COCN + C_6H_5MgBr \longrightarrow C_6H_5COC_6H_5 + MgBrCN$$

$$C_6H_5COC_6H_5 + C_6H_5MgBr \longrightarrow (C_6H_5)_3COMgBr \longrightarrow (C_6H_5)_3COH$$

The triphenyl methane is probably formed as follows,

$$(C_6H_5)_3COMgBr + RMgBr \longrightarrow \begin{array}{c}(C_6H_5)_3CMgBr\\ \downarrow\\ (C_6H_5)_3CH\end{array} + ROMgBr$$

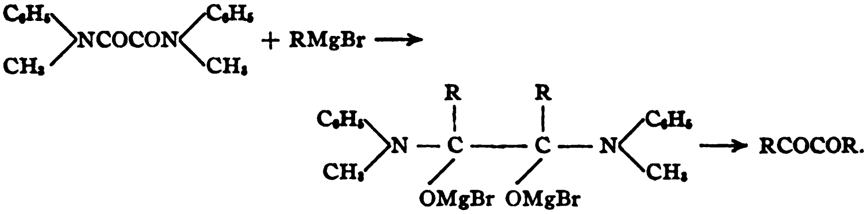
The formation of this compound in reactions of an analogous nature has been observed by previous investigators.[1] The benzoic acid probably comes from the hydrolysis of benzoyl cyanide.

If, instead of 3 moles of Grignard reagent, only one mole is used, triphenyl-acetonitrile, triphenyl-methane and benzoic acid are formed.

$$C_6H_5COCN + C_6H_5MgBr \longrightarrow (C_6H_5)_2C(OMgBr)CN$$

$$(C_6H_5)_2C(OMgBr)CN + C_6H_5MgBr \longrightarrow (C_6H_5)_3CCN + MgBr_2 + MgO.$$

Simultaneous with the study of the Grignard reagent on benzoyl cyanide, which it was hoped would yield 1,2-diketones, the action of the Grignard reagent on dimethyl-oxanilide was investigated in order to obtain diketones as follows.



$$\left.\begin{array}{l}C_6H_5\\CH_3\end{array}\right>NCOCON\left<\begin{array}{l}C_6H_5\\CH_3\end{array}\right. + RMgBr \longrightarrow$$

$$\left.\begin{array}{l}C_6H_5\\CH_3\end{array}\right>N-\underset{OMgBr}{\overset{R}{C}}-\underset{OMgBr}{\overset{R}{C}}-N\left<\begin{array}{l}C_6H_5\\CH_3\end{array}\right. \longrightarrow RCOCOR.$$

The results showed, however, that no matter how large an excess of Grignard reagent was used only one of the carbonyl groups reacted;

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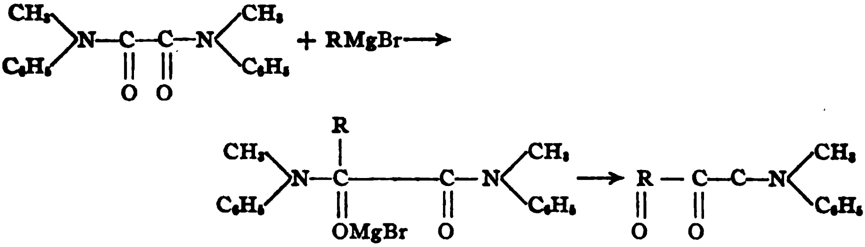
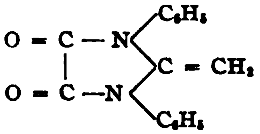
[1] THIS JOURNAL, 39, 2012 (1916).

consequently, on decomposition, the methylphenyl amides of α-keto acids were produced.



The nonreactivity of the second carbonyl is probably due to steric hindrance. That both carbonyls do not react is strange, when it is considered that vinylidene-oxanilide[1]  with methyl- or ethyl-magnesium halides is reported to give, respectively, diacetyl and dipropionyl, although no details or yields are given.

Experimental.

Isoamyl Thiocyanate and Ethyl-Magnesium Bromide.

Forty g. (1 mol) of *iso*-amyl thiocyanate and an equal volume of dry ether were added slowly to a well-cooled solution of 3 moles of ethylmagnesium bromide (2.3 g. of magnesium and 105 g. of ethyl bromide). After the reaction mixture had stood at room temperature for 2 hours, the ether was decanted from the solid material into a flask and treated with hydrochloric acid. When the ether layer, separated and dried over anhydrous sodium sulfate, was fractionally distilled, the main portion, which boiled between 158° and 161°, proved to be ethyl-*iso*-amyl sulfide. The solid material from the original reaction mixture was decomposed with hydrochloric acid and extracted with ether. By fractional distillation, the main portion boiled between 120° and 122° and proved to be *iso*-amyl mercaptan.

If the ethyl-magnesium bromide was added to the *iso*-amyl thiocyanate and the reaction mixture was allowed to stand, when it was decomposed in the usual way, fractionation of the product into definite substances was more difficult. The amount of mercaptan was very small and, in addition to the main product, *iso*-amyl-ethyl sulfide, a higher boiling portion was obtained which, on analysis proved to be di-*iso*-amyl disulfide.

Isoamyl Thiocyanate and Propyl-Magnesium Bromide.

One mole of *iso*-amyl thiocyanate was allowed to react with 3 moles of propyl-magnesium bromide as described under the reaction with ethyl-

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[1] *Ber.*, 40, 186 (1907).

magnesium bromide. The reaction mixture, without separating the solid and the ether, was then decomposed directly with hydrochloric acid and the ether layer separated, dried and fractionally distilled. Two main fractions were obtained, one boiling between 118° and 122° consisted of *iso*-amyl mercaptan; and the other boiling between 179° and 181° at 740 mm. (d_{20} 0.851; n_D^{20} 1.4495) was *iso*-amyl propyl sulfide.

Calc. for $C_8H_{18}S$: S, 21.3. Found: S, 21.9.

Isobutyl Thiocyanate and Ethyl-Magnesium Bromide.

One mole of thiocyanate and 3 moles of the Grignard reagent were allowed to react as described above. The reaction mixture was treated with hydrochloric acid. *Iso*-butyl mercaptan and ethyl-*iso*-butyl sulfide were obtained, but the volatility of these products with ether, caused the yields to be very small.

Heptyl Thiocyanate and Ethyl-Magnesium Bromide.

By the interaction of these 2 substances, heptyl mercaptan boiling between 174° and 176° and heptyl-ethyl sulfide boiling between 188° and 192° at 732 mm. (d_{20} 0.871; n_D^{20} 1.4518) were obtained.

Calc. for $C_9H_{20}S$: S, 20.0. Found: S, 20.1

Isoamyl Thiocyanate and Phenyl-Magnesium Bromide.

One mole of *iso*-amyl thiocyanate was added to 3 moles of phenylmagnesium bromide. Upon treatment of the reaction mixture with hydrochloric acid, a large amount of yellow solid still remained undecomposed. This was filtered and purified by dissolving it in chloroform and precipitating it with dry ether. It did not melt below 240°, was insoluble in water, in hydrochloric acid and in ether. Analysis showed it to be the hydrochloride of benzophenone-imide. When it was warmed with a solution of sodium hydroxide and extracted with ether, benzophenone was obtained.

The ether layer obtained by the decomposition of the original reaction mixture was dried and distilled. In this way, small amounts of *iso*-amyl mercaptan boiling between 120° and 122°, phenyl-*iso*-amyl sulfide and benzophenone were isolated.

Benzyl Thiocyanate and Isobutyl-Magnesium Bromide.

By the interaction of one mole of thiocyanate and 3 moles of the Grignard reagent, a product was obtained which, by careful fractionation, gave benzyl mercaptan boiling between 194° and 195° and benzyl-*iso*-butyl sulfide, a yellowish oil, boiling between 243° and 244° (d_{20} 0.968; n_D^{20} 1.4912).

Calc. for $C_{11}H_{16}S$: S, 17.6. Found: S, 17.0.

Benzyl Thiocyanate and Phenyl-Magnesium Bromide.

After allowing one mole of the thiocyanate and 3 moles of phenylmagnesium bromide to react, the mixture was decomposed with hydrochloric acid. An insoluble substance separated which was the hydrochloride of benzophenone-imide. Upon fractional distillation the ether solution yielded benzyl mercaptan and benzophenone.

Benzyl Thiocyanate and Ethyl-Magnesium Bromide.

When one mole of the thiocyanate and 3 moles of the ethyl-magnesium bromide reacted, and the solid and the ether were worked up separately, the substances isolated were benzyl-ethyl sulfide, boiling between 218° and 220° and benzyl mercaptan boiling between 194° and 195°.

Benzoyl Cyanide and Phenyl-Magnesium Bromide.

An ether solution of 32.5 g. (one mole) of benzoyl cyanide was allowed to run slowly into an ice-cooled ether solution of phenyl-magnesium bromide (78 g. of phenyl bromide and 12 g. of magnesium). A liter of ether was used as solvent. When this product was treated with hydrochloric acid in the usual way, the ether gave a solid which, on purification from alcohol, proved to be triphenyl carbinol, m. p. 159°. The ether mother-liquor yielded an impure solid, which on purification from benzene, melted at 93° and was triphenyl methane.

If instead of using such a large volume of ether as a solvent only 500 cc. was used, the reaction took place in a different manner; after evaporation of the ether, if the residue was fractionally distilled, an excess of bromobenzene, together with triphenylmethane and benzoic acid were the products obtained.

When benzoyl cyanide and phenyl-magnesium bromide were allowed to react in the proportion of 1 : 1, the ether solution submitted to fractional distillation, gave benzophenone, benzoic acid, and triphenylacetonitrile. The yields were poor.

Benzoic acid and a small amount of substance which was probably phenyl-diethyl-aceto-nitrile were isolated when benzoyl cyanide and ethyl-magnesium bromide reacted in the proportion of one mole to 3 moles.

Derivatives of Dimethyl-Oxanilide.

Dimethyl-oxanilide.[1]—Four parts of technical monomethyl-aniline was dissolved in an equal volume of benzene. This solution in a flask attached to a reflux condenser was cooled with a slush of ice and water, and one part of oxalyl chloride dissolved in an equal volume of benzene was allowed to drop slowly from a separatory funnel through the condenser. After all of the oxalyl chloride had been added, the reaction mixture was allowed to stand in an open dish until the benzene evaporated. The solid which remained was treated with cold water to dissolve the methyl-aniline hydrochloride and the crystals remaining were filtered by suction, washed thoroughly with water and dried. The dimethyl-oxanilide crystallized from 75% alcohol and melted at 110°. The yield is about 95%.

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[1] *J. prakt. Chem.* 90, 275 (1914).

Methylanilide of α-Ketobutyric Acid.—To 4 moles of ethyl-magnesium bromide in dry ether one mole of dry dimethyl-oxanilide was added in small portions; during the addition, the reaction mixture should be kept cold and stirred constantly. As soon as the addition was completed, ice and dil. hydrochloric acid were added until the solution was clear. The ether layer was separated, dried over calcium chloride and distilled. A clear, yellow liquid, weighing 27 g. was obtained. Distilled under reduced pressure a light yellow oil was produced; b. p., 165° at 17 mm. In every case a considerable portion of decomposition product remained in the distillation flask.

Subs., 0.2551: 16.2 cc. N_2 at 25° and 770 mm.
Calc. for $C_{11}H_{13}O_2N$: N, 7.3. Found: 7.4.

Methylanilide of Pyruvic Acid.—To 4 moles of methyl-magnesium iodide, one mole of dimethyl-oxanilide was added gradually. The reaction products were worked up in the usual way; an ether solution was obtained which, on distillation, gave a brown oil. This oil solidified to a crystalline mass after 48 hours. The crystals were filtered with suction from the oil and washed first with a little petroleum ether and ether, and finally crystallized from the same mixture. White needles, melting at 83–84° were obtained.

Subs., 0.2230: 11.6 cc. N_2 at 24° and 765 mm.
Calc. for $C_{15}H_{13}O_2N$: N, 5.8. Found: 6.0.

Methylanilide of *p*-Toluyl formic Acid.—The reaction was carried out in the same way as the preceding one except that *p*-tolyl-magnesium bromide was used. Upon decomposition with acid, a solid product separated which was insoluble both in the ether layer and in the water layer. It was filtered, dried, and recrystallized from 85% alcohol. It melted at 128–29°.

Subs., 0.2485: 12.4 cc. N_2 at 24° at 752 mm.
Calc. for $C_{16}H_{15}O_2N$: N, 5.5. Found: 5.7.

Summary.

1. Alkyl thiocyanates react with the Grignard reagent to give a mixture of thio-ether and mercaptan.

2. Benzoyl cyanide (one mole) with phenyl-magnesium bromide (2 moles) give triphenyl carbinol and triphenyl methane; in the proportion one mole to one mole, the products are benzoic acid, benzophenone and triphenyl acetonitrile.

3. Dimethyl-oxanilide with excess of the Grignard reagent yields methylphenyl amides of α-ketonic acids.

URBANA, ILLINOIS.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

THE REACTIONS OF THE ARSINES. PRELIMINARY PAPER. CONDENSATION OF PRIMARY ARSINES WITH ALDEHYDES.[1]

BY ROGER ADAMS AND CHARLES SHATTUCK PALMER.

Received August 16, 1920.

The discovery of arsphenamine greatly stimulated research on organic arsenic compounds. The aim in these investigations has been not only to discover some substance with a higher therapeutic value but, more particularly, some substance of greater stability than arsphenamine. A large number of arsenic compounds have been prepared, but it is noticeable that most of them contain the arseno or arsenic acid groupings, namely, the same groupings which occur in those substances of proved therapeutic value, such as arsphenamine, sodium cacodylate and arrhenal. Comparatively little has been done, however, in attempts to obtain arsenic linked in new ways in organic compounds to determine whether the resulting substances might not be equal or superior therapeutically to those arsenic compounds already found valuable. The research, of which this is a preliminary report, had such an object in view.

A study of the condensation reactions of phenyl arsine with various organic reagents has been undertaken. The experiments have led to such interesting results that a number of investigations have been started to compare carefully the reactions of primary and secondary arsines and arsine itself with the corresponding nitrogen compounds. Experiments have also shown that the phosphines and stibines react similarly, so that a thorough study of these fields is to be taken up.

The previous work on the reactions of the arsines has been very limited. It has been shown that halogens and alkyl halides react with primary and secondary arsines[2] to give respectively arsine halides and arsonium halides. More recently a number of patents[3] have described the condensation of primary aryl arsines with aryl arsenious oxides or chlorides, with aryl stibinous oxides or chlorides, with arsenic, antimony or bismuth trichlorides or tribromides. A more complete review and discussion of these reactions will be given in a future communication.

The present paper deals with the condensation of aldehydes with phenylarsine. Addition products are formed between 2 molecules of aldehyde and one molecule of arsine. The probable structure of the compounds produced is represented by the formula in the following equation

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[1] This work was done under a grant from the U. S. Interdepartmental Social Hygiene Board, Washington, D. C., Dr. T. A. Storey, Secretary.

[2] *Ber.*, 34, 3598 (1901); *Am. Chem. J.*, 33, 101 (1905); 35, 1 (1906); 40, 88 (1907).

[3] *D. R. P.*, 254,187; *Frdl.* 11, 1068 (1912–14); 275,216; 251,571; 254,187; *D. R. P.*, 251,104; 253,226; 270,254; 269,699; 269,700; 269,743; 269,744; 269,745.

$RCHO + RAsH_2 \longrightarrow (RCHOH)_2AsR$. When the aldehyde and arsine are mixed, no apparent reaction takes place until a few drops of hydrochloric acid are added as a catalyzer. Considerable heat is then generated and within a few minutes the reaction is complete. During this procedure, care must be used in handling the arsines as they are easily oxidized by the oxygen of the air to arsenobenzene and phenylarsinic acid. The condensation must be carried out in an atmosphere of carbon dioxide or nitrogen.

Up to the present time, benzaldehyde and butyraldehyde have been condensed with phenylarsine. It seems probable that this reaction may be extended to any aromatic or aliphatic arsines and aldehydes. The compounds may be looked upon as corresponding somewhat to aldehyde ammonias except that only one hydrogen atom on the nitrogen atom reacts, whereas both hydrogen atoms on the arsenic atom take part in the change. The compounds, however, in their chemical reactions do not resemble aldehyde ammonias. They are perfectly stable in cold water, 10% sodium hydroxide solution or dil. hydrochloric acid. Even after boiling them 5 minutes with these reagents, no decomposition takes place except with hydrochloric acid, and only a slight change occurs in this case. Other reactions of these substances will be discussed in a later paper.

Whereas the compounds already made are not soluble in water, it is hoped to obtain certain derivatives in this series which will be soluble in water and capable of therapeutic testing.

Experimental.

Phenylarsinic Acid.—This substance is prepared in 150–200 g. lots by a modification of Bart's reaction which was employed in Germany during the war.[1] It consists in the action of benzene diazonium chloride on sodium arsenite at 15° in the absence of free alkali and in the presence of a copper salt. The yields of pure, recrystallized acid are 40–50%, calculated from the aniline.

Phenylarsine.[2]—For the preparation of this primary arsine, phenylarsinic acid in 50 g. lots is reduced with amalgamated zinc dust and hydrochloric acid. The yields obtained are 40–70%.

Di-α-hydroxy-*n*-butyl phenylarsine (Phenylarsine and *n*-butyraldehyde).—A 250-cc. Erlenmeyer flask is fitted with a 3-hole rubber stopper. A tube through which carbon dioxide may be passed into the flask is placed in one hole, an exit tube and a 100 cc. separatory funnel in the other holes. The air in the apparatus is completely replaced by carbon dioxide, then 20 g. of phenylarsine is poured in through the funnel. This is followed by 5 or 6 drops of conc. hydrochloric acid, and, finally,

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[1] *D. R. P.*, 254,092; *Frdl.* 11, 1030 (1913); *J. Ind. Eng. Chem.*, 11, 825 (1919).

[2] *Ber.*, 34, 3598 (1901); *Am. Chem. J.*, 35, 1 (1906).

20 g. of *n*-butyraldehyde is added in small portions. The reaction takes place immediately; enough heat is evolved to cause the mixture to boil. Carbon dioxide is passed in until the reaction mixture is completely cold (30 to 40 minutes). The product is shaken out with 50 cc. of dil. sodium carbonate solution to remove phenylarsinic acid formed by the oxidation of phenylarsine during the manipulations, and then distilled under diminished pressure.

The fraction boiling 226–230°$_{28 \text{ mm.}}$ is collected and redistilled. Thus 18 g. of product boiling at 228°$_{26 \text{ mm.}}$ is obtained. Although it boils very constant, the cold distillate is slightly turbid, probably due to a trace of phenylarsinic acid not removed by the sodium carbonate. It has the following constants: d_{30}, 1.114; $[n]^{80}$, 1.686.

The compound was analyzed for arsenic by a combination of methods. It was first burned by the method reported by Palmer[1] in a current of oxygen in a tube packed with zinc oxide, the product then dissolved in conc. hydrochloric acid and precipitated with hydrogen sulfide. From this point, the procedure was the same as reported by Little.[2]

Subs., 0.1966, 0.2380: CO_2, 0.4120, 0.5027; H_2O, 0.1371, 0.1602.

Subs., 0.2206: 17.6 cc. iodine (1 cc. sol. = 0.0031 g. arsenic).

Calc. for $C_{14}H_{23}O_2As$: C, 56.36; H, 7.71; As, 25.17. Found: C, 56.47, 57.22; H, 7.29, 7.53; As, 24.74.

This substance is a slightly volatile oil, readily soluble in organic solvents, but practically insoluble in water. It is a stable substance which remains undecomposed in cold water, 10% sodium hydroxide solution and dil. hydrochloric acid. Even when boiled with these reagents, the substance seems to be stable to all except the dilute acid.

Di-α-hydroxybenzyl phenylarsine (Phenylarsine and Benzaldehyde).—The procedure for the preparation of this substance is similar to the one just described. When 20 g. of phenylarsine, 29 g. of pure benzaldehyde and a few drops of hydrochloric acid are mixed, heat is evolved and within a few minutes the mixture has solidified. The crude product crystallized directly from benzene yields fine white needles with a constant m. p. of 193°. The compound must be dried to constant weight at 110° before it is analyzed.

For the analysis for arsenic, the method of Erwins[3] was used.

Subs., 0.2187, 0.2163; CO_2, 0.5301, 0.4471; H_2O, 0.0895, 0.0709.

Subs., 0.2163, 0.2296: 14.0 cc., 14.95 cc. iodine (1 cc. = 0.0031 g. As).

Calc. for $C_{20}H_{19}O_2As$: C, 65.58; H, 5.19; As, 20.66. Found: C, 66.06, 66.28; H, 4.53, 4.31; As, 20.07, 20.19.

The substance is stable to water, dil. hydrochloric acid and in alkali. It is soluble in most organic solvents, but insoluble in water.

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[1] Palmer, *Ber.*, **34**, 3597 (1901).

[2] Little, *J. Chem. Soc.*, **95**, 478 (1909).

[3] Erwins, *ibid.*, **109**, 1356 (1916).

Summary.

1. Phenylarsine has been condensed with butyraldehyde and benzaldehyde to give compounds consisting of two moles of aldehyde and one of arsine and probably having the following structure, $C_6H_5As(CHOH)_2R$.

2. The condensation products are stable toward dilute acid, alkali and water.

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[CONTRIBUTION FROM THE DIVISION OF AGRICULTURAL BIOCHEMISTRY, MINNESOTA AGRICULTURAL EXPERIMENT STATION.]

THE HUMIN FORMED BY THE ACID HYDROLYSIS OF PROTEINS. VI. THE EFFECT OF ACID HYDROLYSIS UPON TRYPTOPHANE.[1]

BY GEORGE E. HOLM AND ROSS AIKEN GORTNER.

Received Aug. 28, 1920.

In previous articles of this series[2] we have shown "that the formation of black acid insoluble humin in a normal protein hydrolysate is dependent upon the presence of tryptophane in the protein molecule." While tryptophane reacts readily with aldehydes to give a black insoluble product, it also undergoes some unknown reaction even when allowed to stand in an acid solution. This was noted by Abderhalden[3] who found that the mother liquor from a tryptophane preparation, which had been allowed to stand for a long time, slowly darkened, lost its ability to absorb bromine, gave no glyoxylic test, and finally deposited a dark brown product, soluble in acids and alkalies, and which when heated gave a strong indole odor.

Harries and Langheld[4] studied the effect of ozone upon hydrolytic products of proteins and found that tryptophane treated with ozone colored very dark, gave no glyoxylic reaction, reduced Fehling's solution in the cold, was precipitated by barium hydroxide, lead acetate, basic lead acetate, and liberated ammonia when treated with sodium hydroxide.

Van Slyke states[5] "tryptophane is known to be precipitated partially by phosphotungstic acid even from fairly dilute solution. When it is boiled with mineral acids, however, it is, to a large extent, at least, destroyed, the nature and fate of the products being unknown." In order to ascertain the behavior of tryptophane under the conditions of protein

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[1] Published with the approval of the Director as Paper No. 208, Journal Series of the Minnesota Agricultural Experiment Station. Presented before the Biological Division of the American Chemical Society at the Spring Meeting, St. Louis, April 12–16, 1920.

[2] Gortner and Blish, THIS JOURNAL, 37, 1630–36 (1915); Gortner, *J. Biol. Chem.*, 26, 177–204 (1916); Gortner and Holm, THIS JOURNAL, 39, 2477–2501 (1917); 42, 821–827 (1920); Holm and Gortner, *ibid.*, 42, 632–40 (1920).

[3] Abderhalden, *Z. physiol. Chem.*, 78, 159–160 (1912).

[4] Harries and Langheld, *ibid.*, 51, 371–383 (1907).

[5] Van Slyke, *J. Biol. Chem.*, 10, 39 (1911).

hydrolysis he boiled pure tryptophane for 12 hours with 20% hydrochloric acid and studied the solution with regard to melanin (humin nitrogen), ammonia, amino nitrogen and total nitrogen, and also with regard to the amounts precipitated by phosphotungstic acid. He draws the following conclusions. 1. Tryptophane is responsible for none of the nitrogen estimated as ammonia, arginine or melanin. 2. Boiling with 20% hydrochloric acid does not alter the ratio 2 : 1 of total nitrogen to amino nitrogen in tryptophane. 3. It appears improbable that tryptophane affects the composition of the phosphotungstic acid precipitate under the usual conditions of analysis, but it is advisable, in the latter, as a precaution, to test a few drops of the solution of the bases for tryptophane.

Homer[1] later studied the effect of acid hydrolysis upon tryptophane and found that after 42 hours' hydrolysis with 25% sulfuric acid almost a complete recovery of the tryptophane was possible, but under the same conditions in a 21–24 hours' hydrolysis and in the presence of ferrous sulfate there was pigmentation and no recovery of tryptophane. She therefore, concludes that hydrolysis changes tryptophane to a compound which absorbs bromine, but does not precipitate with mercuric sulfate.

Johns and Jones[2] in studying the quantitative estimation of tyrosine by use of the Folin-Denis phenol reagent state "it is well known that tryptophane is decomposed by acid hydrolysis" and "the tryptophane was completely decomposed and its decomposition products gave no blue color with the reagent of Folin and Denis." The evidence which they submit in substantiation of the latter statement we have recently shown[3] to be in error, due to the fact that they decolorized their hydrolysate with "Norit" and that carbon adsorbs tyrosine, tryptophane and tryptophane decomposition products.

In the present study our interest is confined primarily to the "acid insoluble" and "acid soluble" humins formed on protein hydrolysis. Our previous studies[4] have shown that aldehydes, when present during the acid hydrolysis of a protein greatly increase the amount of acid-insoluble humin which may be formed, the amount of acid-insoluble humin rapidly increasing to a maximum, at which point the tryptophane is entirely converted into acid-insoluble humin. When the hydrolysis is conducted in the presence of an optimum amount of formaldehyde the nitrogen present in the acid-insoluble humin may be taken as a quantitative measure of the tryptophane nitrogen of the protein. Certain of our experiments have been taken as evidence that proteins contain some unknown component which reacts with tryptophane to form the small

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[1] Homer, *J. Biol. Chem.*, 22, 382–85 (1915).

[2] Johns and Jones, *ibid.*, 36, 319–322 (1918).

[3] Gortner and Holm, THIS JOURNAL, 42, 1678–1692 (1920).

[4] *Loc. cit.*

amount of insoluble humin which is present in a normal protein hydrolysate.[1] We therefore, wished to ascertain if the tryptophane molecule contributes to the "acid insoluble" or "acid" soluble humins when no aldehydes or other reacting compounds are present.

This paper reports the results of a study of the effect of prolonged boiling with 20% hydrochloric acid upon the tryptophane molecule, with especial reference to the nitrogen distribution.

Experimental.

The Method.—Five hundred milligrams of tryptophane was added to exactly 100 cc. of 20% hydrochloric acid. An aliquot of 2 cc. was then removed with a pipet and amino nitrogen determined upon this sample by the Van Slyke method. One cc. was also removed, diluted to 25 cc. volume, and a colorimetric determination of the tryptophane content made upon 5 cc. (representing one mg. of tryptophane), using the phenol reagent of Folin and Denis.[2,3] The flask was then weighed, fitted with, a reflux condenser and heated to boiling upon a sand-bath. At intervals of 12, 24, 36, 48, 96 and 144 hours, the flask was allowed to cool and was weighed. In case of a loss of weight, 20% hydrochloric acid was added at each interval to make up exactly for the acid lost by evaporation thereby insuring correct aliquots in each sample taken. The samples were taken at intervals as designated until the boiling had continued for 144 hours. The contents were then filtered, the residue washed thoroughly and nitrogen determined upon the residue by the Kjeldahl method. The filtrate was evaporated to dryness *in vacuo* and "soluble humin" and "ammonia" determined in the usual manner. The filtrate from these determinations was acidified, concentrated to about 35 cc., and precipitated by phosphotungstic acid in the usual manner. After a separation of "filtrates" and "bases" had been made, both "amino" and "total nitrogen" determinations were made upon each fraction.

This method enabled us to follow the rate of deaminization and also gave the amounts of tryptophane converted into the black "insoluble humin" and "acid-soluble humin." The amount of "acid-insoluble humin" formed is also indicated by the decrease in the tryptophane as

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[1] For our evidence on this point, see Holm and Gortner, THIS JOURNAL, **42**, 632–40 (1920).

[2] *J. Biol. Chem.*, **12**, 239–43 (1912).

[3] We have recently (THIS JOURNAL, **42**, 1678–1692 (1920)), studied the colorimetric values obtained by adding the phenol reagent to tryptophane solutions, and have shown that the reagent cannot be used on protein hydrolysates to obtain reliable data because of the fact that more than one reactive compound may be present. Our criticisms of the use of this reagent for quantitative work do not apply in the present instance, because all of the color developed in these solutions can be definitely ascribed to the indole nucleus.

determined colorimetrically. The effect of acid hydrolysis upon the precipitability of tryptophane by phosphotungstic acid is also shown.

The Experimental Data.—The color changes observed in the solution were as follows, before the boiling began the solution of the tryptophane in the acid was perfectly colorless; at the end of 12 hours' boiling the solution was transparent but dark red-brown; at the end of 24 hours' boiling the solution was a deep brownish-black and was no longer transparent (depth of liquid about 4 cm.); while the formation of dark, amorphous particles floating in the liquid was first noted after 48 hours' boiling.

The changes in amino nitrogen due to the prolonged boiling with hydrochloric acid are shown graphically in the upper curve of Fig. 1. This curve shows that boiling with 20% hydrochloric acid causes a gradual decrease in amino nitrogen, more rapid at first than during later periods.

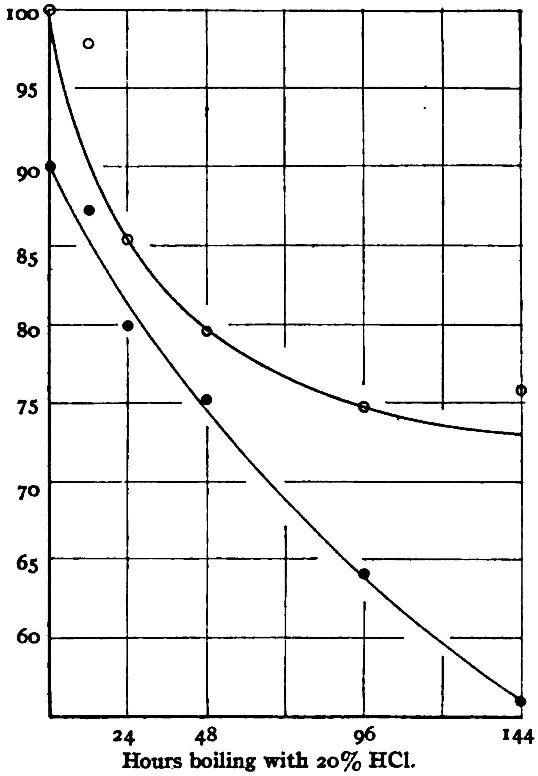

Fig. 1.—Showing (upper curve) the decrease in amino nitrogen (deaminization) in percentage of original amino nitrogen, and (lower curve) the decrease in color values of a tryptophane solution with increasing length of boiling with 20% hydrochloric acid.

A colorimetric determination at each interval serves to indicate the amount of tryptophane which has been destroyed or the amount or portion of the indole nucleus in which the α-position[1] has so been changed or combined that no oxidation is possible. It may indicate even to a greater extent than humin formation or deaminization the total changes in the indole nucleus. The lower curve in Fig. 1 shows the colorimetric values at the different

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[1] That it is the α-position of the indole nucleus of tryptophane which reacts with the phenol reagent is indicated by the fact that α,β-di-phenyl indole did not produce the blue color when added to the phenol reagent. Of course, the failure to produce the blue color with the diphenyl compound may have been due to the insolubility of the indole.

periods, in terms of tyrosine color equivalents (tyrosine, one mg. in 100 cc. of final volume being used as a standard).

At the end of 144 hours' hydrolysis 72 cc. of the solution remained which represented 49.39 mg. of nitrogen upon which the separations of the different fractions were made as has already been described.

Table I (Sample 1) shows the distribution of nitrogen in each fraction.

Table I.—The Distribution of Nitrogen in Two Samples of Tryptophane Boiled for 144 Hours with 20% Hydrochloric Acid.

	Sample I.		Sample II.			
Fraction.	Nitrogen. Mgr.	Fraction of total nitrogen. %	Nitrogen. Mgr.	Fraction of total nitrogen. %	Tryptophane as tyrosine equivalents (colorimetric). Mgr.	Tryptophane actually present (calc. from N.) Mgr.
Total	49.39	.....	34.30	.....	.....	.....
"Acid-insoluble" humin N	4.14	8.38	1.05	3.06	.....	.....
Ammonia N	12.62	25.55	6.42	18.71	.....	.....
"Acid-soluble" humin N	19.78	40.04	9.80	28.57	7.40	71.43
"Phosphotungstic acid humin" N	0.45	0.91	1.25	3.64	.....	.....
Total N in "bases"	5.27	10.66	11.90	34.69	70.00	86.74
Amino N in "bases"	(2.09)	.....	5.25	.....	.....	.....
Total N in "filt. from bases."	6.32	12.78	5.00	14.57	20.45	36.44
Amino N in "filt. from bases"	(2.80)	.....	(3.23)(?)	.....	.....	.....
Total recovered	48.58	98.32	35.42	103.24		

In order to verify these results and also to investigate more closely the nature of the "soluble humin" in its relation to color formation with the phenol reagent, we boiled 250 mg. of tryptophane for 144 hours with 20% hydrochloric acid. At the end of that time the solution was filtered, concentrated and the separations made as in the earlier experiment with the following exceptions: the soluble humin was filtered off and, after thorough washing, was dissolved in dil. hydrochloric acid and made up to 100 cc. volume. Both a total nitrogen determination and a colorimetric determination were made upon this dark solution. Colorimetric determinations were also made upon the "bases" and "filtrates from the bases." Table I (Sample 2) shows the results which were obtained.

Discussion.

While the figures for the nitrogen distribution as shown in Table I are not in exact agreement, they indicate clearly that the nitrogen distribution of tryptophane is altered very markedly by boiling the amino acid with 20% hydrochloric acid. Moreover, the fact that the 2 samples were boiled with 20% hydrochloric acid for equal periods of time and yet exhibit a difference in nitrogen distribution, indicates the ease with which the hydrolysate of a protein containing tryptophane may be altered by slightly varying the conditions of hydrolysis.

We are undecided as to whether or not some of the changes which take place are due to oxidizing reactions. The work of Abderhalden and others would tend to indicate this. Our experimental conditions were such that this could easily be the case, for all hydrolysates were freely open to air. We have also stated[1] that "the vigor of boiling seems to influence both ammonia and insoluble humin formation." This difference (since the 2 samples were not boiled at the same time) might, and we believe does, account for the differences in the nitrogen distribution. However, as stated above, we are interested in possible changes in the nitrogen distribution of tryptophane under conditions comparable with those obtained in the acid hydrolysis of a protein over extended periods of time, whether they be due to oxidizing effects, or directly due to the effect of the acid, or to both.

The data for the acid-insoluble humin show that no detectable amount was formed during the first 24 hours. At the end of that time a few black amorphous particles could be seen in the dark reddish-brown liquid. At 48 hours there were a great number to be seen and these increased in amount with prolonged boiling. Our figures show that, at the end of 144 hours' boiling, from 4 to 8% of the tryptophane nitrogen appeared in this fraction. The figures for the ammonia fraction substantiate the evidence that we have already put forth in a former publication[2] where we state "a part of this (ammonia fraction) must be due to the breaking up of tryptophane." Fig. 1 indicates that deaminization proceeds quite rapidly at first as is the case in a protein hydrolysate.[3] This rate diminishes as the concentration of unaltered tryptophane in the solution decreases. The concordant results obtained for ammonia in each of the 2 hydrolysates appear to indicate that acid concentration and length of hydrolysis are alone responsible for the deaminization. The "soluble humin" nitrogen in these experiments is probably an intermediate product in "acid-insoluble" humin formation. No tyrosine is present and consequently tyrosine could not contribute to this fraction. This would appear to conflict with some of our earlier conclusions and it may be possible that some of the nitrogen in the soluble humin fraction of a normal protein hydrolysate is derived from tryptophane. We have already shown that traces of the tryptophane may appear in this fraction.[4] However, the experiments referred to show conclusively that only a small fraction of the tryptophane is converted into "soluble" humin in a 24-hour hydrolysate (0.20 mg. of soluble humin *N* from 100 mg. of tryptophane). In the same experiments no "insoluble humin" *N* was found.

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[1] Gortner and Holm, THIS JOURNAL, 39, 2738 (1917).

[2] *Ibid.*, 39, 2742 (1917).

[3] Cf. Fig. 1, *ibid.*, 39, 2736–2745 (1917).

[4] Gortner and Holm, *ibid.*, 42, 821–827 (1920).

A colorimetric determination upon the soluble humin fraction also shows that it still retains some of the properties of the tryptophane molecule; at least it gives color with the phenol reagent. A separation of the clear filtrate from the soluble humin into a "basic" and "non-basic" fraction by means of phosphotungstic acid indicates, as we have formerly pointed out, that there is no clear-cut separation of tryptophane into the "bases" or into the "filtrate from the bases." The result in case of a Van Slyke analysis will be that, if tryptophane is present, all of the non-amino nitrogen of a filtrate cannot with certainty be calculated as proline nitrogen and, in fact, might with equal certainty be calculated as non-amino tryptophane nitrogen. The bases, on the other hand, will be in error just to the extent of precipitated tryptophane which, as we have already suggested, will appear and be calculated largely as histidine.

The colorimetric determinations indicate that the "bases" and the "filtrate from the bases" contain substances, which, if they are not unchanged tryptophane, are, at any rate, tryptophane which has been only slightly altered. The color produced by solutions of the bases is approximately equal (82% of a tyrosine equivalent) to that given by unaltered tryptophane (85–90% of a tyrosine equivalent), while the substances in the filtrate from the bases gives a somewhat lower color value, indicating a somewhat greater alteration.

We intend in the near future to make a more exact study of some of the factors involved in tryptophane decomposition.

Summary.

We have studied certain changes produced by boiling tryptophane with 20% hydrochloric acid for various lengths of time and have reached the following conclusions.

1. Tryptophane is slowly altered and parts of the molecule are broken down by long acid-hydrolysis.

2. Tryptophane, in the absence of aldehydes or other reactive compounds, contributes but an insignificant fraction of its nitrogen to the "acid-insoluble" humin. A much larger amount of the tryptophane appears in the "soluble humin" after 144 hours' boiling with acid. Since, however, a normal protein hydrolysis rarely requires more than 24 hours' boiling, it appears extremely improbable that the "total" humin of such a hydrolysate is derived from tryptophane without the intervention of some other reactive compound, which we have postulated in our earlier papers to be of the nature of an aldehyde.

3. Tryptophane is relatively easily deaminized by boiling with 20% hydrochloric acid. Probably some of the ammonia of a normal protein hydrolysate is derived from tryptophane instead of being entirely derived from amide groupings.

4. When tryptophane has been boiled with 20% hydrochloric acid the

distribution of the nitrogen is such that errors may be introduced into both the "basic" nitrogen and the "non-basic nitrogen" fractions of a Van Slyke determination.

St. Paul, Minn.

[Communication from the Chemical Laboratory of Johns Hopkins University.]

A SULFIDE ACID OR THE BUTYL ETHER OF THIOGLYCOLIC ACID.

By Yoshisuke Uyeda and E. Emmet Reid.

Received August 30, 1920.

Introduction.

Sulfur, when present in an organic compound in the sulfide condition, $=CH—S—CH=$, may have comparatively slight influence on the chemical and physical properties of the compound while in some cases it gives rise to peculiar properties, as in β,β'-dichloro-ethyl sulfide. In this remarkable compound the presence of the sulfur atom renders the chlorine atoms very reactive.

It seemed of interest to prepare other compounds containing a sulfide grouping along with some other group with a distinctive function. The present investigation is a study of the acid, $CH_3CH_2CH_2CH_2 — S — CH_2COOH$, and some of its derivatives. Thiophene has nearly the same boiling point as benzene but a considerably higher density and the same may be said of ethyl sulfide as compared with hexane. In physical properties the above acid and its esters should resemble caprylic acid, $C_8H_{16}O_2$, and its esters to which they are nearest in molecular weight. This has been found to be true in a general way, though the acid boils at 282.2°, which is 45° higher than caprylic.

The sulfide acid forms salts readily, the sodium salt being very soluble in water while the barium and calcium salts are only moderately so. When mineral acids are added to water soltuions of its salts the acid separates readily as a heavy oil which would easily be mistaken for one of the fatty acids of about its molecular weight, even to the odor. It is very slightly soluble in water and distils without decomposition. The odors of its esters are somewhat like those of the higher aliphatic esters.

The acid is readily prepared by the action of sodium chloro-acetate on the sodium salt of butyl mercaptan in water solution. Its esters and many of its salts are easily obtained by the usual methods. The esters give good results on quantitative saponification as the acid is accurately titrated with phenolphthalein.

The remarkable fact about β,β'-dichloro-ethyl sulfide is that the influence of the sulfur renders the chlorine atoms quite movable.[1] This

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[1] Marshall, *J. Am. Med. Assoc.*, 73, 684 (1919); *C. A.*, 13, 2929 (1919).

same influence appears in the instability of the corresponding acetate as recently brought out by Helfrich and Reid.[1] It appears here that the amide of this new acid decomposes readily and its anilide and toluidide were found too unstable to prepare for analysis.

Historical.

Letts and Collie[2] prepared the methyl ether of thioglycolic acid by the action of methyl sulfide on ethyl iodoacetate and made the sodium and barium salts of the corresponding acid.

Claesson[3] obtained the corresponding ethyl derivative by the action of the ethyl chloro-acetate on sodium ethyl mercaptide in alcohol solution and the saponification of the ethyl ester with a solution of barium hydroxide in a sealed tube. They prepared a number of its salts and the amide (m. p. 44°). The amyl ether was made in the same way but was not studied. His method is cumbersome and round about.

Experimental.

To 600 cc. of water are added 120 g. of sodium hydroxide and 360 g. of crude butyl mercaptan (containing 75% BuSH) and into this solution, while it is stirred and cooled, is poured a concentrated solution of 285 g. of chloro-acetic acid previously neutralized with sodium carbonate. Much heat is evolved in the reaction and efficient cooling is required. After some hours, the mixture is heated and then steam distilled to drive off volatile impurities derived from the crude mercaptan. On addition of dil. sulfuric acid to the filtered solution, the free acid forms as an oily layer, which is separated, dried, and distilled under diminished pressure. From the above amounts, 395 g. of crude acid or 87% of that calculated, was obtained. The fraction, 245 g., boiling 140–4° at 10–15 mm., was collected.

Properties.—It is a slightly yellowish oil, still liquid at —14°; it boils with only slight decomposition. It is almost insoluble in water but mixes with alcohol and ether.

Identification Derivative.—The *p*-nitrobenzyl ester[4] was found to be an oil but the *p*-bromophenacyl ester[5] was readily obtained, m. p. 95°.

Salts.—The barium and calcium salts were made by adding the respective carbonates to the acid suspended in hot water, after which the solutions were filtered and cooled. The barium salt separates as transparent tablets with the peculiar property of being quite flexible. It is readily soluble in hot water and only sparingly so in cold water. The calcium salt separates as an aggregate of white leaflets, readily soluble in water. The

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[1] Helfrich and Reid, THIS JOURNAL, 42, 1208 (1920).

[2] Letts and Collie, *Jahresb.*, 1878, p. 685.

[3] Claesson, *Bull. soc. chim.* [2] 23, 444 (1875).

[4] THIS JOURNAL, 39, 124 (1917).

[5] *Ibid.*, 42, 1043 (1920).

strontium salt was made from solutions of the sodium salt by precipitation with strontium chloride. It is obtained as transparent tablets, rather soluble in water. The nickel and cobalt salts were prepared from solutions of the barium salt and of the sulfates of these metals. The nickel salt is obtained as minute faintly green crystals, sparingly soluble in water.

The zinc salt was prepared from the carbonate and a suspension of the acid in hot water. It separates as fine silky needles rather soluble in water.

The cadmium and manganese salts were prepared by double decomposition from the sodium salt and sulfates of these metals. The cadmium salt forms minute colorless crystals sparingly soluble in water. The manganese salt separates as faintly pink flakes, rather soluble in water.

The copper salt was prepared from the barium salt and copper sulfate and came down as minute blue crystals, fairly soluble in water. The silver salt was obtained from the barium salt with silver nitrate solution, as minute gray crystals only sparingly soluble in water. It is anhydrous and melts at 137.5°.

By passing dry ammonia into an ether solution of the acid according to McMaster's method[1] the ammonium salt separated as a crystalline mass but it is unstable and analysis showed partial decomposition.

The magnesium and lead salts could not be obtained in crystalline form. The sodium salt is left as a syrupy very soluble mass when its water solution is evaporated but could not be obtained in condition for analysis.

For the corresponding ethyl acid, Claesson found the calcium and barium salts to be anhydrous. His zinc, cadmium, cobalt, nickel and copper salts agree with ours, while his silver salt contained one molecule of water of crystallization.

COMPOSITION AND ANALYSES OF SALTS.

	Water.		Metal.	
$R = C_6H_{11}O_2S$.	Calc. %.	Found. %.	Calc. %.	Found. %.
Ba $R_2 \cdot 0.5H_2O$	2.04	2.18	31.13	31.55
Ca $R_2 \cdot 0.5H_2O$	2.62	2.71	11.66	11.71
Sr $R_2 \cdot 1.5H_2O$	6.61	6.61	21.32	21.57
Ni $R_2 \cdot 2H_2O$	9.25	9.20	15.16	14.98
Co $R_2 \cdot 2H_2O$	9.25	9.25	15.16	15.32
Zn $R_2 \cdot 2H_2O$	9.13	9.65	16.45	15.72
Cd $R_2 \cdot H_2O$	4.24	4.08	26.41	26.16
Mn $R_2 \cdot H_2O$	4.90	5.14	14.98	15.45
Cu $R_2 \cdot 2H_2O$	9.16	9.09	16.03	16.43
Ag R	....	....	42.36	42.96

Acid Chloride, $C_4H_9SCH_2COCl$.—A mixture of 150 g. of the acid and 70 g. of phosphorus trichloride (calc. 45 g. for $^1/_3$ mol.) was heated for 2

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[1] McMaster, *Am. Chem. J.*, 49, 84 (1913).

hours at 100°, then cooled to 0° and the acid chloride decanted.[1] The product was fractionated and the portion which boiled from 89–91° at 8 to 9 mm. was collected as the pure substance. Yield, 155 g. or 93%. The chloride is a colorless liquid with a peculiar odor; it fumes only slightly in the air. It boils at 218° (corr.) at 758 mm. with considerable decomposition. It has d^{25}_{25} 1.0956 and n_D 1.4810. Analysis gave 21.20% Cl, calculated 21.32.

Amide.—The amide is readily obtained by pouring the chloride into strong cold ammonium hydroxide. It melts at 65° and is not stable in contact with moist air.

Calc.: S, 21.76; N, 9.52. Found: S, 21.20; N, 9.30, 9.46.

Attempts were made to prepare the anilide and *p*-toluidide, but they could not be obtained pure.

Esters.—The esters were made from the acid chloride and the alcohols. The products were washed with water and sodium carbonate solution, dried and fractionated at reduced pressures. Weighed samples were saponified with standard sodium butylate in butyl alcohol according to method of Pardee and Reid.[2] The sulfur was determined by the Carius method. The properties and analyses are given in the table.

ANALYSES OF ACIDS AND ITS ESTERS.

	Mol. wt.		Subs.	BaSO$_4$.	Sulfur.	
	Calc.	Found.	G.	G.	Calc. %.	Found. %.
Acid	148	149	0.1707	0.2635	21.62	21.14
Methyl ester	162	160	0.1730	0.2480	19.75	19.65
Ethyl ester	176	179	0.1795	0.2347	18.18	17.93
Propyl ester	190	189	0.1750	0.2100	16.84	16.45
Butyl ester	204	202	0.2130	0.2365	15.68	15.25

PROPERTIES OF ACID AND ITS ESTERS.

	B. p. pressure. Mm.	B. p. cor. pressure. Mm.	d^0_0.	d^{25}_{25}.	Mol. vol. 0°.	$[n]^{25°}_D$.
Acid	$140°^{10}$	282.2^{764}	1.0771	1.0631	137.6	1.4780
Me ester	$85°^{10}$	224.0^{758}	1.0299	1.0125	157.5	1.4590
Et ester	$89–90°^{10}$	235.5^{758}	1.0044	0.9881	175.5	1.4560
Pr ester	$93–4°^{6}$	250.2^{758}	0.9892	0.9723	192.3	1.4555
Bu ester	$105–6°^{6}$	263.8^{758}	0.9794	0.9630	210.2	1.4555

Comparing the boiling points of our acid and its esters with those of *n*-hexoic acid and its esters, we find the following differences: acid, 77°; Me ester, 74°; Et, 67°; Pr, 65°; Bu, 59°. These differences are about as we would expect, when we consider that dibutyl sulfide (b. p. 182°) boils 57° higher than *n*-octane (b. p. 125°).

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[1] Aschan, *Ber.*, **31**, 2346 (1898).

[2] Pardee and Reid, *J. Ind. Eng. Chem.*, **12**, 129 (1920).

Summary.

The *n*-butyl ether of thioglycolic acid, $C_4H_9SCH_2COOH$, and some of its salts and derivatives have been studied. The following new compounds have been prepared. In each case R indicates the radical $C_4H_9SCH_2$.

$RCOOH$
$RCOCl$
$RCONH_2$
RCO_2CH_3
$RCO_2C_2H_5$
$RCO_2C_4H_9$
$(RCO_2)_2Ba.0.5H_2O$
$(RCO_2)_2Ca.0.5H_2O$
$(RCO_2)_2Sr.1.5H_2O$
$(RCO_2)_2Ni.2H_2O$
$(RCO_2)_2CO.2H_2O$
$(RCO_2)_2Zn.2H_2O$
$(RCO_2)_2Cd.H_2O$
$(RCO_2)_2Mn.H_2O$
$(RCO_2)_2Cu.2H_2O$
RCO_2Ag

BALTIMORE, MD.

[FORTY-FOURTH CONTRIBUTION FROM THE COLOR LABORATORY, U. S. BUREAU OF CHEMISTRY.]

ISOCYANINE DYES FROM LEPIDINE AND ITS HOMOLOGS.

BY ELLIOT Q. ADAMS AND HERBERT L. HALLER.

Received Sept. 7, 1920.

The mixed alkyl halides[1] of quinoline[2] and lepidine[3] give with alcoholic alkalies blue dyes known as "cyanines;"[4] when quinaldine[5] replaces lepidine, pink "isocyanines"[6] are formed. In both cases the quinoline may be replaced by quinaldine so that the mixed alkyl halides of quinaldine and lepidine give with alcoholic alkalies a blue;[7] and alkyl halides of quinaldine only, a pink color.

From these and other data it has been concluded that "cyanine"[8] is a derivative of 4,4-diquinolyl-methane and "isocyanine" of 4,2-diquinolyl-methane. It needs hardly to be stated that the hydrogens (1) and (1′) must be replaced to permit the formation of dyes capable of existence in alkaline solution.

The formation of a dye with alkali and quinaldine alkyl halides alone is explained as a condensation of the 2-methyl and 4-hydrogen, respectively,

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[1] It is now known that other quaternary addition compounds react similarly but the earliest dyes of all the types mentioned were halides.

[2] Benzene-substituted quinolines react similarly.

[3] *I. e.*, 4-methyl quinoline; benzene-substituted lepidines react similarly.

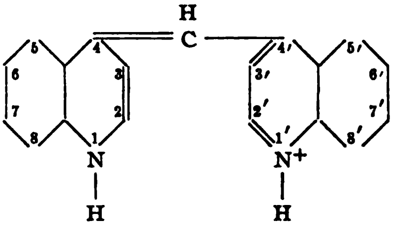
[4] C. Greville Williams, *Chem. News*, 1, 15 (1860).

[5] *I. e.*, 2-methyl quinoline. Benzene-substituted quinaldines react similarly.

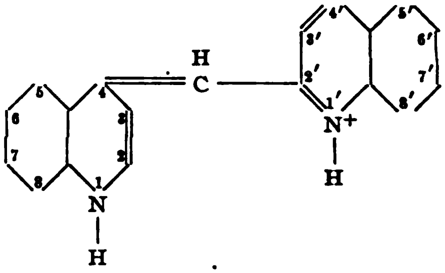
[6] Spalteholz, *Ber.*, 16, 1849 (1883). Hoogewerff and V. Dorp, *Rec. trav. chim.* 2, 28, 41 (1883); 2, 317–26 (1883); 3, 336–62 (1884).

[7] The results obtained with this combination appear to be nowhere recorded in the literature available to us; since the blue solution thus prepared is a mixture of at least 5 dyes, no one of which can be obtained crystalline, this omission is hardly to be wondered at.

[8] This nomenclature was first suggested by Hoogewerff and V. Dorp, *loc. cit.* A more detailed explanation, together with a more complete bibliography, will be given in a paper from this laboratory by L. E. Wise.



Cyanine(ion).



Iso-cyanine (ion).

of 2 molecules of the intermediate. If this explanation be correct, it should be possible to get a similar dye by the action of alkali on a lepidine alkyl halide by condensation of a 4-methyl and a 2-hydrogen. All the published accounts of dye formation from lepidine describe a blue or violet color. This is probably due to the presence of quinoline in the lepidine used, for lepidine made from cinchonine is certain to contain quinoline. Synthetic lepidine should contain no quinoline, but may contain quinaldine, and as mentioned above, this impurity likewise permits the production of a dye of the cyanine type. When lepidine ethiodide of sufficient purity is treated with alcoholic alkali in hot concentrated solution, the principal product is an *iso*-cyanine. In dilute solution or in the presence of formaldehyde other products result, which will be described in a later article. The isocyanine is presumably isomeric with that from quinaldine ethiodide, but is crystallographically[1] very different; its photosensitizing action is similar. Since other isocyanines possess greater photosensitizing power, these new isocyanines are interesting chiefly from the light which their existence throws on the nature of the isocyanine condensation; this type of dye can be formed alike from a 2-methyl and from a 4-methyl-quinoline alkyl halide, hence the only possible formulation of the reaction is as a 4,2′ condensation.

Preparation of Isocyanine from Lepidine Methiodide.—One hundredth of a mole (2.85 g.) of lepidine methiodide, was dissolved in 25 cc. methyl alcohol and the solution heated to boiling. 10 cc. of 0.5 N solution of sodium methylate (0.005 mole, equivalent to 0.115 g. of sodium) was gradually added to the boiling solution. Boiling was continued for a few minutes after the addition of the alkali, the flask loosely stoppered and the slightly concentrated solution allowed to cool very slowly. After 24 hours very fine bluish-black crystals separated. These were filtered off with suction, washed with ice-cold methyl alcohol, methyl alcohol-ether, and finally ether alone. The yield was about 0.8 g.

Preparation of Isocyanine from Tolu-lepidine Methiodide.—The same

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[1] The crystallography of these 2 and of 2 other isomers is being studied by Dr. E. T. Wherry, of the Crystallography Laboratory of the Bureau of Chemistry.

procedure, starting with 2.99 g. of tolu-lepidine methiodide (1,4,6-trimethyl-quinolium iodide) gave 0.75 g. of a crystal felt with a bluish-green sheen.

Preparation of Isocyanine from Tolu-lepidine Ethiodide.—The same procedure, starting with 3.13 g. of tolu-lepidine ethiodide (1-ethyl-4,6-dimethyl-quinolinium iodide) gave 0.47 g. of a purplish-black powder, containing many crystals showing brassy and blue-green metallic reflections.

Preparation of Isocyanine from Lepidine Ethiodide.—Starting with 1.5 g. of lepidine ethiodide, the same procedure was followed (half the quantity of all reagents being used) except that the solution was concentrated to a volume of 5 cc. and allowed to stand for 2 weeks. The dye separated in blunt (apparently) square prisms, with a brass-like luster, and showing peculiarly mottled reflection colors. The yield was 0.16 g.

Preparation of Isocyanine from Tolu-lepidine Methnitrate.—A solution of 4.50 g. of tolu-lepidine methiodide in 40 cc. of methyl alcohol was added to a solution of 2.56 g. of silver nitrate in 80 cc. of methyl alcohol, and the precipitated silver iodide filtered off. As the solution gave a test for silver, a small amount of the solution of the intermediate was added, and the filtration repeated. The solution was concentrated to 50 cc. and 15 cc. of 0.5 *N* sodium methylate (0.1725 g. of sodium in 15 cc. of methyl alcohol) was added to the boiling solution, which was then concentrated to 25 cc. and allowed to cool very slowly. The blue-black crystals which separated were washed with ice-cold methyl alcohol, methyl alcohol-ether, and finally ether alone. The yield was 0.43 g.

Summary.

1. The quaternary addition products of sufficiently pure lepidine (or homologs of lepidine) give when treated with alcoholic alkalies in hot, concentrated solution, dyes of the isocyanine type, similar to, but not identical with, those given by the corresponding derivatives of quinaldine.

2. The preparation of 5 such dyes is described.

3. The formation of isocyanines from lepidine confirms the hypothesis, now generally accepted, that these dyes contain 2 quinoline nuclei attached to a central carbon atom in Positions 4 and 2 respectively.

WASHINGTON, D. C.

[FORTY-THIRD CONTRIBUTION FROM THE COLOR LABORATORY OF THE BUREAU OF CHEMISTRY.]

SYNTHESIS OF PHOTOSENSITIZING DYES (II), DICYANINE A.[1]

BY LOUIS A. MIKESKA, HERBERT L. HALLER AND ELLIOT Q. ADAMS.

Received September 9, 1920.

The photosensitizing dyes (derived from quinoline) in use prior to 1919 were of 4 general types: isocyanines, *e. g.*, pinaverdol, sensitizing to green and yellow; cyanines and pinacyanols, both sensitizing to orange and red; and dicyanines, which extend the sensitiveness of the plate to, or even beyond 9000 Å. The dye of this last type which, from the point both of preparation and of use, we have found most satisfactory is that termed by the German manufacturers "Dicyanin A."

We have prepared this dye by the action of sodium methylate (or ethylate) in absolute methyl (or ethyl) alcoholic solution, in the presence of air, on 2,4-dimethyl-6-ethoxy-quinoline ethnitrate, obtained by the action of silver nitrate on the ethiodide of the same base. The base is prepared from *p*-phenetidine by condensation with paraldehyde and acetone.[2]

The corresponding dicyanine A iodide is more difficult to use in the plate-staining bath, but has somewhat better keeping qualities.

Preparation of 2,4-dimethyl-6-ethoxy-quinoline.—A mixture of 300 g. of acetone and 200 g. of paraldehyde, cooled on ice, is saturated with hydrogen chloride. After standing at 0° for 2 hours, the saturation is repeated, the mixture removed from the ice-bath and allowed to stand at room temperature for 20 hours. It is then added slowly to a solution of 300 g. of phenetidine in 600 g. of conc. hydrochloric acid (sp. gr. 1.2). The mixture, in a flask attached to a reflux condenser, is heated in a water-bath for 2 hours, then it is cooled, neutralized with a concentrated solution of sodium hydroxide, and extracted with ether. The ether extract is dried with anhydrous sodium sulfate, the ether removed by distillation and the residue distilled under reduced pressure. To the distillate is added an equal weight of acetic anhydride; this mixture is heated on a steam-bath for half an hour and poured into water. The phenacetine and unchanged anhydride are removed by filtration, the filtrate neutralized with a concentrated solution of sodium hydroxide, and extracted with ether; then the ether is removed and the residue distilled as before. The distillate is dissolved in twice its weight of conc. hydrochloric acid and a slight excess of sodium nitrate solution added at 0°. The solution is extracted with ether at 0°, and the extract discarded. The diazo-compounds are

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[1] The preparation of pinaverdol and pinacyanol has been described by L. E. Wise, E. Q. Adams, J. K. Stewart and C. H. Lund. *J. Ind. Eng. Chem.*, **11**, 460 (1919).

[2] The preparation of 2,4-dimethyl-quinoline is described by L. A. Mikeska, J. K. Stewart and Louis E. Wise. *J. Ind. Eng. Chem.*, **11**, 456 (1919).

destroyed by heating the solution on the steam-bath; the solution is neutralized with conc. sodium hydroxide solution and extracted with ether, the ether removed by distillation and the residue distilled under reduced pressure. The distillate is dissolved in its own weight of 95% alcohol, and an equal weight of alcohol containing about 10% in excess of the theoretical amount of sulfuric acid added. The precipitated sulfate is collected on a filter, washed with alcohol and then with ether. The base is recovered as before and recrystallized from petroleum ether. A yield of 75 g. of base boiling between 314° and 316° should be obtained.

A preparation made as above, except that the final purification was made by fractional distillation, gave in 4 analyses:

Calc. for $C_{13}H_{15}NO$: N, 6.96. Found: 6.96, 6.95, 6.97, 6.88.

Preparation of 2,4-dimethyl-6-ethoxy-quinoline Ethiodide.—To 10 g. of 2,4-dimethyl-6-ethoxy-quinoline is added an equal weight of ethyl iodide. The mixture in a flask attached to a reflux condenser is heated for 20 hours on the steam-bath. After it has cooled the solid reaction product is washed in the flask with ether. It is then recrystallized several times from boiling 95% alcohol. A yield of 10 g. should be obtained.

Calc. for $C_{15}H_{20}NOI$: N, 3.92. Found: Kjeldahl, 3.76, 3.71.

Preparation of Dicyanine A Nitrate (A VI).—A solution of 5.36 g. of 2,4-dimethyl-6-ethoxy-quinoline ethiodide (0.015 mol) in 25 cc. of absolute ethyl alcohol is slowly added to a solution of 2.55 g. of silver nitrate in 175 cc. of hot absolute ethyl alcohol. The precipitated silver iodide is removed by filtration. If the filtrate is found to contain silver, a slight excess of the ethiodide solution is added and the filtration repeated. The solution is concentrated to 60 cc., cooled to 10°, and air passed through it while a solution of sodium ethylate, prepared by dissolving 0.1725 g. of metallic sodium in 15 cc. of absolute ethyl alcohol, is added slowly. The aeration is continued for 16 hours, the precipitated sodium nitrate removed by filtration with the aid of suction, and the solution placed in a vacuum desiccator for 24 hours.

The grass-green crystals which separate are collected on a filter and washed with ice-cold ethyl alcohol, ethyl alcohol-ether, and finally, ether alone. The yield is about 0.15 g.

Preparation of Dicyanine A Iodide (A IV).—A solution of sodium methylate was prepared by dissolving 0.345 g. of metallic sodium in 30 cc. of absolute methyl alcohol. This sodium methylate was added slowly to a solution of 10.72 g. of 2,4-dimethyl-6-ethoxy-quinoline ethiodide (0.03 mol.) in 100 cc. of methyl alcohol, the mixture cooled to 10° and shaken continuously. The solution is then allowed to stand at room temperature in an open Erlenmeyer flask for 60 hours. The beetle-green crystals which separate are collected on a filter and washed with ice-cold methyl alcohol, then with methyl alcohol-ether mixture, and finally, with ether alone. The yield is about 0.25 g.

Summary.

Directions are given for the preparation of 2,4-dimethyl-6-ethoxy-quinoline from *p*-phenetidine; for the preparation of the ethiodide of this base, and, from it, the nitrate and iodide of Dicyanine A.

WASHINGTON, D. C.

[FORTY-SIXTH CONTRIBUTION FROM THE COLOR LABORATORY OF THE BUREAU OF CHEMISTRY.]

TETRAMETHYL-QUINOLINES.

BY LOUIS A. MIKESKA AND ELLIOT Q. ADAMS.

Received September 14, 1920.

Among the photosensitizing dyes prepared from quinoline derivatives, those which extend the sensitiveness of the photographic plate farthest into the infra-red are the dicyanines. They are prepared by treating with alkali the quaternary halides of 2,4-dimethyl-quinoline or its homologs. 2,4-Dimethyl-quinoline is obtained from aniline, acetone and paraldehyde by a condensation similar to the well-known Skraup synthesis. The substitution of toluidines for aniline in this reaction gives rise to derivatives of 2,4-dimethyl-quinoline with one methyl group in the benzene ring. As the dicyanine obtained from 2,4,6-trimethyl-quinoline seems to be somewhat superior to that obtained from 2,4-dimethyl-quinoline, a study of the effect of the introduction of another methyl group in the benzene ring was undertaken. To do this, xylidines were substituted for aniline in the synthesis. Since this reaction required an unsubstituted hydrogen in the *ortho* position to the amino group it is evident that it is inapplicable to *m*-2-xylidine. On the other hand, *o*-4-xylidine can theoretically yield 2 isomers, so that it should be possible to obtain 6 tetramethyl-quinolines from the 6 known xylidines.

A search of the literature has revealed that this reaction has been applied to *m*-4-xylidine by Levin and Riehm,[1] who obtained a tetramethyl-quinoline to which they assigned the alternative constitutions of 2,4,5,6- and 2,4,6,7-tetramethyl-quinolines, based on the erroneous assumption that *m*-4-xylidine is 1,2-dimethyl-4-aminobenzene. Since the name and structure applied to the xylidine used do not accord it was necessary to repeat their work in order to ascertain whether *m*-4-xylidine or *o*-4-xylidine was actually used. Levin and Riehm employed acetone alone in this condensation, whereas we used a mixture of acetone and paraldehyde. The melting point of the tetramethyl-quinoline obtained from *m*-4-xylidine agrees with that of the base obtained by Levin and Riehm, thus indicating that they used *m*-4-xylidine.

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[1] J. Levin and P. Riehm, *Ber.*, 19, 1394 (1886).

Symmetrical xylidine, obtained from mesitylene according to the method described by Haller and Adams[1] was used in the synthesis of 2,4,5,7-tetramethyl-quinoline; and *p*-xylidine served as an intermediate in the preparation of the corresponding 2,4,5,8-tetramethyl derivative.

The work on 2,4,7,8-, 2,4,5,6- and 2,4,6,7-tetramethyl-quinoline will be begun as soon as the necessary *o*-xylidines can be obtained in pure state.

The 3 tetramethyl-quinolines so far isolated[2] are obtained by the general procedure described below.

Experimental Part.

A mixture of 30 g. of acetone and 20 g. of paraldehyde is saturated with dry hydrogen chloride at 0° and is allowed to stand for 18 hours at room temperature. The reaction mixture is then poured into a solution of 27 g. of xylidine in 54 g. of conc. hydrochloric acid. The reaction begins at once with slight evolution of heat and is completed by heating for 1 to 2 hours on a water-bath under a return condenser. The dark brown mass is next neutralized with conc. sodium hydroxide solution, whereupon a brown oil is obtained, which is separated from the mother liquor by extraction with ether. The ether extract is dried with sodium sulfate, the ether removed, and the residue distilled under reduced pressure. In order to remove the unchanged xylidine the distillate is heated on a water-bath for 2 hours with an equal weight of acetic anhydride and is then poured into several volumes of cold water. The acetxylid is thus precipitated and removed by filtration, the filtrate treated with an excess of alkali to regenerate the base which separates in the form of an oil but solidifies on cooling and stirring. For 2,4,5,7- and 2,4,6,8-tetramethyl-quinolines the yield at this stage of purity is about 22 to 25 g. For 2,4,5,8-tetramethyl-quinoline the yield is somewhat less. The last traces of unchanged xylidine, together with small amounts of the corresponding tetrahydro-quinolines, are removed from the acid solution by diazotization with sodium nitrite. The nitroso tetrahydro-quinolines are removed by extracting the acid solution with ether, the diazonium salts are decomposed by heating and the quinoline bases are regenerated by treating with excess of alkali. The free base is then recrystallized from petroleum ether. 2,4,5,7- and 2,4,6,8-, tetramethyl-quinoline are readily obtained in the form of snow-white crystals melting at 59° and 86° respectively. It is somewhat more difficult to purify the corresponding 2,4,5,8-tetramethyl derivative which melts at 131°.

Summary.

1. The only 2,4-dimethyl-benzene-dimethyl-quinoline hitherto described, was incorrectly named by Levin and Riehm, who prepared it.

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[1] H. L. Haller and E. Q. Adams, This Journal, 42, 1840–2 (1920).

[2] As the senior author has left the Color Laboratory, it has been thought best to publish the work completed to date.

2. The synthesis of 2,4,6,8-, of 2,4,5,7-, and 2,4,5,8-tetramethyl-quinoline is described, and the properties of these bases noted.

WASHINGTON, D. C.

[FORTY-FIFTH CONTRIBUTION FROM THE COLOR LABORATORY OF THE BUREAU OF CHEMISTRY.]

THE PREPARATION OF LEPIDINE AND RELATED BASES.

BY LOUIS A. MIKESKA.

Received September 14, 1920.

The first of the cyanine dyes was prepared by Williams,[1] from what we now know to have been a mixture of lepidine and quinoline, by treatment first with amyl iodide and then with alcoholic potash. The importance of lepidine as a source of cyanine has been considerably diminished by the introduction of pinacyanol, derived from the more easily obtained quinaldine,[2] possessing the same sensitizing properties as cyanine, and obtained in considerably better yield. The recent discovery that from the alkyl halides of lepidine and related bases can be obtained, not only a number of hitherto unknown dyes of the isocyanine (or pinaverdol) type, but also dyes of a new type,[3] possessing interesting and useful sensitizing properties in the infra-red, renders the preparation of pure lepidine in good yield again a matter of importance.

Several different methods for the preparation of lepidine are quoted in Beilstein's "Handbook," but without exception they are difficult to carry out and disappointing in yield and purity of product. The following procedure has been found to give a fair yield of pure lepidine.

Preparation of Lepidine.—A mixture of 300 g. of acetone and 300 g. of 40% formaldehyde is cooled in ice and saturated with hydrogen chloride. After standing overnight at room temperature, it is cooled and saturated with hydrogen chloride as before, and again allowed to stand overnight. It is then slowly added to a cooled mixture of 300 g. of aniline and 600 g. of hydrochloric acid (sp. gr. 1.2). The mixture is heated on a water-bath for 3 hours, under a reflux condenser. After cooling it is neutralized with conc. sodium hydroxide solution and extracted with ether. The extract is dried over sodium sulfate, the ether distilled off and the residue distilled under reduced pressure. To the distillate is added an equal weight of acetic anhydride, and the mixture is heated on the steam-bath half an hour and then poured into water. The acetanilide and unchanged anhydride are filtered off, and the lepidine recovered by neutral-

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[1] C. Greville Williams, *Chem. News*, 1, 15 (1860).

[2] By treatment with formaldehyde and alcoholic alkali, with exclusion of air. Cf. L. E Wise, E. Q. Adams, J. K. Stewart and C. H. Lund, THIS JOURNAL, 11, 460 (1919).

[3] Kryptocyanines. E. Q. Adams and H. L. Haller, will be published later.

izing, extracting and distilling as before. Traces of acetanilide may be removed at this point by dissolving the lepidine in petroleum ether, filtering, and distilling off the solvent. The lepidine is dissolved in 1.5 times its own weight of hydrochloric acid (sp. gr. 1.2) and cooled. A slight excess of sodium nitrite is added and the cold solution extracted with ether (to remove nitroso-tetrahydro-lepidine). The solution is boiled to decompose the diazo-compound and the phenol formed removed by extracting the acid solution with ether. The lepidine is recovered by neutralizing, extracting and distilling as before. It is then dissolved in an equal weight of 95% alcohol, and twice as much alcohol containing a 10% excess of sulfuric acid is added. After cooling the sulfate is filtered off, washed with cold alcohol and then ether. From the snow-white sulfate the lepidine is recovered as before. A yield of 20 g. of lepidine boiling at 262° (atmospheric pressure) may be expected.

Preparation of *p*-Tolu-lepidine.—When the aniline is replaced by an equal weight of *p*-toluidine, the same procedure gives *p*-tolu-lepidine (*i. e.*, 4,6-dimethyl-quinoline).

Preparation of *p*-Ethoxy-lepidine.—When the aniline is replaced by an equal weight of *p*-phenetidine, the same procedure gives *p*-ethoxy-lepidine (*i. e.*, 4-methyl-6-ethoxy-quinoline). The product, being solid, may be recrystallized from petroleum ether. It then melts at 77°.

Calc. for $C_{12}H_{13}NO$: N, 7.48. Found: (Kjeldahl) 7.40, 7.32, 7.33.

The base gave an ethiodide melting at 187° (uncorr.).

The preparation of other related bases will be discussed in articles shortly to appear on trimethyl- and tetramethyl-quinolines.

Summary.

Recent developments in the field of photosensitizing dyes have brought lepidine and related bases again into prominence.

A procedure is given for the preparation of lepidine, *p*-tolu-lepidine and *p*-ethoxy-lepidine.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE OIL, FAT AND WAX LABORATORY, BUREAU OF CHEMISTRY, DEPARTMENT OF AGRICULTURE.]

CANTALOUP SEED OIL.

BY WALTER F. BAUGHMAN, DIRK BRAUNS, AND GEORGE S. JAMIESON.

Received September 14, 1920.

Considerable quantities of unmarketable cantaloup (*Cucumis melo* L.) are allowed to remain on the fields. If the melons are collected and dumped into shallow pits, they soon decompose so completely that the seeds can readily be recovered by raking them from the pits.

A large sample of cantaloup seed was received from the Imperial Valley, California. An ether extraction showed that these seeds contained about 30.4% of oil. The seeds were pressed by H. S. Bailey, formerly in charge of this laboratory, in an expeller, and the oil was used for this investigation, the results of which are given below.

Physical and Chemical Examination.—The cold-pressed virgin oil has a pale yellow color, an odor resembling that of olive oil and a pleasant fruity taste. The physical and chemical characteristics are given in Table I. The iodine number indicates that it might be a semi-drying oil, but no film developed even after the oil had been exposed to the air on a glass plate for one week. The acetyl value indicates the presence of a small amount of hydroxylated acids. Glycerides of volatile acids are almost completely absent as shown by the low Reichert-Meissl and Polenske numbers. Only 0.4% of acids soluble in water was found. The oil does not easily become rancid. This sample had been stored for 2 years at room temperature in a stoppered-glass bottle yet it had acquired no rancid odor nor taste and the acid value (mg. of potassium hydroxide required to neutralize the free acids in one g. of oil) was only 0.43. The saturated and unsaturated acids were determined by the lead-salt ether method. It is well known that it is not possible to effect a complete separation by this procedure. The saturated acid fraction always absorbs some iodine showing the presence of unsaturated acids. Also the unsaturated acid fraction is contaminated with small amounts of saturated acids, but this error is much smaller than the first. By refraining from excessively washing the precipitated lead salts of the saturated acids with ether the error caused by their slight solubility in ether is reduced. Of course, the amount of unsaturated acids remaining with the saturated acid fraction is greater. However, the amount can be calculated and the proper correction made as follows: $\frac{\text{iodine number of saturated acid fraction}}{\text{iodine number of unsaturated acid fraction}} \times 100 = A$ (per cent. of unsaturated acids contaminating the saturated acid fraction). The proper correction is then obtained by means of the formula $(A \times B)/100$ in which B is the per cent. of impure saturated acids. This correction is subtracted from the per cent. of impure saturated acids and added to the per cent. of unsaturated acids actually determined.

TABLE I.—CANTALOUP SEED OIL.
Chemical and Physical Characteristics.

Specific gravity 25°/25°	0.9210	
Refractive index 20°	1.4725	
Iodine number (Hanus)	125.9	
Saponification value	192.3	
Reichert-Meissl number	0.33	
Polenske number	0.26	
Acetyl number	15.8	
Acid value	0.43	
Unsaponifiable matter, %	1.1	
Soluble acids (% butyric acid)	0.4	
Insoluble acids %	94.0	
Unsaturated acids (determined) %	79.2	(Iodine No. 151.8)
Saturated acids (determined) %	15.3	(Iodine No. 10.0)
Unsaturated acids (corrected) %	80.2	
Saturated acids (corrected) %	14.3	

Unsaturated Acids.—The bromine addition derivatives[1] of the unsaturated acids were made. No hexabromide was obtained, which indicates the absence of linolenic acid. A large quantity of linolic tetrabromide was obtained melting at 113–114°. The theoretical iodine number of linolic acid is 181.4 while the iodine number of the unsaturated acid fraction is 151.8; so oleic acid whose iodine number is 90.1 must also be present. Using the iodine numbers to calculate the proportions of these 2 acids we get 67.6% of linolic acid and 32.4% of oleic acid in the unsaturated acid fraction, or 56.6% of the glyceride of linolic acid and 27.2% of oleic acid glyceride in the original oil.

Saturated Acids.—The saturated acids obtained by the lead salt ether method were esterified with methyl alcohol. The mixture of methyl esters was subjected to fractional distillation under diminished pressure. The data of this distillation are given in Table II. As indicated, a preliminary distillation resulted in 5 fractions designated by letters, and a residue. Fraction A was redistilled into Fractions 1, 2 and 3. Fractions B and C were combined and redistilled, resulting in Fractions 4, 5 and 6. Fraction D was not redistilled but E was combined with the original residue and redistilled into Fractions 8, 9 and 10

The iodine numbers and the saponification values of the various fractions are given in Table III, Cols. 2 and 3. From this data it is possible to calculate the saponification values and mean molecular weights of the saturated acid esters uncontaminated with unsaturated acid esters as explained in previous papers.[2]

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[1] Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats and Waxes," 5th Ed., Vol. I, pp. 568–578.

THIS JOURNAL, 42, 152, 1197 (1920).

TABLE II.—CANTALOUP SEED OIL.
Fractional Distillation of Methyl Esters of Saturated Acids.
85.5 G. of Esters subjected to Distillation.

Original fractions.	Final fractions.	Temperature, ° C.	Pressure. Mm.	Weight. G.
A		165–165.5	4.0	(23.3)[a]
	1	165–169	6.0	3.3
	2	168–173	5.0	18.2
	3	175–176	5.0	1.8
B		165–167	4.0	(23.8)[a]
C		167	3.5	(8.4)[a]
	4	158–163	3.0	3.9
	5	164–166	3.0	21.8
	6	167–175	3.5	6.5
D	7	167–171	3.5	11.0
E		171–186	3.5	(15.2)[a]
Residue				(3.8)[a]
	8	179–183	3.0	13.4
	9	183–195	3.0	3.0
	10	195–220	3.0	1.0
	Residue			1.5
		Total..................		85.4

[a] Not included in total.

In Col. 6 are given the mean molecular weights of the methyl esters of the saturated acids in the various fractions. Inspection of these results indicates the possible saturated acids that may be present. The molecular weights of Fractions 1 and 4, 262.6 and 266.4 are between the molecular weight of methyl myristate (242.3) and methyl palmitate (270.3) and suggest, therefore, the presence of these 2 acids. The molecular weights of all the other fractions lie between methyl palmitate and methyl stearate (298.4).

The following acids were isolated and identified by recovering the free acids from the various fractions and subjecting them to fractional crystallization from alcohol until constant melting points were obtained.

Stearic acid, $C_{18}H_{36}O_2$, m. p. 69°. Several recrystallizations of the free acids recovered from Fractions 9 and 10 gave a product which melted at 68–69°. An elementary analysis was made with the following results:[1]

Calc. for stearic acid: H, 12.76; C, 75.98. Found: H, 12.50; C, 76.04.

Palmitic acid, $C_{16}H_{32}O_2$, m. p. 62.6°. From Fractions 1 and 2 acids were isolated having a melting point of 62–63°. Elementary analysis gave the following results:

Calc. for palmitic acid: H, 12.58; C, 74.92. Found: H, 12.47; C, 74.72.

Myristic acid, $C_{14}H_{28}O_2$, m. p. 53.8. The Fraction 1, alcoholic mother-liquor from the palmitic acid crystallization, was diluted with a small amount of water and a crop of crystals obtained which, after several

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[1] (Analysis by Charles E. F. Gersdorff.)

recrystallizations, melted at 54°. The fraction was not large enough for an elementary analysis.

It is now established that the saturated acids present are myristic, palmitic and stearic and the proportions present in each fraction have been calculated from the molecular weights with the results given in Table III.

TABLE III—CANTALOUP SEED OIL.

Results of Analyses of Fractions Obtained by Distilling Methyl Esters of Saturated Acids.

Fractions.	Iodine number.	Saponification value.	Unsaturated acids. %	Unsaturated acids. G.	Mean molecular weight of esters of saturated acids.	Myristic acid. %	Myristic acid. G.	Palmitic acid. %	Palmitic acid. G.	Stearic acid. %	Stearic acid. G.
1.....	6.2	212.6	4.1	0.14	262.6	24.9	0.82	66.1	2.18	....	....
2.....	8.5	204.9	5.6	1.02	272.6	....	....	82.3	15.00	7.4	1.35
3.....	20.8	197.2	13.8	0.25	282.9	....	....	44.9	0.81	36.8	0.66
4.....	6.5	209.7	4.3	0.17	266.4	12.6	0.50	78.3	3.05	....	....
5.....	10.3	203.8	6.8	1.48	274.1	....	....	76.5	16.68	12.1	2.64
6.....	20.8	197.2	13.8	0.90	282.9	....	....	44.9	2.92	36.8	2.39
7.....	20.7	196.9	13.8	1.52	283.5	....	....	43.2	4.75	38.6	4.25
8.....	26.1	192.5	17.3	2.32	291.0	....	....	20.4	2.73	57.9	7.76
9.....	27.3	190.9	18.1	0.54	293.9	....	....	12.1	0.36	65.5	1.96
10.....	31.5	189.1	20.9	0.21	297.5	....	....	2.1	0.02	72.8	0.73
							1.32		48.50		21.74

Table IV gives in Col. 2 the percentage composition of the saturated acid fraction, in Col. 3 the percentages present in the original oil, and in Col. 4 the percentages of glycerides in the original oil.

TABLE IV.—CANTALOUP SEED OIL.

Composition of Saturated Acids.

	G.	%.	Original oil. %.	Glycerides in original oil. %.
Myristic................	1.32	1.8	0.3	0.3
Palmitic................	48.50	67.8	9.7	10.2
Stearic................	21.74	30.4	4.3	4.5
Total..............	71.56	100.0	14.3	15.0

Summary.

A sample of cantaloup seed was found to contain 30.4% oil. The chemical and physical characteristics of the oil were determined. A study was also made of the chemical composition, the results of which are given in the following table.

COMPOSITION OF CANTALOUP SEED OIL.

Glycerides of	Myristic acid........................	0.3
	Palmitic acid........................	10.2
	Stearic acid........................	4.5
	Oleic acid........................	27.2
	Linolic acid........................	56.6
Unsaponifiable matter		1.1
		99.9

WASHINGTON, D. C.

[CONTRIBUTION FROM THE DEPARTMENT OF PHARMACOLOGY, HARVARD MEDICAL SCHOOL.]

HYPOPHOSPHOROUS ACID PREPARATION OF ARSPHENAMINE. (3,3^1-DIAMINO-4,4^1-DIHYDROXY-ARSENOBENZENE DIHYDROCHLORIDE.)[1]

BY WALTER G. CHRISTIANSEN.

Received September 16, 1920.

In the course of our work it was found that the reduction of 3-amino-4-hydroxy-phenyl-arsonic acid by hypophosphorous acid consistently gives arsphenamine of low toxicity. The amino acid was secured most readily by reducing 3-nitro-4-hydroxy-phenyl-arsonic acid with sodium hydrosulfite[2] and then purified by precipitation from a hydrochloric acid solution with sodium acetate. Instead of isolating the arsphenamine base after the reduction of the amino acid, as done by Fargher and Pyman, the reduced solution was poured into hydrochloric acid, thereby precipitating the arsephenamine as the dihydrochloride, which, although difficultly soluble in cold water, conforms to the qualitative tests for arsphenamine outlined in the Public Health Reports.[3]

It has been found that by oxidizing toxic arsphenamine to the 3-amino-4-hydroxy-phenyl-arsonic acid and then reducing this intermediate with hypophosphorous acid arsphenamine of low toxicity was obtained.

Fargher's[4] modification of Lehmann's method was used in the arsenic determinations, and the toxicity of the products was determined by intravenous injection into albino rats according to the standard method adopted by the U. S. Public Health Service.

The amino acid was synthesized by 4 different methods, and the arsphenamine secured from it was, in each case, of low toxicity.

Experimental.

Oxidation of Arsphenamine.[5]—Thirty-five g. of arsphenamine is dissolved in 360 cc. of water, 40 cc. of 10 *N* sodium hydroxide solution is added, and then hydrogen peroxide (3%) slowly. The reaction is quite exothermic, and the solution becomes dark brown. After a while, a precipitate forms which is redissolved by adding a little 10 *N* sodium hy-

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[1] This is the first of a series of studies on the properties contributing to the toxicity of arsphenamine being made under a grant from the Interdepartmental Social Hygiene Board to the Harvard Medical School; the work is under the general direction of Dr. Reid Hunt, who is also responsible for the biological tests reported in this paper.

The experimental work reported here was largely completed before the publication of the paper by Fargher and Pyman, *J. Chem. Soc.*, 117, 370 (1920).

[2] Fargher, *ibid.*, 115, 982 (1919).

[3] Myers and Du Mez, *Public Health Reports*, 33, 1004 (1918).

[4] *Loc. cit.*

[5] This method is suggested by Ehrlich and Bertheim, *Ber.*, 45, 756 (1912), but details were not given.

droxide solution. More hydrogen peroxide is now added until the precipitate reappears. This alternate addition of the sodium hydroxide and hydrogen peroxide is continued until a precipitate no longer appears when the oxidizing agent is added. The total quantity of hydrogen peroxide used is about 310 cc., and 14 cc. of 10 *N* sodium hydroxide was added to redissolve the precipitates. The solution is acidified with glacial acetic acid (39 cc.); if a mineral acid is used care must be taken to reach the point when the solution is acid to litmus, but not to congo red, as the amino-hydroxy-arsonic acid is soluble in an excess of mineral acid. Yields, 60% of brown solid.

Purification of Crude 3-Amino-4-hydroxy-phenyl-arsonic Acid.—Ten g. of the crude acid is dissolved in 100 cc. of water plus 8 cc. of hydrochloric acid (1.19), super-filtchar[1] is added and the solution agitated for 15 minutes at room temperature. Heating was found to hinder the decolorization. After filtering, 20% sodium acetate solution (about 90 cc.) is added to the colorless or light yellow filtrate until the latter is no longer acid to congo red. White or slightly pink, minute plates crystallize, and after thorough cooling, they are filtered off and air-dried. The yield is 78%.

Subs., 0.1999: 34.91 cc. of 0.04889 *N* $Na_2S_2O_3$ solution.
Calc. for $C_6H_8O_4NAs$: As, 32.17. Found: 31.99.

Preparation of Arsphenamine.—Twenty-three g. of purified 3-amino-4-hydroxy-phenyl-arsonic acid is dissolved in 736 cc. of water plus 138 cc. of 50% hypophosphorous acid plus 11.5 cc. of 3% potassium iodide solution. The mixture is heated gradually to 55° and maintained at 55–60° for 90 minutes. The deep yellow solution is cooled to 10° and poured with vigorous stirring into 1640 cc. of 1 : 1 hydrochloric acid which has been previously cooled to 2°. The precipitate is filtered and washed with 100 cc. of cold 1 : 1 hydrochloric acid and dried in thin layers *in vacuo* over flake sodium hydroxide. Yield, 98.3% of light yellow powder of high specific gravity.

Subs., 0.2007: 13.38 cc. of 0.1280 *N* $Na_2S_2O_3$.
Calc. for $C_{12}H_{14}O_2N_2Cl_2As_2.H_2O$: As, 32.82. Calc. for $2H_2O$: As, 31.58. Found: 31.99.

The product is yellow, dissolves readily in warm water, and its aqueous solution is clear bright yellow. With cold water it forms a jelly. The material was found to be free from inorganic arsenic and sulfur and conformed to the qualitative tests for arsphenamine.

Arsenic Content.—The average of the analyses of 25 samples prepared by hydrosulfite reduction[2] and Kober's[3] conversion of the base into

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[1] A high grade of decolorizing carbon prepared by the Industrial Chemical Co., N. Y., who kindly placed a supply at our disposal.

[2] Ehrlich and Bertheim, *loc. cit.*

[3] THIS JOURNAL, 41, 442 (1919).

dihydrochloride shows 31.30% of arsenic, while the average of the analyses of 10 samples prepared by hypophosphorous acid reduction followed by hydrochloric acid precipitation of the dihydrochloride showed 31.00% of arsenic. Theoretically, arsphenamine with 2 molecules of water of crystallization should contain 31.58% of aresnic.

Toxicity.—The average tolerated dose of 44 samples prepared by hydrosulfite reduction and methyl alcohol-ether[1] or Kober's method of conversion of the base into the dihydrochloride is 100 mg./kg. bodyweight, and the doses ranged from below 60 to 140 mg./kg. The average tolerated dose of 10 samples prepared by the method outlined above is 140 mg./kg. and ranged from 120 to 160 mg./kg.

Reworking of Toxic Arsphenamine.—Four samples of arsphenamine which would not pass the present U. S. P. H. S.[2] requirements were oxidized to the amino-hydroxyphenyl-arsonic acid which, after purification, was reduced to arsphenamine with hypophosphorous acid and precipitated by pouring into 1 : 1 hydrochloric acid.

Ext. No.	Tolerated dose of original.	Tolerated dose of arsphenamine obtained.
51	Below 100 mg./kg.	150 mg./kg.
53	Below 80 mg./kg.	140 mg./kg.
38	Doubtful at 80 mg./kg.	Above 140 mg./kg.
42	Below 80 mg./kg.	140 mg./kg.

In order to try this procedure on a little larger scale, Mr. Lewis I. Nurenberg, chemist in charge of the arsphenamine laboratory of the Massachusetts Health Department prepared arsphenamine by this method from some amino-hydroxyphenyl-arsonic acid which was secured by oxidation of an old toxic lot of arsphenamine and obtained a product which had a tolerated dose of 130 mg./kg. Another batch gave a product which had a tolerated dose of 130–140 mg./kg.

Summary.

1. A method for the preparation of 3,3^1-diamino-4,4^1-dihydroxy-arsenobenzene dihydrochloride directly from the aminohydroxyphenyl-arsonic acid has been developed which, in every case in this laboratory, has given a relatively non-toxic product and which, when carried out in another laboratory by other manipulators, gave equally good results.
2. By application of this method toxic arsphenamine has been converted into relatively non-toxic material.
3. Although the product obtained by this method is less readily soluble in water than that obtained by the methyl alcohol-ether method, the use of warm water in dissolving it has not been found to be injurious.
4. The isolation of arsphenamine base and its possible oxidation during manipulation are avoided.

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[1] Ehrlich and Bertheim, *loc. cit.*

[2] U. S. Public Health Service.

5. The qualitative tests and the analyses of the product show that it is chemically the same as that obtained by the older method.

6. The source of the amino-hydroxyphenyl-arsonic acid does not affect the toxicity of the arsphenamine obtained from it.

The writer wishes to express his thanks to Dr. Reid Hunt for his interest in the work, his helpful suggestions and his kindness in determining the toxicity of the preparations.

Boston, Mass.

[Contribution from the Chemical Laboratory of the University of California.]

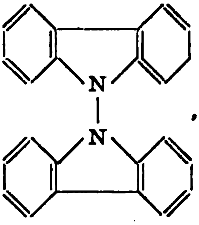
A BIVALENT NITROGEN DERIVATIVE OF CARBAZOLE.

By Gerald E. K. Branch and Julian F. Smith.

Received September 13, 1920.

Introduction.

The two series of compounds



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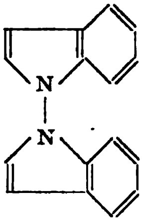

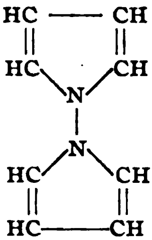

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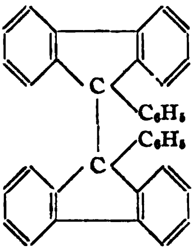
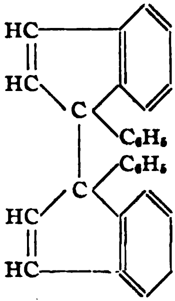
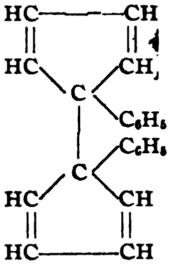
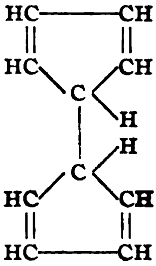
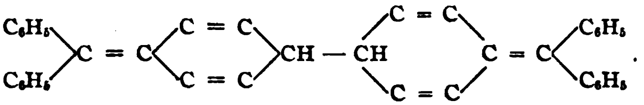






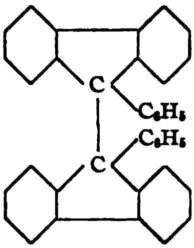


are of interest since they vary by graduated steps from compounds closely allied to the tetra-aryl hydrazines and hexa-arylethanes to purely aliphatic types which are similar in form to the quinoid modifications such as

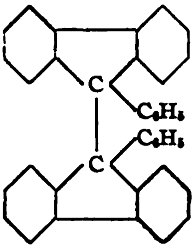


$$\begin{array}{l}C_6H_5\\C_6H_5\end{array}\!\!>C=C<\begin{array}{l}C=C\\C=C\end{array}>CH-CH<\begin{array}{l}C=C\\C=C\end{array}>C=C<\begin{array}{l}C_6H_5\\C_6H_5\end{array}.$$

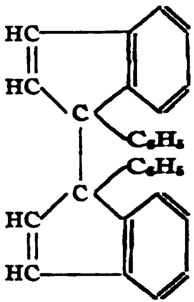
Substances of Type I p. 2406 have been prepared and appear to show some evidence of dissociation, but to a less extent than the corresponding hexa-aryl ethanes. They do not give colored solutions and no dissociation has been shown by molecular weight determinations, but, on the other hand,



(I).



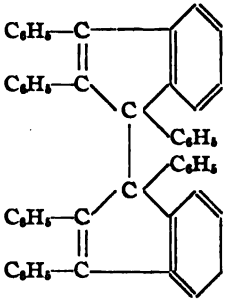
(II).



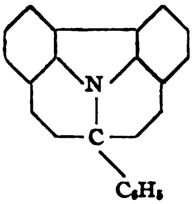
(III).

they absorb oxygen to form peroxides.[1] Thus it would appear from the evidence at present in our possession that the change from a compound of the type of hexaphenyl ethane to one of Type II is associated with a decrease in dissociation.

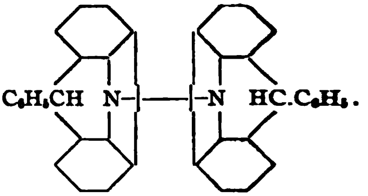
Only one compound of Type III is known, namely IV. This is a colored substance which readily absorbs oxygen, the description of which is very similar to that of hexaphenyl ethane. The molecular weight, however, was not determined.[2]



(IV).



(V).



(VI).

None of the corresponding nitrogen compounds is known, with the possible exception of a substance obtained by Bizzari by the reduction of the compound V which he believed to be the compound VI. He gives little evidence in favor of this view, neither a combustion nor a molecular-weight determination. He based his belief chiefly on the amount of silver solution which it could reduce, assuming that this would give the amount of reduction which the mother substance had undergone. But his figures show too large a variation to be very convincing. Thus he obtained in 2 experiments 2.45 and 1.72 equivalents of silver for a calculated value of 2. He describes the substance as giving a yellow solution and being unstable to the action of mineral acids.[3]

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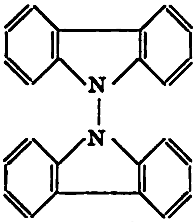
[1] Gomberg and Cone, *Ber.*, **37,** 3546 (1904); Schmidlin and Garcia-Benus, *ibid.*, **45,** 1344 (1912); Herzenstein, *Dissertation* Zurich 1911.

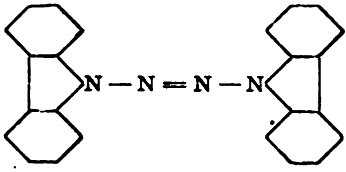
[2] Kohler, *Am. Chem. J.*, **40,** 317–333 (1908).

[3] Bizzari, *Gazz. chim. ital.*, **20,** 407–17 (1890).

Wieland and his co-workers describe 3 unsuccessful attempts to prepare a compound of the structure VII. First by the oxidation of carbazole

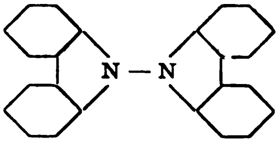


(VII).



(VIII).

[1]



(IX).

with lead dioxide,[2] second by the expulsion of nitrogen from a substance corresponding to VIII and third by boiling *N*-nitroso-carbazole in xylene which gave a mixture of carbazole and 3-nitro-carbazole.[3]

A Di-bi-phenylene Hydrazine.

By oxidizing carbazole with silver oxide we obtained 2 substances, one soluble, the other insoluble in ether. The former we have not as yet investigated any further, but the latter appears to be a poly-carbazyl derivative of the substance IX which dissociated to a great extent in solution.

This substance is an almost white powder, but gives red-brown solutions with blue fluorescence. It melts at 283–287°, with decomposition; stem corrected 292–296. It is very soluble in benzene or any benzene derivative, in chloroform, bromoform, ethylene bromide, carbon disulfide, thiophene and pyridine; slightly soluble in carbon tetrachloride and ethyl acetate, and insoluble in ligroin, ether, alcohol, acetic acid and water. On evaporation of a solution it leaves a brown vitreous mass from which the unchanged substance may be obtained as a white powder on treatment with alcohol. The vitreous mass above described retains the solvent, for if chloroform be used it gives a strong test for halogen even after standing in the air for 2 weeks. This strong affinity for the solvent is also indicated by its high solubility (more than 50 g. in 100 g. of benzene) in spite of its high melting point.[4] The color is approximately the same in all solvents, but the fluorescence varies considerably. Thus in carbon tetrachloride a saturated solution, though markedly colored, shows no fluorescence, although as judged by color it is noticeable in even more dilute solutions in benzene or ethyl acetate. The fluorescence of a nitrobenzene solution is green instead of blue.

Found: C, 86.0; H, 4.44; N, 8.22; Ag, 1.4.
Found (corrected for Ag as impurity): C, 87.2; H, 4.50; N, 8.33.

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[1] Fussel, *Dissertation*, Univ. Muenchen, 1912.

[2] Wieland and Gambarjan, *Ber.*, 39, 1506 (1906).

[3] Lecher, *Dissertation*, Univ. Muenchen, 1913.

[4] Hildebrand, THIS JOURNAL, 38, 1452–73 (1916).

The molecular weight in benzene varies directly with the concentration as shown in Table I.

TABLE I.

Wt. C_6H_6. G.	Sample. G.	F. p. lowering. ° C.	Apparent mol. wt.	Dissociation. %.	K in mols./1000 g. of solvent.
26.31	0.1192	0.048	472	40	7.5×10^{-3}
26.31	0.4748	0.180	501	31.8	12.9×10^{-3}
26.31	0.9828	0.351	544.5	21.4	13.4×10^{-3}
				Mean	11.3×10^{-3}

The substance adds nitric oxide to give a yellow crystalline substance melting above 270°. It does not give a precipitate with oxygen in a benzene solution, nor does it decolorize iodine. In benzene solution it reacts violently with bromine giving off some hydrogen bromide; and forms a slight precipitate, but the major portion goes to a benzene soluble bromine compound with a very high melting point. In benzene solution with hydrochloric acid it gives a slightly yellow precipitate, soluble in pyridine, which contains no chlorine. In conc. sulfuric acid it dissolves with a brilliant green color, and a green sulfate is obtained on dilution. The base from this sulfate is not, however, the original substance, but is similar to the substance obtained by treating it with hydrochloric acid, being of a high melting point, insoluble in benzene, and soluble in pyridine. Carbazole forms similar sulfates when oxidized in sulfuric acid solution which give bases which are insoluble in benzene, but soluble or insoluble in pyridine according to the methods of oxidation.

Discussion of the Constitution.

The method of preparation and the analysis show that the substance is made up of carbazole nuclei linked together by the removal of hydrogens.

The way the molecular weight varies with dilution shows that the substance dissociates in solution, for, as has been mentioned already, the substance has a strong affinity for the solvent. This would necessitate that variations from the law of dilute solutions would be in the sense of producing a greater lowering of fugacity of the benzene than would be expected from Raoult's law. This would mean that the molecular weight would appear too low. But such an effect must be more marked in the concentrated than in the dilute solutions and would, therefore, produce a lower molecular weight in the former than in the latter, which is just the opposite from what was observed. Error would also be introduced into the molecular weight determination if both solvent and solute crystallized out as a solid solution. This point was tested by freezing out some of the benzene from the solution, filtering it off, and washing rapidly with a little cold benzene and then re-melting. By comparing the color of this solution with the mother liquor it was apparent that the former must be less than one hundredth as concentrated as the latter.[1] We thus see

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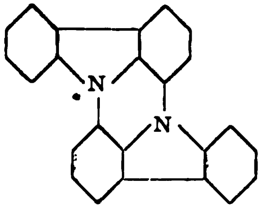
[1] The solution obtained by melting the crystallized benzene was colorless but had

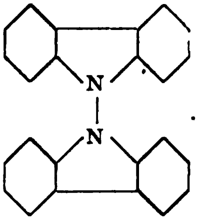
that the molecular weight determinations are not appreciably in error from the formation of a solid solution.

The error introduced into the molecular weight determinations by the presence of the silver depends upon the form in which it appears. The most probable assumption is that it is present as colloidal silver, in which case a deduction of 1.4% from the observed will give the corrected values. In this case the substance can contain only 4 or 5 carbazole nuclei.[1]

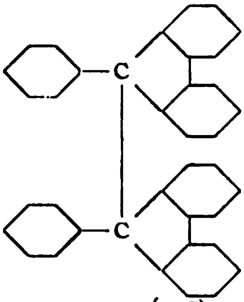
If the substance contains 4 carbazole nuclei, the possibilities which we have to consider fall into the following 6 types: (1), a double molecule of the simple hydrazine, $C_{12}H_8NNC_{12}H_8$; (2), a double molecule of the corresponding benzidine or semidine, $HNC_{12}H_7.C_{12}H_8NH$; (3) a double molecule in which 2 carbazole nuclei are linked in 2 places such as the substance X; (4) a dicarbazyl hydrazine $C_{12}H_8NC_{12}H_7N.NC_{12}H_7NC_{12}H_8$; (5) the corresponding benzidine or semidine; (6) the dicarbazyl derivative of single molecules of Type 3, $C_{48}H_{26}N_4$.



(X).



(XI).



(XII).

Types 1 and 2 should give hydrogen = 4.82%. Types 3 and 6 hydrogen = 4.28%; and 4 and 5, hydrogen = 4.56%. The value found was 4.5%. This alone is almost sufficient to show that the substance does not belong to Types 1, 2, 3 or 6.

The addition of nitric oxide is characteristic of dissociating hydrazines, and likewise the instability to acids is a property common to all hydrazines, whereas they are not the reactions we should expect from Types 2, 3, 5 and 6.

If the substance is the hydrazine $C_{12}H_8N.NC_{12}H_8$, and reacted with nitric oxide it would give *N*-nitroso-carbazole, 3-nitroso-carbazole, or 3-nitro-carbazole.[2] The substance actually formed melted too high to be any of these.

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a slight fluorescence. The mother liquor on diluting 120 times was still perceptibly colored and more markedly fluorescent. The trace of solute in the benzene crystals is due more probably to incomplete washing than to the formation of a solid solution.

[1] The assumption made here is that the dissociation is only into 2 molecules.

[2] As has been mentioned above, *N*-nitroso-carbazole when boiled in xylene will give 3-nitro-carbazole.

There is no reason to believe that compounds of Types 5 or 6 would dissociate, nor that those of Types 1, 2 or 3 would associate in dilute solution.[1]

Similarly, if the compound contains 5 carbazole nuclei only a hydrazine formula could explain the properties. The analysis agrees just as well with a tricarbazyl dibiphenylene hydrazine as with the dicarbazyl derivative, although the equilibrium constant of dissociation varies less if calculated on the assumption that it is the latter. However, the experimental error is too great to allow us to reject the possibility of the former, as it is obvious that the error made in the determination of the molecular weight will be greatly exaggerated when the results are calculated as equilibrium constants.

If the silver is present as a benzene soluble salt the effect on the molecular weight determination is greater the smaller the equivalent weight of the acid radical, and assuming this equivalent weight to be zero it can only give a range to the molecular weights from 490 to 575, and although this brings a compound of 6 carbazole nuclei within the range of the molecular weight, the substance cannot be completely dissociated at the lowest concentration and at the same time exist to so appreciable an extent at the higher concentrations. If, on the other hand, we assume that the silver exists as a colloidal salt of silver, the error introduced into the molecular weight determinations is greater the higher the equivalent weight of the acid, but unless we make preposterous assumptions concerning the molecular weight of this imaginary acid we cannot do more than bring a substance containing 3 carbazole nuclei within the range of determined molecular weights, and we should have to assume that the substance is practically undissociated at the highest concentrations but very markedly at the lower. It would thus appear that the substance is almost certainly a dicarbazyl or a tricarbazyl derivative of the substance XI.

Observations.

There are 2 points of interest in this work, the anomalous reaction which has taken place and the high dissociation of the compound obtained. The reaction consists of an alternate oxidation and an isomerization similar to that of the benzidine conversion, but at present we have no evidence as to whether it is a benzidine or semidine shift nor whether it is *ortho* or *para*, though presumably the latter. Such a process might be repeated almost indefinitely and give a class of compounds almost as complicated as the proteins. It is probable that oxidation of carbazole in acid solution would give a similar set of reactions, only in that case isomerization would take place much more readily, and the products obtained would be expected to be benzidines rather than hydrazines. This corresponds

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[1] A possible exception to this may be the high molecular weights obtained for $(C_6H_5)_2As.As(C_6H_5)_2$ by Porter and Borgstrom, THIS JOURNAL, 41, 2048–51 (1919).

with the work on the oxidation of ditolylamine in conc. sulfuric acid by Kehrmann and Micewicz.[1]

The fact that this compound is one of the most highly associated hydrazines known[2] is of exceptional interest because by analogy with the *ortho* linked hexaphenyl ethane, such as the compound XII, we should have expected very little dissociation.

We have no explanation to offer, but we do not think that the high dissociation of the compound can be explained entirely by the complicated nature of the compound, but believe that it indicates a real difference in the play of forces within the pyrrol nucleus from those within the nucleus of cyclo-pentadiene.

Experimental.

A mixture of 36.3 g. of silver oxide and 26.4 g. of carbazole was shaken up with 600 cc. of dry benzene, a little pyridine was added, and the mixture was boiled for 2 days under a reflux condenser protected from the air. The product was nearly a quantitative yield of the 2 substances described in the preceding pages. The purification was effected by filtering off the silver and silver oxide, evaporating the benzene off *in vacuo*, triturating the gummy residue with alcohol till it became granular, filtering and washing with alcohol, and drying. The 2 compounds were then separated by extracting with ether for several hours in a Soxhlet extractor.

An oxidation with ether as solvent was carried out under similar conditions, using 3.97 g. of silver oxide and 2.88 g. of carbazole in 100 cc. of dry ether. A few drops of pyridine were added as a catalyst. In the product the ether-soluble compound predominated.

Analysis.—The compound was analyzed by the combustion methods for carbon, hydrogen and nitrogen. The substance was mixed with finely powdered cupric oxide.

Subs., (I) 0.2673, (II) 0.2644, (III) 0.5634: CO_2 (I) 0.8442, (II) 0.8325; H_2O (I) 0.1045, (II) 0.1063, (III) 0.2243.

Subs., 0.3482, 0.3596: dry N, 24.1 cc. (10° and 749.3 mm.), 25.7 cc. (19° and 747 mm.).

Subs., 0.34: AgCl, 0.0063.

Calc. for $C_{48}H_{30}N_4$ with 1.4% of silver: C, 85.75; H, 4.50; N, 8.34; Ag, 1.40. Found: C, 86.15, 85.89; H, 4.37, 4.49, 4.45; N, 8.23, 8.21; Ag, 1.4.

Molecular Weight Determination.—Barrett's pure benzene, further purified by recrystallization, was used as a solvent. The amount was 26.31

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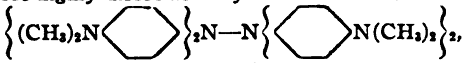
[1] Kehrmann and Micewicz, *Ber.*, 45, 2641–53 (1912).

[2] The most highly dissociated hydrazine which the authors found described in the literature is  which is 21% dissociated in nitrobenzene solution at concentrations between 1 × 10^{-2} and 1.5 × 10^{-2} total mols per 1000 g. of solvent. Wieland, *ibid.*, 48, 1078–95 (1915).

g. The weights of samples added were: I, 0.1192 g.; II, 0.4748 g.; III, 0.9828. The readings were:

Pure benzene......	5.260	5.260	5.258	5.254	5.257	mean 5.258
Sample I..........	5.213	5.205	5.210	5.215	5.210	mean 5.210
Sample II.........	5.075	5.078	5.079	5.078	...	mean 5.078
Sample III........	4.909	4.905	4.907	...	...	mean 4.907

Molecular weight calculated from I = 472, from II = 501, from III = 544.5. The constant for benzene has been taken as 50° per mol of solute per 100 g. of solvent.

Chemical Reactions.

Nitric Oxide.—A mixture of pure dry nitric oxide and carbon dioxide was passed through a solution of 0.8 g. of the substance in 10 cc. of boiling benzene for one hour. A yellow crystalline precipitate was formed, soluble in pyridine, and melting above 270°.

Hydrogen Chloride.—A current of dry hydrogen chloride was passed through a dilute solution of the substance in benzene for 2 hours at room temperature. A yellowish precipitate was formed which was soluble in pyridine, and which had a high melting point. It contained no chlorine. The filtrate yielded more of the precipitate on standing.

Sulfuric Acid.—Treated with cold conc. sulfuric acid, the substance gives a deep green solution, and on dilution with water a green precipitate which, when shaken with alkali, gives a discolored powder, insoluble in benzene but soluble in pyridine.

Oxygen.—A current of pure dry oxygen was passed through a solution of 0.3 g. of substance in 10 cc. of xylene at room temperature for 7 hours. Traces of a precipitate formed within the first hour, which apparently did not increase after that time.

Iodine.—A solution of the substance in benzene was mixed with a solution of iodine in benzene. The solutions were not decolorized, and only a slight trace of precipitate was formed.

Bromine.—On treatment of a benzene solution of the substance with bromine a vigorous reaction takes place, and some hydrogen bromide was liberated. There was some precipitation, similar to that obtained with hydrogen chloride, but the major portion forms a brown solution, and on evaporating off the benzene a brown residue is left, which, on heating, gives a white powder, giving a strong flame test for halogens. It chars before melting, and dissolves in benzene with a yellow-brown color somewhat less intense than the original substance, and gives no fluorescence.

Colorimetric Measurements.

The colors of many free radicals of the trivalent carbon series have been found to deviate from Beer's law, owing to the dimolecular species being colorless. This proof of dissociation has not so far been demonstrated in the case of the divalent nitrogen compounds. In this case it was found impossible to match, both for hue and depth, the color of the solutions of different concentrations. However, by three observers taking several readings and averaging all the results, it was found that the color was approximately proportional to the concentration. If this is not due to experimental error, it indicates either that both the dissociated and the undissociated forms are colored, or that the color is largely due to impurity.

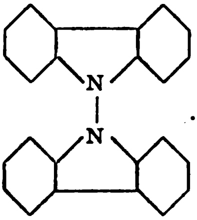
The results are given in Table II, in which the sixth column gives the relative values calculated from the assumption that only the dissociated form is colored, and the dissociation constant is 1.1×10^{-3} mols/1000 g. of solvent, as given by the cryoscopic method.

Table II.

Conc. in mols. of $C_{48}H_{30}N_4$ per 1000 g.	No. of readings.	Range of readings.	Average.	Calc. by Beer's law.	Calc. assuming only dissociated molecules colored.
3.62×10^{-2}	35	37–41	39.1	40.2	61.5
2.17×10^{-2}	21	62–70	66.8	67.2	82.6
1.30×10^{-2}	33	107–116	112.0	112.0	112
7.82×10^{-3}	9	170–181	176.8	187.0	155

Summary.

A substance was obtained by oxidizing carbazole with silver oxide which from analysis, molecular weight determinations, and chemical reactions appeared to be either a dicarbazyl or tricarbazyl derivative of the substance



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By the cryoscopic method it was shown that the substance is very highly dissociated into odd molecules, in which the nitrogen is probably divalent.

No verification of this was obtained by the colorimetric method.

It is a pleasant duty to make grateful acknowledgment to H. E. Hudson Branch for assistance in the study of the compound described in these pages. Much of the application of physical methods was carried out with her help.

Thanks are also due to Dr. C. G. Derick and Dr. R. W. Hess of the Research Laboratory of the National Aniline and Chemical Company in Buffalo, New York, for helpful suggestions and material aid in the prosecution of the work. Through their courtesy, a liberal supply of pure carbazole was obtained from the Research Laboratory of the Company.

Berkeley, Calif.

NEW BOOKS.

Laboratory Manual of Colloid Chemistry. By EMIL HATSCHEK. 135 pages. P. Blakiston's Son and Co., Philadelphia, 1920. Price, $2.00.

This is the first manual of its kind on the market and will be found very helpful to teachers of colloid chemistry. Instruction in this subject has been held back for lack of any sort of a laboratory manual although texts are reasonably numerous.

There is much merit in the book as was to be expected coming from the pen of such an authority as Emil Hatschek. Yet a more generous use of references to the literature would have improved it. Soaps deserve fuller treatment, and peptization is distinctly slighted. Nor do we find more than passing reference to that important group, the hydrated oxides of iron, aluminum and chromium. The chapter on dialysis is good although it might well include some mention of Neidle's hot dialysis.

The chapter on emulsions is far too brief, considering their great importance. It contains no discussion of the difference between sodium and calcium soaps. for example, as emulsifiers and ignores the water-in-oil type of emulsions. It would be well to have in this chapter some clear experiments illustrating the different theories of emulsification. The chapter on viscosity is good.

Much material is given on Liesegang's rings but too little importance is attached to the use of silicic acid gels as a medium for their formation. The most remarkable banding is to be secured by the use of these gels if directions in the recent literature are followed.

The book is too strictly a laboratory manual. In the present pioneer stage of laboratory instruction in colloid chemistry a moderate amount of comment would greatly increase the effectiveness of the work.

The first book of its kind must necessarily be subject to improvement but the author is to be congratulated on a very useful contribution.

HARRY N. HOLMES.

Standards and Tests for Reagent Chemicals. By BENJAMIN L. MURRAY. D. Van Nostrand Co., New York, 1920. x + 385 pp. 15 × 23 cm. $2.00 net.

In the words of the author "certain desired degrees of purity in our laboratory chemicals must be insured. Recognizing the above condition, this text has been prepared." Although the text follows very closely along the lines of other well-known texts dealing with the same subjects, the author has seen fit to make no acknowledgments whatever.

The arbitrary changing, in this book, of the limits of allowable impurities published elsewhere (such as 0.25% salts of the alkalies, earths, etc., in copper sulfate as against 0.033% in Merck's "Chemical Reagents," and 0.0343% sulfates and 0.025 chloride in sodium hydroxide, pure, as against $<0.025\%$ and $<0.005\%$ respectively in Merck) emphasizes the fact that the "Standards" are standards chosen by the author and that therefore a more appropriate title would be "Proposed Standards."

The tests are, for the most part, tests already given in Krauch (authorized translation of the third edition, Van Nostrand Co., 1902), Krauch-Merck (authorized translation of first edition, Van Nostrand Co., 1907), and Merck (authorized translation of a second edition, Merck and Co., 1914). The reviewer regrets that the author has omitted practically all of the helpful notes and references to original papers dealing with reagents and tests, which were given by Krauch and, to a lesser extent, by Merck.

The author has substituted the term "mil" for "cc." throughout the text, which is a step in the right direction, the final step being the adoption of the correct designation "ml."

In the absence of any chemists' standard such as the pharmacists have in their Pharmacopeia, this book can well be recommended as a reference text on proposed standards and tests for reagent chemicals.

G. E. F. LUNDELL.

Introduction to General Chemistry. Second Edition, first impression. By HERBERT N. McCOY AND ETHEL M. TERRY. McGraw-Hill Book Co., Inc., New York and London. 1920. x + 648 pp, 128 figures. 15.5 × 23.5 cm. Price, $3.00.

The book has been written for college freshmen, and has been in process of growth at the University of Chicago since 1913. The choice and arrangement of topics vary from the familiar order, beginning with a chapter upon the gas laws, followed by 5 chapters introducing the fundamental concepts of the indestructibility of matter, pure substances, elements, analysis, percentage composition, the law of definite proportions and the derivation of formulas; vapor densities are developed by methods independent of the atomic-molecular hypothesis. Chapters VII to X include descriptive matter upon the common acids, bases and salts, water and solutions, introduced chiefly "to supply the indispensable data needed later for the understanding of the ionic hypothesis." Chapters X and XI present the kinetic-molecular hypothesis and the atomic hypothesis, followed by a chapter upon the halogens and one upon chemical equilibrium. Hydrogen and oxygen are treated in Chapter XIV, followed by a discussion of oxidation and reduction. The next 5 chapters cover the topics of heat and energy, the ionic hypothesis and its applications, and electrochemistry. Several descriptive chapters are then given to nitrogen, phosphorus, sulfur and their compounds, after which are 2 chapters given to an elementary presentation of organic chemistry. The concluding 7 chapters are upon special topics,—the theory of dilute solutions, disperse systems, the atmosphere, some additional elements and their compounds, the classification of the elements, radioactivity and metallurgy.

The text is written in a style that is colloquial and straightforward.

Typographical errors are very few, and complicated or obscure statements are almost wholly missing. There are frequent references to the history of the science, and likewise to chemical warfare and war industries.

The text makes a strong appeal to college teachers by its unusually complete and well-written treatment of the laws and theories of chemistry,—what are generally comprehended in the title physical chemistry. Some of the chapters on these topics deserve especial praise. The chapter on electrochemistry is written from the standpoint of the electron theory, and presents the subject with a degree of clearness and completeness which the reviewer has not met with in other first texts in chemistry. The electron theory is not only stated and explained, but is put into a form in which it can be used and is used throughout the remaining body of the text. The chapter on radioactivity is also of a superior character, and is carried through to a clear presentation of X-ray spectra, atomic numbers, and the structure of matter. The chapter on disperse systems is of the highest order of interest, and complete to a degree not usual in common texts. It is a well-informed college teacher who will not find his information increased and his horizon broadened by reading the chapters on theory and on special topics which McCoy and Terry have written, and the material is so clearly given as to be within the intellectual grasp of college freshmen at all times. The chapters are not burdened with mathematics, but on the other hand contain lucid explanations of physical principles which are needed in their elaboration.

Of the descriptive chapters, that upon nitrogen and its compounds is exceedingly well done, and the chapters on organic chemistry are fuller than is usual. There are also good chapters upon the halogens, phosphorus and sulfur, giving all the information usually put before freshmen under those headings. With the forcing of the metals and their compounds into the background, however, the reviewer is not in sympathy. Where, if not in the freshmen course, is the student to acquire the extensive knowledge of properties of materials which every good chemist must have? And what of the student whose chemistry stops with this course? Though it must be conceded that any college first text in chemistry is a compromise between being all principles and all description, yet the point at which the ratio is put is of supreme importance. It is to be wished, therefore, that McCoy and Terry's chemistry might have a systematic treatment of the alkali metals, of the alkaline earths, and of the various groups of heavy metals, concerning all of which the information in the present book is scattered and not extensive. As examples, the manufacture, properties and manifold uses of sodium carbonate and bicarbonate might well have more than the few lines accorded them; and it is hardly true that "silver is so familiar a metal that we need not describe its properties," at least if we wish the student to know more than that it is white and expensive.

The text under review stops far short of the ambition expressed by a recent writer, who desires that we might have in chemistry a book like a college text in physics, a body of principles instead of a catalogue of facts. But there is in this text and some others a tendency, conscious or unconscious, to go some distance in that direction. If the habit should fix itself upon the present generation of text-book writers in chemistry who have themselves acquired their foundation under an older system, the logical result might well happen; if the freshman course becomes as thoroughly reduced to principles as the college work in physics, it might well acquire the same standing in our colleges—taken by those who must, elected by a few, and pursued by almost none.

McCoy and Terry's text could have its descriptive matter, especially that of the metallic derivatives, expanded and systematized without becoming over-bulky and without detracting from its very obvious merits.

ARTHUR E. HILL.

Chemical Calculation Tables. Second edition revised. By HORACE L. WELLS, Professor of Analytical Chemistry and Metallurgy in the Sheffield Scientific School of Yale University. John Wiley & Sons, Inc., New York (Chapman and Hall, Ltd., London), 1919. v + 43 pp. 15.5 × 24.5 cm. Price $1.35.

This book contains about 20 pages of data very useful to chemists and a 5-place table of logarithms with double thumb index. Much care has been taken to insure its accuracy. Individual opinions may differ as to what should be included in a book so limited in size. The gravimetric factors are not always well chosen and the analyst will need to supply many more. For example, nickel is commonly weighed as the salt of dimethylglyoxime, and lead as PbO_2, but no mention is made of factors involving these compounds. No date is give for the table of atomic weights. The stiff red cloth covers in which the book is bound do not seem well suited in color or style for a book of this kind which is used at the laboratory desk. The book will, on the whole, be found very convenient.

H. H. WILLARD

Les Colloides. By J. DUCLAUX. 18 × 12 cm. pp. vii + 288. Paris: Gauthier-Villars et Cie, 1920.

Most people nowadays consider a colloidal ferric oxide solution as consisting of suspended particles of ferric oxide stabilized by an adsorbed salt, ferric chloride for instance. The author prefers to look upon it as a salt with iron as cation and an anion consisting of the ferric oxide plus the chlorine. If one postulates that the amount of chlorine in the anion can vary considerably and if one also postulates that the anions behave like suspended particles, the two views lead to similar conclusions so far as cases of this type are concerned. The disadvantage is that Duclaux is forced to treat adsorption from solution by a solid as a fundamentally different phenomenon from the formation of a colloidal solution. This does not trouble him because he likes antitheses and still holds to Graham's distinction between colloids and crystalloids, though admitting that the distinction is not absolute.

The subject is treated under the following general heads: General methods of making colloidal solutions; general properties of colloidal solutions; optical properties and filtration; constitution of colloidal particles; colloids and the ionic theory; adsorption; colloids and adsorption; physical properties in living organisms; osmotic pressure in living organisms; colloids in living organisms; technique of the study of colloids.

While the author, like most authors, is convinced that he has explained everything, his apparent success is due chiefly to the general vagueness of the discussion. Dyeing is cited as a case of adsorption, p. 138; but there is no reference to the effect of acids, alkalies, or salts. When discussing coagulation by salts, p. 229, he takes the ground that one cannot tell whether the precipitation is due to the sodium ion or the chlorine ion. On p. 197 he states that the permeability of tissues depends on their structure, which is undoubtedly true; but which is not distinctly helpful.

There are some interesting facts in the book which were entirely new to the reviewer. In 1810 a lot of mercury in the hold of an English ship escaped from the containers. Inside of three weeks two hundred men on board suffered from mercury poisoning and all the animals died, p. 172. In the dried venom of the cobra, p. 183, the zinc content is about 15% of the total mineral matter. This means a specific concentration, because iron which is much more abundant than zinc, is not concentrated in the venom. The case is analogous to the concentrating of potassium and iodine in sea-weed, to the taking up of lime by soft shell crabs, and to the concentrating of phosphate by mistletoe.

The author is not much impressed by the terminology of the biological chemists. He considers the precipitation of arsenious sulfide by barium chloride adsorbed by something, and points out, p. 241, that if we had the two reagents enclosed separately in gelatine capsules which suddenly became permeable, we should call the arsenious sulfide an arseniogen before it was precipitated and an arsenine after it was precipitated while the adsorbed barium chloride would be called an arsenine ferment.

WILDER D. BANCROFT.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, SYRACUSE UNIVERSITY.]

THE CHEMISTRY AND CRYSTALLOGRAPHY OF SOME FLUORIDES OF COBALT, NICKEL, MANGANESE AND COPPER.[1]

BY FLOYD H. EDMISTER AND HERMON C. COOPER.

Received November 3, 1919.

Introduction.

The fluorides of the bivalent heavy metals, such as cobalt, nickel and copper, have never been fully investigated; neither have their compositions and crystalline forms, including isomorphous relations, been satisfactorily established. An examination of the description of these compounds in the handbooks[2] leaves one in doubt as to the facts and relationship.

In 1824 Berzelius[3] prepared the fluorides of cobalt, nickel and copper and regarded them as so similar that he described them together. "If the carbonate (of the metal) is treated with hydrofluoric acid, it will dissolve with effervescence, but soon a salt is precipitated as a heavy powder. If more and more of the carbonate be added, the effervescence continues, but the salt already formed decomposes, especially if warmed, and

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[1] A more detailed account of this work was submitted to the Faculty of the Graduate School of Syracuse University by Floyd H. Edmister in May, 1918, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] *E. g.*, "Gmelin-Kraut."

[3] Berzelius, *Pogg. Ann.* I, **1824**, p. 28; *Ann. chim. phys.* [2] **24,** 61 (1823).

there results a pulverulent basic salt. If the addition and decomposition of the carbonate be stopped before this salt (powder) forms and the solution be evaporated, there separates out a crystalline crust. * * * In this process there is given off the excess of acid which the dissolved salt contains. If the crystallized salt be covered with a very small amount of water and the mixture be allowed to stand for a long time at room temperature, there results a saturated solution which will deposit these same crystals on evaporation. If, however, the mixture is heated to boiling with much water, decomposition occurs, part of the salt dissolving in the liberated acid and another part remaining undissolved as a basic salt."

Berzelius selected the copper salt for analysis and found that on heating it with lead oxide there were given off 2 molecules of water, not in the least acid. The green pulverulent salt resulting from the decomposition of the neutral salt by boiling water proved, by the same method of analysis, to be a basic salt of the formula $CuO.CuF_2.H_2O$.

The 3 metals, cobalt, nickel and copper, were thus regarded by Berzelius as forming entirely analogous fluorides: a crystallized normal fluoride, $MF_2.H_2O$, and an amorphous basic fluoride.

About fifty years later F. W. Clarke[1] described the preparation of a supposedly new fluoride, made by evaporating a solution of nickel hydroxide in hydrofluoric acid, whereby a crystalline crust is formed. The analysis of this crust gave the formula, $NiF_2.3H_2O$.

In 1884 Balbaino[2] stated that he prepared the hydrated cupric fluoride ($CuF_2.2H_2O$) of Berzelius by dissolving copper carbonate in hydrofluoric acid and adding 95% alcohol, which precipitated a pale blue crystalline powder.

Poulenc[3] is credited with the first description of the anhydrous fluorides. They are only of incidental interest to us here, but it may be noted that, according to Poulenc, the anhydrous nickel fluoride is formed as an amorphous yellow powder or as green crystallized prisms. The anhydrous cobalt fluoride is either a rose-red amorphous powder or red prismatic crystals.

In 1905 Böhm[4] reviewed the work on the fluorides of the heavy metals, called attention to the lack of accurate investigations of well-crystallized material, and prepared, along with several other complex fluorides, the acid fluorides of cobalt, nickel and copper. He stated merely that he obtained these by dissolving the freshly precipitated hydroxides or carbonates of the metals in hydrofluoric acid and concentrating until crystals appeared. His cobalt and nickel fluorides are described as, respectively,

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[1] Clarke, *Am. Chem. J.*, 13, 290 (1887).

[2] Balbaino, *J. Chem. Soc.*, 2, 1264 (1884).

[3] Poulenc, *Compt. rend.*, 114, 1426 (1892); *Ann. chim. phys.*, [7] 2, 47 (1894); *Ber.*, 25, R. 662 (1892).

[4] Böhm, *Z. anorg. Chem.*, 43, 330 (1905).

red and green prisms, having similar form and composition. They are stable in the air and easily soluble in water and dilute acids. The metal was determined by electrolysis from a sulfate solution, the fluorine by heating the salt with pure Iceland spar and the water by heating a mixture of the salt with lead chromate in a combustion tube. Böhm found the copper-fluoride crystals to be different from the others in that they soon lose their water of crystallization in the air and that they decompose completely when heated in a closed tube, water and hydrogen fluoride escaping, while copper oxide remains. In the case of copper fluoride the fluorine was determined by neutralizing with an excess of sodium hydroxide and titrating back with standard hydrochloric acid. The formulas assigned by Böhm for these fluorides are of a strongly acid fluoride type.

Purpose of the Investigation.

It is hardly possible that the conclusions of Berzelius, Clarke and Böhm can all be correct, since all of them offer different formulas for salts prepared by methods which should yield the same type of fluoride for a single metal. It is reasonable to suspect that the old master, Berzelius, drew too hasty conclusions from his brief experiments.

Notwithstanding the slight experimental foundation on which the existence of the normal fluorides is based, one is inclined to prefer a normal salt formula to an acid salt formula for a halide obtained from the hydroxide or carbonate and acid, because it is in this way that the most familiar normal chlorides and bromides are prepared.

We have undertaken a combined chemical and crystallographic study of these fluorides, not merely to ascertain the facts in question, but to see whether an isomorphous series is involved.

Preparation of Materials.

The following general methods were investigated. (1) Treating the hydroxide of the metal with an excess of hydrofluoric acid. The excess is necessary for avoiding the formation of the basic salt. (2) Decomposing the carbonate with hydrofluoric acid. In either of these cases the resulting solution is evaporated until crystals appear. Both methods yield satisfactory results. (3) "Dissolving" the metal in hydrofluoric acid. In most cases the action was so slow that only a very small concentration could be obtained. (4) Treating a salt of the metal (the acetate) with hydrofluoric acid. (5) Double decomposition of an alkali fluoride and a salt of the metal. A complex fluoride resulted.

The first general method was ordinarily employed. The hydroxides were precipitated from the acetate solution with sodium hydroxide, the precipitate being washed repeatedly by decantation with cold water and finally with hot water, until the filtrate gave no color with phenolphthalein. The washing must be very thorough, since the gelatinous hydroxide adsorbs the alkali greedily. An excess of alkali was avoided and the precipitate was heated in an excess of water to boiling repeatedly before bringing it upon the filter. The moist hydroxide was then dissolved in C. P. hydrofluoric acid in a platinum basin and the solution was filtered through a wax funnel into a wax bottle, from which it was taken as needed.

Böhm specifies that the solution should be evaporated in a vacuum desiccator over sulfuric acid until crystals appear. Attempts to follow this procedure resulted in the formation, not of crystals, but of a crystalline crust on the sides and bottom of the container and an arborescent creeping growth extending often over the sides of the vessel. The walls of the container and the desiccator were bedewed with a strongly acid solution, which was not absorbed by the sulfuric acid. If the evaporation took place in the open air, the crust was drier and harder and more difficultly soluble.

Under the microscope this crust looked different according to the conditions under which the evaporation took place. In some cases the crust was only a mass of nodules, while in others it appeared to be a mixture of amorphous material and of small but fairly definite crystals. In the case of copper the crust was, fortunately, almost wholly crystalline.

In view of the fact that the analyses of Berzelius and Clarke were made on material prepared in this way, special attention was given to preparing a product which could be regarded as suitable for analysis, but examination with the petrographic microscope showed the preparations—except in the case of the copper salt—to be either amorphous and of indefinite water content or mixtures of amorphous and crystalline material. Analyses of these products were made and indicated roughly a ratio of cobalt or nickel to fluorine of 1 : 2, but the character of the crystals was too indefinite to warrant careful investigation of their composition.

Recrystallization.—If this crust is placed in about an equal weight of water, the crystalline portion can be seen to dissolve out, while the amorphous portion remains. If the amount of water is increased and the temperature raised, all of the material dissolves. Except in the case of cobalt no well-defined crystals, capable of measurement, were obtained from the original solution of the hydroxide in hydrofluoric acid. All of the crystals used for analysis and measurement have been obtained from the water extract of the crystalline crust, the extract being allowed to evaporate slowly in the air. Even then some of the crust is nearly always formed around the crystals and a second recrystallization is necessary to free them entirely from the crust. Each recrystallization reduces the acid concentration until in the third it is practically negligible.

We hesitated to recrystallize from pure water because of the possibility of hydrolysis and, particularly, because of the possible loss of acid in case the salts should be acid fluorides, as our investigation as well as

Böhm's disclosed. Contrary to expectations, the proportion of amorphous material lessened, rather than increased, with decreasing acidity, indicating that it is not a basic salt. The acid concentration, however, appears to control the equilibrium involving the crystal and amorphous phases.

Preparation of Cobalt Fluoride.—Our first preparation of cobalt fluoride was by treating the hydroxide with hydrofluoric acid. Because of the tendency of the cobalt (ous) hydroxide to oxidize in the air during the long washing process to cobaltic hydroxide, which is insoluble in hydrofluoric acid, we generally used the carbonate instead. It is permanent in the air, filters more quickly and is more easily washed. It is, however, less soluble than the cobaltous hydroxide. To be sure, the carbonate, when added to the hydrofluoric acid, is decomposed as long as there is any acid present, but, as Berzelius stated, there is precipitated a fine rose-red powder, which is dissolved only upon the addition of more acid and water.

The original solution was evaporated on a water-bath until solid appeared, whereupon it was removed to a heat-insulated box of the Swedish box, or fireless cooker type, and allowed to cool slowly. No crystals formed. Even after standing in the box until half of it had evaporated, the solution continued to yield a brittle crystalline crust, the last portion being the same as the first.

The next trial was made in the open air, using the mother liquor from this crust, but no real crystals were obtained. The same method was tried, starting with a dilute solution and allowing it to evaporate slowly at an even temperature, with no better results. Böhm's method of letting stand in an evacuated desiccator over sulfuric acid was then tried. The evaporation proceeded slowly because, as stated above, the escaping vapor was not absorbed by the sulfuric acid but condensed upon the inner wall of the desiccator. Solid fluoride formed upon the sides of the basin and then crept over the edge. Under the microscope this crust appeared to have no crystal form and no definite composition.

The cobalt fluoride crust, however formed, is slowly soluble in very dilute hydrofluoric acid. For this reason a few drops of hydrofluoric acid were added to the water on dissolving. Upon evaporation the same results were obtained as in the first evaporation. Since the crust appeared to consist of more than one form of material, differing in solubility, a comparatively large amount was treated with a small quantity of water and warmed. The filtered solution upon standing for 6 hours began to deposit crystals which, though accompanied by crust, were sufficiently distinct from it to be separated mechanically. When these crystals were recrystallized from slightly acid water, very clean, well-defined crystals were obtained.

Preparation of Nickel Fluoride.—For the preparation of nickel fluoride either the hydroxide or the carbonate may be used, since the hydroxide, unlike that of cobalt, is stable in the air. The first product was a crystalline crust, as for cobalt. The crust forming on the surface of the evaporating solution is identical in appearance under the microscope with that deposited on the bottom. Satisfactory crystals were obtained in the same way as for cobalt, the cleanest ones resulting from a second recrystallization from water.

Preparation of Manganese Fluoride.—Of all the fluorides investigated that of manganese is the most difficult to prepare. The hydroxide is less stable in the air than that of cobalt; so that, before it can be thoroughly washed, much of it has become insoluble in hydrofluoric acid; but a more serious difficulty is the comparatively slight solubility of the manganous hydroxide in hydrofluoric acid. The carbonate likewise dissolves only to about 10%; further addition of the carbonate produces a marked effervescence and the precipitation of a fine powder, which does not dissolve upon the addition of more acid and water. The solution of the fluoride is consequently very dilute.

If the manganous fluoride solution be heated on the water-bath, the fluoride precipitates as the powder, so that all evaporation must be done at room temperatures, requiring on the average 6 weeks to produce crystals. The crust also forms as in the case of cobalt and nickel, but decomposes when digested with water. We attempted to obtain manganese fluoride by dissolving the metal in hydrofluoric acid, but obtained only manganese dioxide, which was formed by an unusually vigorous reaction between the metal and acid.

Preparation of Copper Fluoride.—For the preparation of copper fluoride the hydroxide is to be preferred to the carbonate, since the hydroxide reacts faster with hydrofluoric acid. Although it forms a basic salt upon standing in the air, the product is soluble in more acid. If the copper fluoride solution be evaporated slowly, small irregular blue crystals form on the bottom of the basin; while, if the evaporation takes place on the water-bath, the fluoride appears as a clear crystalline crust of constant composition. Both the small crystals and the crystalline crust were free from the granular, amorphous material so persistent in the deposition of cobalt and nickel fluorides. They were regarded as sufficiently well defined for analysis. The analyses showed the 2 products to be identical in composition, *viz.*, to be a normal fluoride.

These normal fluoride crystals are difficultly soluble in water, a white coat forming upon the surface. If an excess of water is added and the solution is heated, the filtrate yields upon evaporation well-defined 3- or 6-sided prismatic crystals. These are very soluble in water and, strange to say, have the composition of an acid fluoride. On exposure to the air they effloresce rapidly. If they are heated, water and hydrogen fluoride are evolved, leaving copper oxide in the tube. Presumably the hydrogen fluoride is driven off first, whereupon the water of crystallization hydrolyzes the copper fluoride.

Observations on Dissociation.

The crystal fluorides of cobalt, nickel, manganese and copper all evolve hydrogen fluoride when exposed to the air. After a portion of one of these substances is washed and dried and set aside on the watch glass the latter is found to be etched in 3 minutes. The gradual loss of hydrogen fluoride is a very important property of these fluorides. It means that the compound cannot be preserved with certainty of its retaining its original composition and that analyses must be made with the freshest possible product. This phenomenon will be referred to in the discussion of the analysis. It would be interesting to determine the rate of decomposition, but no work has been done upon it thus far.

The crystals are soluble in water and dilute acids. When heated, they give off water and hydrofluoric acid and are themselves converted to the oxides, as stated by Böhm, for the copper salt.

Analysis of the Fluorides.

For the *metal* the following general methods are applicable: (1) precipitation as the hydroxide or sulfide with subsequent reduction in a stream of hydrogen; (2) evaporation with sulfuric acid and weighing as the anhydrous sulfate; (3) heating at red heat to convert the fluoride into the oxide; (4) electrolytic deposition.

The *total fluorine* can be determined volumetrically by adding an excess of standard alkali and titrating back with standard acid. In this case the precipitated hydroxide is filtered off before the titration, else it will obscure the end-point. With nickel and copper, using phenolphthalein as an indicator, a very good end-point can be obtained if the alkali be added slowly to the warm solution until the free hydrofluoric acid is neutralized and the hydroxide of the metal is precipitated.

The gravimetric determination of fluorine is based upon its precipitation as an insoluble fluoride. A number of metals form insoluble fluorides, calcium being the one most commonly used. Lead chloride precipitates the fluorine as the double halide, $PbFCl$,[1] and lithium chloride is said to give accurate results.[2] In our work with the fluorides lead chloride gave results uniformly low and lithium chloride failed in some cases to give a precipitate. The difficulties of precipitation are well known. Calcium fluoride is an extremely finely divided, slimy precipitate, which passes through nearly all filters the first time. Refiltering through the same filter proved to be exceedingly tedious, and washing was impracticable because of the time consumed in filtration of the solution. However, a

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[1] G. Starck, *Z. anorg. Chem.*, 70, 173 (1911); *J. Chem. Soc. Abs.*, 100, ii, 436 (1911).

[2] Deladrier, *J. Chem. Soc.*, 86, 440 (1904).

number of determinations for fluorine were made by precipitating it with calcium chloride or calcium acetate. While the results were not accurate, they afforded independent confirmation of those obtained by other methods so far as the interpretation was concerned.

The purpose of adding the carbonate to the fluoride in the calcium fluoride method (Berzelius) is to assist in the filtration. A modification of this procedure has given good results in our work. Instead of adding sodium carbonate we made the solution slightly acid with acetic acid. An amount of standard ammonium oxalate was then added so that the calcium oxalate precipitated would be approximately the same as the weight of calcium fluoride. The 2 precipitates were then filtered off together in a Gooch crucible, dried and weighed. The difference between the weight of the combined precipitate and the weight of the calcium oxalate, corresponding to the ammonium oxalate added, gave the calcium fluoride. The decided advantage lies in the elimination of the decomposition and, furthermore, it does not necessitate a second filtration. The calcium oxalate serves the same purpose as the calcium carbonate and does it equally well. None of the absorption methods was used in the analysis for fluorine.

The determination of *crystal hydrate water* is the most difficult, since a temperature sufficiently high to expel the last traces will cause a loss of at least a part of the hydrogen fluoride. The method used by Böhm—heating the fluoride with lead oxide—is the only one described as being satisfactory. In the analyses that follow the water determinations were so variable that they were used only as rough indications of the amount present. For calculating formulas use was made of the percentage of water by difference.

Cobalt Fluoride Analysis.—The fluorine of the cobalt fluoride was determined by adding an excess of standard alkali to the water solution. The precipitate was 4 times washed by decantation with hot water, whereupon it was brought upon the filter and washed with hot water until the washings gave no test for alkali with phenolphthalein. The filtrate was then titrated with standard hydrochloric acid and the weight of sodium hydroxide used was calculated. In order to check this method determinations were made by precipitating the fluorine with calcium acetate. The results were lower than by titration and are not considered reliable.

All of the general methods were used for determining cobalt metal. The first method employed was that of precipitating with sodium hydroxide, filtering the precipitate and washing it with hot water. The dried hydroxide was ignited and the oxide decomposed with conc. sulfuric acid. This acid solution was then evaporated to dryness and the anhydrous cobalt sulfate weighed.

Another method used for cobalt was to treat the fluoride with sulfuric acid and evaporate. This should volatilize all of the constituents except the metal. Consistent results were obtained by this method which agree with the electrolytic determinations. The reaction with sulfuric acid is vigorous and complete within a few minutes. The sulfuric acid is then driven off in an air-bath, the residue heated for 5 minutes and eventually weighed as anhydrous cobalt sulfate.

In electrolytic deposition cobalt does not behave ideally; it does not always form a good coating on the cathode, but often scales off before the deposition is complete. We carried out the electrolysis as specified by Treadwell-Hall.[1] Our experience has been that, if the voltage exceeds 1.5 volts, the cobalt will precipitate as the hydroxide and, if the solution is not kept strongly alkaline, a black ring will be deposited, particularly around the edge. A voltage of 1.0 to 1.5 and an amperage of 1.0 to 1.3 gave the best results. A 100-cc. platinum basin served as the cathode. It is not necessary to precipitate the hydroxide of cobalt, but the crystals may be dissolved in water, ammonium hydroxide added and the solution electrolyzed directly. The possibility of contamination with alkali is eliminated and accurate results are to be expected, but no determination of fluorine can be made on the same sample.

Cobalt hydroxide was also reduced to the metal by the Rose method. Unfortunately, the ignited precipitate was always in masses, which would not reduce unless removed from the crucible and ground. If this was not done, the reduction was incomplete and the results were too high.

Nickel Fluoride Analysis.—In the nickel fluoride the fluorine was determined as in the case of cobalt. The metal also was determined (1) as the anhydrous sulfate, after evaporating the fluoride crystals with sulfuric acid; (2) by electrolysis; and (3) as the oxide. Unlike cobalt oxide nickel oxide has a constant composition and the metal can be calculated from the weight of the oxide.

Anhydrous nickel sulfate is hygroscopic and must be weighed quickly after removal from the desiccator. The electrolysis was conducted in a strongly alkaline solution with a voltage of about 1.5 and an amperage of 1.5. In all cases the platinum basin was used as the cathode.

No analyses for nickel were made by the Rose method.

Copper Fluoride Analysis.—The copper is best determined (1) by electrolysis in the water solution of the crystals, which are acid with hydrofluoric acid, unless the fluorine is to be determined in the same sample. In the latter case the copper is precipitated as the hydroxide, dissolved in dil. nitric acid and subjected to electrolysis. Copper was also determined (2) by evaporating the crystals with sulfuric acid. (3) When the copper fluoride crystals are heated alone, they give off water and hydrofluoric acid and are converted to the oxide. The weight of copper calculated

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[1] Treadwell-Hall, "Analytical Chemistry" II, 1915, p. 138, 4th Ed., N. Y.

from the oxide thus obtained agrees approximately with that obtained by other methods.

Manganese Fluoride Analysis.—The fluorine was determined by the same method as for the other fluorides. The metal was determined (1) by decomposing with sulfuric acid, and (2) by converting to the pyrophosphate. For the latter method the manganese is first precipitated as the hydroxide, washed free from alkali and dissolved in dil. sulfuric acid.

The Analytical Data.—The results of the analyses are tabulated in the following tables. The numbers in the first column are analytical reference numbers; the method employed in the analysis is indicated in the second column; the weights of salt and constituent, respectively, are given in the next 2 columns; the computed percentage is found in the fifth column; while the last column is used for memoranda that might aid in the appraisal of the results.

COBALT FLUORIDE.

Prepared by the action of HF on the hydroxide or carbonate, no difference being seen in the products.

Reference No.		Salt. G.	Fluorine. G.	%.
6	Pptd. as CaF_2	0.3000	0.1214	39.97
3	Titration	0.5000	0.1310	41.30
63	Titration	0.3000	0.1221	40.78
64	Titration	0.4007	0.1695	41.45
90	Titration	0.3000	0.1285	42.85[a]
130	Pptd. as CaF_2 + CaC_2O_4	0.2934	0.1458	42.79[a]
131	Pptd. as CaF_2 + CaC_2O_4	0.2280	0.1232	43.79[a]

Reference No.		Salt. G.	Metal. G.	%.	
37	Dissolved hydroxide in H_2SO_4 and electrolyzed	0.3026	0.0591	19.53	Crystals were washed in alcohol
39	Dissolved hydroxide in H_2SO_4 and electrolyzed	0.4483	0.0864	19.27	
50	Decomposed with H_2SO_4 and weighed as $CoSO_4$	0.3520	0.1793	19.36	
63	Electrolysis	0.3000	0.0571	19.40	
78	Electrolysis	4.4007	0.7840	19.40	Very clean crystals
93	Electrolysis	0.3000	0.0590	19.60	Dissolved in water and electrolyzed
51	Electrolysis	0.2544	0.0484	19.03	Dehydrated

[a] Taken from solution, washed, dried and analyzed immediately.

Reference No.		Salt. G.	Metal. G.	%.
51	Heating and collecting the water	0.2544	0.1036	40.70
130	Heating and collecting the water	0.3024	0.1195	39.52
133	Heating with PbO	0.3313	0.1363	41.14
135	Heating with PbO	0.1853	0.7440	41.15
137	Heating and collecting the water	0.2107	0.8650	41.05

Nickel Fluoride.

Prepared from the hydroxide and hydrofluoric acid.

Reference No.		Salt. G.	Fluorine. G.	%.	
58	Titration	0.3000	0.1259	41.99	Washed in alcohol
80	Titration	0.3000	0.1658	41.36	Old crystals
89	Titration	0.3000	0.1296	43.27	Clean crystals fresh from solution
96	Titration	0.3000	0.1292	43.05	Clean crystals fresh from solution
97	Titration	0.3000	0.1248	41.67	Old crystals
131	Pptd. as CaF_2 + CaC_2O_4	0.1876	0.0914	43.76	Crystals fresh from solution

Reference No.		Salt. G.	Metal. G.	%.
54	Electrolysis	0.3070	0.0677	19.80
58	Electrolysis	0.3000	0.0584	19.60
62	Electrolysis	0.3000	0.0574	19.50
64	Electrolysis	0.2497	0.0489	19.58
91	Electrolysis	0.3000	0.0478	19.26

Reference No.		Salt. G.	Water. G.	%.
110	Heating and collecting water in H_2SO_4	0.2764	0.1149	41.50

Manganese Fluoride.

Reference No.		Salt. G.	Fluorine. G.	%.	
76	Titration	0.3537	0.1313	43.02	Crystals fresh from solution
69	Titration	0.3004	0.1190	39.63	
92	Titration	0.3020	0.1220	40.68	

Reference No.		Salt. G.	Metal. G.	%.
76	Heating with H_2SO_4 and weighing as $MnSO_4$	0.0365	0.1817	18.09
60	Heating with H_2SO_4 and weighing as $MnSO_4$	0.3537	0.1810	18.89
77	Heating with H_2SO_4 and weighing as $MnSO_4$	0.2892	0.1457	18.35

Reference No.		Salt. G.	Water. G.	%.
127	Heating with PbO and collecting the water	0.3171	0.1221	38.2

Copper Fluoride (Crystals).

Reference No.		Salt. G.	Fluorine. G	%.	
43	Titration	0.3000	0.1282	42.76	
59	Titration	0.3000	0.1281	42.71	
65	Titration	0.4220	0.1808	43.05	
127	Precipitation	0.3612	0.1519[b]	42.20	[b]$CaF_2 + CaC_2O_4$
Reference No.		**Salt. G.**	**Metal. G.**	**%.**	
59	Electrolysis	0.3000	0.0610	20.30	
60	Electrolysis	0.3000	0.0602	20.07	
61	Electrolysis	0.3009	0.0604	20.06	
79	Electrolysis	0.4112	0.0838	20.38	

Copper Fluoride (Crystalline Crust).

Reference No.		Salt. G.	Fluorine. G.	%.	
52	Titration	0.6087	0.1692	27.80	These two are the same preparation
53	Titration	0.6896	0.1270	27.00	
56	Titration	0.5000	0.1437	28.75	
74	Titration	1.1751	0.3323	28.28	
83	Titration	0.9401	0.2646	28.13	
Reference No.		**Salt. G.**	**Metal. G.**	**%.**	
52	Electrolysis	0.0609	0.2814	46.10	
53	Electrolysis	0.6896	0.3158	45.80	
82	Electrolysis	0.8219	0.3767	45.83	
83	Electrolysis	0.9401	0.4306	45.82	
49	Electrolysis	0.3621	0.1643	45.40	

Calculations.—In the computation of the formulas for the fluorides use was made of the analyses on crystals which were taken from the solution, washed, dried and analyzed immediately. The average of these analyses was used.

In the case of fluorine results from the precipitation by calcium chloride alone were discarded, as they had been proven to be inaccurate. The results used are the average of the fluorine determinations by titration and by precipitation by calcium chloride in the presence of calcium oxalate.

For the metal the calculations in the case of cobalt, nickel and copper are the average of results obtained from the anhydrous sulfate and by electrolysis, with emphasis upon the latter, since in this method the sources of error are reduced to a minimum. For manganese metal the calculations are based upon the weight found in the anhydrous sulfate and in the pyrophosphate.

For the water use was made of the percentage difference.

In some cases only selected determinations were utilized for the calculations. The selection is given in the last column of the following tables. A great many more determinations were made than are recorded in the preceding tables, in order to familiarize ourselves with the possible sources of error.

FORMULAS.

Cobalt Fluoride.

$\mathrm{Co} = 19.40 \div 58.97 = 0.3291 = 1.000$. All determinations.
$\mathrm{F} = 43.14 \div 19.00 = 2.2705 = 6.899$. Nos. 90, 130, 131.
$\mathrm{H_2O} = 36.06 \div 18.00 = 2.0033 = 6.087$. By difference.
$\mathrm{H} = 1.6$.
The formula is $\mathrm{CoF_2.5HF.6H_2O}$.

Nickel Fluoride.

$\mathrm{Ni} = 19.50 \div 58.68 = 0.3323 = 1.0000$. All determinations.
$\mathrm{F} = 43.32 \div 19.00 = 2.2800 = 6.8610$. Nos. 89, 96, 131.
$\mathrm{H_2O} = 35.58 \div 18.00 = 1.9767 = 5.9485$. By difference.
$\mathrm{H} = 1.6$.
The formula is $\mathrm{NiF_2.5HF.6H_2O}$.

Manganese Fluoride.

$\mathrm{Mn} = 18.09 \div 55.00 = 0.3283 = 1.000$. No. 76.
$\mathrm{F} = 43.02 \div 19.00 = 2.2640 = 6.889$. No. 76.
$\mathrm{H_2O} = 35.58 \div 18.00 = 2.0772 = 6.327$.
$\mathrm{H} = 1.5$.
The formula is $\mathrm{MnF_2.5HF.6H_2O}$.

Copper Fluoride.

(Crystals by recrystallization from water.)

$\mathrm{Cu} = 20.09 \div 63.57 = 0.316 = 1.000$. All determinations.
$\mathrm{F} = 42.70 \div 19.00 = 2.250 = 7.100$. All determinations.
$\mathrm{H_2O} = 35.61 \div 18.00 = 1.978 = 6.260$. By difference.
$\mathrm{H} = 1.6$.
The formula is $\mathrm{CuF_2.5HF.6H_2O}$.

Copper Fluoride.

(Small crystals and crust deposited slowly from original mixture.)

$\mathrm{Cu} = 45.82 \div 63.57 = 0.747 = 1.000$.
$\mathrm{F} = 28.13 \div 19.00 = 1.480 = 2.036$.
$\mathrm{H_2O} = 26.05 \div 18.00 = 1.440 = 2.000$.
The formula is $\mathrm{CuF_2.2H_2O}$.

We append here the results of a few determinations and calculations on the crust or powder formed in the preparation of crystals of cobalt and nickel fluorides.

Cobalt Fluoride—Crystalline Crust.

Reference No.	Fluorine. %.	Metal.	Ratio.	
84	25.09	33.99	1.0 : 2.29	
			Powder.	
104	24.42[*]	35.19	1.0 : 2.154	
		Nickel Fluoride—Powder.		
100	Not det'd.	34.51		
101	25.46	34.66	1.0 : 2.26	Made by boiling the crust.

[*] Average of 2 determinations on the same material; fluorine also determined on same powder.

The results approximate the neutral salt formula and correspond to the result for the copper fluoride crust. We do not, however, feel warranted in assigning formulas.

Crystallography.

From the second recrystallization in the open air crystals were obtained in ample quantity for crystallographic investigation and analysis. Some of them were as large as 20 × 8 mm. Measurements were made with a Goldschmidt reflecting goniometer. In general, the specimens were found to be extensively etched because of their high solubility. The etching caused so much dispersion of light that the reflected image was not as sharp as was desirable; therefore the readings were only reliable to about 30 seconds.

Cobalt Fluoride, $CoF_2.5HF.6H_2O$, Rhombohedral.—The cobalt fluoride is orange-red; equivalent wave-length 610 $\mu\mu$ for a plate 2 mm. thick.[1] The crystals are flattened hexagonal prisms capped by 2 rhombohedrons of the opposite order to the prisms. The average angle between the prism faces $m:m'$ is 60° 0′. For the rhombohedrons the angles from the base are 30° 59′ and 50° 6′, both within ±8′. From the measurements $\dot{c} = 1.039$; $c \wedge r\ (10\bar{1}1) = 50° 9'$ and $c \wedge e\ (01\bar{1}2) = 30° 55'$. Distinct prismatic cleavage was observed. Optically the crystals are uniaxial postive with approximate refractive indices measured by immersion: $\omega = 1.38(5)$, $\epsilon = 1.39(7)$. Extinction is parallel. The sp. gr. by the Jolly balance, using alcohol as immersion liquid, is 2.0445.

It does not seem worth while to make drawings of the crystals because of their distortion, which was probably due to their growing attached by one side to the dish.

Nickel Fluoride, $NiF_2.5HF.6H_2O$, Rhombohedral.—The nickel fluoride is blue-green; equivalent wave-length 510 $\mu\mu$ for a plate 2 mm. thick; non-pleochroic, with habit, cleavage and general optical properties like cobalt fluoride. Measurements of the rhombohedrons gave the same angles as the coblat salt. Refractive indices measured on a small prism gave the following results for the mercury lines; the other values are interpolated:

	ω.	ϵ.
Hg 436	1.398	1.413
F	1.395	1.410
Hg 578	1.392	1.408
D	1.392 −	1.408 −
C	1.390	1.406

Sp. gr. in alcohol, 2.006.

Manganese Fluoride, $MnF_2.5HF.6H_2O$.—The manganese fluoride is light red with habit and general optical properties like those of cobalt fluoride. The average angle between the prism faces $m:m'$ is 60° 8′. The pyramid faces were so poorly developed that it was impossible to measure them. Sp. gr. in alcohol, 1.921.

Copper Fluoride, $CuF_2.5HF.6H_2O$, Monoclinic.—The copper fluoride is blue-green-blue, equivalent wave-length 490 $\mu\mu$ for a plate 2 mm. thick., and is distinctly pleochroic. The crystals were not perfect enough to determine by form. Microscopically they apparently show 3 cleavages, to one of which they extinguish parallel. This cleavage seems to be parallel to a set of faces. The extinction observed against another apparent cleavage is very oblique. A few elongated rough crystals and cleavage fragments were elongated in the direction of α'. Good biaxial interference figures showed $-2E = 48° \pm 2°$, with no observable axial dispersion. The refractive indices were measured carefully under the microscope by immersion as follows: $\alpha = 1.395$, $\beta = 1.440$, $\gamma = 1.444$. Therefore $-2V = 32°$. α is least absorbed.

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[1] A considerable number of these observations were made or confirmed by H. E. Merwin, of the Geophysical Laboratory, to whom we are accordingly greatly indebted.

The evidence of monoclinic symmetry is thus almost conclusive. The examination of the optical properties was rendered very difficult by the rapid loss of crystal hydrate water. Sp. gr. in alcohol, 2.4055.

The crystals of the normal fluoride, $CuF_2.2H_2O$, were too small to measure. Recrystallization yielded the acid fluoride.

Isomorphism.—The chemical and optical examination thus showed that the acid fluorides of cobalt, nickel and manganese are isomorphous, while the similarly prepared copper fluoride, of the same chemical formula, has a different crystal form. The first 3 are rhombohedral, forming flattened hexagonal prisms, capped by 2 rhombohedra of the opposite order to the prisms. All 3 showed prismatic cleavage, are uniaxial positive and give parallel extinction. The refractive indices of the cobalt and nickel fluorides differ by less than 1%. The indices of the manganese fluoride were not measured.

Summary.

The fluorides of cobalt, nickel, manganese and copper can be prepared by dissolving either the hydroxide or the carbonate of the metal in hydrofluoric acid, the same product being obtained, whichever is used. In all cases a crust-like product was obtained as the result of evaporating the original solution. From the water extract, slightly acidulated with hydrofluoric acid, crystals of the acid fluorides were formed and analyses and measurements of these crystals were made.

The formulas of all 4 fluorides are of the same acid fluoride type: $MF_2.5HF.6H_2O$. It was a surprise to obtain the acid fluoride by recrystallization from water, it being considered more likely that a basic salt would be obtained under these circumstances.

The acid fluorides are not permanent in the air but decompose, losing hydrogen fluoride, and in the case of copper losing water also, so that the crystals used for analyses must be carefully selected and preserved. Investigation of the rate of loss of hydrogen fluoride was not undertaken, but our analyses were made with crystals soon after being taken from the solution and in our opinion the results are the most reliable obtainable.

The formation of a hydrated, non-crystalline crust is distinct from that of the hydrated acid fluoride crystals. In this crust the ratio of metal to fluorine, for the cases of cobalt and nickel, was found to be, roughly, one to two, with varying water content. This crust differs from the crystals in solubility and form, as well as in composition. We have arrived at the conclusion that the crust described by Berzelius as containing 2 molecules of water, the crust later described by Clarke as containing 3 molecules of water, and the crust and powder obtained by use are the same, the water content being variable and the crystal form undeveloped. All were obtained in the same manner.

The acid fluorides of cobalt, nickel and manganese give rhombohedral crystals, with prismatic cleavage, parallel extinction and uniaxial positive character. Since they have the same type of chemical formula, the same crystal form and the same habit, cleavage and general optical properties, we consider that they constitute an isomorphous series.

The acid fluoride of copper has the same type of formula, but differs crystallographically.

From the original preparation of copper fluoride small crystals of the normal fluoride, $CuF_2.2H_2O$, were obtained, which were not good enough for measurement and which reverted unexpectedly to the acid fluoride on recrystallization from water.

The experimental work upon which this article is based was completed in May, 1918.

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[Contribution from the Department of Chemistry of Columbia University. No. 332.]

A STUDY OF THE SATURATED POTASSIUM CHLORIDE CALOMEL CELL.

By Harold A. Fales and William A. Mudge.

Received February 6, 1920.

The increasing use of the electromotive force method for hydrogen-ion measurements, and the variety of combinations employed, have intensified the desirability of devising a single combination which will not only minimize, as far as possible, the inherent errors of this important method, but will give, in addition, an improved technique for working over a wide range of temperature, 5–60°.

The combinations which have been used to the greatest extent are those employing either the 0.1 N or N calomel cell in conjunction with either the 0.1 N,[1] N,[2] 3.5 N,[3] or saturated[4] potassium chloride salt bridge.

In the use of such combinations the difficulties are two-fold: (*a*) those due to the changes in value of the contact potentials brought about by the interdiffusion of the respective solutions at their several junctions; and (*b*) those due to the change in value of the calomel cell resulting from the diffusion of the potassium chloride of the salt bridge into the more dilute solution of the salt in the calomel cell.

Fales and Vosburgh,[5] in a study of Planck's formula for contact poten-

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[1] Loomis and Acree, *Am. Chem. J.*, 46, 585 (1911); Myers and Acree, *ibid.*, 50, 398 (1913); Harned, This Journal, 37, 2475 (1915); Fales and Vosburgh, *ibid.*, 40, 1302 (1918).

[2] Ostwald. Ostwald-Luther, "Physico-chemische Messungen," 3rd Ed., p. 445.

[3] Bjerrum, *Z. physik. Chem.*, 53, 430 (1905); Fales and Nelson, This Journal, 37, 2781 (1915).

[4] Loomis and Acree, *loc. cit.*; Harned, *loc. cit.*; Fales and Vosburgh, *loc. cit.*

[5] This Journal, 40, 1291 (1918).

tials, deduced the value of zero for the contact potential 1.0 *M* HCl—sat. KCl, and 0.1 *M* HCl—sat. KCl at 25°.[1] Inferentially it follows that the same value of zero applies for concentrations of hydrochloric acid between 1.0 *M* and 0.1 *M*, and also for concentrations less than 0.1 *M*, *e. g.*, that the use of saturated potassium chloride in contact with concentrations of hydrochloric acid up to 1.0 *M* gives zero contact potential at 25°.[2]

The selection of the saturated salt bridge, therefore, minimizes difficulty *a*, but still leaves difficulty *b*, when 0.1 *M* or *M* calomel cells are used. The simple device of substituting the saturated potassium chloride calomel cell for the others will also remove difficulty *b*. In view of the above considerations the logical procedure is to use the saturated potassium-chloride calomel cell in conjunction with a saturated salt bridge, and thereby eliminate or minimize both difficulties.[3]

The purpose of the present investigation is therefore as follows: to study the applicability of the saturated potassium chloride calomel cell for use in systems of the type,

Combination (1) Hg—HgCl sat. KCl—sat. KCl—0.1 *M* HCl—H_2(Pt),[4]

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[1] According to Planck's formula, the values for the contact potential 1.0 *M* HCl - sat. KCl and 0.1 *M* HCl-sat. KCl at 25° are, respectively, 0.0170 and 0.0055 volt. The main argument that the values are each zero, as deduced by Fales and Vosburgh, is that the acceptance of this value leads to consistent results when taken in conjunction with the corresonding electrode potentials, and applied to the 28 combinations studied by them, whereas Planck's values lead to inconsistent results.

The matter of the exact value of contact potentials cannot, however, be considered as settled in its finality until (1) it is shown that no other set of values but the ones selected will give consistent results, or until (2) some method is devised by which either electrode potentials or contact potentials can be measured independently. The difficulty in dealing with individual electrode potentials, as has always been realized, is that there are always at least *n* + 1 potentials to be considered for every set of *n* combinations chosen, that is to say, the experimental observations always give rise to a set of indeterminate equations; this indeterminateness of the problem was pointed out by Fales and Vosburgh (*loc. cit.*, p. 1304). For a further appreciation of the difficulties in this regard, see Lewis, Brighton and Sebastian, THIS JOURNAL, 39, 2256 (1917).

[2] Loomis and Acree, *Am. Chem. J.*, 46, 621 (1911), had previously inferred that the use of a saturated potassium chloride salt bridge would eliminate the contact potential between it and 0.1 *M* hydrochloric acid at 25°.

[3] Michaelis, it seems, was the first to propose the use of the saturated potassium chloride calomel cell in conjunction with a saturated salt bridge. In his monograph, "Die Wasserstoffionen-Konzentration," Julius Springer, Berlin, 1914, p. 150, he recommends this scheme, and gives figures for the combination:

$$\text{Hg-HgCl sat. KCl-sat. KCl-}\left\{\begin{matrix} 0.1\ M\ NaC_2H_3O_2 \\ 0.1\ M\ HC_2H_3O_2 \end{matrix}\right\}\text{-}H_2(\text{Pt})$$

for the temperature range 15–38° with the comment, however, that his values may be in error by 2 or 2.5 millivolts.

Fales and Ware, THIS JOURNAL, 41, 487 (1919), used this combination, and provisionally gave the value of the electrode potential Hg-HgCl sat. KCl- as 0.5272 volt at 25°.

and to compare its use for such purposes with the 0.1 *M* and *M* potassium-chloride calomel cells respectively, throughout the temperature range 5–60°.

Experimental.

Water-baths, Potentiometer, and Galvanometer.—Two baths, Nos. 1 and 2, were used; the former was controlled to within ±0.02°, and the latter to within ±0.01°. From Combination 8, Table IV, it will be seen that the difference in e. m. f. between any 5° is about 0.003 volt; this is equivalent to 0.000006 volt per 0.01°, and shows that both temperature regulations were well within the required precision.

The null method was employed and the e. m. f. determined by means of a Leeds and Northrup potentiometer and a D'Arsonval galvanometer. The latter had a sensibility of 280 megohms, a period of 2.5 seconds, and a total resistance of 444 ohms. A Weston cell was used as a primary standard of reference; it had been calibrated by the U. S. Bureau of Standards, checked against another standard cell in the department, and found to have a value of 1.0183 volts at 20°.

Types of Cells.—The calomel electrode described by Fales and Vosburgh,[1] and the bubbling hydrogen cell were used throughout the work.

Making New Calomel Cells.—At first the mercury and the calomel in a calomel cell were not removed from the cell when it was desired to make up a new cell; only the solution of 0.1 *M* or *M* potassium chloride above the calomel was replaced. In every case the value of the new cell was not appreciably different from the old value before the fresh potassium chloride solution had been added. One case is cited as an illustration: a 0.1 *M* calomel cell, B_6, was employed in Combination 6 and gave an observed value for the combination at 25° of 0.3934 volt (theory 0.4016 volt).[2] When the potassium chloride solution in the cell had been replaced by some fresh solution, the value of the combination was 0.3935 volt. The entire contents of the cell were then removed, the cell thoroughly cleaned and prepared again with all fresh materials. The resulting value of the combination was 0.4015 volt.

This would seem to indicate that whenever a new cell is prepared an entire change of materials must be effected if accurate values are desired. It is quite possible that there is an adsorption of the potassium chloride by the calomel, and this phenomenon would not be altered by a simple substitution of some fresh solution. This point would undoubtedly bear further investigation.

Hydrogen Electrodes and Hydrogen.—Platinum electrodes of plate form, 2 cm. long × 1 cm. wide × 0.025 cm. thick, platinized with plat-

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[1] THIS JOURNAL, 40, 1305 (1918).

[2] This particular cell had shown a decrease in its e. m. f., due to diffusion into it of potassium chloride from the salt bridge; hence the low value of the combination.

inum black, were used. They were reblacked several times during the work, whenever any 2 gave a greater difference than 0.0002 volt.

Compressed hydrogen was used exclusively; it was passed successively through alkaline permanganate solution, alkaline pyrogallate solution, water, and cotton wool to purify it; then through a hydrochloric acid solution of the same concentration as that employed in the hydrogen cell; the rate of flow was about 2 or 3 bubbles per second.

Liquid Junctions.—The liquid junctions were made by dipping the ends of the siphon tubes of the component cells into a saturated solution of potassium chloride contained in a small beaker, the amounts of the solutions in all parts of a combination being so adjusted that all meniscuses were on the same level. At the beginning of the work small wooden plugs or toothpicks were used in the ends of the siphon tubes to prevent any mechanical mixing of the solutions. With these it was often found that duplicate measurements of a combination did not agree to a closer precision than ±0.0005 volt.[1] Investigation showed that this variation was due solely to the change in contact potential and not to any change in the value of the electrode potential; a conclusion which is confirmed by the fact that the loosening or tightening of the wooden plugs in the ends of the siphon tubes would cause an immediate change in the value of the combination. By using small cones of cotton wool fitted snugly, but not tightly, into the siphon tubes of all the cells of a combination, the present authors found that they could duplicate their results with ease at any time with a precision of ±0.0001 to ±0.0002 volt. This method was, therefore, adopted and the values reported in this work are, unless otherwise specified, those obtained by using cotton plugs.

With respect to the reproducibility which is thus gained by the use of cotton plugs, it is possible that the greater space between the fibers of the cotton than between the cells of the wood allows a more even and rapid diffusion of the 2 liquids to their point of juncture, with the result that contact is made through the plug when cotton is used, instead of around the plug as is the case when wood is used.[2]

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[1] See the work of Fales and Vosburgh, *loc. cit.*, who used wooden plugs, and commented on the variability of measurements caused by the interdiffusion which occurs at liquid junctions.

[2] Attention must be called to the admirable and quite different "flowing junction" method of Lewis, Brighton and Sebastian, THIS JOURNAL, 39, 2254 (1917), and of Lamb and Larson, *ibid.*, 42, 1229 (1920), for establishing constancy of contact conditions and insuring reproducibility of results. In view of the theoretical excellence of the "flowing junction" method, it would be of great service to the study of e. m. f. measurements to have all other methods critically compared with it. In the meantime it is certainly worth while to state that the L. B. and S. method allows duplication of results to be obtained within one or two minutes after making contact, and it would seem, therefore, to be particularly desirable for those combinations, where large contact potentials exist.

Preparation of Materials and Solutions.—Conductivity water was obtained by distilling ordinary distilled water through a block tin condenser from alkaline permanganate solution, and kept in Non-sol bottles. It was used throughout the work except for making saturated potassium chloride solution for the salt bridge, when ordinary distilled water was used. In order to prevent any contamination of the salt bridge it was renewed every 2 or 3 days with fresh solution.

The mercury employed in the preparation of the calomel cells was washed several times with nitric acid according to the method of Hildebrand,[1] then filtered through a clean dry towel, and finally distilled under reduced pressure with access of air as proposed by Hulett.[2]

But one lot of calomel was used, a commercial "C. P." grade; it was tested for iron and non-volatile residue and found satisfactory. A sufficient amount was put in a Non-sol bottle together with a little pure mercury and about 400 cc. of potassium chloride solution of the desired concentration; this mixture was then shaken intermittently for 2 days before being used.[3]

TABLE I.—SPECIFIC GRAVITIES AND DENSITIES OF SOLUTIONS.

	(1.0 *M* HCl).	1.022 $\underline{M}$ HCl[a]		(0.1 *M* HCl)	0.1003 $\underline{M}$ HCl	
Temp. °.	Sp. gr. t°/t°.	Density t°/4°.	Mols per liter.	Sp. gr. t°/t°.	Density t°/4°.	Mols per liter.
5	1.0188	1.0188	1.004	1.0020	1.0020	0.1003
10	1.0182	1.0179	1.003	1.0018	1.0015	0.1002
15	1.0179	1.0170	1.002	1.0018	1.0010	0.1001
20	....	....	1.000	....	....	0.1000
25	1.0176	1.0146	0.999	1.0018	0.9990	0.0999
40	1.0169	1.0091	0.993	1.0016	0.9939	0.0993
45	1.0169	1.0071	0.991	1.0016	0.9920	0.0991
50	1.0169	1.0049	0.989	1.0016	0.9898	0.0989
55	1.0167	1.0023	0.987	1.0016	0.9875	0.0987
60	1.0166	0.9997	0.984	1.0015	0.9848	0.0984
	(1.0 *M* KCl)	1.030 $\underline{M}$ KCl		(0.1 *M* KCl)	0.1004 $\underline{M}$ KCl	
5	1.0482	1.0482	1.004	1.0049	1.0049	0.1002
10	1.0473	1.0470	1.003	1.0050	1.0047	0.1001
15	1.0466	1.0457	1.002	1.0049	1.0040	0.1001
20	....	....	1.000	....	....	0.1000
25	1.0462	1.0431	0.999	1.0048	1.0019	0.0999
40	1.0454	1.0374	0.993	1.0044	0.9967	0.0993
45	1.0453	1.0352	0.991	1.0043	0.9946	0.0991
50	1.0452	1.0329	0.989	1.0044	0.9925	0.0989
55	1.0452	1.0304	0.986	1.0045	0.9902	0.0987
60	1.0451	1.0277	0.984	1.0044	0.9877	0.0984

[a] By $\underline{M}$ is understood the No. of mols per 1000 g. of water. *M* indicates true mols.

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[1] THIS JOURNAL, 31, 933 (1909).

[2] *Z. physik. Chem.*, 33, 611 (1900).

[3] Fales and Vosburgh, *loc. cit.*, used 3 lots of calomel: an imported, a domestic, and that prepared by the electrolytic method of Ellis, THIS JOURNAL, 38, 740 (1916). They noticed no difference between cells prepared with any one of the 3 lots of calomel.

The various standard solutions employed in preparing the several cells were made up as described by Fales and Vosburgh. In order to extend the data given by those authors,[1] the specific gravities, densities and molar concentrations of the standard solutions are given above in Table I for temperatures not considered by them.

Comparison of the Values of the Saturated Potassium Chloride Calome Cell with Potassium Chloride Calomel Cell of Different Concentrations, at 25°.

The starting point in the investigation was to study the system, Combination 2

$$\text{Hg—HgCl}xM\text{ KCl—sat. KCl—}0.1\,M\text{ HCl—H}_2\text{ (1 Atmos.) Pt, at }25°,$$

where x varies from 0.1 M to saturation (4.12 M). The results are given in Table II.

TABLE II.—VALUES OF COMBINATION 2 AT 25°.

Conc. KCl.	Av. obs. value of combination 2 (volt).	No. of detns.	Av. bar. reading (mm. Hg).	Av. corr. value[a] to 1 atmos. H_2 (volt).
0.1 M	0.4016 ± 0.0002	39	759	0.4020 ± 0.0002
0.5	0.3642 ± 0.0001	8	761	0.3646 ± 0.0001
1.0	0.3479 ± 0.0002	90	760	0.3483 ± 0.0002
2.0	0.3321 ± 0.0001	8	760	0.3325 ± 0.0001
3.0	0.3209 ± 0.0001	8	760	0.3213 ± 0.0001
Saturated	0.3099 ± 0.0002	101	761	0.3103 ± 0.0002

[a] For correction of values to 1 atmos. H_2, see paragraphs headed "Correction for Barometric Pressure."

From the values given in the last column of Table II, the values of the several electrode potentials

$$\text{Hg—HgCl}xM\text{ KCl}$$

may be obtained by correcting for the small contact potentials existing between the saturated potassium chloride solution of the salt bridge and the less concentrated solution of the same salt in the calomel electrode. These values for the 0.1, 0.5, 1.0, 2.0 and 3.0 M potassium chloride solutions in contact with the saturated salt bridge have been calculated from Nernst's formula,

$$E = RT\frac{u - v}{u + v}\log\frac{C_2}{C_1},$$

and found to be: 0.0006, 0.0003, 0.0002, 0.0002 and 0.0001 volt, respectively. Using these values and the value 0.5648 volt for the electrode potential, Hg—HgCl 1.0 M KCl at 25°[2] we get as the values of the several electrode potentials the results given in Table III and expressed graphically in Fig. 1.

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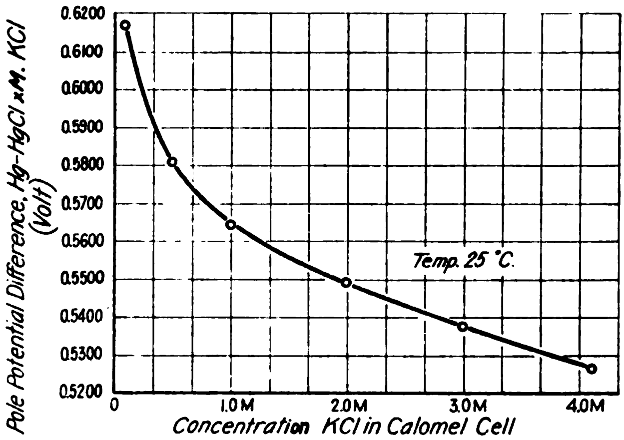
[1] *Loc. cit.*, p. 1309. It is also desired to point out that the values for the several solutions at the temperatures of 15° and 18°, as given by F. and V., are incorrect due to an error in calculation.

[2] See Fales and Vosburgh, *loc. cit.*, for the selection of the value 0.5648 volt.

TABLE III.—ELECTRODE POTENTIALS OF SEVERAL POTASSIUM CHLORIDE CALOMEL CELLS AT 25°.

Cell Hg–HgCl xM KCl.	Electrode potential (volt).
0.1	0.6177
0.5	0.5808
1.0	0.5648
2.0	0.5488
3.0	0.5377
Sat. KCl	0.5266



Relation of Pole Potential Difference to Concentration of KCl at 25°C.

Fig. 1.

From Fig. 1 it can readily be seen that the e. m. f. of the calomel cell changes more rapidly when the concentration of the potassium chloride is more dilute. From this one consideration alone, neglecting for the moment the fact that the saturated cell would eliminate both the error due to diffusion and that due to the change of contact potential, it is obvious that the saturated potassium chloride calomel cell would be the safest cell to use.

Correction for Barometric Pressure.

In order to obtain the absolute value of any combination in which a hydrogen cell is employed, it is necessary to determine the correction which must be applied to the electrode potential of the hydrogen cell on account of the barometric pressure and the temperature at which the measurement is made. In the combination

$$\text{Hg—HgCl } xM \text{ KCl—} yM \text{ KCl—} zM \text{ HCl—H}_2\text{(Pt)}$$
$$\xleftarrow{a} \qquad\qquad\qquad\qquad \xrightarrow{b}$$

if we decrease the pressure of the hydrogen, the value of b will increase. Therefore, when the pressure of the hydrogen is less than one atmosphere the value of b will be greater than the value which it has when the pressure of hydrogen is equal to one atmosphere, while the value of the whole combination will be correspondingly low because the electrode potentials a and b are oppositely directed. Consequently if we know the variation in b, we can apply the necessary correction by subtracting it from the electrode potential $2M$ HCl—H_2(Pt), or by adding it to the observed value of the combination.

Two standards of reference may be adopted: correction to one atmosphere of hydrogen; or correction to one atmosphere total pressure, *e. g.*, one atmosphere as indicated by the barometer.

Correction to One Atmosphere of Hydrogen.

Assuming that the partial pressure of the hydrogen above the solution bathing the hydrogen electrode is equal to the observed barometric pressure less the vapor pressure of water,[1] and making the calculations according to the formula

$$E = \frac{RT}{2F \ln 1/P}$$ [2]

we obtain the graph given in Fig. 2, where the correction is plotted as a function of the observed barometric pressure.

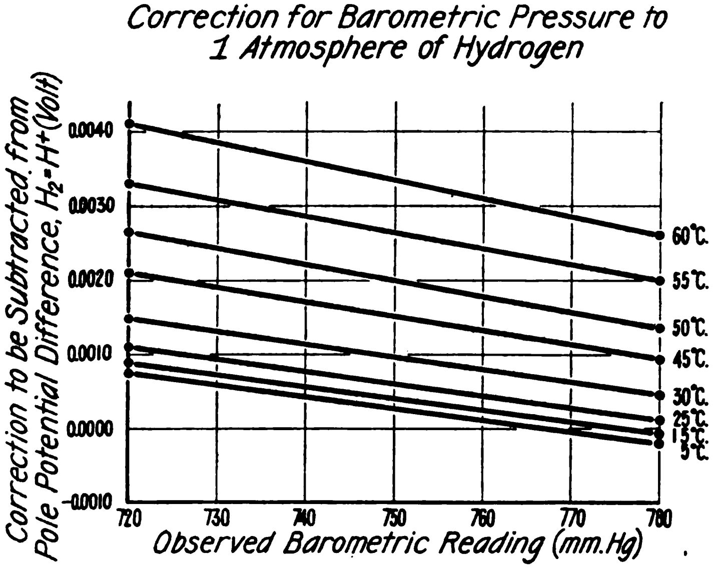


Fig. 2.

While this assumption holds for dilute solutions and temperatures around 25°, it is very probable that the relationship is different for con-

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[1] For concentrated solutions, this would not be strictly true, since the vapor pressure of concentrated solutions may depart considerably from that of water.

[2] See Harned, This Journal, 37, 2465 (1915).

centrated solutions and high temperatures, say above 50°. It would seem a safer procedure, in general, therefore, to refer all measurements to one atmosphere total pressure.

Correction to One Atmosphere Total Pressure.

In the present work the extreme barometric pressures observed over a period of 8 months were 755 mm.—770 mm., with an average of 762.5 mm. It can readily be seen that this deviation of about 10 mm. from the average would correspond to a correction which is less than the experimental error involved in the measurements of the systems. The authors, therefore, propose to neglect the correction when one atmosphere total pressure is used as a standard, and to employ it only when it shall be necessary to refer to one atmosphere of hydrogen, as in Table II, where the ultimate or absolute value of the different combinations was desired.

Comparison of Cells at 30°, 35°, and 40°.

In order to compare the relative merits of the saturated, *M* and 0.1 *M* potassium chloride calomel cells, 3 of each type, which we shall, respectively designate "S," "A," and "B" were placed in a constant temperature bath along with three 0.1 *M* hydrochloric acid cells, "D." The calomel cells were not disturbed from day to day, but the hydrogen cells were removed from the bath after each day's measurements, thoroughly washed, and each platinum electrode allowed to stand overnight in distilled water. The next day the hydrogen cells were prepared with fresh acid. This procedure gave many duplicate determinations of the same calomel cell, and served to make the results more reliable. After the value of the various combinations had been obtained at any one temperature, the temperature of the bath was raised through an interval of 5°. It was originally intended to extend the measurements for all 3 calomel cells over the range of 25° to 60°, but it was soon plainly evident that the lack of merit of the *M* and 0.1 *M* calomel cells did not warrant the necessary time or labor.

Each cell in the bath was measured against the other 11, using a saturated potassium chloride salt bridge. This gave the following combinations.

(3) Hg—HgCl 0.1 *M* KCl—sat. KCl— sat. KCl HgCl—Hg,
(4) Hg—HgCl 1.0 *M* KCl—sat. KCl—sat. KCl HgCl—Hg,
(5) Hg—HgCl 0.1 *M* KCl—sat. KCl—1.0 *M* KCl HgCl—Hg
(6) Hg—HgCl 0.1 *M* KCl—sat. KCl—0.1 *M* HCl—H_2(Pt),
(7) Hg—HgCl 1.0 *M* KCl—sat. KCl—0.1 *M* HCl—H_2(Pt)
(8) Hg—HgCl sat. KCl—sat. KCl—0.1 *M* HCl—H_2(Pt)

The combinations were always kept at one temperature until observations of 2 successive days, with renewals of the hydrochloric acid in the hydrogen cells, did not differ from each other by more than the experimental error, ±0.0002 volt. Combination 8 was measured throughout the temperature range, 5° to 60°, but measurements of the other 5 combinations were abandoned at 40°. The results are given in Table IV, all observations being expressed in volts, and the values for Combinations 6, 7, and 8 being referred to one atmosphere total pressure.

TABLE IV.—THE e. m. f. OF THE SATURATED, *M*, AND 0.1 *M* POTASSIUM CHLORIDE CALOMEL CELLS AT 25–40°.[a]

Temp. °C.	No. of detns.	Time. Days.	Average bar. reading (mm. Hg).	Average e. m. f. (volt).
(3) Hg–HgCl 0.1 *M* KCl–sat. KCl–sat. KCl HgCl–Hg.				
25	36	4	760	0.0918 ± 0.0002
30	27	3	760	0.0904 ± 0.0034
35	9	1	761	0.0902 ± 0.0033
40	9	1	757	0.0759 ± 0.0149
(4) Hg–HgCl 1.0 *M* KCl–sat. KCl–sat. KCl HgCl–Hg.				
25	36	6	760	0.0387 ± 0.0002
30	27	3	760	0.0397 ± 0.0005
35	6	1	761	0.0404 ± 0.0004
40	6	1	757	0.0386 ± 0.0022
(5) Hg–HgCl 0.1 *M* KCl–sat. KCl–1.0 *M* KCl HgCl–Hg.				
25	28	4	760	0.0533 ± 0.0002
30	27	3	760	0.0508 ± 0.0035
35	9	1	761	0.0513 ± 0.0028
40	9	1	757	0.0407 ± 0.0148
(6) Hg–HgCl 0.1 *M* KCl–sat. KCl–0.1 *M* HCl–H_2(Pt).[b]				
25	39	5	760	0.4016 ± 0.0002
30	27	3	760	0.3971 ± 0.0035
35	18	2	760	0.3967 ± 0.0031
40	27	3	756	0.3782 ± 0.0123
(7) Hg–HgCl 1.0 *M* KCl–sat. KCl–0.1 *M* HCl–H_2(Pt).[c]				
25	90	10	759	0.3479 ± 0.0002
30	18	2	760	0.3462 ± 0.0005
35	18	2	760	0.3443 ± 0.0005
40	27	3	756	0.3411 ± 0.0029
(8) Hg–HgCl sat. KCl–sat. KCl–0.1 *M* HCl–H_2(Pt).				
25	108	12	761	0.3099 ± 0.0002
30	27	3	760	0.3070 ± 0.0001
35	27	3	760	0.3042 ± 0.0001
40	36	4	756	0.3014 ± 0.0001
45	27	3	762	0.2996 ± 0.0002
50	27	3	758	0.2966 ± 0.0001
55	36	4	762	0.2942 ± 0.0002
60	18	2	763	0.2919 ± 0.0002

[a] The following individual cells were used: B_7, B_8, B_9; A_4, A_6, A_7; S_1, S_2, S_3, S_4; and D_1, D_2, D_3.

[b] For combination 6 at 25° and one atmos. H_2 the following values are reported in the literature: Fales and Vosburgh, THIS JOURNAL, 40, 1314 (1918), 0.3991 volt; Bjerrum, *Z. physik. Chem.*, 53, 430 (1905), 0.4012 volt; Harned, *loc. cit.*, 0.4000 volt; Myers and Acree, *Am. Chem. J.*, 50, 411 (1913), 0.4012 volt.

[c] For combination 7 at 25° and one atmos. of H_2, Fales and Vosburgh, *loc. cit.*, found 0.3470 volt; Harned, *loc. cit.*, 0.3491 volt.

The results given in Table IV show that the *M* and 0.1 *M* potassium chloride calomel cells are entirely unreliable above 25° when used in conjunction with a saturated potassium chloride salt bridge. In every case the average deviation increases with temperature and is far greater than the experimental error, being 0.012–0.015 volt at 40°, and due as we shall show later, to the diffusion of the saturated solution from the salt bridge into the *M* or 0.1 *M* solution in the calomel cell. It is also evident that the saturated potassium chloride calomel cell shows marked superiority over the other 2 calomel cells for use under the above conditions.

The System, Hg—HgCl sat. KCl—sat. KCl—0.1 *M* HCl—H_2(Pt), from 5° to 60°, Also Four Other Systems.

In order to test the saturated potassium chloride calomel cell further and to obtain its temperature coefficient, the saturated cells S_1 and S_2,[1] together with 8 new ones, S_3, S_4, ... S_{12}, were used in conjunction with four 0.1 *M* hydrochloric acid hydrogen cells, D_1, D_2, D_3, D_4, as follows the odd-numbered cells of each kind were placed in Bath 1, which was maintained at 25°, while the even-numbered cells were placed in Bath 2, which was varied from 5° to 60°. The saturated potassium chloride solution serving as a salt bridge in Bath 1 was connected to that serving in Bath 2, by means of a siphon tube of 0.5 cm. diameter; this tube contained saturated potassium chloride, and had its ends stopped with small cotton plugs, similar to those used in the ends of the siphon tubes of the component cells. Before any measurements were made, the platinum electrodes of the hydrogen cells were carefully blackened with platinum

TABLE V.

(8) Hg–HgCl sat. KCl–sat. KCl–0.1 *M* HCl–H_2(Pt).

5–60° 5–60°

Temperature.					
Calomel. °.	Hydrogen. °.	No. of detns.	Time. Days.	Average bar. reading (mm. Hg).	Average e. m. f. 1 atmos. total pressure (volt).
5	5	8	2	767	0.3183 ± 0.0001
10	10	6	3	765	0.3161 ± 0.0001
15	15	6	2	766	0.3143 ± 0.0001
20	20	8	2	764	0.3122 ± 0.0001
25	25	20	3	765	0.3100 ± 0.0001
30	30	4	1	770	0.3070 ± 0.0001
35	35	4	1	765	0.3043 ± 0.0001
40	40	4	1	770	0.3016 ± 0.0001
45	45	4	1	766	0.2997 ± 0.0002
50	50	4	1	755	0.2966 ± 0.0001
55	55	4	1	762	0.2942 ± 0.0002
60	60	4	1	762	0.2917 ± 0.0002

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[1] The 2 cells S_1 and S_2 had already been employed in obtaining the values given in Table IV; their further use was to give information as to their reliability for continued use after having been passed through the temperature range 25° to 60° and back again to 25°.

TABLE V (*continued*).

(9) Hg–HgCl sat. KCl–sat. KCl–sat. KCl HgCl–Hg,
5–60° 25°

Temperature.					
Calomel. °	Calomel. °	No. of detns.	Time. Days.	Average bar. reading (mm. Hg).	Average e. m. f. 1 atmos. total pressure (volt).
5	25	8	2	767	0.0042 ± 0.0001
10	25	8	3	765	0.0035 ± 0.0002
15	25	8	3	766	0.0025 ± 0.0001
20	25	8	2	764	0.0014 ± 0.0001
25	25	4	1	765	0.0001 ± 0.0001
30	25	4	1	770	0.0011 ± 0.0001
35	25	4	1	765	0.0023 ± 0.0001
40	25	4	1	770	0.0030 ± 0.0002
45	25	4	1	766	0.0040 ± 0.0001
50	25	4	1	755	0.0050 ± 0.0001
55	25	4	1	762	0.0059 ± 0.0001
60	25	4	1	762	0.0068 ± 0.0002

(10) Hg–HgCl sat. KCl–sat. KCl–0.1 *M* HCl–H_2(Pt),
5–60° 25°

Calomel. °	Hydrogen. °				
5	25	8	2	767	0.3052 ± 0.0001
10	25	12	3	765	0.3061 ± 0.0002
15	25	8	2	766	0.3072 ± 0.0001
20	25	6	2	764	0.3086 ± 0.0001
25	25	20	3	765	0.3100 ± 0.0001
30	25	4	1	770	0.3111 ± 0.0001
35	25	4	1	765	0.3119 ± 0.0001
40	25	4	1	770	0.3129 ± 0.0001
45	25	4	1	766	0.3136 ± 0.0001
50	25	4	1	755	0.3142 ± 0.0001
55	25	4	1	762	0.3150 ± 0.0001
60	25	4	1	762	0.3162 ± 0.0002

(11) (Pt)H_2–0.1 *M* HCl–sat. KCl–0.1 *M* HCl–H_2(Pt).
5–60° 25°

Hydrogen. °	Hydrogen. °				
5	25	8	2	767	0.0122 ± 0.0001
10	25	8	3	765	0.0096 ± 0.0002
15	25	12	3	766	0.0066 ± 0.0001
20	25	8	2	764	0.0034 ± 0.0001
25	25	4	1	765	0.0001 ± 0.0001
30	25	4	1	770	0.0049 ± 0.0002
35	25	4	1	765	0.0087 ± 0.0001
40	25	4	1	770	0.0125 ± 0.0001
45	25	4	1	766	0.0146 ± 0.0001
50	25	4	1	755	0.0181 ± 0.0002
55	25	4	1	762	0.0216 ± 0.0002
60	25	4	1	762	0.0260 ± 0.0002

TABLE V (*continued*).

(12) Hg–HgCl sat. KCl–sat. KCl–0.1 *M* HCl–H_2(Pt).

25° 5–60°

Temperature.					
Hydrogen. °.	Calomel. °.	No. of detns.	Time. Days.	Average bar. reading (mm. Hg).	Average e. m. f. 1 atmos. total pressure (volt).
5	25	8	2	767	0.3230 ± 0.0001
10	25	8	3	765	0.3194 ± 0.0001
15	25	8	2	766	0.3163 ± 0.0002
20	25	6	2	764	0.3128 ± 0.0002
25	25	20	3	765	0.3100 ± 0.0001
30	25	4	1	770	0.3070 ± 0.0002
35	25	4	1	765	0.3031 ± 0.0001
40	25	4	1	770	0.3003 ± 0.0002
45	25	4	1	766	0.2964 ± 0.0002
50	25	4	1	755	0.2926 ± 0.0002
55	25	4	1	762	0.2886 ± 0.0002
60	25	4	1	762	0.2842 ± 0.0002

black until, on subsequent trial, identical values were obtained when they were checked against a saturated calomel cell of known value. When the hydrogen cells containing these electrodes were measured against each other, there was no difference in e. m. f. Each cell in Bath 1 was measured against each cell in Bath 2, thus giving additional data for Combination 8 as well as data for 4 other combinations, namely, 9, 10, 11 and 12, as contained in Table V.

The Electrode Potentials of the Calomel and Hydrogen Cells.

The value of the electrode potential Hg—HgCl 1.0 *M* KCl at 18° is taken as the standard as adopted by Ostwald[1] with the value 0.5600 volt. This is equivalent to 0.5648 volt at 25°[2] and is the standard to which we shall refer all our calculations.

The value of the electrode potential Hg—HgCl sat. KCl is found in terms of the standard calomel cells by means of Combination 4 to be 0.5263 volt at 25°, by solving for *a:*

(4) Hg—HgCl 1.0 *M* KCl—sat. KCl—sat. KCl HgCl—Hg; 0.0387 volt.

$\xleftarrow{0.5648}$ $\xleftarrow{0.0002}$ zero $\xrightarrow{a}$

Likewise the electrode potential Pt (1 atmos.) H_2—0.1 *M* HCl is found in terms of the standard calomel cell to be 0.2167 volt at 25° by solving for *b* in Combination 7:

(7) Hg—HgCl 1.0 *M* KCl—sat. KCl—0.1 *M* HCl—H_2(1 atmos.) Pt; 0.3483 volt.

$\xleftarrow{0.5648}$ $\xleftarrow{0.0002}$ zero $\xrightarrow{b}$

Also from Combination 8 at 25°:

(8) Hg—HgCl—sat. KCl—sat. KCl—0.1 *M* HCl—H_2 (1 atmos.) Pt; 0.3103 volt.

$\xleftarrow{a}$ zero zero $\xrightarrow{0.2167}$

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[1] *Z. physik. Chem.*, 35, 333 (1900).

[2] Fales and Vosburgh, THIS JOURNAL, 40, 1300 (1918).

we obtain a second value, 0.5270 volt, for the electrode potential Hg—HgCl sat. KCl, by solving for a.

The value of the electrode potential Hg—HgCl 0.1 M KCl at 25° may be obtained from Combination 5, by solving for c:

(5) Hg—HgCl 0.1 M KCl—sat. KCl—1.0 M KCl HgCl—Hg; 0.0533 volt.

$\xleftarrow{c}$ $\xleftarrow{0.0006}$ $\xrightarrow{0.0002}$ $\xrightarrow{0.5648}$

It is found to be 0.6177 volt. Using this value in Combination 3

(3) Hg—HgCl 0.1 M KCl—sat. KCl—sat. KCl HgCl—Hg; 0.0918 volt.

$\xleftarrow{0.6177}$ $\xleftarrow{0.0006}$ zero $\xrightarrow{a}$

we obtain a third value for a, which is 0.5265 volt. Likewise using the same value for c, 0.6177 volt, in Combination 6, we find a second value of b which is 0.2163 volt:

(6) Hg—HgCl 0.1 M KCl—sat. KCl—0.1 M HCl—H_2 (1 atmos.) Pt; 0.4020 volt.

$\xleftarrow{0.6177}$ $\xleftarrow{0.0006}$ zero $\xrightarrow{b}$

By averaging the respective values we find that the value of the electrode potential Hg—HgCl sat. KCl is equal to 0.5266 ± 0.0003 volt at 25°, while that of Pt (1 atmos.) H_2—0.1 M HCl is equal to 0.2165 ± 0.0002 volt at the same temperature. These values, along with the value of the standard calomel cell of 0.5648 volt at 25°, were used for the calculation of the results given in Table III and Fig. 1.

The Temperature Coefficient of the Saturated Potassium Chloride Calomel Cell.

From Combinations 9 and 10, Table V, it will be seen that the difference in e. m. f. for the saturated calomel cell between 5° and 60° is 0.0110 volt, and that the e. m. f. is sensibly a linear function of the temperature. Consequently the temperature coefficient of the cell is

$$\frac{0.0110}{55} = 0.00020 \text{ volt per degree C.}$$

This shows that the saturated calomel cell has a very small temperature coefficient.

The Free Energy Change of the Several Systems.

In order to accomplish the change in state,

$$H_2 \text{ (1 atmos.)} + 2HgCl \rightleftarrows 2\,Hg \text{ (liquid)} + 2HCl$$

it is necessary that 2 faradays pass through the system. Therefore, the free energy decrease accompanying this reaction where the system is maintained at the constant temperature t, may be obtained by the use of the thermodynamic relationship,

$$(\Delta F)_t = 2\ (\text{e. m. f.})_t \times 96{,}500.$$

This is true for systems of the type represented by Combinations 8 and 11. When we have systems like Combinations 3, 4, or 5, the same change will be effected by the passage of one faraday so that we have for the decrease in free energy in such cases

$$(\Delta F)_t = (\text{e. m. f.})_t \times 96{,}500.$$

Behavior of the Saturated Potassium Chloride Calomel Cell on Falling Temperature.

When the systems employing the saturated potassium chloride calomel cell were subjected to an increase in temperature, it was necessary to add a slight excess of solid potassium chloride to the solution of the salt in the cell in order to maintain the solution at the point of saturation. This was easily accomplished and caused no difficulty in technique, because of the construction of the calomel cell. However, the amount of salt necessary to produce a saturated solution at 60° was much greater than the amount needed for the lower temperatures. The result was that a considerable excess of the salt always crystallized out when the temperature was lowered. This excess of salt in the cell caused no variation in the observed e. m. f. of the system except when the temperature drop was from 30° to 25°. In this interval it was noticed for Combination 8 using cells S_1 and S_2 that the readings were about one millivolt high when the cells were being taken through the temperature cycle 25° to 60° a second time, and descending temperatures were being used. The precise values after dropping from 30° to 25° were 0.3114 and 0.3107 volt, respectively, whereas the initial values at the start of the cycle were 0.3100 and 0.3101 volt (theory 0.3100 volt). These values of 0.3114 and 0.3107 remained constant for 4 days. To see the effect of further cooling, followed by subsequent warming, the cells were cooled down to 15° for 5 minutes and then placed in the constant temperature bath at 25°. Two hours later both cells gave a value of 0.3104 volt. Four days later S_1 gave its original value of 0.3100 volt. In view of the fact that the solid phase of potassium chloride was always present during the changes in temperature, the variation in e. m. f. cannot be ascribed to supersaturation, but must be attributed to some other cause. On ascending temperatures no such variation was encountered.

Variation in e. m. f. of the Molar and Tenth-molar Potassium Chloride Calomel Cells.

It has been noticed by several workers that the values of the *M* and 0.1 *M* calomel cells, when used in conjunction with a potassium chloride salt bridge of greater concentration than that employed in the calomel cell, varied from time to time. Richards and Archibald[1] described the decrease in potential as due to the formation of a complex mercuric ion by the interaction of the alkali chloride and the calomel. They also

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[1] Richards and Archibald, *Z. physik. Chem.*, 40, 385 (1902).

offered a mathematical proof of their theory. Gewecke[1] almost simultaneously corroborated Richards' results. Loomis and Acree,[2] by careful preparation of materials, were able to obtain 0.1 *M* calomel cells that would remain constant for about 3 weeks and then change gradually. Ellis[3] observed a similar effect in his work, but offered no explanation. Loomis and Meacham[4] adopt the view of Richards. Fales and Vosburgh[5] ascribed the decrease to the diffusion of the saturated potassium chloride from the salt bridge into the more dilute solution in the calomel cell; they made an unsuccessful attempt to eliminate it by the use of a jelly salt bridge of agar agar. Lewis, Brighton and Sebastian[5] made frequent renewals of the liquid junction in a specially designed form of apparatus in order to overcome this gradual diffusion.

The present authors found no confirmation of Richards'[5] theory in their work; they are of the opinion that the decrease in value is due only to the diffusion of the saturated potassium chloride from the salt bridge into the *M* and 0.1 *M* potassium chloride solution in the cell, and offer the following evidence in support of this belief. After the e. m. f. of Combinations 6 and 7 had undergone a considerable decrease, they withdrew from each 0.1 *M* and *M* calomel cell employed, 10 cc. of its potassium chloride solution. Each portion was carefully withdrawn by means of a small pipet, diluted with water, aliquoted as necessary and then titrated with 0.01 *M* silver nitrate solution, using potassium chromate as indicator. In some cases, that part of the potassium chloride solution which was in the siphon tube of the cell was excluded, but no great difference was noticed in the chloride content, thus showing that the solution in the cell had practically a uniform concentration throughout.

Table VI gives the detailed information.

During their use, Cells B_1, B_2, B_3, and A_3 were allowed to stand in contact with a molar salt bridge with stopcocks closed. When a measurement was to be made the cells were transferred to a saturated potassium chloride salt bridge and the stopcocks opened. The other cells were kept in contact with a saturated bridge at all times, the stopcocks being closed except when a measurement was being made. It will be noticed that the original values of Cells B_4, B_5 and B_6 are somewhat lower than the accepted value for the 0.1 *M* calomel cell (0.4016 volt). This is probably due to the fact that diffusion had already begun since they had been in contact with the saturated salt bridge for 2 days before the initial measurements were made. The addition of methyl orange to the potassium chloride solution in the cells showed no trace of hydrochloric acid which

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[1] Gewecke, *ibid.*, 45, 685 (1903).

[2] Loomis and Acree, *Am. Chem. J.*, 46, 621 (1911).

[3] Ellis, THIS JOURNAL, 38, 737 (1916).

[4] Loomis and Meacham, *ibid.*, 38, 2312 (1916).

[5] *Loc. cit.*

might have diffused into the cell due to the salt bridge having become contaminated with acid from the hydrogen cell.

TABLE VI.—VARIATION IN E. M. F. OF THE TENTH MOLAR AND MOLAR CELLS DUE TO DIFFUSION.

Cell.	Time in use (days).	Original value at 25°. 1 atmos. total pressure.	Final value at 25°. 1 atmos. total pressure.	Final conc. of KCl. *M*.
		0.1 *M* KCl.		
B_1	16	0.4006 volt	0.3884 volt	0.197
B_2	16	0.4006	0.3855	0.210
B_3	16	0.4003	0.3912	0.186
B_4	8	0.3989	0.3903	0.155
B_5	8	0.3985	0.3921	0.138
B_6	8	0.3994	0.3855	0.152
B_7	19	0.4015	0.3824[a]	0.170
B_8	19	0.4015	0.3819[a]	0.179
B_9	19	0.4017	0.3585[a]	0.657
		1.0 *M* KCl.		
A_3	16	0.3469	0.3458	1.106
A_4	23	0.3479	0.3355[a]	1.61
A_5	23	0.3481	0.3390[a]	1.44
A_7	23	0.3474	0.3442[a]	1.12

[a] The final values of these cells were measured at 40° as they were being used to compare the different kinds of cells.

In the case of Cell B_9 a very pronounced decrease in potential was noticed over a comparatively short period of time. At the start B_9 against D_1, D_2 and D_3 at 35° gave an average observed value of 0.3991 volt. Twenty-two hours later it gave an average of 0.3960 volt; 2.5 hours later its value had decreased to 0.3864 volt. The next day its value was 0.3843 volt. This shows a decrease in potential of 0.0100 volt in 2.5 hours following a decrease of about $^2/_3$ this amount during the previous day, and followed by a further decrease of about $^1/_3$ this amount during the next 24 hours. The cell was also measured against the *M* and saturated calomel cells, and they, in turn, against the hydrogen cells, in order that there might be no doubt in ascribing the drop in potential to the 0.1 *M* cell B_9. It should also be mentioned at this point that the diffusion of the saturated potassium chloride solution, from the salt bridge, into the more dilute solution in the calomel cell is greatly increased by a rise in temperature, as might be expected.

By comparing the final concentrations of the potassium chloride solutions withdrawn from the cells, as given in the last column of Table VI, with the theoretical concentrations of potassium chloride corresponding to the e. m. f. given in the fourth column of the same table, it is seen that the decrease in e. m. f. corresponds almost exactly to the increase in the concentration of the solution in the cell; see Fig. 3.

To further confirm the belief that the decrease in the e. m. f. of the cell is not due to the formation of a complex mercuric ion, 5 cc. of the potassium chloride solution from a 0.1 *M* cell, which had shown a decrease in potential due to diffusion, was made approximately 3 *M* with respect to hydrochloric acid, hydrogen sulfide passed into the solution, and the solution then allowed to stand for one hour in a stoppered bottle; no trace of a precipitate of mercuric sulfide was formed.

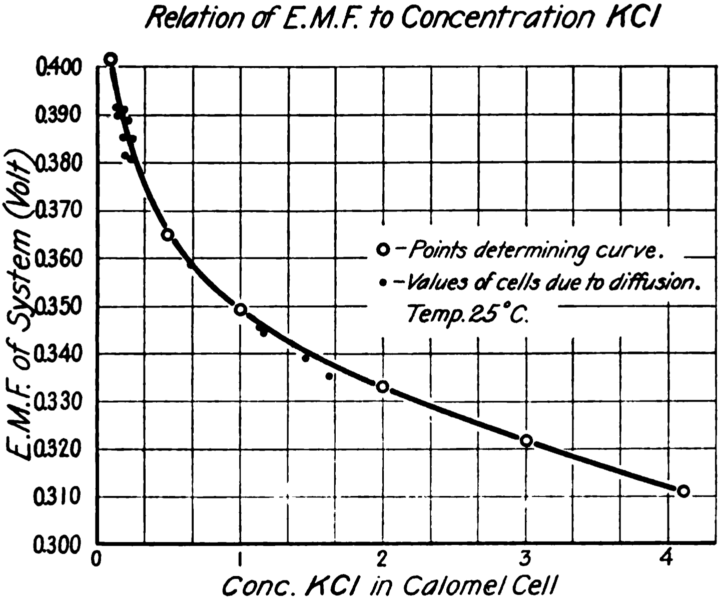

Fig. 3.

It is also to be remarked that the 0.1 *M* and *M* cells when used at 25° in conjunction with a saturated salt bridge were not found reliable over any great length of time, usually not longer than a week. Thus at 25° three 0.1 *M* cells decreased 0.1069 volt (average) after 12 days, while another 3 decreased 0.0016 volt (average) after 7 days; 3 molar cells decreased 0.0014 volt (average) after 15 days; another 3 decreased 0.0013 volt (average) after 6 days, and in the same time their average deviation increased from ±0.0002 to ±0.0006 volt.

Diffusion of the Saturated Potassium Chloride Solution into the Tenth-molar Hydrochloric Acid Solution of the Hydrogen Cell.

So far mention has been made only of the diffusion of the saturated potassium chloride solution from the salt bridge into the calomel cell, an occurrence which happens when the concentration of the salt solution in the cell is less than that in the salt bridge. There is also a diffusion of the saturated potassium chloride solution from the salt bridge into the hydrochloric acid solution of the hydrogen cell, and it was to offset the effect of this as completely as possible, that the acid of this cell was renewed each day that new measurements were to be made. At 40° this diffusion is quite rapid, while at 55° to 60° it is so rapid that considerable difficulty was encountered in obtaining satisfactory measurements. The best procedure is to draw off the acid solution which is in the siphon tube just before a reading is to be made, then to lower the siphon tube of the cell into the salt bridge and measure the e. m. f. of the combination at once. At 50–60°, when it so happened that the cotton plug had not been fitted snugly enough into the end of the siphon tube, the reading of the potentiometer could be seen to change as much as a millivolt per minute during the first and second minutes in which the siphon tube had been immersed in the salt bridge. At 25°, however, the diffusion into the hydrogen cell is not rapid enough to prevent one from duplicating their values with ease.

Superiority of the Saturated Potassium Chloride Calomel Cell.

With respect to the durability, accuracy and reproducibility of the saturated potassium chloride calomel cell, the following table, giving the history and measurements of 12 such cells, speaks for itself. Each value represents the average of 3 determinations, using Combination 8 at 25°.

TABLE VII.—HISTORY OF TWELVE SATURATED POTASSIUM CHLORIDE CALOMEL CELLS.

Cell.	Time in use (days).	E. m. f. of combination 8 (1 atmos. total pressure). Initial Volt.	E. m. f. of combination 8 (1 atmos. total pressure). Final Volt.	Remarks.
S_1	147	0.3100	0.3101	Carried around cycle 25–60°
S_2	147	0.3101	0.3103	
S_3	71	0.3100	0.3009	Destroyed to test KCl for acidity
S_4	143	0.3009	0.3104	Carried around cycle 25–60°
S_5	20	0.3101	0.3102	
S_6	20	0.3009	0.3100	Kept at constant temperature 25°
S_7	8	0.3008	0.3008	
S_8	8	0.3008	0.3007	Carried around cycle 25–5°
S_9	8	0.3100	0.3100	
S_{10}	8	0.3100	0.3009	
S_{11}	8	0.3009	0.3009	
S_{12}	8	0.3009	0.3009	
	Average,	0.3009	0.3100	

Cells S_1, S_2, S_6 and S_7 were used again around the temperature cycle 25–60°, and gave the following results:

S_1	20	0.3101	0.3100
S_2	20	0.3103	0.3104
S_6	8	0.3102	0.3008
S_7	8	0.3008	0.3008

Conclusions.

1. The e. m. f. of the combination,

(8) Hg—HgCl sat. KCl—sat. KCl—0.1 *M* HCl—H_2(Pt),

has been measured for the temperature range 5–60°, in intervals of 5°.

2. Taking the value of the normal calomel cell at 25° as 0.5648 volt, the value of the saturated potassium chloride calomel cell at 25° is 0.5266 volt. Its temperature coefficient is +0.00020 volt per degree rise in temperature for temperatures within the interval 5–60°.

3. The e. m. f. of the system,

(2) Hg—HgCl xM KCl—sat. KCl—0.1 M HCl—H_2 (1 atmos.) Pt,

at 25°, and the value of the electrode potential Hg—HgCl xM KCl in the above system, where x ranges from 0.1 M to saturation (4.12 M), have been given.

4. The e. m. f. of the combinations,

(3) Hg—HgCl 0.1 M KCl—sat. KCl—sat. KCl HgCl—Hg,
(4) Hg—HgCl 1.0 M KCl—sat. KCl—sat. KCl HgCl—Hg,
(5) Hg—HgCl 0.1 M KCl—sat. KCl—1.0 M KCl HgCl—Hg,
(6) Hg—HgCl 0.1 M KCl—sat. KCl—0.1 M HCl—H_2(Pt),
(7) Hg—HgCl 1.0 M KCl—sat. KCl—0.1 M HCl—H_2(Pt),

have been measured for the temperature range 25–40°, in intervals of 5°, and it has been found that these combinations are quite unreliable above 25°, and only reliable at 25° for about one week.

5. It appears that the decrease in the e. m. f. of the 0.1 M and M potassium chloride calomel cells, when used in conjunction with a saturated salt bridge, is due to the diffusion of the concentrated solution of potassium chloride from the bridge into the cell, and not due to the formation of a complex ion as a result of the interaction of the calomel and the potassium chloride solution.

6. In preparing new calomel cells it is necessary to use all new materials, and not simply replace the potassium chloride solution.

7. The saturated potassium chloride calomel cell is the best cell for use in conjunction with a saturated salt bridge, because it has a very small temperature coefficient, is easily reproducible, can safely be used at temperatures from 5° to 60°, and can be relied upon for its constancy of value over long periods of time.

NEW YORK, N. Y

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF LELAND STANFORD JUNIOR UNIVERSITY.]

THE CONDUCTIVITY AND VISCOSITY OF SOLUTIONS IN DIMETHYLAMINE, TRIMETHYLAMINE, ETHYLAMINE, DIETHYLAMINE, TRIETHYLAMINE, AND PROPYLAMINE.[1]

BY HOWARD McKEE ELSEY.

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Introduction.

The work described in this paper was undertaken as a contribution to our knowledge of the properties of the ammono alcohols[2] and ethers (alkyl amines) as electrolytic solvents.

It seemed desirable to gather data on the properties of solutions in that class of ammono alcohols of which dimethylamine is a representative member and also to study the ammono ethers or tertiary amines. Though it was to be expected, from the low dielectric constants of the solvents,[3] that the solutions would have very high resistances the improved type of apparatus available made it possible to measure the conductivity with a high degree of accuracy. In fact, it was found that the conductivity of a given solution could be measured very much more accurately than the solution could be duplicated.

The surprising observations of Shinn[4] that potassium iodide is insoluble in ethylamine led to a study of the solubility of salts in the amines, preliminary to beginning the other work. Potassium iodide is very soluble in liquid ammonia, Franklin[5] having measured the conductivity of a 7.1 molar solution. The salt is also very soluble in methylamine, Fitzgerald[6] having measured the conductivity of a 1.7 molar solution. As accurate data[7] for the conductivity of potassium iodide in liquid ammonia through a wide range of concentrations is already available for comparison, this solute would have been most desirable to work with in the amines.

The solubility tests[8] were disappointing in that they showed that only a very few salts were sufficiently soluble to be of any value for use in making conductivity measurements, though in a surprising number of cases on the introduction of the solvent an "addition" compound was

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[1] Submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy at Stanford University.

[2] For the development of the ammonia system of compounds, together with the nomenclature. See Franklin, *Am. Chem. J.*, 47, 285 (1912).

[3] Schlundt, *J. Phys. Chem.*, 5, 503 (1901).

[4] Shinn, *ibid.*, 11, 537 (1907).

[5] Franklin, *Z. physik. Chem.*, 69, 272 (1909).

[6] Franklin, Gibbs and Fitzgerald, THIS JOURNAL, 29, 1389 (1907).

[7] *Loc. cit.*

[8] Elsey, THIS JOURNAL, 42, 2080 (1920).

formed, and though, on allowing the tube to stand, the bulky precipitate first formed became crystalline and showed evidences of being somewhat soluble only a few even fairly soluble salts were found. Many salts which are quite soluble at room temperature are only very slightly soluble at —33.5°, the temperature of the conductivity measurements. The tendency to form addition compounds seemed to be almost wholly lacking in the tertiary amines.

Of the 80 salts which were tested, the following were the only ones which seemed to be sufficiently soluble and which could be obtained sufficiently pure to warrant further investigation: silver nitrate, silver iodide, lithium chloride, hydrogen chloride (that is, the amine addition compound, as ethylamine hydrochloride) and barium thiocyanate.

Preparation of Substances.

Solutes.—The silver nitrate was prepared by twice recrystallizing a commercial sample of the salt and drying over sulfuric acid.

Silver Iodide.—A solution of silver nitrate was treated with a slight excess of potassium iodide solution and the resulting precipitate washed free from potassium nitrate and potassium iodide, then dried over sulfuric acid.

Lithium Chloride.—A recrystallized sample of lithium chloride was carefully dried over sulfuric acid in a vacuum desiccator.

Barium Thiocyanate.—A pure commercial sample of this salt was dried in a vacuum desiccator over sulfuric acid.

Amine Hydrochlorides.—These salts were all pure commercial preparations and were simply dried in a vacuum desiccator over sulfuric acid.

The slightest trace of moisture in an amine solution of either silver nitrate or silver iodide causes the salt to blacken and deposit metallic silver. Also, the amine hydrochlorides and lithium chloride are so deliquescent that it is almost impossible to weigh out these salts in the open air or even transfer from one container to another without their suffering contamination from the water vapor in the atmosphere. For this reason, the bottling arrangement described later was devised and proved very satisfactory.

Solvents.

The amines were pure commercial samples which had been stored in sealed glass containers over metallic sodium for several years and were thus thoroughly dry. To decrease the risk in working with the limited amount of solvent available, at the beginning of work with a given amine it was distilled over into an evacuated steel cylinder which was fitted with a good fitting steel needle-valve. The nipple of this valve was silver-soldered to a platinum tube and this in turn was sealed to the glass measuring apparatus by means of sealing-in glass.

Apparatus.

Conductivity Measuring Set.—The source of current was a small Vreeland oscillator, built to give frequencies of either 500 or 1000 cycles per second. The measurements were all made using the higher frequency as the tone obtained is much easier to hear in the telephone, which was tuned to this frequency. The resistance box was a 5-dial 100,000-ohm Curtis coil box. In working with dilute solutions, the capacity in the bridge arms was balanced by means of small variable rotary condensers, but with concentrated solutions these proved insufficient and a subdivided mica condenser, having a total capacity of 0.9 microfarad, was built and used. All precautions suggested by Washburn[1] were taken as to the shielding of cables and the individual parts of the apparatus from each other, the shields being carefully grounded.

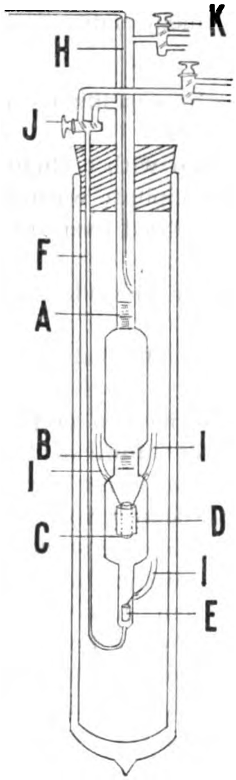

Fig. 1.

Conductivity Cell.—At the boiling point of liquid ammonia (—33.5°),[2] which was the temperature at which the measurements were made, the alkyl amines have too low a vapor pressure to be conveniently adjusted to a given volume by the method used by Franklin and his students[3] in working with liquid ammonia and methylamine.[4] For this reason the conductivity cell used was designed as shown in Fig. 1.

Two scales, A and B, graduated in millimeters, were etched on the cell as shown. The volume of the solution was found by reading the position of the meniscus with respect to these scales by means of a telemicroscope having an eyepiece graduated in tenths of a millimeter. The capillary F, through which the solution was removed, was large, to avoid risk of stoppage, and it was necessary, either always to make a volume reading with the liquid in the capillary at the same point, which was difficult, or else to apply a correction which varied with the position of the meniscus in the capillary. This second method was the one used, the correction applied to

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[1] Washburn and Bell, This Journal, 35, 177 (1913). Also see Catalog 48 of Leeds and Northrup Company.

[2] Franklin, *Ann. Phys.*, 24, 367 (1907). From the recent work of Cragoe, Meyers and Taylor, This Journal, 42, 206 (1920), it appears that the most probable value for the boiling point of ammonia is —33.35°, but the measurements here described were all carried out at a temperature of —33.5°.

[3] *Ibid.*, 27, 191 (1905).

[4] Gibbs, *ibid.*, 29, 1389 (1907); Fitzgerald, *J. Phys. Chem.*, 7, 254 (1903).

a given volume reading never being greater than 0.3 scale divisions, corresponding to a volume of 0.02 cc.

The volume of the cell was found by filling it to various points on the scale with water from a weighing pipet, the temperature being adjusted to 20°. In this way, the volume of the cell was found over the whole range of the 2 scales with an error of less than 0.1%. The volume of liquid required to fill the cell at room temperature to the first graduation of the lower scale was 6.093 cc. and to the top line of this scale 6.336 cc., while the volumes required to fill the cell to the top and bottom graduations of the upper scales were 11.96 cc. and 12.75 cc., respectively.

If the coefficient of expansion of soft glass is 8.5×10^{-6} then the cell would decrease in volume by 0.14% in changing from 20° to —33.5°, the temperature of the measurements. Moreover the decrease in the area of the platinum electrodes on changing to —33.5° would be 0.10% and would tend to increase the cell constant, K, by that amount. Also, the decrease in length of the glass rivets holding the electrodes apart would be 0.04% and would decrease K, leaving the probable increase in K about 0.06%. This uncorrected increase in K will partially balance an uncorrected decrease in the cell volume leaving a probable error in the results of about 0.08%. Since the error is undoubtedly small and cannot easily be experimentally determined, no attempt has been made to apply any of the above corrections to the conductivity results.

The 3 platinum electrodes C, D, and E, which were lightly coated with platinum black, each have an area of about 3 sq. cm. Electrodes C and D are concentric cylinders, held in position with relation to one another by glass rivets. The platinum leading-in wires ended in glass mercury wells I, I, I. Assuming the specific conductivity of a 0.02 N potassium chloride solution to be 0.002501 at 20°,[1] the cell constant K_1, for the pair of electrodes C and D, was 0.05374 Kohlrausch unit. The constant K_2, for the pair of electrodes C and E, was 10.95 units. These values were checked frequently and found to be constant. Electrodes C and E were used for measuring good conducting solutions. Electrodes C and D were used for solutions where the resistance between these electrodes was greater than 100 ohms. With solutions having a lower resistance between them the heating effect of the current was very noticeable, and where the resistance fell below 75 ohms there was a marked discrepancy between molecular conductivities calculated from these electrodes and Electrodes C and E.

Viscometer.—The viscometer used is shown in Fig. 2 and was an adaptation of a 2-capillary instrument suggested by Bingham,[2] the chief modification being in the method used in introducing the liquid to be

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[1] Kohlrausch and Holborn, "Leitvermögen der Elektrolyte," 1898.

[2] *J. Ind. Eng. Chem.*, 6, 233 (1914).

measured. This was forced in through Stopcock F and Capillary H, until the viscometer was filled to Mark A in Arm L, and Mark C in Arm R. Bingham used an automatic pipet method which filled the cell with exactly the same quantity of liquid each time, but this method was not applicable here, because of the difficulty of manipulation. In using the cell, after the proper amount of liquid had been introduced, Arm L was opened to atmospheric pressure by turning Stopcock E, and the liquid was forced to rise in Arm L, by means of hydrogen pressure applied through the 2-way stopcock D, until Bulb K was almost empty. The stopcocks D and E were now reversed, causing Arm R to be open to atmospheric pressure and the liquid in Arm L to be under a known hydrogen pressure. The time required for the meniscus to fall from Mark A to Mark B was then noted. The pressure was measured by means of a water manometer which was connected to the apparatus through a drying tube, both the drying tube and the hydrogen reservoir being protected against sudden changes in temperature by wrapping with hair felt.

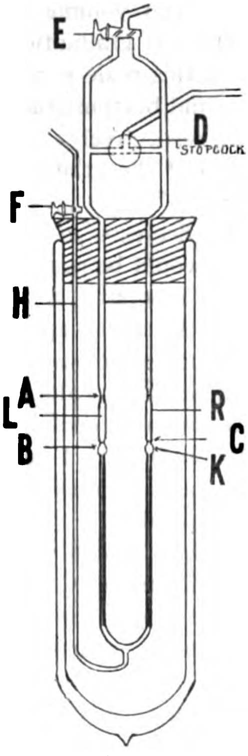

Fig. 2.

If the 2 arms of the instrument had been identical as to size and shape, the time taken to reverse the above process, the pressure remaining constant, should have been the same as the first time of flow from left to right. If the volume of liquid used each time is the same, then it is possible, according to Bingham, to apply a correction factor so that the viscosity may be determined from a single reading in either direction. As it was impossible in our case to control the filling of the cell within better than ±0.05 cc. in a total volume of less than 2 cc. a reading was taken in each direction and the mean of the 2 calculated results taken as the viscosity of the solution.

The equation given by Bingham for the use of the above viscometer is

$$\eta = Ctp - (mn\rho v/8\pi tl) \qquad (1)$$

where η is the viscosity in absolute units, C a constant for the given instrument, p the pressure in grams per sq. cm., m a constant, n the number of capillaries, v the volume of flow, ρ the density, and l the length of the capillaries. Substituting for the constants the values $m = 1.12$, $n = 2$, $v = 1.24$, $\pi = 3.1416$, $l = 20$, the above equation reduces to

$$\eta = Ctp - (0.0054\rho/t) \qquad (2)$$

Assuming the viscosity of water at 25° to be 0.01006[1] and the density to be 0.997 and substituting these values in Equation 2 together with the experimentally determined times of outflow with the corresponding pressures, the value of C was found to be 5.66×10^{-7}.

Density Apparatus.—In order to determine ρ for use in correcting the viscosity equation, a modification of Hare's method[2] of balancing columns was used. A diagram of the apparatus is shown in Fig. 3. The solution whose density was to be determined was forced into the U-tube which was surrounded by an ammonia bath at —33.5° through the stopcock and capillary Tube A. The stopcock B, which had been set to connect the 2 arms of the U-tube, was then turned to open the left arm to atmospheric pressure. By means of a third stopcock, C, the right arm was opened momentarily to a hydrogen reservoir which was fitted with a water manometer. Then the stopcocks were all closed and the heights of the solution column and of the water column measured with a cathetometer and compared. The results obtained were very inaccurate as the small quantity of solution available for each measurement made it necessary to make the U-tube of rather small-bore glass tubing and the difference in level in the 2 arms of the tube was usually less than 10 cm. In addition to this, trouble was had from an improper cathetometer mounting. However, the measurements were sufficiently accurate for the correction of the viscosity, as the value of the expression $0.0054\ \rho/t$ rarely exceeded 0.4% of the total value for the viscosity. Indeed it was found that for any but the most concentrated solutions it was sufficient to calculate the density of a solution from the normality, assuming no volume change in the solvent on the solution of the salt.

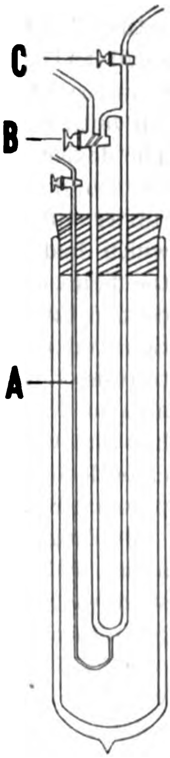

Fig. 3.

Recovery of the Solvents.—As the amines are expensive, their recovery from the solutions was essential and all the discarded solutions were run into a waste jar which was placed in a liquid ammonia bath. The hydrogen gas used for stirring and transferring the solutions was necessarily saturated with the solvent vapor, therefore it also was passed into the waste jar, whence it escaped through a gas wash-bottle containing dil. sulfuric acid. To recover the amine, the hydrogen was removed from the waste jar and the ammonia in the Dewar tube bath replaced

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[1] Bingham and White, *Z. physik. Chem.*, 80, 670 (1912).

[2] The use of this method is a suggestion of Professor H. P. Cady, of the University of Kansas.

by warm water. By adjusting the proper stopcocks, the amine was then distilled directly back into its steel container.

Temperature Control.—All the measurements were made at the boiling point of ammonia, —33.5°, the different units of the apparatus being fitted with rubber stoppers and placed in Dewar tubes containing liquid ammonia. The temperature was maintained constant within ±0.05° by means of a toluene regulator opening or closing an electric circuit which actuated a telegraph sounder to whose arm was fastened the stem of a small steel needle-valve. The opening of this valve allowed a suction pump to increase the rate of boiling of the ammonia, causing the temperature to fall until the regulator functionated and closed the needle-valve again. The device is similar to that used by Franklin and Cady[1] excepting that the sounder arm controls a valve stem rather than pinching down on a rubber tube. The temperature was read on mercury thermometers which had been carefully checked against a certified thermometer. In the figures, for simplicity, the thermometers, toluene bulbs, and bath control tubes are omitted. The hydrogen used in transferring the solution from one part of the apparatus to another was generated by the electrolysis of 10% sulfuric acid. The hydrogen was then passed through an alkaline pyrogallic acid solution, traces of oxygen were burned out in a hot-wire tube, the gas was then dried by means of a chain of calcium chloride and phosphorus pentoxide drying tubes and was then stored under pressure in a glass reservoir.

Bottling Device.—This was devised to transfer the deliquescent amine hydrochlorides and lithium chloride from the large glass-stoppered stock-weighing bottles to the small tube for the sample to be used in a given measurement. This last tube was made from the neck and stopper of a small graduated flask and was of such a size that it would slip conveniently into the mouth of the accessory cell of the apparatus. An old balance case was fitted with a movable platform which carried spring-brass 2-fingered clamps for the two bottles, the movement of the platform being controlled by a rod fitted into the hole which ordinarily carries the balance-beam raising and lowering device. Into the left side of the case, opposite this central platform, were fitted 3 short brass sleeves, and, through these, 3 steel rods. The 2 outer rods each ended in 2 fingers of sheet spring-brass while the center rod ended in a platinum spoon. The door of the case was lined around the edge with felt and the joints between the iron rods and the brass sleeves were made tight with rubber tubing. To use the apparatus, the stock bottle and weighing tube were placed in their proper clamps, the door was tightly closed and a stream of dry air passed through the apparatus for some time. Then by pushing the platform back so that the back weighing tube was opposite the rear

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[1] Franklin and Cady, This Journal, 26, 499 (1904).

rod, its stopper could be removed by manipulation of the rod. The platform was then pulled to the front and the stopper removed from the second weighing bottle. The first tube was now in a position so that a spoonful of salt could be removed from it by the platinum spoon on the second rod and transferred to the smaller tube on pushing the platform again to the rear. The stoppers could now be replaced in the bottles, as, by the proper twisting of the rods the stoppers would "set" in the tubes and allow the clamps to be pulled off. This device proved to be very convenient.

Method of Making Measurements.

A weighed quantity of the solute was introduced into a small accessory cell adjacent to the conductivity cell. This cell was then closed with a ground-glass stopper, which was held in place by a brass cap, and the whole apparatus was swept free of air with a stream of pure dry hydrogen. The Dewar-tube thermostats were then filled with liquid ammonia and solvent was distilled into the accessory cell by opening the proper stopcocks. To hasten distillation a bath of warm water was usually held around the steel storage cylinder in order to overcome the cooling effect due to the rapid evaporation. On leaving the cylinder, the amine vapors were filtered through glass wool to remove solid impurities. After 2 or 3 cc. of solvent had distilled over, the stopcocks were reversed and a stream of hydrogen gas was bubbled through the mixture of salt and solvent in the accessory cell until solution was complete. Hydrogen pressure was then applied to the surface of the solution, the 3-way stirring stopcock was reversed and the solution forced over into the conductivity cell, entering through Tube H, Fig. 1. The accessory cell was washed with successive small portions of fresh solvent in the conductivity cell. Gaseous solvent could be introduced into the accessory cell either through a capillary tube reaching to the bottom, when it would condense at the bottom of the cell, or through a tube at the top, when it would condense all over the inner surface of the cell and thus the walls could be easily washed free of solute. The accessory cell was washed until the washings plus the original solution filled the conductivity cell to some point on the lower scale B, Fig. 1. The solution in the conductivity cell was then stirred until homogeneous by means of hydrogen forced in through the capillary F. The temperature of the bath was checked and the resistance of the solution measured. The volume of the solution was then determined by reading, by means of the telemicroscope, the position of the meniscus with respect to the glass scale B, and noting the height of the liquid in the capillary F. After again reading the resistance, the solution was diluted by the addition of fresh solvent until the cell was filled to a point on the upper glass Scale A. If the boiling point of the solvent was below room temperature, this fresh portion was added by distilling it in through the capillary F. The introduction of this layer of solvent under a denser solution very greatly decreased the time required for stirring the new solution. In this first dilution, advantage was usually taken of the opportunity for rinsing the accessory cell again as in the case of the more concentrated solutions very little washing could be done without filling the conductivity cell above Scale B. Also in the case of solvents boiling above room temperature, the fresh additions of solvent were made from the accessory cell. These solvents were forced into this cell from the glass storage vessel into which they had been distilled in vacuum from the original glass containers where they had been stored over metallic sodium. All connections were made of glass to avoid contamination.

After the solution had been made up to the scale A and thoroughly stirred, the scale and capillary were read and the resistance measured. Hydrogen pressure was turned on and the solution forced out through the capillary F until the meniscus had fallen to Scale B, when the stopcocks were closed, the pressure released, and the scale and capillary meniscus read. This remaining portion of the solution was then diluted with fresh solvent and measured as before.

The first portion of the "discarded" solution was, by proper adjustment of the stopcocks, led into the viscometer and density meter and used to rinse these cells after which it was run into the waste jar. The viscometer and density tube were filled with the remainder of the "discarded" solution. The viscosity and density of this solution were then determined as previously described, after which it also was forced into the waste jar.

The measurements were carried from the most concentrated solutions, which could be handled without risking the stoppage of the capillary tubes, to dilutions where the error in setting the bridge was greater than one part in 500. Due to the high resistance of even the most concentrated solutions, the measurements could not be carried out to very low concentrations. In most cases, the upper limit to the concentration of the solution measured was the limit of solubility of the salt.

Experimental Data.

Conductance Data.—In the following tables, c is the concentration in gram moles per liter. Λ is the molecular conductance, which is equal to 1000 χ/c, where χ is the specific conductance in reciprocal ohms, η is the absolute viscosity in c. g. s. units, and ρ is the density.

TABLE I.—SILVER NITRATE IN ETHYLAMINE.

c.	Λ.	η.	ρ.
	I.		
0.4917	5.310	......	.....
0.2508	3.820	......	.....
0.1220	2.283	......	.....

TABLE I (*continued*).

c.	Λ.	η.	ρ.
II.			
0.5184	5.204	......	.....
0.2731	3.982	......	.....
0.1358	2.517	......	.....
0.06791	1.522	......	.....
0.03311	1.102	......	.....
0.01673	0.8937	......	.....
0.008196	0.9528	......	.....
0.004140	1.090	......	.....
III.			
0.7411	5.762	0.01374	0.888
IV.			
0.02559	1.107	......	.....
0.01260	0.9945	......	.....
0.006240	1.052	......	.....
0.003117	1.254	......	.....
0.001485	1.651	......	.....
0.0007315	2.208	......	.....
0.0003533	2.864	......	.....
0.0001771	3.960	......	.....
V.			
0.1797	3.263	......	.....
0.08535	1.951	......	.....
0.04400	1.280	......	.....
0.02201	0.9874	......	.....
0.01086	0.9284	......	.....
0.005428	1.007	......	.....
VI.			
1.004	5.633	......	.....
0.5420	5.587	0.009700	.....
0.2785	4.231	0.008069	.....
0.1402	2.715	0.007101	.....
0.07045	1.690	0.006271	.....
VII.			
1.999	3.180	0.07098	.....
VIII.			
0.06665	1.700	......	.....
0.03436	1.191	0.005948	.....
0.01719	0.9944	0.005849	.....
0.008500	0.9814	0.005764	.....
0.004277	1.008	0.005757	.....
0.002170	1.336	0.005757	.....
IX.			
0.0009003	2.196	......	.....
0.0004566	3.003	0.005823	.....
0.0002293	4.132	0.005752	.....
0.0001016	5.618	0.005737	.....
0.00006145	7.621	0.005754	.....

TABLE I (*continued*).

Silver Iodide in Ethylamine.

c.	Λ.	η.	p.
	I.		
0.2253	0.00739	......	.....
0.1012	0.01002	0.006046	.....
0.05629	0.01349	0.005951	.....
0.02888	0.01820	0.005894	.....
0.01460	0.02562	0.005856	.....
	II.		
0.6641	0.004841	......	.....
0.3494	0.006337	0.006922	.....
0.1728	0.008318	0.006373	.....
0.08780	0.01093	0.005977	.....
	III.		
1.023	0.003331	......	.....
0.6339	0.004707	0.007994	.....
0.3246	0.006216	......	.....
	IV.		
2.156	0.001913	......	.....
1.116	0.003600	0.009965	.....
1.068	0.003721	......	.....
0.5514	0.005085	......	.....

Barium Thiocyanate in Ethylamine.

c.	Λ.	η.	p.
	I.		
0.09393	0.4023	......	.....
0.08937	0.3882–0.3899	0.006747	.....
0.04576	0.2518	0.006244	.....
0.02364	0.2035	0.006067	.....
0.01234	0.2017	......	.....
0.01234	0.2063	......	.....
0.006275	0.2086	......	.....
	II.		
0.4099	1.251	......	.....
0.2120	0.8549	......	.....
0.1121	0.4747	......	.....
0.1121	0.4802	......	.....
	III.		
0.5550	1.284	......	.....
0.2809	0.9333	0.009230	.....
0.1393	0.5180	......	.....
0.1392	0.5557	0.007192	.....
0.07076	0.3159	......	.....
0.07088	0.3298	0.006475	.....
0.03618	0.2386	0.006154	.....
0.01893	0.2052	0.006067	.....

TABLE I (*continued*).
Ethylamine Hydrochloride in Ethylamine.

c.	Λ.	η.	ρ.
I.			
2.872	2.557	......	.....
1.489	3.755	0.01863	0.811
0.7518	2.854	0.009860	0.771
0.3817	1.461	0.007614	0.767
0.1898	0.6276	0.006634	.....
0.09458	0.3308	0.006165	.....
II.			
0.2105	0.6787	......	.....
0.1071	0.3560	......	.....
0.05406	0.2383	......	.....
0.02711	0.1980	......	.....
0.01342	0.1980	......	.....
0.006492	0.2255	......	.....
0.003181	0.2815	......	.....
0.001575	0.3686	......	.....

The conductivities of solutions of silver nitrate and of ethylamine ydrochloride in ethylamine have been measured by Fitzgerald[1] at —33.5°, ut he was unable to carry the measurements past a minimum of molecular conductivity. However, in the present experiments in both of these olutions, it has been possible to pass a minimum of molecular conductivity. In Fig. 4 one may see the general form of the conductivity curves n ethylamine, the molecular conductivities being plotted against the ogarithms of the concentrations. The curve for silver nitrate shows the

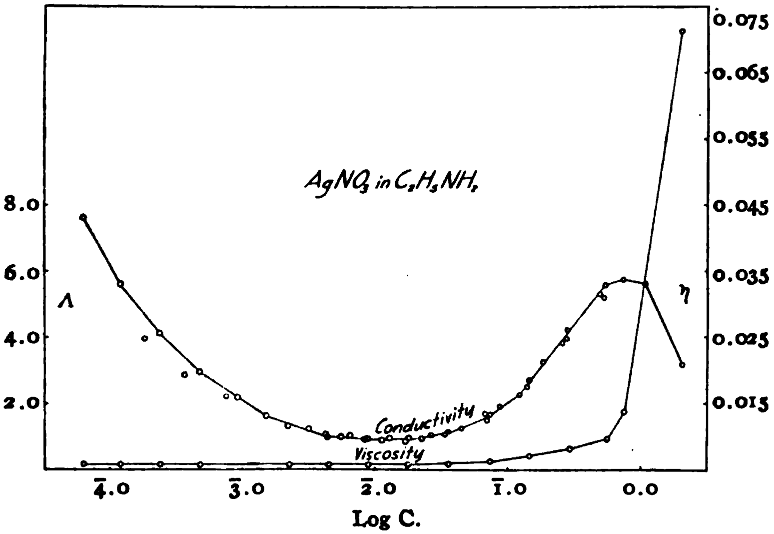

Fig. 4.

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[1] *Loc. cit.*

form first noted by Gibbs[1] in methylamine solutions. With decreasing concentration the molecular conductivity rises to a maximum, then falls to a minimum, and rises to a final maximum in very dilute solutions.

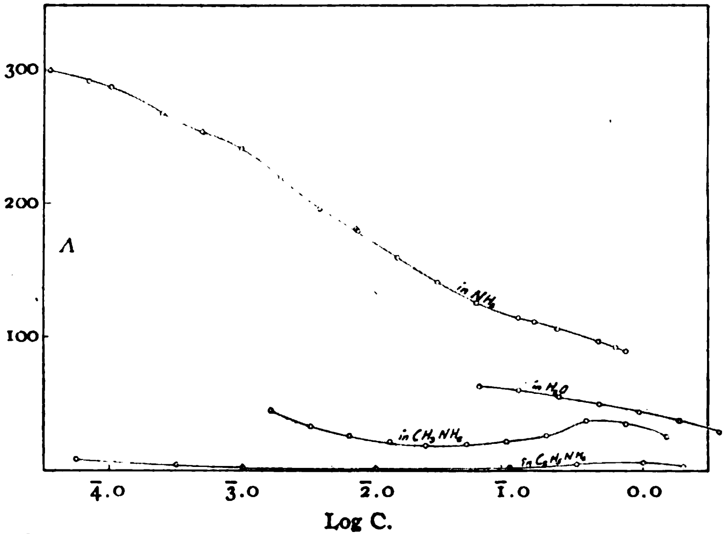

Fig. 5.—Conductivity of silver nitrate.

Only the final rise to a maximum of molecular conductivity at infinite dilution does not appear on account of our inability to work with the higher resistances met with in dilute solutions. In Fig. 5 are plotted the

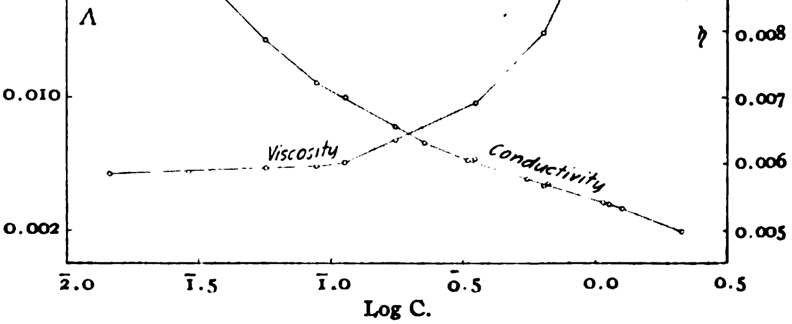

Fig. 6.

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[1] *Loc. cit.*

conductivity curves for silver nitrate in water, ammonia, methylamine and ethylamine. Data for the conductivity of silver nitrate in concentrated water solutions is plotted from data given by Sloan.[1]

Silver iodide (Fig. 6), which is extremely soluble in both ethyl and dimethylamine, melting down in the vapors of ethylamine at room temperature, apparently is dissociated to a very much less extent even than the other salts, as one is forced to use units only $^1/_{1000}$ as great in order to plot the curve for silver iodide on the same sheet as silver nitrate. It will also be noticed that for this salt there is no indication of a maximum in concentrated solutions, the equivalent conductivity rising regularly from the most concentrated to the most dilute solutions. In solutions of silver nitrate and ethylamine hydrochloride (Fig. 7) in ethylamine, the maximum of equivalent conductivity for each salt is in a solution of about normal strength while in the case of silver iodide solutions the equivalent conductivity was still decreasing at much higher concentrations. It is interesting to note that the 2 former solutions begin to increase rapidly in viscosity at about the same point while the rapid rise for silver iodide solutions does not come until greater concentrations are reached, and the marked increase in viscosity apparently does not alter the rate of decrease of the equivalent conductivity.

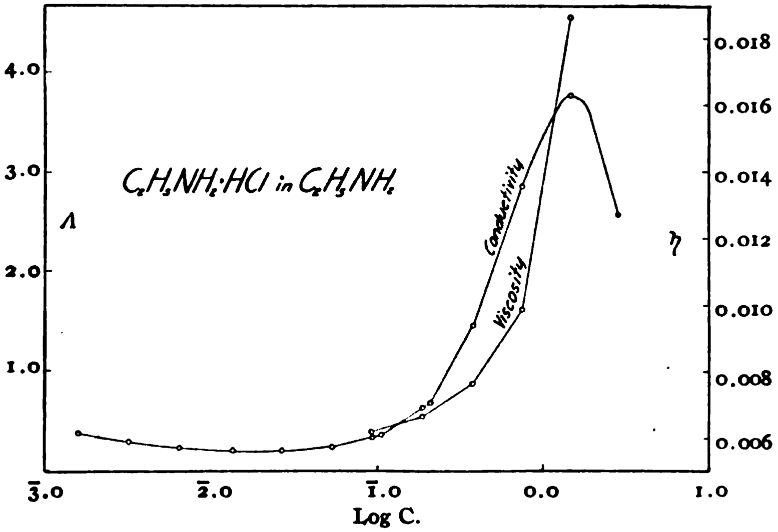

Fig. 7.

The above action in the case of "normal" electrolytes is further evidence, tending to show the close connection between the maximum in molecular conductivity which occurs in concentrated solutions and the viscosity. No attempt has been made to correct the conductivities of

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[1] Sloan, This Journal, 32, 946 (1910).

the concentrated solutions for the viscosity according to the method of Sakhanov,[1] for, while the relation between viscosity and conductivity is recognized, we believe it futile, arbitrarily to apply a correction which considers only one of the several factors which determine the course of the conductivity curve in concentrated solutions.

An attempt was made to measure the conductivity of a solution of cadmium iodide in ethylamine, but it was found that the bulky aminate formed on contact of solute and solvent is only slightly soluble in ethylamine at liquid ammonia temperatures. This is interesting as Kahlenberg and Ruhoff[2] were able to prepare and measure the conductivity of a 1.3 *N* solution of this salt in amylamine. Their measurements, it is true, were made at 0°, but the cadmium iodide showed no signs of possessing any such solubility in ethylamine at room temperatures as they found it to possess in amylamine at 0°.

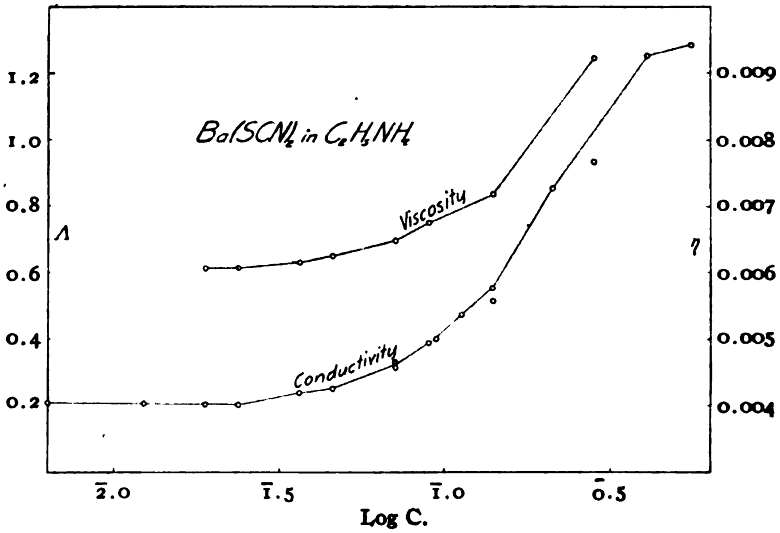

Fig. 8.

In measuring the conductivity of solutions of barium thiocyanate in ethylamine, it was noticed that the resistance seemed to vary with the time, and in order to check this observation a dilute solution of the salt was prepared and the molecular conductivities observed with the time of measurement are given.

If the conductivity is plotted against the time the form of the curve seems to indicate that perhaps we are dealing with an example of aminolysis (solvolysis) which proceeds slowly enough to be followed with ease by this conductivity method.

[1] Sakhanov, *J. Phys. Chem.*, 21, 169 (1917).

[2] Kahlenberg and Ruhoff, *ibid.*, 7, 254 (1903).

TABLE II.

Aminolysis of Barium Thiocyanate in Ethylamine.

($c = 0.0651$).

Time (hours).	Λ.
0.767	0.3754
1.067	0.3754
1.158	0.3772
1.384	0.3778
1.650	0.3783
1.966	0.3789
2.684	0.3799
3.516	0.3812
4.384	0.3822
5.267	0.3841
6.200	0.3853
8.117	0.3878
10.267	0.3912
11.500	0.3922
12.017	0.3929
23.70	0.4036
83.45	0.4057
95.45	0.4061

In water solutions such examples are rare as the rate of reaction of electrolytes brings almost instant equilibrium between solute and solvent, but in a few instances[1] it has been possible to follow the rate of hydrolysis by the conductivity method as above.

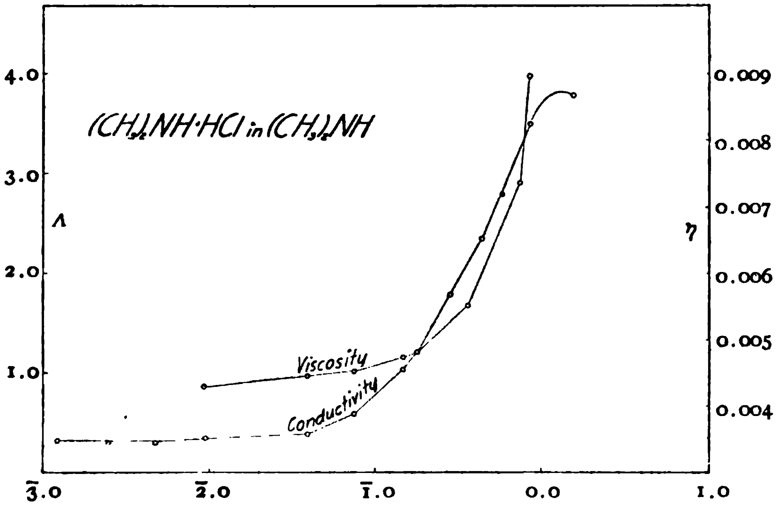

Fig. 9.

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[1] Furman, "Hydrolysis of Stannic Fluoride," THIS JOURNAL, 40, 906 (1918). For other examples see Foster, *Phys. Rev.*, 9, 41 (1899), and Kohlrausch, *Z. physik. Chem.*, 33, 257 (1900).

TABLE III.

Dimethylamine Hydrochloride in Dimethylamine.

c.	Λ.	η.	ρ.
I.			
0.009399	0.3417	0.004290	.....
0.004713	0.3061	......	.....
0.002437	0.3003	......	.....
0.001201	0.3206	......	.....
II.			
0.5697	2.775	......	.....
0.2843	1.786	0.005284	.....
0.1459	1.030	0.004720	.....
0.07458	0.5909	0.004523	.....
0.03855	0.3851	0.004451	.....
III.			
1.557	3.774	......	.....
0.8535	3.487	0.008947	.....
0.4346	2.342	......	.....
IV.			
0.7847	.....	0.007360	0.740
0.3585	.....	0.005496	0.734
0.1788	.....	0.004802	0.728
Silver Iodide in Dimethylamine.			
I.			
1.259	0.002431	......	.....
0.6375	0.0004819	0.005558	.....
0.3195	0.0007660	0.005023	.....
0.1592	0.001110	0.004612	.....
II.			
2.695	0.000059	......	.....
1.366	0.0002217	0.007992	.....
0.7011	0.0004584	......	.....
III.			
2.03	......	......	1.17
IV.			
0.1285	0.006503	......	.....
0.06389	0.008974	0.004415	.....
0.03197	0.01109	0.004394	.....
0.01629	0.01438	0.004368	.....
0.008316	0.01919	0.004360	.....

In Table III are shown the results obtained in dimethylamine solutions. The curve for dimethylamine hydrochloride shows the typical form obtained in ethylamine curves. A maximum in concentrated solutions is indicated and apparently the minimum had been passed in a 0.005 *N* solution. Silver iodide, although quite soluble, gave a very poorly conducting solution, the slight molecular conductivity falling off rapidly with increasing concentration, in every way behaving as the solution in ethylamine. Franklin[1] has previously noted the fact that silver

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[1] *Loc. cit.*

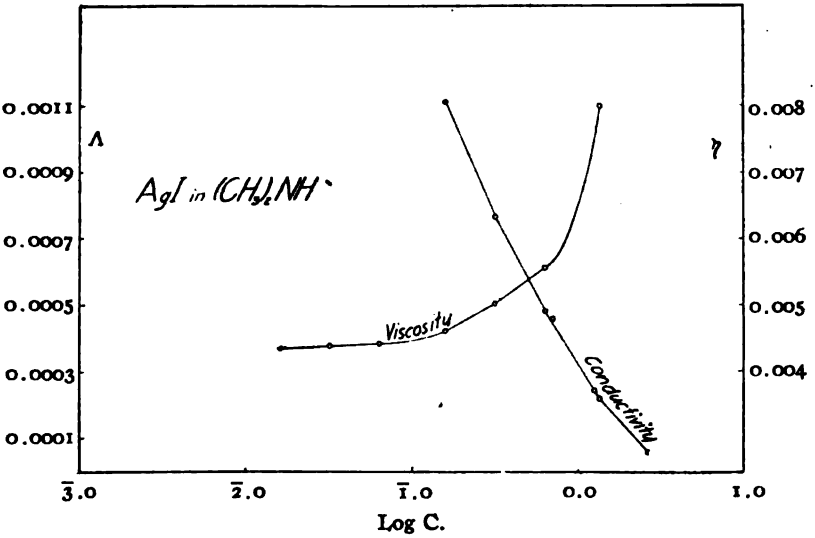

Fig. 10.

iodide has an abnormally low conductivity in ammonia solutions. This abnormality is apparently merely accentuated in the amine solutions.

TABLE IV.

Lithium Chloride in Diethylamine.

c.	Λ.		
0.1998	0.0004988	......	.....
0.1021	0.0006138	......	.....
0.05199	0.0009478	......	.....
0.02544	0.001205	......	.....

TABLE V.

Silver Nitrate in Propylamine.

c.	Λ.	η.	ρ.
0.4588	3.270 (this value is at 20° C.).		.....
0.4588	1.660	......	.....
0.2802	1.230	0.01500	0.841
0.1387	0.6031	0.01218	.....
0.06789	0.2479	0.01112	.....
0.03376	0.1224	0.01066	.....
0.01657	0.07865	......	.....
0.008183	0.06476	0.01033	.....
0.003994	0.06434	0.01028	.....

Lithium chloride was the only one of the several salts used which was at all soluble in diethylamine at —33.5° and it was only moderately soluble. The solutions in dimethylamine were conductors of the same order as ethylamine solutions, but diethylamine proved to be an extremely poor electrolytic solvent, the conductivity of the lithium chloride solution in it being of the same order as the conductivity of the silver iodide solution in dimethylamine, a 0.1 *N* solution having a molecular conductivity of only 0.0006 Kohlrausch unit.

Only one series of measurements was made in propylamine. Silver nitrate is only fairly soluble, a 0.26 *N* solution being approximately saturated with the salt at —33.5°, the limited solubility thus preventing the appearance of a maximum of conductivity in concentrated solutions.

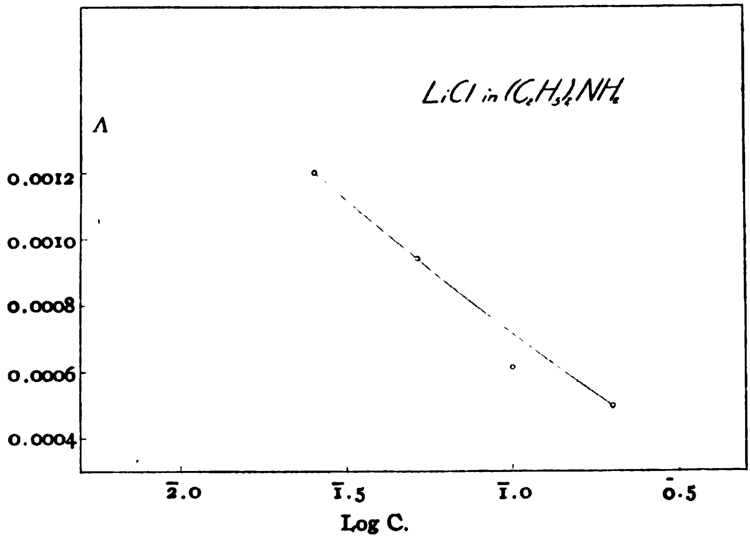

Fig. 11.

The molecular conductivity was about the same as for the corresponding solution in ethylamine, the lower values being doubtless due more to the greater viscosities encountered than to a difference in the dielectric constants.

None of the salts used in the preceding measurements would form a conducting solution in trimethylamine or triethylamine or diethylamine other than as noted. In Table VI, the specific conductivities of solutions saturated at —33.5° with these salts in the above solvents are given. In the table, *a* is one arm of the bridge where the total length is 1000 units, χ is the specific conductivity, *f* is the capacity in microfarads which must be introduced in parallel with the resistance box to get a good minimum in the telephone, and *m* is the fraction of the bridge over which a perfect minimum is secured.

TABLE VI.

Solute.	Solvent.	*a.*	χ.	*f.*	*m.* %.
$(CH_3)_3N.HCl$	$(CH_3)_3N$	999.4	3.2×10^{-10}	0.1288	0.02
$(C_2H_5)_2NH.HCl$	$(C_2H_5)_2NH$	988.1	6.5×10^{-9}	0.001	0.02
AgI	$(C_2H_5)_2NH$	995.2	2.6×10^{-9}	0.019	0.02
LiCl	$(C_2H_5)_3N$	997.4	1.4×10^{-9}	0.027	0.05

The above solutions were saturated at room temperature by stirring the solvent and solid salt together by the use of hydrogen. The solutions were then transferred to the conductivity cell at —33.5°. In no instance was solid salt observed to separate out on cooling to the lower temperature and apparently but very little, if any, salt had been dissolved in any case.

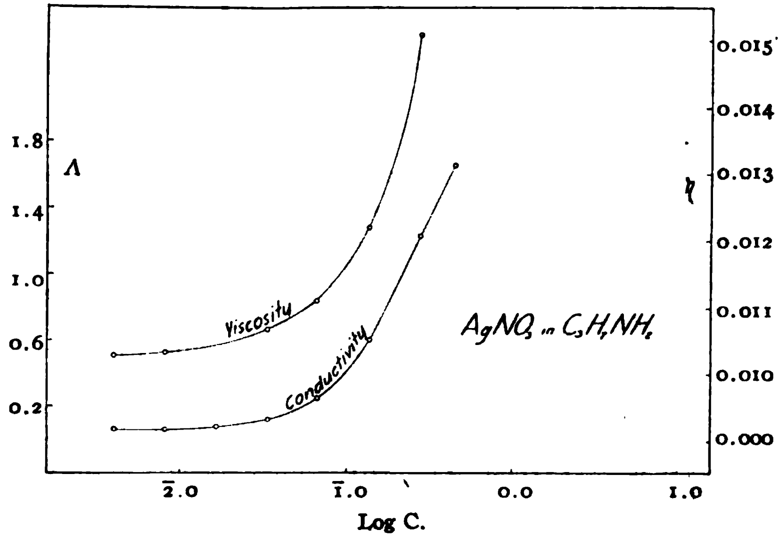

Fig. 12.

In Table VII are given the specific conductivities of the different solvents used, and it will be seen that the so-called solutions listed in Table VI are but little, if any, better conductors than the pure solvents.

TABLE VII.

Specific Conductivities of Amines.

	a.	*x.*	*f.*	*m.*
$(CH_3)_3N$	999.6	2.2×10^{-10}	0.1378	0.02
$C_2H_5NH_2$	923.0	4.6×10^{-8}	0.001	0.05
$(C_2H_5)_2NH$	995.4	2.5×10^{-9}	0.019	0.05
$(C_2H_5)_2NH$	996.0	2.2×10^{-9}	0.024	0.05
$(C_2H_5)_2NH$	995.5	2.4×10^{-9}	0.024	0.05
$(C_2H_5)_2NH$	995.9	2.2×10^{-9}	0.025	0.05

Since the dissociation of the solute is far from complete even in the most dilute solution measured (0.00006 *N*), some more delicate type of detector than the simple telephone is essential to enable any further study of these high resistance solutions to be made. For this use, one of the thermionic detectors or oscillation valves used in wireless work (such as the "audion" or "pliotron"), should be readily adaptable. The audion valve circuit could replace the telephone across the bridge arms and the resulting unilateral oscillating current detected either by a telephone or by a galvanometer.[1]

In Table VIII are given the results of the measurements of the viscosities of the various solvents used. The viscosities of a number of samples

TABLE VIII.

Viscosity of Ammonia at —33.5°.

s.	*d.*	*p.*	*t.*	η'.	η.
1......	L to R	78.69	58.4	0.002542	
	R to L	78.44	58.9	0.002556	0.002549
	L to R	78.24	58.9	0.002549	
	R to L	77.74	59.0	0.002531	0.002540
	L to R	67.12	67.7	0.002520	
	R to L	66.77	68.9	0.002553	0.002537
	L to R	66.47	69.0	0.002545	
	R to L	66.22	69.5	0.002554	0.002550
2......	L to R	78.46	58.2	0.002526	
	R to L	78.26	59.2	0.002564	0.002545
	L to R	78.16	58.3	0.002520	
	R to L	78.04	59.2	0.002556	0.002538
3......	R to L	78.02	58.9	0.002542	
	L to R	77.87	59.3	0.002556	0.002549
	R to L	77.80	59.1	0.002545	
	L to R	77.65	59.1	0.002539	0.002542
4......	L to R	51.50	87.8	0.002518	
	L to R	51.50	88.8	0.002548	0.002553
	R to L	51.45	87.9	0.002519	
	L to R	51.42	89.0	0.002550	0.002535
	R to L	40.31	112.2	0.002528	
	L to R	40.32	113.5	0.002558	0.002543
	R to L	40.33	112.2	0.002529	
	L to R	40.40	113.7	0.002568	0.002549
				Mean..........	0.002543

Viscosity of Ethylamine at —33.5°.

s.	*d.*	*p.*	*t.*	η'.	η.
1......	L to R	46.13	221.2	0.005757	
	R to L	46.07	221.7	0.005762	0.005760
2......	L to R	46.38	219.7	0.005747	
	R to L	46.15	220.2	0.005733	0.005740
3......	L to R	47.36	215.3	0.005751	
	R to L	47.21	216.0	0.005753	0.005752
4......	L to R	47.99	212.2	0.005746	
	R to L	47.71	212.8	0.005727	0.005737
5......	L to R	48.36	210.9	0.005754	
	R to L	48.26	211.3	0.005753	0.005754
				Mean.........	0.005749

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[1] Hall and Adams, THIS JOURNAL, 41, 1515 (1919).

TABLE VIII (*continued*).

s.	*d.*	*p.*	*t.*	*η'.*	*η.*
Viscosity of Dimethylamine at 33.5°.					
1......	L to R	40.5	191.1	0.004360	
	R to L	40.35	192.1	0.004365	0.004363
2......	L to R	40.56	191.9	0.004387	
	R to L	40.51	191.5	0.004370	0.004379
3......	L to R	43.64	177.5	0.004361	
	R to L	43.50	177.8	0.004358	0.004360
4......	L to R	43.48	178.8	0.004367	
	R to L	43.30	179.2	0.004368	0.004368
				Mean.........	0.004368
Viscosity of Trimethylamine at —33.5°.					
1......	L to R	40.42	140.3	0.003183	
	R to L	40.37	140.5	0.003184	0.003184
	L to R	35.37	160.3	0.003185	
	R to L	35.18	161.2	0.003187	0.003186
2......	L to R	37.04	155.6	0.003237	
	R to L	36.90	155.5	0.003222	0.003230
	L to R	38.92	148.5	0.003245	
	R to L	38.72	147.9	0.003215	0.003230
				Mean.........	0.003208
Viscosity of Diethylamine at —33.5°.					
1......	L to R	73.35	200.4	0.008301	
	R to L	73.25	201.2	0.008322	0.008312
	L to R	73.15	201.0	0.008302	
	R to L	72.98	201.1	0.008287	0.008295
2......	L to R	73.43	196.8	0.008160	
	R to L	73.25	198.4	0.008168	0.008164
	L to R	73.05	198.3	0.008179	
	R to L	72.91	199.7	0.008223	0.008201
3......	L to R	73.22	198.9	0.008166	
	R to L	73.08	200.0	0.008253	0.008209
				Mean.........	0.008236
Viscosity of Triethylamine at —33.5°.					
1......	L to R	52.26	262.9	0.007760	
	R to L	53.26	256.1	0.007703	0.007732
	L to R	53.21	257.4	0.007735	
	R to L	53.16	257.1	0.007719	0.007727
2......	L to R	53.51	255.6	0.007724	
	R to L	53.36	256.0	0.007713	0.007718
				Mean.........	0.007726

of each solvent were measured all at —33.5°. In the table *s* is the number of the sample; *d*, the direction of flow between the capillaries; *p*, the pressure in grams per sq. cm.; *t*, the time; and η', the calculated viscosity. The mean of the L to R and R to L values or η is the true viscosity.

The viscosity of liquid ammonia at —33.5° has also been measured by Fitzgerald,[1] who found the average value $\nu = 0.00266$, using a viscometer of the Ostwald type. The average value found in the present work was 0.00254. The only possible claims for consideration of this latter value over that of Fitzgerald are that it is the mean of a greater number of observations and that the type of viscometer used gave a much longer time of flow, very greatly reducing the possibility of eddy currents.

TABLE IX.
Density of Amines at —33.5°.

Amine.	Density.
Dimethylamine	0.727
Trimethylamine	0.702
Ethylamine	0.742
Diethylamine	0.713
Triethylamine	0.778

In Table IX are given the mean values of measurements of the densities of the amines. These results were obtained by use of the densitimeter in the manner described for solutions. The experimental values are not given as the results are very inaccurate indeed.

Summary.

Viscosity and conductivity measurements have been made on a number of solutions in ethyl, dimethyl, trimethyl, diethyl, triethyl and propyl amines.

Dimethylamine proved to be a poorer solvent than ethylamine, though the salts which did dissolve formed solutions having about the same molecular conductivity.

Diethylamine is a still poorer solvent and a distinctly poorer ionizing agent, a lithium chloride solution in it being no better conductor than a solution of silver iodide in ethylamine.

The tertiary amines are distinctly not electrolytic solvents, no evidence of salt solution being found in any case and solvent in equilibrium with solid solute did not appreciably gain in conductivity.

In conclusion, the writer wishes to thank Dr. E. C. Franklin for his kindly guidance and to express his appreciation of him, both as a friend and a teacher.

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LAWRENCE, KANSAS.

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[1] *Loc. cit.*

[Contribution from the Chemistry Department of Columbia University. No. 345.]

THE MOLECULAR STATE OF WATER VAPOR.[1]

By James Kendall.

Received April 27, 1920.

Up to a few years ago it was universally considered that water vapor at ordinary temperatures was, so far as could be deduced from vapor density determinations, entirely monomolecular H_2O and obeyed the gas laws within the limits of experimental error. Regnault's measurements gave 18.0 for the molecular weight, Gay-Lussac's 18.01 and Leduc's 18.1, while the formula H_2O requires the value 18.016.[2] In the derivation of equations for osmotic pressure, vapor pressure lowerings etc. in dilute aqueous solutions the assumption was accordingly made, without any question, that water vapor could be treated as a perfect gas. Some measurements by Winkelmann[3] appeared to indicate a tendency towards association at temperatures slightly above normal, but even as late as 1907, in a discussion at the Faraday Society,[4] the different results quoted for saturated vapor at 15° varied more among themselves than from the theoretical value, and the conclusion that the vapor behaved as a perfect gas was undisputed.

In 1908, however, some calculations were published by Bose,[5] based upon new vapor density determinations by Kornatz,[6] claiming that association in the saturated vapor was considerable even at ordinary temperatures. The equilibrium $(H_2O)_2 \rightleftarrows 2H_2O$ was assumed to exist in the vapor phase and an equation for the variation in the equilibrium constant with temperature was derived. This equation indicated for the saturated vapor at 0°, 6.6% association; at 50°, 8.2% association; at 100°, 8.9% association.

In 1915 Oddo,[7] evidently ignorant of the work of Bose, calculated from the tables of Landolt-Börnstein[8] (Regnault's data, reproduced from Zeuner's "Technische Thermodynamik") the molecular weight of saturated water vapor between —20° and 200°, obtaining values steadily increasing from 17.03 at —20° to 19.92 at 200°. Only at 32° did the experimental value agree with that required by monomolecular H_2O. The conclusion was drawn that at temperatures below 32° a *dissociation*

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[1] Presented at the Buffalo Meeting of the American Chemical Society, April 10, 1919.

[2] Abegg, "Handbuch der anorganischen Chemie," [1] 2, 67, (1908).

[3] Winkelmann, *Wied. Ann.*, 9, 208 (1880).

[4] Wilsmore, *Trans. Faraday Soc.*, 3, 85 (1907).

[5] Bose, *Z. Elektrochem.*, 14, 269 (1908).

[6] Kornatz, *Inaug-Diss.*, Königsberg 1908.

[7] Oddo, *Gazz. chim. ital.* [1] 45, 319 (1915)

[8] "Tabellen," 1912, p. 369.

equilibrium, $H_2O \rightleftarrows H^+ + OH^-$, existed, and above 32° an *association* equilibrium: $(H_2O)_2 \rightleftarrows 2H_2O$. At —20° the degree of "ionization" was calculated to be 5.79%; at 200° the "association" reached 19.11%. Great emphasis was laid upon the former phenomenon—*the spontaneous ionization of water vapor*—as opening up a new field in science, and in a second article[1] remarkable deductions were drawn therefrom upon such diverse topics as atmospheric electricity, the influence of temperature on vegetation, the respiratory processes of plants and animals, the electrolytic reactions in a monocellular organism, and the first experimental mechanism for the origin of life.

An adequate discussion of so many important questions cannot be entered into here, but since the molecular weight of water vapor is a matter of fundamental interest in a few minor fields (such as the modern theory of solutions and steam engineering practice) it has been thought profitable to subject the mutually contradictory conclusions of Bose and Oddo to a critical examination, particularly since these conclusions are now quoted without reserve in standard monographs.[2] The results below 32° may first be considered.

According to Oddo, saturated water vapor below 32° is partly dissociated into hydrogen and hydroxyl ions. At 0° the calculated degree of ionization is 2.6%, the vapor pressure being 4.6 mm. From these figures we can determine the concentration of hydrogen and hydroxyl ions in saturated vapor at 0°. The value obtained is 7×10^{-6} g. ions per liter, in other words, just 200 times as great as the corresponding concentration in pure liquid water[3] at 0°. Since the mobility of the ions in the vapor phase would certainly be enormously greater than in the liquid, owing to the diminished viscosity of the medium, it follows that the conductivity of saturated water vapor (or air saturated with water vapor) at 0° should be comparable with that of a fairly concentrated salt solution. Now this is admittedly not the case, hence Oddo's whole argument must be quite invalid.

The explanation is not far to seek. Regnault's data at temperatures below the normal (although smoothed off on a curve to render them consistent) are far too inaccurate to be employed as a basis for determinations of molecular weights to the second place of decimals. In fact, the density of the saturated vapor at pressures so low as 4.6 mm. becomes so small that it is impossible to measure it with anything approaching the above order of accuracy. Even the exceedingly careful determinations of Young[4] on the specific volumes of the saturated vapor of 30 organic liquids

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[1] Oddo, *Gazz. chim. ital.*, [1] **45**, 395 (1915).

[2] See Turner, "Molecular Association," **1915**, p. 89.

[3] Kohlrausch and Heydweiller, *Z. physik. Chem.*, **14**, 317 (1894).

[4] Young, *Proc. Roy. Soc. Dublin*, **12**, 374 (1910).

are conceded to be uncertain at the lower temperatures investigated, for this same reason. Consequently, until more definite proof of this spontaneous ionization of water vapor is brought forward,[1] we cannot consider the molecular weight of water vapor to be appreciably diverted from the normal value as a consequence of such ionization.

It remains to examine the abnormally high vapor densities for temperatures above normal, upon which both Bose and Oddo postulate the equilibrium $(H_2O)_2 \rightleftarrows 2H_2O$. Bose's calculations are dependent entirely upon a series of 19 determinations at 13 different temperatures (T ranging from 50° to 182°, p ranging from 52.6 to 790 mm.) by Kornatz. It is true that a few isolated measurements of previous investigators are quoted, which are in fair agreement with these results, but of the many determinations which do not agree no mention is made.

While Kornatz's measurements certainly indicate a greater vapor density than the theoretical for monomolecular water throughout the whole series, yet examination shows that *at any one temperature* the observed variation in density with pressure is *systematically* different from that calculated by the use of Bose's equation for the equilibrium: $(H_2O)_2 \rightleftarrows 2H_2O$. The following table will illustrate this clearly. Densities are given relative to air; the theoretical ratio for monomolecular water is 0.6216.

T (abs.).	p (mm. Hg).	Density (obs.).	Variation with p.	Density (calc.).	Variation with p.
348	86.8	0.6324	0.0095	0.6307	0.0139
348	231.5	0.6419		0.6446	
353	71.0	0.6308	0.0063	0.6276	0.0144
353	249.0	0.6371		0.6420	
358	86.76	0.6307	0.0052	0.6278	0.0116
358	260.3	0.6359		0.6394	
363	52.6	0.6286	0.0061	0.6247	0.0119
363	263.0	0.6347		0.6366	
368	63.4	0.6282	0.0051	0.6247	0.0091
368	253.6	0.6333		0.6338	

It will be evident from the above table that the observed variation is approximately only 50% of the calculated. Bose remarks, in a passing comment on this fact, that it is possible that the experimental results are affected by systematic errors, which may be partially explained by assuming that the equilibrium $(H_2O)_2 \rightleftarrows 2H_2O$ in the vapor phase is only slowly established. It is extremely improbable that this assumption is correct, since even in liquid water no indication of anything but instantaneous equilibria between the different molecular species present has ever been obtained. If Kornatz's data *are* trustworthy, Bose's in-

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[1] The dielectric constant of water vapor is so near to unity as to appear to preclude more than the merest trace of ionization (Büdeker, *Z. physik. Chem.*, 36, 305 (1901).

terpretation of them is not justified; if they are *not* trustworthy, no such interpretation should have been attempted.

We are consequently left to face the fact that, while vapor density measurements for temperatures above the ordinary give abnormally high results, these high results cannot be adequately explained by assuming association in the vapor phase. Indeed, other evidence renders it certain that such association is negligible even at 100°. Let us compare the abnormality in the density of saturated water vapor at this temperature with the abnormalities shown by the saturated vapors of other liquids at their boiling points. The data in the following table are taken from Washburn.[1]

Liquid.	Boiling point. ° C.	Vapor density $\left(\frac{\text{observed}}{\text{calculated}}\right)$.	Vapor density $\left(\frac{\text{observed}}{\text{corrected}}\right)$.
Benzene..........	80.1	1.024	0.990
Pentane..........	36.3	1.046	1.002
Heptane..........	98.4	1.055	1.007
Chlorobenzene.....	132.0	1.055	1.019
Nitrogen..........	—195.7	1.05	1.00
Helium...........	—268.5	1.09	.....
Water............	100.0	1.028[a]	1.018[b]

[a] Value taken from Regnault's determinations; see Oddo, *Gazz. chim. ital.*, [1] 45, 328 (1915).

[b] Critical data employed were taken from Holborn and Baumann, *Ann. Physik.*, [4] 31, 945 (1910).

The ratios obtained in the third column show that *all* substances (even such generally accepted non-associated liquids as the saturated hydrocarbons and the inert gases) give saturated vapors of abnormally high density even at pressures as low as one atmosphere. As has been pointed out by Guye,[2] the assumption of the merest trace of association in the vapor phase involves extreme association in the more concentrated liquid phase, consequently if the above abnormalities are due to molecular complexity in the vapor state than even the so-called "normal" liquids are all exceedingly complex. While it would be going too far to state that we have *no* indications of association in the liquid state for the substances listed above,[3] yet their general physical properties show conclusively that any deviations from ideality are very slight.

To what, then, are the abnormalities due? To the simple fact that the saturated vapors under discussion do not exactly follow the gas laws, but require a correction according to the equation of state. When such a correction is applied (as has been done in the last column of the above table

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[1] Washburn, "Principles of Physical Chemistry," 1915, p. 31.

[2] Guye, *Trans. Faraday Soc.*, 6, 84 (1910).

[3] Dolezalek has recently claimed (*Z. physik. Chem.*, 93, 585 (1919)), that liquid argon is slightly associated, but rightly notes that such association does not extend appreciably unto the vapor phase.

by means of Berthelot's modification of van der Waal's equation)[1] the abnormalities practically disappear.

It will be noticed that water vapor diverges *less* from the "theoretical" than the majority of substances listed. Have we any more reason to attribute the abnormalities here to the presence of dimolecular $(H_2O)_2$ than we have to postulate polymerization in pentane vapor or the existence of He_2 in helium gas? It is true that liquid water is highly associated, and that the vapors of certain similarly associated liquids such as acetic acid[2] show unmistakable association even at low temperatures, yet from the values obtained in the table above it is evident that, below 100° at least, association in water vapor can only be minute. While the observed vapor density is still slightly above the corrected theoretical value, yet the excess is not so great as in the case of chlorobenzene and may be accounted for in part by uncertainty in the critical data.[3] At temperatures approaching the critical, where the pressure is very high, association of the saturated vapor may become appreciable,[4] but the extensive association claimed by Bose and Oddo at temperatures below the boiling point is certainly an exaggeration of the facts.

In conclusion, it is necessary to record a protest against the optimistic habit, prevalent among writers of text books as well as of original articles, of treating all gases as perfect. In work on gaseous systems, it is rare to find any correction applied for "the equation of state," although frequently intricate calculations which presuppose considerable accuracy are carried out with the use of the observed densities. In technical processes (probably following Haber's "Thermodynamics of Technical Gas Reactions" and similar monographs) no regard at all is commonly paid to possible abnormalities, even when reactions under high pressures are considered. That the quantities of different gases introduced into the reaction vessels under such conditions are quite at variance from the correct proportions has been strikingly shown in recent work on the Haber process.[5] The extended discussion of this general question given by Lewis in several articles[6] does not appear to have attracted the attention which it deserves.

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[1] See Washburn, *loc. cit.*, p. 33.

[2] Young, *loc. cit.*

[3] If association exists at the critical point, the critical data are not strictly applicable to the Berthelot equation.

[4] The experiments of Ramsay and Young (*Phil. Trans.*, 183, 107 (1892)), indicate a rapid increase in the ratio (obs./calc.) above 200°. At 270° the observed vapor density is more than 15% in excess of the corrected theoretical.

[5] "Physical and Chemical Data of Nitrogen Compounds," p. 5–6 (M. I. D. Research Laboratory, University College, London, 1918).

[6] G. N. Lewis, *Proc. Am. Acad.*, 37, 66 etc. (1901); 43, 262 (1907); THIS JOURNAL, 37, 2309 (1915).

For the same reason, vapor density determinations upon dissociating substances, such as phosphorus pentachloride and the ammonium halides,[1] will not furnish exact values for their dissociation unless correction is made for the appreciable divergence from the perfect gas laws of all of the substances concerned in the equilibrium. The possible error in functions derived from *variations* in the calculated degrees of dissociation (such as the heat of dissociation)[2] will naturally be much greater. To attempt to obtain quantitative values for the association of *liquid* water from uncorrected vapor density measurements, as has been done by Guye,[3] is obviously altogether futile.

In the standard Victor Meyer vapor-density experiment the textbooks on practical physical chemistry "allow" the student an error of "less than 5%," although the abnormalities in the vapor densities of many common liquids exceed that value. Since corrections of less than 1% (*e. g.*, for the water vapor content of the atmosphere)[4] have been proposed, it would evidently be well worth while to introduce the equation of state factor into the discussion. Otherwise, the accurate student and the conscientious instructor will inevitably clash, without prospect of reconciliation.

Summary.

The monomolecular nature of water vapor has recently been questioned, "spontaneous ionization" of H_2O into H^+ and OH^- at low temperatures and association into $(H_2O)_2$ at higher temperatures being postulated. It has been shown here that the evidence for the existence of the equilibria $H_2O \rightleftharpoons H^+ + OH^-$ and $2H_2O \rightleftharpoons (H_2O)_2$ is in each case entirely insufficient, that the abnormalities in the vapor densities of normal substances at their boiling points are similar to that in water vapor at 100°, and that such abnormalities practically vanish on applying the corrections for deviation from the perfect gas laws.

An "equation of state" correction is similarly necessary in gas reactions at high pressures, in calculations on dissociation in the vapor state and in Dumas or Victor Meyer vapor-density determinations.

NEW YORK, N. Y.

[1] Smith and Lombard, THIS JOURNAL, 37, 38, 2055 (1915).

[2] Smith and Lombard, *loc. cit.*, p. 55.

[3] Guye, *Trans. Faraday Soc.*, 6, 84 (1910).

[4] Evans, THIS JOURNAL, 35, 958 (1913).

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO AND THE FURMAN CHEMICAL LABORATORY OF VANDERBILT UNIVERSITY.]

THE PROPERTIES OF SUBSIDIARY VALENCE GROUPS. I. THE MOLECULAR VOLUME RELATIONSHIPS OF THE HYDRATES AND AMMINES OF SOME COBALT COMPOUNDS. II. SUBSIDIARY GROUP MOBILITY AS STUDIED BY THE HEAT DECOMPOSITION OF SOME COBALTAMMINES.

BY GEORGE L. CLARK, A. J. QUICK, AND WILLIAM D. HARKINS.

Received August 13, 1920.

The problem of the nature of subsidiary valence, together with the factors determining Werner's "coördination numbers," is now assuming renewed importance and interest in the light of the newer ideas on the space structure of the atom as outlined by Parson, Lewis, Born and Landè, Langmuir, and others, and on the space lattice structure of crystals as based on the researches of Laue, the Braggs, Hull, and others, together with the experimental work of Ephraim and of Biltz upon new compounds exhibiting this type of valence. The present investigation was begun 4 years ago in the endeavor to show that the interatomic and intermolecular electromagnetic fields are the largest factor in determining the stability of these compounds. The present paper treats of the closely related molecular, atomic, and group volumes. It seemed to the writers to be probable that the relative volumes of the anion, cation, and of the groups held by subsidiary valence, as they exist in the complex molecules would be of great importance in determining the stability. Ephraim[1] had already proved that the volumes of the cation and anion before entering into this combination, are of importance. The necessity for a careful study of these and other properties of subsidiary valence groups has been accentuated by the recent work of Clark and Quick[2] on the preparation of *p*-phenylene-diamine by the action of ammonia on *p*-dichloro-benzene in the presence of certain salts capable of forming ammines, thus pointing to a catalytic activation of the ammonia in the intermediate subsidiary valence stage.

The usual number of subsidiary valences is of course 6 as postulated by Werner, but it is incorrect to assign this number rigidly to all possible cases. Ephraim, as cited above, has shown that only the metals with an atomic volume less than 14 are able to form hexammines, and that the stability of the compounds containing 6 ammonia molecules and a common anion, decreases with increasing atomic volume of the cation. This is what might be expected from the general relations, since a relatively

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[1] Ephraim, *Z. physik. Chem.*, 81, 513–39 (1913); 83, 196 (1915); *Ber.*, 45, 1323 (1912).

[2] Clark and Quick, THIS JOURNAL, 42, 1033 (1920).

small atomic volume for an atom in a solid is an indication of the existence around it of a relatively intense electromagnetic field.[1]

If, as it is postulated by Ephraim, each metal atom is surrounded by 8 anion groups in the space lattice, it is reasonable to expect that when the relative volumes of the anion and cation are varied the packing will become more or less compact, and it may, therefore, be expected that, provided the group volume of the anion becomes sufficiently great, there will be the possibility of packing more than 6 ammonia groups around the cation.

Some experimental work which will be described later in this paper, and which, though it seems to be correct, is nevertheless less well verified than any of the other work of the paper on account of its sudden interruption by the war, indicates that we have been able to attach 10 ammonia groups to one cobalt atom. Certain features of the results have led us to use the term "cavity" to indicate a position in molecule, or in the space lattice of a crystal, where an extra atom may be squeezed in without adding appreciably to the total volume of the crystalline substance. It is obvious that these results may be the consequence of an entire change in the crystal and its rearrangement into a much closer state of packing.

Ephraim's work on the dissociation temperatures of the hexammines shows that with the same metal the dissociation temperature is higher for the compound with an anion of higher atomic or group volume. In his more recent work[2] he describes some octammines. Now it may be noticed that these are invariably compounds containing anions (organic aromatic radicals) which are very large compared to the metal, with the result that the "cavities" around the metal atom can actually hold *2 more* than the usual number of ammonia groups. The influence of volume thus receives a further verification.

That the addition of the 2 extra groups does not produce any remarkable change in the general characteristics of the molecules, is shown by the fact that there is little color change, thus indicating that the vibration of the more loosely bound electrons is only very slightly affected. In our own work even the addition of the 4 extra ammonia groups did not greatly change the color, though there was a definite change.

Biltz and Fetkenheur[3] have recently isolated alpha and beta, or what they consider to be *cis* and *trans* stereoisomers of the diammines of the cobaltous halides. That these are different compounds they concluded from the fact that the colors are entirely different. It will be shown in this paper that their densities are also different.

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[1] Harkins and King, "An Electromagnetic Hypothesis of the Kinetics of Heterogeneous Equilibrium, the Structure of Liquids, and Cohesion." THIS JOURNAL, 41, 970–92 (1919).

[2] Ephraim, *Ber.*, 51, 644–69 (1918).

[3] Biltz and Fetkenheur, *Z. anorg. Chem.*, 89, 97 (1914).

With all the points just outlined in view, it was considered of fundamental importance in the further study of the position and number of subsidiary valence groups and the stability of the compound to know how the groups themselves change in volume as they are packed into the space-lattice cavities of the crystal, for this would at once serve to indicate the size of the cavities, the limiting compressibility of the subsidiary groups, and the effects of both anion and cation. The purpose of this paper, therefore, is to make such an interpretation in a preliminary way from accurate measurements and comparisons of molecular volumes. It is limited to the hydrates and ammines of the chloride and sulfate of bivalent cobalt and 3 cobaltic chloride ammines for purposes of comparison. Of intrinsic value are, first, the study of the methods of preparation and the actual composition of the compounds, concerning which there is a surprisingly wide difference of opinion; and second, the specific gravity determinations. It is a reflection upon present day chemistry that the specific gravity of cobalt sulfate, for example, which is generally quoted in tables, was determined in 1845 without any refinement in method, and that several others now accepted were made with water as the liquid. A few compounds are described and specific gravities given for the first time.

Part II of this paper gives the interesting results of experiments upon the effect of heat on the cobaltammines, from which information may be gained as to the stability of the subsidiary valence unions, the constrained mobility of the groups, and the possible secondary chemical reactions when heat energy has overcome the electric and magnetic forces which enable the ammine molecule to hold together.

Experimental.

Specific Gravity Determinations.—The specific gravity determinations were carried out by means of a pycnometer having a side-arm capillary tube such as is used for the accurate determination of the densities of liquids. The stoppers were specially ground so carefully that there was no need for the use of phosphoric acid or grease as a lubricant, thereby removing any possibility of contamination. The pycnometer was repeatedly carefully standardized with freshly distilled water. The liquids used in the determinations were kerosene, xylene and toluene. They were purified by allowing them to stand over solid sodium hydroxide for several days, further dehydrated with metallic sodium, and then fractionated, the middle portion being collected. The boiling point and the specific gravity of the fraction taken at 25° and compared to water at 4° were as follows:

Liquid.	Boiling point, ° C.	Sp. gr.
Kerosene	145–180	0.78824
Toluene	106–107	0.86584
Xylene	133–134	0.86286

It might be mentioned that no vacuum correction for the pycnometer was made since the air displaced by it was always the same. The object in using 3 liquids was to avoid as far as possible any errors due to solubility of the compounds in perhaps one or another of the liquids.

The determination of the specific gravity of the various compounds to be described was based on the replacement of one of the 3 liquids by a known weight of the solid. This was weighed directly in the pycnometer, covered with the liquid and the occluded air removed by suction. The latter process was repeated after the pycnometer had been left in the thermostat for at least 30 minutes. Hygroscopic materials were introduced into the pycnometer by means of a wide funnel in a box kept desiccated. Every compound whose specific gravity was determined was passed through a 100-mesh sieve, and in the case of anhydrous salts the dehydrated salt was ground to the desired fineness, passed through the sieve and then redehydrated.

As a final check on the measurements many were repeated using instead of the pycnometer a tube 5 mm. in diameter graduated in 0.1 cc. and carefully calibrated as recommended by LeChatelier and Bogitch.[1] This was filled with the liquid, the meniscus carefully read, and then a weighed quantity of the solid introduced and the volume noted from the movement of the meniscus. Results by the pycnometric and the tube methods were entirely concordant in every case.

The results are tabulated in Table I, each single value representing an average of 3 to 6 determinations. The utmost care was exercised in every particular so that the values are probably accurate to within 0.2%. In 2 cases variations from values derived in Harvard atomic weight determinations were less than this.

Analytical Methods.—*Ammonia.* A weighed amount of the ammine was put into a small weighing bottle, dropped through a wide closed funnel into a solution of sodium hydroxide, and the liberated ammonia distilled into standard acid solution. The usual precautions were taken, including a blank test showing that the reagents were pure and that no fixed alkali was swept over.

Water.—The sample was put into a combustion tube and heated to the necessary temperature. A slow current of dry air was passed over the sample and the liberated water collected in a U-tube filled with fused calcium chloride, or, in the case of compounds containing both water and ammonia, with potassium hydroxide. Horn and Taylor[2] have shown that this latter method is entirely rigorous.

Compounds Studied.—*Anhydrous Cobaltous Chloride.* This was prepared from Kahlbaum's purest crystallized cobaltous chloride hexa-

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[1] LeChatelier and Bogitch, *Compt. rend.*, 163, 459 (1916).

[2] Horn and Taylor, *Am. Chem. J.*, 32, 256 (1904).

hydrate, by heating to 160–170° until a uniformly light blue product was obtained. It was found very advisable to conduct the dehydration in an atmosphere of dry hydrogen chloride. The preparation of the perfectly anhydrous salt presents a problem in itself. The usual recommendation for the temperature of dehydration is 140°,[1] but the salt dehydrated at this temperature always has a purplish tinge indicative of minute traces of moisture. The extremely delicate color sensitiveness to moisture shows that only the pure blue salt is really in a state of perfect dehydration, and is obtained at 160–170° in the presence of dry hydrogen chloride or hydrogen. The temperature may be raised to 400° for a short time without apparent decomposition, but at this point dark spots begin to appear. It has been found possible in this work to sublime anhydrous cobaltous chloride below 500° in a brick-lined electric oven under slight pressure of hydrogen chloride into *colorless*, but wonderfully iridescent fluffy crystals, which crumble into a pink powder in the presence of a minute amount of water vapor.

Specific gravities are as follows: in xylene, 3.360; in toluene, 3.352; in kerosene, 3.356; average, 3.356. Baxter and Coffin,[2] who made a careful determination, found practically the same value, 3.348.

Cobaltous Chloride Hexahydrate.—A pure commercial product was used. An analysis for water gave the following results:

Calc. for $CoCl_2.6H_2O$: H_2O, 45.38. Found: 45.15.

Values of the specific gravity are 1.923 in toluene, 1.925 in xylene, or 1.924 average. The only other value of this constant found in the literature and the one now generally used is 1.84, determined by Bödeker,[3] whose work has been found inaccurate in many cases.[4]

Cobaltous Chloride Dihydrate.—This compound was formed by keeping the hexahydrate over conc. sulfuric acid at 50° for 36 hours. A dark purple compound was formed giving the following analysis for water.

Calc. for $CoCl_2.2H_2O$: H_2O, 21.70. Found: 21.60.

All attempts to prepare definite intermediate hydrates between 2 and 6 failed, confirming the results of Derby and Yngve.[5] Specific gravity values are: 2.470 in kerosene, 2.485 in xylene, 2.477 average.

Cobaltous Chloride Hexammine.—This ammine was prepared in 4 different ways. The first method, following the method described by Ephraim,[6] consisted in passing dry ammonia gas over anhydrous cobaltous chloride. The first trace turned the salt deep blue, then red, then finally

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[1] Wyrouboff, *Bull. soc. chim.* [3], 5, 462 (1871); Potilitizer, *Ber.*, 17, 280 (1884).

[2] Baxter and Coffin, THIS JOURNAL, 28, 1587 (1906).

[3] Bödeker, "Die Beziehung zwischen Dichte und Zusammenhang bei festenund liquiden Stoffen." Leipzig, 1860.

[4] *Am. Chem. J.*, 31, 228 (1904).

[5] Derby and Yngve, THIS JOURNAL, 38, 1439 (1916).

[6] Ephraim, *Ber.*, 45, 1323 (1912).

flesh colored. Using the perfectly dehydrated salt, a number of samples have been prepared in this way, giving practically theoretical analyses. Using, however, some of the chloride dehydrated without precautions, the ammonia content of the ammine always approximated 5.5 moles instead of 6. In the effort to raise the content the experiment was repeated at a temperature of —10°, and finally liquid ammonia was added to the salt in a Dewar bulb; but in either case the resulting product showed no appreciable increase in ammonia. Average specific gravity values of the pure hexammine prepared in the dry way are: 1.495 in toluene, 1.489 in kerosene, 1.507 in xylene, or 1.497 average in the 3 liquids.

The compound was prepared a second way by passing dry ammonia gas through a solution of anhydrous cobaltous chloride in absolute alcohol, producing first a pale red precipitate which gradually changed to the light flesh color identical in shade with that produced by the dry method. A specific gravity determination in kerosene gave 1.533.

The ammine was also prepared in the wet way, by bubbling ammonia through a saturated solution of the chloride in water. Surprisingly good results were obtained for, as the solution approached saturation perfect octahedral crystals, dark red in color, separated. These were filtered off in an atmosphere of hydrogen, washed with conc. ammonium hydroxide, then alcohol saturated with ammonia, and finally ether. The product was fairly stable in air after being dried in an atmosphere of hydrogen at slightly above room temperature. Analysis of the compound gave the following results:

Calc. for $CoCl_2.6NH_3$: Cl, 30.57; NH_3, 43.99. Found: Cl, 30.43; NH_3, 43.68.

The specific gravity of this sample is 1.506. In this connection a number of experiments were performed to ascertain whether ammonia groups will always displace water when held by subsidiary valence bonds. Dry ammonia was passed over cobaltous chloride hexahydrate and the water was absorbed by solid potassium hydroxide as it was liberated. An exceedingly unstable series of compounds is formed as the process continues, and these compounds are instantly oxidized at first contact with air. After several hours, however, all the water of hydration is replaced by ammonia and the perfectly stable hexammine is left. The greater ease with which ammonia molecules can exist as subsidiary valence groups is thus clearly demonstrated.[1]

The hexammine was finally prepared under pressure. No mention of this method could be found in the literature, although it affords a convenient process especially for cobaltous ammines which oxidize easily. By means of it the tedious process of bubbling ammonia through the solution or passing over the dry salt is eliminated, and at the same time

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[1] Ephraim and Rosenberg, *Ber.*, 51, 130 (1918), show that the hexammine of cobaltous nitrate is very easily prepared in this way.

the yield is markedly increased and a beautifully crystalline product is obtained. The details of the method are as follows. 35 g. of hydrated chloride, 50 cc. of conc. ammonium hydroxide, and 10 cc. of alcohol were put into a pressure flask and heated in a bath of boiling water. In about an hour complete solution took place, whereupon the bath was allowed to cool very slowly. Large, well defined crystals separated. The supernatant liquid was decanted off and the crystals washed successively by decantation with conc. ammonium hydroxide, alcohol and ether. The crystals were identical in color, form and composition with those obtained by the wet method.

Cobaltous Chloride Pentammine Monohydrate.—It was found that by using the third or wet method described for the hexammine except that the solution of the chloride is first heated to boiling and then cooled down during the passage of the ammonia to —10°, a product quite different from the red octahedral crystals was obtained. It was a fine pink powder which gave the following analysis:

Calc. for $CoCl_2.5NH_3.1H_2O$: Co, 25.26; Cl, 30.31; NH_3, 36.60; H_2O, 7.73. Found: Co, 25.24; Cl, 30.39; NH_3, 36.51; H_2O, 7.55.

The cobalt in this case was determined by electrolysis as metallic cobalt from a solution made alkaline with ammonium hydroxide and containing 4 times the weight of cobalt of ammonium chloride. It is doubtful whether this is as definite a compound as the hexammine, since other samples gave a somewhat higher ammonia and lower water content. That the compound differs from the hexammine, however, is shown by the difference in their hydrolysis by water. The hexammine is completely decomposed, forming a precipitate of cobaltous hydroxide and a clear supernatant solution of ammonium chloride. This compound, however, produces a green precipitate containing about 6 moles of hydroxide to one of cobaltous chloride, and a red supernatant liquid from which separated, after 4 weeks spontaneous evaporation *in vacuo*, red octahedral crystals having the approximate composition, $CoCl_2.12NH_4Cl.8NH_3$. Hydrolysis therefore, would seem to proceed according to the following equations.

$$CoCl_2.6NH_3 + 2H_2O \longrightarrow Co(OH)_2 + 2NH_4Cl + 4NH_3;$$

$$CoCl_2.5NH_3.1H_2O + 4H_2O \longrightarrow CoCl_2.6Co(OH)_2 + 20NH_3 + CoCl_2.12NH_4Cl.8NH_3.$$

This compound also has a higher specific gravity, 1.559 in kerosene.

Cobaltous Chloride Pentammine.—Only 5 molecules of ammonia combine when the gas is conducted into a *boiling* solution of the chloride in absolute alcohol. A pale yellowish-pink colored ammine which gave the following analysis for ammonia results:

Calc. for $CoCl_2.5NH_3.NH_3$, 39.60. Found: 39.78.

The average specific gravity of this compound was found to be 1.580.

Cobaltous Chloride Tetrammine.—This was prepared in 2 entirely different ways. By keeping the hexammine prepared in the dry way over conc. sulfuric acid at 50° for 36 hours a light pink-colored product was formed giving an almost exact analysis for the tetrammine, and having a specific gravity of 1.593 in xylene. The same result is accomplished by subjecting the hexammine to continued evacuation over acid at room temperature. The loss of ammonia seems to proceed gradually and quite slowly, but after the tetrammine is reached no further loss is noted.

The other method consisted in heating cobaltous chloride pentammine monohydrate in a closed vessel at 150° in the presence of potassium hydroxide and allowing the dry ammonia gas to be reabsorbed. By doing this ammonium hydroxide (one NH_3 and the one H_2O) failed to recombine. The compound was a very pale pink in oclor and could be melted to a dark blue liquid. The following remarkable analysis was obtained:

Calc. for $CoCl_2.4NH_3$: Co, 29.58; Cl, 35.80; NH_3, 34.40. Found: Co, 29.68; Cl, 35.82; NH_3,34.31.

The only direct method recorded is by H. Rose[1] by passing dry ammonia gas over anhydrous cobalt chloride giving a blue compound. Bersch[2] later showed that the hexammine was formed instead.

When dry ammonia gas was passed through a cold solution of cobalt chloride in amyl alcohol a compound containing 38.53% ammonia was obtained, corresponding to 4.79 moles of ammonia. Curtis and Burns,[3] working under similar conditions, obtained a pale red ammine whose composition corresponded to the formula $CoCl_2.3NH_3$, and considered by Biltz and Fetkenheur[4] to be a mixture of the hexammine and the diammine which they obtained by heating the hexammine above 130°. It has been found impossible in the work of this paper to prepare any compound corresponding to a triammine, which must indicate that the solution with which Curtis and Burns worked was not completely saturated with ammonia. Experiments which need not here be detailed have been performed with amyl alcohol solutions at temperatures in 5° intervals from —10 to 125°. The tendency is for the formation of ammines and mixtures of ammines containing between 5 and 6 molecules of ammonia at temperatures below the boiling point irrespective of the method of preparation. Acetone and ethyl alcohol solutions are exactly analogous, so that the temperature of the experiment is the determining factor and not the chemical nature of the solvent in which the ammines are insoluble.

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[1] Rose, *Pogg. Ann.*, **20**, 151 (1830).

[2] Bersch, *Ber. Wien. Akad.* [2], **56**, 729.

[3] Curtis and Burns, THIS JOURNAL, **39**, 33 (1917).

[4] Biltz and Fetkenheur, *Z. anorg. Chem.*, **97**, 133 (1914).

Cobaltous Chloride Diammine.—When ammonia is passed through a *boiling* solution of the anhydrous chloride in pure anhydrous amyl alcohol a distinctly pink colored compound was precipitated containing 20.74% ammonia, while 20.774% is the calculated value for the diammine. The alcohol was carefully dehydrated by allowing it to stand over solid sodium hydroxide and fractionating. The specific gravity of the diammine was 2.095 in both xylene and toluene. Two methods for the preparation of the diammines are to be found in the earlier literature: a light blue compound from heating the hexammine to 120°,[1] and a dark blue one[2] by precipitation with ammonia from acetone solution. Great interest is attached to this compound, however, by a recent isolation by Biltz and Fetkenheur[3] of 2 isomeric diammines. In order to obtain these the method was followed exactly. The pink α or *cis*-diammine was prepared by heating the pure hexammine rapidly between 152° and 175°, and was identical with the one prepared in boiling amyl alcohol solution; the blue β, or *trans*-diammine was obtained by heating the hexammine *in vacuo* at 65°. The following analyses indicate the purity of the isomers,

Calc. for $2NH_3$: NH_3, 20.74. Found: α, 20.82; β, 20.75.

The specific gravities have not been heretofore determined and are of course of fundamental importance. The values are, α, 2.097 and β, 2.073, in xylene.

Cobaltic Chloride Pentammine (*Chloro-pentammine*).—This compound was prepared for very special work at the University of Chicago and was obtained from there. The following analysis shows its purity,

Calc. for $CoCl_3.5NH_3$: NH_3, 33.95. Found: 34.00.

The specific gravity was 1.809 in xylene and 1.829 in toluene, or 1.819 average.

Aquo-pentammine Cobaltic Chloride.—The compound was prepared from the corresponding oxalate according to the directions given in Biltz' "Laboratory Methods of Inorganic Chemistry," and twice recrystallized. The specific gravity was 1.774 in xylene and 1.778 in toluene, or 1.776 average.

Cobaltic chloride hexammine was also prepared according to Biltz and purified by several recrystallizations Specific gravity, 1.740 in xylene; 1.748 in toluene; 1.744 average.

Cobaltous Sulfate Anhydrous.—A current of dry air was passed over the hydrated salt kept at 280° for 4 hours. At the end the product was perfectly anhydrous and had a light lavender color. Different samples gave the following specific gravities: 3.717 and 3.705 in xylene, and 3.707 in kerosene, or an average of 3.710. The value of this constant

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[1] F. Rose, "Unters. uber ammoniak Kobaltverb.," 1871, p. 26.

[2] Naumann, *Ber.*, 37, 4334 (1904).

[3] *Z. anorg. Chem.*, 89, 97 (1918).

quoted in tables was determined in 1845 by Joule and Playfair,[1] who obtained 3.531.

Cobaltous Sulfate Heptahydrate.—A pure commercial product was carefully recrystallized from water and the crystals thoroughly dried. An analysis for water showed 44.95%, while the calculated value for the heptahydrate is 44.83. Specific gravities were 1.955 in toluene, 1.942 in kerosene, or 1.948 average.

Cobaltous Sulfate Hexahydrate.—By keeping the heptahydrate in an air-bath at 45° for several hours, a compound containing 40.80% water was obtained, corresponding to the hexahydrate which should analyze 41.06. The specific gravity was 2.029 in toluene.

Cobaltous Sulfate Tetrahydrate.—This was made by placing the heptahydrate over conc. sulfuric acid for 48 hours at 50°. One sample was found to contain 31.80% of water, while the calculated value for the tetrahydrate is 31.72. Two different samples gave specific gravities of 2.366 and 2.370 in xylene, for an average of 2.368.

Cobaltous Sulfate Pentammine.—In at least 15 trials in passing dry ammonia over dehydrated cobaltous sulfate, it was found impossible to prepare the hexammine of this salt, but instead always the pentammine, a light, fluffy, pink powder, was obtained, contrary to the findings of Ephraim.[2] One sample gave the following representative analysis for ammonia.

Calc. for $5NH_3$: 35.41. Found: 35.52

At —18° an ammine containing 5.2 moles of ammonia was formed. The specific gravity of the purest pentammine was 1.692 in kerosene and 1.715 in xylene, an average of 1.703.

Cobaltous Sulfate Tetrammine Dihydrate.—This compound was prepared for the first time by passing ammonia gas through a hot concentrated solution of the sulfate. By allowing the solution to cool slowly as it approached saturation, red crystals separated out, which were washed by decantation with conc. ammonium hydroxide, alcohol and ether. They are stable when dry but oxidized rapidly when dry, hence the drying and washing were done out of contact of air. The compound undergoes no change when submitted to reduced pressure for a short time, and is not decomposed when heated at 50° for 25 hours. Analysis gave the following results:

Calc. for $CoSO_4.4NH_3.2H_2O$: SO_4, 37.06; NH_3, 26.25; H_2O, 13.90. Found: SO_4, 36.85; NH_3, 26.38; H_2O, 13.20.

The compound may also be prepared by the pressure method already described, by heating together 20 g. of hydrated sulfate, 40 cc. of conc. ammonium hydroxide and 10 cc. of alcohol in the pressure flask. The

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[1] Joule and Playfair, *Chem. Soc. Memoirs*, 2, 401 (1845).

[2] Ephraim, *Z. physik. Chem.*, 83, 196 (1915).

average specific gravities were 1.808 and 1.807 in xylene, and 1.797 in toluene.

Discussion.

In the table are listed for each compound the specific gravity as experimentally determined in xylene, toluene and kerosene, the molecular volume, the apparent volume of the groups held by subsidiary valence, and the percentage compression of these groups from the volume in the free state at the same temperature. The latter two columns are not to be construed directly as the volume of the cavities in the space lattice of the crystal, since not only the free volume but also the electrical and magnetic stray fields of anion, cation and subsidiary group will determine

TABLE I.—VOLUME RELATIONS OF COMPLEX COBALT COMPOUNDS.

(Note that the atomic and group volumes given below are *apparent* volumes only. Thus the volume of the ammonia is calculated on the basis of the assumption that in the complex compounds the cobalt and chlorine have the same volume as in pure cobaltous chloride. This assumption should be kept in mind in considering the discussion presented in the paper.)

	Specific gravity at 25°.						
Compound.	Xylene.	Toluene.	Kerosene.	Av.	Mol. vol.	Apparent vol. subsidiary group.	% compression.
NH_3	.....	.....	.....	.....	28.416	....	.....
H_2O	.....	.....	.....	.....	18.069	....	.....
$CoCl_2$ anhyd.	3.360	3.352	.....	3.356	38.70	(Co, 6.77	31.95
						Cl_2, 50.104)	
$CoCl_2.6H_2O$	1.925	1.923	.....	1.924	123.69	H_2O, 14.165	21.40
$CoCl_2.2H_2O$	2.485	.....	2.470	2.477	66.97	H_2O, 14.25	20.91
$CoCl_2.6NH_3$	1.507	1.459	1.489	1.497	154.01	NH_3, 19.33	31.97
	1.506	.....	1.533	.....	......	....	.....
$CoCl_2.5NH_3.1H_2O$	.....	.....	1.559	1.559	149.50	NH_3, 19.29	32.12
	.....	.....	.....	.....	......	H_2O, 14.30	20.69
$CoCl_2.5NH_3$	.....	1.575	1.585	1.580	136.20	NH_3, 19.50	31.37
$CoCl_2.4NH_3$	1.593	1.594	.....	1.593	126.84	NH_3, 20.11	29.23
$CoCl_2.2NH_3$	(alpha)	.....	.....	.....	......	....	.....
	2.095	2.095	.....	2.095	78.25	NH_3, 19.77	30.43
	2.097	.....	.....	.....	......	....	.....
$CoCl_2.2NH_3$ (beta)	2.073	.....	.....	2.073	78.25	NH_3, 20.19	28.95
$CoCl_3$	.....	.....	.....	2.940	56.24	....	.....
$CoCl_3.6NH_3$	1.740	1.748	.....	1.744	153.37	NH_3, 16.09	43.37
$CoCl_3.5NH_3.1H_2O$	1.774	1.778	.....	1.776	151.29	NH_3, 16.20	42.86
	.....	.....	.....	.....	......	H_2O, 14.05	22.24
$CoCl_3.5NH_3$	1.809	1.829	.....	1.819	137.69	NH_3, 16.29	42.67
$CoSO_4$ anhyd.	3.717	.....	3.707	3.710	41.78	....	.....
	3.705	.....	.....	.....	......	....	.....
$CoSO_4.7H_2O$	.....	1.955	1.942	1.948	144.34	H_2O, 14.65	18.74
$CoSO_4.6H_2O$	.....	2.029	.....	2.029	129.67	H_2O, 14.65	18.74
$CoSO_4.4H_2O$	2.366	.....	.....	.....	......	....	.....
	2.370	.....	.....	2.368	95.90	H_2O, 13.53	24.90
$CoSO_4.5NH_3$	1.715	.....	1.692	1.703	141.03	NH_3, 19.85	30.14
$CoSO_4.2H_2O.4NH_3$	1.808	.....	.....	.....	......	NH_3, 19.10	32.77
	1.807	1.797	.....	1.804	143.67	H_2O, 13.49	25.28

what the packing in the entire molecule will be. Thus cobaltous chloride forms a hexahydrate and a hexammine, and in both cases the subsidiary forces of the cobalt atom seem completely satisfied, though some recent as yet incompletely verified work by one of the authors indicates that under very special conditions more than 6 ammonia groups may be held. The table shows that the relative volumes of water and ammonia are in the ration 14.265 to 19.33. In both cases the substituent groups must occupy relatively the same positions or cavities in the lattice; but the higher stray field of the water as measured by its higher dielectric apparently compensates for its smaller volume.

Considering the ammines of cobaltous chloride it is evident that the ammonia groups increase in volume passing down from the hexammine, assuming that the volume of the nucleus bound by primary valence forces remains constant. The 2 diammines present an interesting difference in accordance with the view either that they are *cis*- and *trans*- isomers or that their crystal form is different. The former has ammonia groups, each occupying a smaller volume than in the tetrammine, while the latter *trans*-, *β*-, or blue form follows the regular order of increase in volume of the substituent group with decrease in number.

Comparing the influence of bi- and trivalent cobalt upon the molecular volumes of the subsidiary groups, it is at once apparent that ammonia groups occupy volumes 10% smaller in the cobalt*ic* than in the cobalt*ous* ammines. The values for the former may be somewhat less accurate than for the bivalent cobalt compounds because of the larger possible error in the molecular volume of the cobaltic chloride nucleus. Even with this greater compression, however, the cobaltic ammines are more stable, as is to be expected from the much greater strength of the stray fields which give the subsidiary valence unions. It is of interest to note that in aquopentammine cobaltic chloride, the water molecule occupies a volume not greatly different from that in the cobaltous compound, and pointing to the greater susceptibility of the ammonia molecule to compression.

In the cobaltous sulfate series the relationships are somewhat different for the water molecules. These occupy the same volume exactly in both the hepta- and the hexa-hydrate, showing that the addition of the seventh molecule, which must be closely connected with the sulfate group, has no effect upon the symmetrically arranged 6. The tetrahydrate and the tetrammine dihydrate are somewhat anomalous in that the water molecules occupy less volume than the hexahydrate shows. It is quite probable that 2 of the groups occupy considerably greater volume than the other 2, whose contraction may be occasioned by the greater concentration of stray field between the sulfate group and the cobalt atom. Ammonia groups in this series are entirely comparable to their properties in the chloride; hence the tendency for the sulfate group to combine with water, aside from the usual subsidiary grouping about the cobalt atom, must be taken to explain the peculiarities in the relationships of the water molecules. A number of other relationships in the table need not be specifically pointed out here.

Preparation and Properties of Cobaltous Decammine Chloride.

Cobaltous Decammine Chloride was prepared *twice* from cobaltous chloride prepared with great care according to the method already described. One preparation was made at the University of Chicago, and the other at the University of Arizona, the preparation being made in both cases by Clark. *Three* careful and agreeing analyses were made of which 2 are given below.

	Second preparation.	First preparation.	Calc. value.
NH_3	0.5662	0.5661	0.5673
Co	0.1955	0.1966	0.1964
Cl	0.2370	0.2358	0.2362

It is remarkable that no attempt to prepare this compound has proved successful except when the original sample of cobaltous chloride, Kahlbaum's purest grade, has been used, though about 10 such attempts have been made. The compound was prepared by passing ammonia over cobaltous chloride, which is nearly colorless. In about one hour, when the layer of the powdered salt is about $^3/_{16}$ inch thick, the salt is completely changed to the hexammine. During the greater part of this period, and in the middle of the period, it was found that the ammonia adds on at an entirely constant rate. Thus in one experiment carried out in a large box containing ammonia, with the cobaltous chloride spread in a layer of about the above thickness on a watch glass, it was found that the period during which the salt absorbed 10 mg. of ammonia gas determined on a sensitive Troemner balance, gave the period of 60 seconds as accurately as it could be determined by means of a stop watch. The hexammine thus formed is almost colorless, but with a slight flesh tinge.

If no more ammonia is taken up this color remains constant, but if the ammonia addition is to go on to the decammine stage, the color begins to change slightly after many hours, and at the end of a week or more has changed gradually over to a brown. An analysis of this brown powder taken directly from the apparatus showed the presence of about 10.5 to 11 molecules of ammonia, but it was obvious that the powder held some absorbed and adsorbed gas not united chemically. On putting some of the powder in a tube and making a connection to a high vacuum for only about one minute, the compound gave the analyses listed above.

The evidence that such a compound was formed was as follows: (1) it was prepared twice with 3 analyses, together with several other analyses showing more ammonia when the ammonia caught in the powder was not removed; (2) the color change; (3) the vapor-pressure curve lies very much higher than that of the hexammine; (4) the density is altogether different; (5) on standing the compound gradually loses its brown color and changes over to the lighter color of the hexammine. The density was found to be 1.71, the molecular volume, 175.6 cu. cm., the volume of the combined ammonia was thus reduced in a very remarkable way to 13. Only 2 density determinations were made, and although they agreed perfectly, it cannot be said that this density work has been so carefully checked as the other work, since it was interrupted by the war, and now none of the compound is available for the determinations.

This compound is evidently very difficult to prepare, as the conditions for its formation have not yet been discovered. Two experiments by Harkins and about 10 by Clark, using new samples of cobaltous chloride, have proved unsuccessful, and it was evident from the original experiments that the quantity of moisture present had to be very carefully controlled.

Part II. The Effect of Heat on Cobaltous and Cobaltic Ammines.

Just as it is possible to drive water from the crystalline hydrates of the cobaltous salts without secondary reactions, so ammonia may be removed from the ammines by heat leaving the anhydrous salt, providing that care be exercised and the temperature not raised too high. The diammine, for example, is prepared from the hexammine by heating to 150° and the last 2 molecules of ammonia may be removed below 200°, though the diammine may be made to melt without decomposition. If higher temperatures are used, however, ammonium chloride is sublimed from the compound as oxidation to cobaltic oxide takes place. Even when 2 different species of groups are held by the same cobalt atom by the subsidiary valence forces—water and ammonia, for example—the effect of heat is merely to remove ammonium hydroxide without disturbing the relationship of the atoms held by primary valence forces. Thus although the ammonia groups are compressed by about $^1/_3$ of their free volume when ammines are formed (a fact which may account in large measure for the greater activity and the catalytic action of the salt in acting merely as a "compressor" and surface for adsorption) still the expansion of the groups and the ultimate liberation is not sufficient to disrupt the entire molecule, unless secondary reactions such as oxidation by the air are made possible.

On the other hand, heat has a large effect upon salts containing a central atom as easily reducible as the cobalt atom when in its higher valence. It has already been shown that ammonia groups are compressed to perhaps 10% greater amount in the cobaltic ammines than in the corresponding cobaltous compounds, and it would be expected that the cobaltic compounds would be more stable. Experiments were performed on 3 of the cobaltic ammines, the hexammine in which the effect of only one species of subsidiary group could be noted, mononitro-pentammine cobaltic chloride with 2 species, and trinitro-triammine cobalt with 2 species and without the uusal effect of an anion of an electrolyte. From none of these is it possible to remove ammonia alone without effect upon the rest of the molecule.

From the hexammine cobaltic chloride evolution of ammonia began at 173° to a slight extent, and a sublimate of ammonium chloride was apparent at 181°. The first step consisted in the formation of chloropentammine cobaltic chloride, $[Co(NH_3)_5Cl]Cl_2$, agreeing with the work of Biltz.[1] Rapid increase in vapor pressure began at 220°, and at 228° it was 1054 mm. The original orange-red salt was now dark blue. Reabsorption of ammonia reduced the pressure by 392 mm. and caused the residue to become dark maroon in color. The residual gas, 101 cc., was collected above mercury and all but 6 cc. (which later proved to be nitrogen) dissolved in water showing it to be largely ammonia. The pump was now attached to the vessel containing the solid residue, and the gas withdrawn at 260° for one hour. The residue light blue in color and easily dissolved in water to give a wine colored solution. Upon analysis it proved to be cobaltous chloride together with ammonium chloride in the ration 1 : 2, or $CoCl_2.2NH_4Cl$, though this ratio was undoubtedly accidental inasmuch as a considerable quantity of ammonium chloride had sublimed. This experiment was carried on throughout, out of contact with air and represents the spontaneous decomposition of the molecule with heat according to the following equation.

$$6[CoCl_3.6NH_3] \longrightarrow 6CoCl_2 + 6NH_4Cl + N_2 + 28NH_3.$$

This behavior is much more easily explained upon the basis of Werner's structure than Friend's cyclic structure.[2]

Proceeding in similar fashion with mononitro-pentammine cobaltic chloride, it was found that the gas exerted noticeable pressure at 100° and rapid evolution began at 210°. The gas liberated below 248° was drawn off above mercury and analyzed, showing a total of 87.1 cc., composed of nitrogen 70.3 cc., and ammonia 16.8 cc. Oxygen, hydrogen, nitric and nitrous oxides were tested for and found not present. Water was formed in appreciable quantities in the heating bulb, which, together with the large evolution of nitrogen, indicated the intermediate formation of ammonium nitrite. The solid residue left in the bulb was dicobalt trioxide, agreeing in all properties and giving the following analysis

Calc. for $CoSO_4$: Co, 71.08. Found: 70.96.

The mechanism of this reaction is very probably as follows.

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[1] *Z. anorg. Chem.*, 83, 177 (1913).

[2] *J. Chem. Soc.*, 109, 715 (1916).

$$Co(NH_3)_5(NO_2)Cl_2 \longrightarrow NH_3 + 2NH_4Cl + NH_4NO_2 + CoN;$$
$$NH_4NO_2 \longrightarrow N_2 + 2H_2O;$$
$$2CoN + 3H_2O \longrightarrow Co_2O_3 + 3NH_3;$$

or,

$$2Co(NH_3)_5(NO_2)Cl_2 \longrightarrow Co_2O_3 + 5NH_3 + 4NH_4Cl + 2N_2 + H_2O.$$

This case differs, therefore, from the preceding one in that the cobalt atom is not reduced, because of the interaction of 2 species of molecules both with subsidiary valence unions.

The results with trinitro-triammine cobalt are somewhat similar, but very interesting. Slight evolution of gas begins at 158°, but at 164° the decomposition takes place with almost explosive violence, forming pure nitrogen, water and cobaltic oxide, according to the following reactions.

$$2Co(NH_3)_3(NO_2)_3 \longrightarrow 2CoN + 2HNO_2 + 4NH_4NO_2;$$
$$4NH_4NO_2 \longrightarrow 4N_2 + 8H_2O;$$
$$2CoN + 2HNO_2 \longrightarrow Co_2O_3 + H_2O + 2N_2;$$

or,

$$2Co(NH_3)_3(NO_2)_3 \longrightarrow 6N_2 + 9H_2O + Co_2O_3.$$

The writers wish to express their indebtedness to the Gibbs Fund of the National Academy of Sciences for a grant of two hundred dollars made to W. D. Harkins, which was used in purchasing a very rapid vacuum apparatus, consisting of a mercury condensation pump, and a large supporting pump of the mechanical type, for use in this work.

CHICAGO, ILL., AND NASHVILLE, TENN.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN.]

THE PREPARATION OF SELENIUM OXYCHLORIDE.

BY VICTOR LENHER.

Received August 23, 1920.

The first record in the literature that we have of selenium oxychloride is its preparation by Weber[1] in 1859, who heated together in a knee-shaped tube the vapors of selenium tetrachloride and selenium dioxide. Michaelis[2] prepared the oxychloride by the action of phosphorus pentachloride on selenium dioxide. Later, in 1889, in their work on selenic acid, Cameron and Macallan,[3] mention that selenium oxychloride is formed when common salt is distilled with selenium dioxide.

The methods used in this laboratory for the formation of selenium oxychloride may be grouped under 3 heads.

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[1] Weber, *Pogg. Ann.*, **108**, 615 (1859).

[2] Michaelis, *Ann.*, **240**, 150 (1887).

[3] Cameron and Macallan, *Chem. News*, **59**, 267 (1889).

1. Direct Union of Selenium Tetrachloride and Selenium Dioxide at Room Temperatures.

When elementary selenium is suspended in carbon tetrachloride and chlorine gas is passed in, the chlorine first dissolves in the carbon tetrachloride, this being an excellent solvent for chlorine at low temperatures. The dissolved chlorine immediately attacks the selenium, forming selenium monochloride which also dissolves at once in the carbon tetrachlroide. Selenium monochloride, in turn, is an excellent solvent for elementary selenium. The solution and chlorination of the selenium is therefore, much expedited.

An alternate method of preparing the 2 chlorides of selenium which possesses interesting advantages with certain selenium containing materials is to suspend them in carbon tetrachloride, chloroform or similar solvent, and pass in chlorine. This converts the selenium first to the monochloride which is soluble in carbon tetrachloride while most of the metallic chlorides, being insoluble in carbon tetrachloride, can be at once removed by filtration or decantation, while the further chlorination of the selenium monochloride gives white selenium tetrachloride, which being sparingly soluble, separates out and if desired can be removed from the solvent by a second filtration.

To the suspended selenium tetrachloride in carbon tetrachloride it is convenient to add the calculated amount of selenium dioxide. Reaction takes place with formation of selenium oxychloride, which dissolves in the carbon tetrachloride. The liquid can then be distilled. Carbon tetrachloride distills at 76–77° and selenium oxychloride at 176.4°, hence they can be readily separated by distillation. Selenium oxychloride can be conveniently distilled under diminished pressure to a high degree of purity.

The carbon tetrachloride suggested in the above procedure can be replaced by chloroform or still better replaced by selenium oxychloride itself.

Inasmuch as selenium oxychloride is a solvent for elementary selenium the entire operation of its formation can be accomplished by mixing together selenium dioxide and elementary selenium, treating this mixture with selenium oxychloride and then chlorinating.

2. Partial Hydrolysis of Selenium Tetrachloride.—This can be readily accomplished by treatment with water according to the following reaction.

$$SeCl_4 + H_2O— = SeOCl_2 + 2HCl.$$

This reaction can be carried out with solid selenium tetrachloride or with the selenium tetrachloride suspended in carbon tetrachloride, chloroform, selenium oxychloride or other liquids.

3. Dehydration of the Compound $SeO_2.2HCl$.—This substance, first described by Ditte,[1] can be formed by bringing hydrogen chloride into contact with selenium dioxide. The 2 substances unite at moderately low temperatures to form an amber-colored liquid of the formula $SeO_2.2HCl$. It is possible to remove the elements of water from this compound by means of phosphorus pentoxide, calcium chloride, or a similar dehydrating agent. The reaction can be carried out in the laboratory in one of 2 ways.

Selenium dioxide can be treated with hydrogen chloride, the resulting liquid mixed with excess of the dehydrating agent and the oxychloride distilled off, or selenium dioxide can be first mixed with the dehydrating agent and this mixture treated with hydrogen chloride. The operation can be conducted by either first passing hydrogen chloride into the mixture of selenium dioxide and dehydrating agent in the cold and subsequently heating to drive off the selenium oxychloride formed, or the mixture can be heated, hydrogen chloride passed in, and selenium oxychloride distilled from the hot mixture as it forms.

The author takes this opportunity of acknowledging the valuable help rendered by his assistant, Mr. A. J. Snyder, for various preparations of material in the above processes.

MADISON, WISCONSIN.

THE IONIZATION OF AQUEOUS SOLUTIONS OF AMMONIA IN THE PRESENCE OF UREA.

BY WINTHROP M. BURKE.

Received August 27, 1920.

Introduction.

According to the Nernst-Thomson hypothesis,[2] the dielectric constant of a solvent largely determines its power to ionize electrolytes dissolved in it. In cases which have been investigated[3] in solvents of lower dielectric constant than water, the ionization of the electrolyte has in general been found to be lower than in water. It has been found that aqueous solutions of urea have a dielectric constant higher than water; that of water is 78.83, while for a 2 M solution of urea it is 83.98 at 18.0°.[4] Consequently, according to the Nernst-Thomson hypothesis, we should expect to find a greater ionization constant for an electrolyte, which obeys the mass-action law, in an aqueous urea solution than in water alone. Assuming the mass-action law to be obeyed, the ionization constant for binary dissociation may be derived from the expression

$$\frac{(C\gamma)^2}{C(1-\gamma)} = K.$$

[1] *Ann. chim. phys.* [5] 10, 82 (1877).

[2] Thomson, *Phil. Mag.*, 38, 320 (1893); Nernst, *Z. physik. Chem.*, 38, 487 (1901).

[3] Kraus and Bray, THIS JOURNAL, 35, 131 (1913).

[4] Harrington, *Phys. Rev.*, 8, 581 (1916).

where C is the total salt concentration, γ is the degree of dissociation, and K is the ionization constant. In this case the assumption is made that the degree of ionization is equal to the ratio Λ/Λ_0, of the equivalent conductance Λ, at any dilution, to the limiting value Λ_0. The mass-action law may be expressed in terms of Λ and Λ_0, by means of the equation

$$\frac{C\Lambda^2}{\Lambda_0\,(\Lambda_0 - \Lambda)} = K.$$

At the suggestion of C. A. Kraus, an investigation of the conductance of a weak base in the presence of urea was undertaken. Ammonium hydroxide was used as an electrolyte since this substance obeys the mass-action law in dilute solution.

Apparatus.

The Kohlrausch method was employed in determining the conductance of the solutions. A Kohlrausch slide-wire bridge with extension coils was employed. Two resistance boxes were used, one of 110,000 ohms with Curtis wound coils for higher resistance; for the lower resistances a bifilar wound box. A variable air condenser was placed in the circuit for the purpose of compensating the effects of capacity and inductance. All connecting wires were lead-covered and carefully grounded. The thermostat was also grounded.

A small induction coil was used as a source of e. m. f. for determining the conductance of the urea-ammonia solutions, and a Vreeland oscillator was employed in standardizing the cell and in measuring the conductance of the water and the urea solutions.

The temperature was maintained constant at 25° ± 0.01°. The thermostat was filled with kerosene oil and was regulated by means of a mercury filled regulator and a thermometer graduated in 0.1°.

The cell employed consisted of a glass cylinder 45 cm. long and 6 cm. in diameter and was constructed as shown in Fig. 1. The neck having the stopper was inclined at an angle of about 45° to the tube containing the electrodes, which facilitated the tipping of the cell so that the solution could fill the arm containing the electrodes and thus be kept at the same height above them. This was accomplished by the aid of the small tube, shown in Fig. 1, which was fitted with a piece of rubber tubing and a pinchcock.

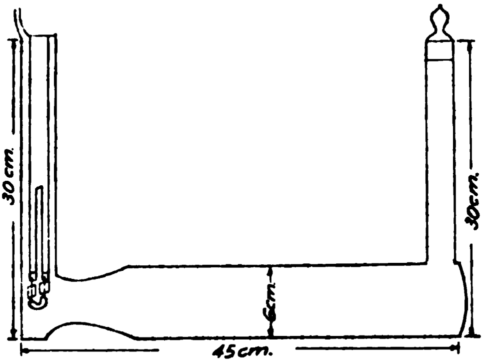

Fig. 1.

The platinum electrodes, coated with platinum black, were about one cm. square and about one cm. apart and were sealed into the bottom of the tubular extensions by stiff platinum wires. These extensions led into a larger tube located within the arm of the cell and connected to it at the top by a Dewar seal.

The cell was standardized by comparing it with a standard pipet cell whose constant had been previously determined. It was found that the constant of the cell was 0.22878.

Materials.

Urea.—The urea used was a commercial sample. As it was impure material it had to be purified. This was effected by crystallizing it 5 times from 95% ethyl alcohol and once from absolute alcohol. The urea obtained in this manner had a high degree of purity, giving a colorless aqueous solution and having a conductance of about 4.0×10^{-6} for a 2 *M* solution.

A small amount of an imported sample of reputed purity was available and the conductance of a molar solution of this was determined. Using water of a conductance of 3.5×10^{-6}, the increase in conductance due to the addition of urea amounted to 3.3×10^{-6}.

Small amounts of the urea in a water solution were tested with phenolphthalein, methyl orange and congo red, and no trace of acid or base could be found. The indicators showed the solutions to be neutral.

Ammonium Hydroxide.—The ammonium hydroxide solutions were made up in approximately *N* and 0.1 *N* concentrations by passing ammonia gas into water.

The solutions were standardized against hydrochloric acid of approximately the same concentrations. The hydrochloric acid was standardized against silver nitrate by weighing the chloride precipitated from a measured amount of the acid. In this manner the normalities of the ammonium hydroxide solutions were found to be 1.0272 *N* and 0.11049 *N*. Density determinations were made; at 25° one g. of the stronger solution was found to contain 0.035581 g. of NH_4OH and occupy 1.0111 cc., and one gram of the weaker solution contained 0.003874 g. of NH_4OH and occupied 1.0037 cc.

The density of a 2 *M* solution of urea at 25° was found to be 1.0291. Also when one gram of urea dissolves in water it displaces 0.8102 cc., the volume of the solution being increased by this amount.

The densities were all referred to water at 4° as 1.0000.

Water.—The water used in this work was distilled directly into the cell from dil. alkaline permanganate solution and the carbon dioxide was further removed by passing air through it. Water of a conductivity of about $1. \times 10^{-6}$ was obtained in this manner.

Procedure.

In making a run about 250 g. of water was weighed in the cell and the amount of urea calculated to make a 2 *M* solution was added. As the urea undergoes gradual decomposition in water, the conductance of the urea solution was measured about 20 minutes after the addition of urea, and then ammonium hydroxide was run in from a previously weighed pipet which was then weighed again. The addition of ammonium hydroxide checked the decomposition and the solution came to equilibrium in about 15 to 20 minutes after the addition of ammonium hydroxide. Immediately following the addition of ammonium hydroxide an amount of urea was added which was calculated to compensate for the change in volume, thus keeping the concentration constant.

Experimental Results.

The results of 6 independent determinations are given in Table I. Expts. 2 to 5 show the data on aqueous solutions of urea and ammonium hydroxide, and Expts. 6 and 7 show the data on aqueous solutions of ammonia.

TABLE I.

	Expt. 2.			Expt. 3.			Expt. 4.		
No.	NH_4OH Conc. $\times 10^4$ $\frac{\text{Equiv.}}{\text{Liter.}}$	Spec. cond. $\times 10^5$ corr.	Λ.	NH_4OH Conc. $\times 10^4$ $\frac{\text{Equiv.}}{\text{Liter.}}$	Spec. cond. $\times 10^5$ corr.	Λ.	NH_4OH Conc. $\times 10^4$ $\frac{\text{Equiv.}}{\text{Liter.}}$	Spec. cond. $\times 10^5$ corr.	Λ.
H_2O	.....	0.1537	....	......	0.1288	....	......	0.0972	....
Urea	.....	0.3979	....	......	0.2992	....	......	0.3879	....
1	2.8365	1.508	53.16	2.7662	1.500	54.23	2.6879	1.393	51.82
2	8.6133	1.778	20.64	9.4245	2.756	29.24	8.5048	2.634	30.97
3	19.627	4.214	21.47	23.263	4.588	19.72	18.834	4.027	21.38
4	42.780	6.197	16.38	50.202	6.707	13.36	41.269	6.089	14.75
5	82.873	8.673	10.47	93.449	9.133	9.773	83.340	8.721	10.46
6	112.06	10.139	9.048	115.87	10.330	8.916	109.46	9.943	9.083
7	167.69	12.432	7.414	191.68	13.237	6.906	161.70	12.169	7.526
8	342.75	17.620	5.141	569.51	22.569	3.963	273.51	15.752	5.759
9	678.05	24.616	3.630	......	.....	....	516.53	21.513	4.165
10	1073.7	30.809	2.869	......	.....	....	935.41	29.293	3.080
	Expt. 5.			Expt. 6.			Expt. 7.		
H_2O	.....	0.08807	....	......	0.112	....	......	0.1358	....
Urea	.....	0.4538	....	......	.....	....	......	.....	....
1	2.4898	1.275	51.21	2.4406	1.257	51.50	4.7535	2.258	47.50
2	9.4494	2.784	29.46	8.5501	2.961	34.63	14.060	3.993	28.40
3	22.333	4.453	19.94	16.793	4.368	26.01	30.413	6.064	19.95
4	47.840	6.510	13.61	33.807	6.400	18.93	54.747	8.238	15.05
5	100.88	9.608	9.524	59.379	8.643	14.56	91.783	10.758	11.72
6	118.55	10.373	8.750	92.582	10.798	11.66	136.52	13.322	9.759
7	173.89	12.659	7.280	121.72	12.479	10.25	225.66	17.104	7.580
8	277.79	15.846	5.704	191.50	15.820	8.261	337.61	22.141	5.863
9	468.06	20.466	4.373	331.70	20.705	6.242	692.91	30.066	4.339
10	874.27	27.448	3.192	528.37	26.215	4.982	......	.....	....
11	.....	.....	....	774.20	31.818	4.110	......	.....	....

The results of the first experiment are omitted because the solution had stood for a day before any data were taken. The urea and water solution did not come to equilibrium; the resistance in the cell dropping about 100 ohms every 15 minutes. This was undoubtedly due to the partial conversion into ammonium cyanate.

All measurements were made at 25° ± 0.01°.

In the first column is given the number of the observation, in the second the concentration of the ammonium hydroxide present, in the third the specific conductance corrected for the conductance of the solvent. This corrected value was obtained by subtracting the value of the specific conductance of the urea solution from that of the urea-ammonium hydroxide solution. In the fourth column is given the value of the equivalent conductance.

Discussion.

The results are shown graphically in Fig. 2. The points of each experiment are marked with the number of the experiment so that they can be identified. The values of $1/\Lambda$ are plotted against those of the specific conductance. This gives a linear curve if the mass-action law holds. At

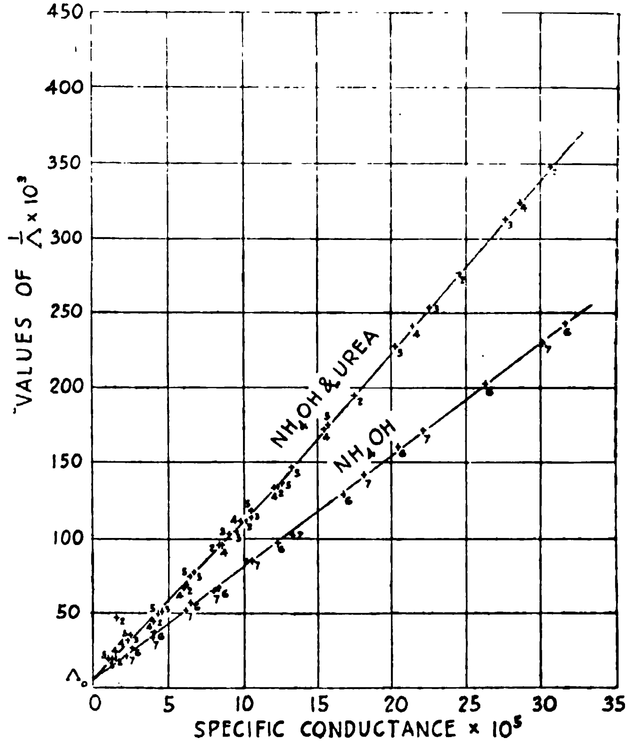

Fig. 2.

the concentration of about 0.01 *N* the slope of the curve increases slightly and then continues in a straight line.

On extrapolating to get Λ_0, a value was obtained approximately equal to that for ammonium hydroxide in water solution,[1] $\Lambda_0 = 270.6$.

On applying the mass-action law and taking values from the lower part of the curve, before the slope changes, the results shown in the following table were obtained.

TABLE II.

$\Lambda_0 = 270.6$.

Specific conductance $\times 10^6$.	$\frac{1}{A} \times 10^3$.	A.	$K \times 10^6$.
2.3	28.0	35.71	12.92
5.7	64.0	15.63	12.91
7.5	83.0	12.05	12.92
11.0	120.0	8.33	12.92

This shows that ammonium hydroxide in urea solution obeys the mass-action law.

On determining the ionization constant of ammonium hydroxide in aqueous solution the following results were obtained.

TABLE III.

Specific conductance $\times 10^5$.	$\frac{1}{A} \times 10^3$.	A.	$K \times 10^6$.
1.9	18.0	55.56	18.14
7.6	61.0	16.39	18.11
15.3	119.0	8.40	18.12
23.8	183.0	5.46	18.13

The concentrations are expressed in equivalents per liter. The value given by A. A. Noyes[2] for *K* at 25° is 18.1×10^{-6}, where the concentration is expressed in equivalents per liter.

The value of $\Lambda_0 = 270.6$ is the one given by Noyes and was used in calculating the results.

From the value of the equilibrium constants we see that in the case of urea and ammonium hydroxide we have an apparent exception to the Nernst-Thomson hypothesis. Instead of the ionization constant being increased, it is decreased about 30%. This difference cannot be wholly accounted for by viscosity effects as the viscosity of the urea solutions does not differ appreciably from that of water.

Landolt and Börnstein give the following data:

M.	*Z.*
1.875	1.026
3.75	1.072

where *M* is the number of moles of urea per liter of water and *Z* is the viscosity at 25° referred to water as 1.0000.

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[1] A. A. Noyes, *Carnegie Inst. Pub.*, 83 (1907).

[2] *Loc. cit.*, 1907, p. 228.

From the great tendency of urea to form complexes with acids, bases and salts,[1] it is possible that an ammonium-urea complex, having an ionization constants less than that of ammonium hydroxide was formed.

WORCESTER, MASS.

[CONTRIBUTION FROM THE FIXED NITROGEN RESEARCH LABORATORY.]

STATISTICAL MECHANICS APPLIED TO CHEMICAL KINETICS.

BY RICHARD C. TOLMAN.

Received September 13, 1920.

I. Introduction.

The rate at which chemical reactions take place has long been one of the most important and most baffling of the problems of theoretical chemistry. The principles of thermodynamics provide a theoretical basis for predicting just which chemical reactions can take place, namely, those accompanied by an increase in entropy, and for predicting just how far they will proceed until equilibrium is attained. Thermodynamics, however, has been powerless to provide information as to the rate at which the thermodynamically possible reactions will actually proceed. Indeed chemical reactions which are accompanied by very large increases in entropy, such, for example, as the union of hydrogen and oxygen to form water, are often the ones which proceed with the slowest rates. The final solution of the problems of chemical velocity will be of extraordinary importance both for theoretical and for applied chemistry, since the chemist will then be able to predict not only the *possible* reactions in a given mixture of chemicals, but also the *actual* reactions which really do take place. The present article aims to make some contribution towards this final solution.

1. Previous Work.—Important contributions to the general theory of chemical velocity have been made by Guldberg and Waage,[2] Arrhenius,[3] Marcelin,[4] Trautz,[5] Perrin[6] and W. C. M. Lewis.[7]

Guldberg and Waage were the first to understand the effect of concentration on rate of reaction.

Considering the reaction

$$aA + bB + \ldots \longrightarrow cC + dD + \ldots \qquad (1)$$

where a mols of the Substance A react with b mols of the Substance B, etc., to form the products C, D, etc., the equation of Guldberg and Waage,

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[1] Meyer and Jacobson, "Lehrbuch der Organischen Chemie," 1, Pt. 2 (1913).

[2] Guldberg and Waage, Ostwald's "Klassiker" No. 104; *J. prakt. Chem.*, 19, 69 (1879).

[3] Arrhenius, *Z. physik. Chem.*, 4, 226 (1889).

[4] Marcelin, *Ann. phys.*, 3, 120 (1915).

[5] Trautz, see summary, *Z. anorg. Chem.*, 102, 81 (1918).

[6] Perrin, *Ann. phys.*, 11, 5 (1919).

[7] W. C. M. Lewis, *J. Chem. Soc.*, 113, 471 (1918); *Phil. Mag.*, 39, 26 (1920).

for the rate at which the concentration of the reactant A is decreasing may be written

$$-\frac{dC_A}{dt} = k_1 C_A^a C_B^b \ldots \qquad (2)$$

where C_A, C_B . . ., etc., are the instantaneous concentrations of the reactive substances at the time t and k_1, the so-called specific reaction rate, is a constant, independent of the concentration, but dependent of course on temperature. Equation 2, which applies to single phase homogeneous systems, is a correct expression, provided the actual mechanism of the reaction is given by Equation 1 and provided the reacting substances are sufficiently dilute. The equation has a familiar and obvious derivation based on a consideration of the number of collisions between reacting molecules.

Arrhenius investigated the relation between temperature and rate of reaction, and showed that the variation of specific reaction rate with the temperature could be satisfactorily expressed by the equation

$$\frac{d\, ln\, k_1}{dT} = \frac{E_1}{RT^2} \qquad (3)$$

where E_1 is a quantity, having the dimensions of energy, which is found experimentally to vary only slightly with the temperature.

Equation 3 has the same form as van't Hoff's well known thermodynamic equation for the relation between equilibrium constant and temperature, namely,

$$\frac{d\, ln\, K}{dT} = \frac{\Delta E}{RT^2} \qquad (4)$$

where K is the (concentration) equilibrium constant and ΔE is the energy absorbed when the reaction takes place at constant volume and temperature.

The analogous forms of Equations 3 and 4 led Arrhenius to a partially satisfactory thermodynamic derivation of Equation 3. He postulated that chemical interaction does not take place between all molecules which collide in reacting proportions but only between molecules which are in a special activated state. These activated molecules are considered as a tautomeric form of the reacting substance existing at very small concentration in equilibrium with the unactivated form. Since the rate of the reaction will depend on the concentrations of the activated molecules, Equation 3 can then be derived by combining the individual van't Hoff equations which control the concentrations of the activated substances. k_1 is found to be proportional to the product of the equilibrium constants for the individual reactions by which the activated substances are formed, and E_1 the "energy of activation" is the sum of the heats of these reactions.

This treatment of Arrhenius is only partially satisfactory. Like any thermodynamic treatment it is powerless to give information as to the internal mechanism of the processes involved and hence cannot ultimately compete with a statistical mechanical treatment. It also seems questionable whether it is entirely justifiable to treat a portion of the molecules of a reactant namely, those having high energy content, as a "thermodynamically" distinct substance. Furthermore, the Arrhenius discussion takes no cognizances of the important rôle played by radiation in furnishing the energy of activation. It should also be noted that the idea of activated molecules which exist as a tautomeric form and react upon collision is apparently inapplicable to the important case of monomolecular reactions. Finally, modifications would have to be introduced to take care of the increased frequency and violence of collision with increased temperature, as well as the change in effective time of contact of the molecules which are to react.

Marcelin was the first to present any elaborate attempt to apply the methods of statistical mechanics to the problems of reaction velocity. His important contribution, however, is marred by a lack of appreciation of the rôle of radiant energy in the activation of molecules and by a confusion of Gibbs' expression for the canonical distribution of an ensemble of systems with Maxwell's distribution law.

Trautz, W. C. M. Lewis and Perrin, were the first to appreciate the importance of radiation as the source from which the energy of activation necessary for chemical reaction is to be obtained. The development of this idea has received its most complete expression in the very persuasive treatment of Perrin, "Matiére et Lumiére."[1] A brief account of Perrin's work will be necessary to indicate the point of departure for the present article.

In order to express the mechanism of a chemical reaction by which the substances A are changed into the substances A′, Perrin writes the equation

$$H\nu + \mathrm{A} = \mathrm{A}' + H\nu' \qquad (5)$$

where ν is the frequency of the light which has to be absorbed in order to activate A, ν' is the frequency of the light which is given out by A′ on formation, and H is Planck's constant h multiplied by Avogadro's number N.

$$H = Nh. \qquad (6)$$

It will be seen that Equation 5 takes cognizance of the quantum theory by making $H\nu$ the energy of activation per mol. of substance, and thus making the energy of activation per molecule exactly one quantum of energy $h\nu$.

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[1] *Loc. cit.*

Equation 5 is regarded as reversible ν' being the frequency of light absorbed by A′ when the reaction proceeds in the reverse direction.

In accordance with Equation 5, Perrin writes for the total energy change accompanying the reaction

$$\Delta E = H(\nu - \nu'). \tag{7}$$

In order to investigate the rate of reaction and its dependence on temperature, Perrin assumes that the specific reaction rate k will be proportional to the intensity of radiant energy of the activating frequency ν. In the case of a purely thermal reaction this will obviously be the intensity of radiation in a hohlraum at the temperature in question. If u is the density of energy in a hohlraum at temperature T we may write in accordance with the Planck law for the distribution of radiant energy,

$$\frac{du}{d\nu} = \frac{8\pi h\nu^3}{c^3}\,\frac{1}{\epsilon^{h\nu/kT} - 1}. \tag{8}$$

On the basis of Planck's distribution law, Perrin then writes the following expression for specific reaction rate,

$$k_1 = \frac{s}{\epsilon^{h\nu/kT} - 1}, \tag{9}$$

s being a composite proportionality factor which in agreement with Perrin may be called the "*sensibility*" of the substances A to the action of radiation of frequency ν.

Since the quantity $\epsilon^{h\nu/kT}$ is in general very large compared with unity, Perrin rewrites Equation 9 in the form

$$k_1 = s\epsilon^{-h\nu/kT} \tag{10}$$

and indeed seems to feel that Equation 10 is presumably the exact form of the equation.

Taking the logarithm of Equation 10 and differentiating with respect to the temperature we obtain

$$\frac{d\,ln\,k_1}{dT} = \frac{h\nu}{kT^2} \tag{11}$$

or since $Nk = R$ and $Nh = H$,

$$\frac{d\,ln\,k_1}{dT} = \frac{H\nu}{RT^2}. \tag{11a}$$

We have thus derived Arrhenius' equation (3). $H\nu$ being the energy of activation previously called E_1.

2. Criticism of Perrin's Treatment.—Perrin's treatment is not entirely satisfactory for the following reasons.

(1) Equation 7 for the energy change accompanying a reaction would make the energy of reaction entirely independent of the temperature. This is known not to be the case.

(2) Perrin's treatment is based on the assumption that light of a single

frequency or rather of a very narrow range of frequencies will be the only light having activating properties. We have, however, very considerable evidence to show that photochemical reactions are produced by the action of light of a considerable range of frequencies. The simplest of all chemical reactions is the dissociation of a substance into positive ions and electrons, and it is well known that the photo-electric effect in metals is produced by a range of frequencies above the limiting threshhold frequency. This is not only true for solid metals, but I am informed by Dr. E. H. Williams that it was also found by Kunz and himself to be true for cesium vapor. The well known reactions of practical photography are also known to be produced by light of a great variety of wave lengths. Work carried on in this laboratory by Dr. Farrington Daniels[1] has also shown that the photo-chemical decomposition of gaseous nitrogen pentoxide is apparently produced by a range of frequencies. It is evident that a more general method of treatment involving integration over the whole range of frequencies is to be desired. Perrin's treatment, even if in other ways correct, would then be the limiting case of a more general theory, applicable when only a spectrum "line" is active. In this connection it should be pointed out that Perrin's s in Equation 9 must be thought of as containing a factor $\Delta\nu$, corresponding to the width of the supposed "line," since Equation 8 gives, not energy density, but change of energy density with frequency.

(3) Perrin's assumption that specific reaction rate is really exactly proportional to $\epsilon^{-h\nu/kT}$ instead of to $\frac{1}{\epsilon^{h\nu/kT}-1}$ as would be expected from Planck's radiation formula, seems arbitrary.

(4) Perrin's treatment makes no allowance for the fact that the different molecules of a reacting substance are undoubtedly in many different internal states. Hence, the rate of reaction and its change with temperature must be thought of as depending on the condition of the molecules as well as on the condition of the surrounding "bath" of radiant energy.

(5) Perrin's treatment does not make what seems to be a necessary differentiation between monomolecular and polymolecular reactions. In the case of monomolecular reactions, we may think of the reaction as being completed as soon as the molecule has received its energy of activation In the case, however, of di- and polymolecular reactions, we shall find it advantageous to consider as 2 separate steps, (*a*) the process by which the proper quota of activated molecules is maintained, and (*b*) the actual chemical interaction. This latter viewpoint has as a matter of fact been appreciated both by Trautz and W. C. M. Lewis.[2]

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[1] To be published in a later number of THIS JOURNAL.

[2] Since this article was written a further criticism of Perrin's development has been made by Langmuir, *ibid.*, 42, 2190 (1920). Langmuir points out (1) that many substances do not have absorption bands for radiant energy of the fre-

II. Method of Treatment Adopted in this Article.

The point of view adopted in the present article is essentially an extension of that of Perrin, the attempt being made to meet the 5 criticisms made above. The method of treatment, however, will differ from that of Perrin in being based as nearly as may be on the fundamental considerations of statistical mechanics.

Since many chemists are not familiar with the methods of statistical mechanics we shall first present a brief introduction to this important science.

All developments of statistical mechanics which have as yet reached any degree of elaboration have been based on the assumption that Hamilton's equation of motion are applicable to the different parts of the system under consideration, and this assumption will be made in the present treatment. In recent years many investigators have objected to such a use of Hamilton's equations of motion, since they have believed that a statistical mechanics founded on these equations necessarily led to the principle of the equipartition of energy which has been shown not to be true for the radiant energy in a hohlraum, and for other systems where "quantum" relations have been found important. The present writer, however, does not believe that the principle of the equipartition of energy is a necessary consequence of Hamilton's equations, but rather a consequence of an unnecessary and incorrect assumption that energy is necessarily a homogeneous quadratic function of the generalized coördinates and momenta. This point of view has already been presented by the author[1] in an article dealing with the general theory of energy partition, where it has been shown that a relation between energy and the generalized coördinates and momenta can be found which will even account for the distribution of energy in the hohlraum in accordance with the Planck radiation formula. For this reason we shall feel justified in using a statistical mechanics based on Hamilton's equations for the present investigation.

Before proceeding to our development, a word must be said about the rôle of radiant energy in the production of chemical reaction. In this connection, it is believed that Perrin's arguments that radiant energy is necessary for chemical reaction are unescapable. If we agree to the

quency which Perrin predicts as necessary for their activation, and (2) that the amount of radiant energy of such frequencies which is actually available in the hohlraum is too small to furnish the necessary energy of activation. The present writer agrees with both these criticisms of Perrin's treatment. He is not inclined at the present, however, to give up, as Langmuir suggests, the whole radiation theory of reaction velocity. As will be evident in the sequel, the present development, by assuming the possibility of a widely extended range of activating frequencies, meets the objections of Langmuir as well as the 5 objections noted above.

[1] Tolman, *Phys. Rev.*, 11, 261 (1918).

general idea, as presented, indeed in the simple Arrhenius treatment, that reaction occurs only between activated molecules, we find experimentally from the temperature coefficient of rate of reaction (see Equation 3) that the energy necessary is usually very large, much larger than ordinary heats of reaction. In order to maintain a steady rate of reaction, the molecules of the reacting substances will have then to obtain in some continuous way this necessary energy of activation. It can come either from collision with other molecules or from the surrounding bath of radiant energy. If the only source of energy were collisional we should expect a decrease in specific reaction rate on increased dilution which is not found to be the case. We may conclude that radiant energy is an important source for the energy of activation and the only source for reactions in gases of high dilution.

III. Statistical Mechanics Applied to Chemistry.

1. The Equations of Motion.—Consider a chemical system such as a gaseous mixture of reacting molecules immersed in a bath of radiant energy of a character corresponding to the temperature. The configuration of the system at any instant will be determined by the specification of the position of the different molecules, the orientation of the atoms composing them, and the electromagnetic displacement in the different modes of vibration which are the seat of the radiant energy. If a statement of the values of n generalized coördinates, $\phi_1\,\phi_2\,\phi_3\,\ldots\,\phi_n$ is just sufficient to specify the configuration, the system is said to have n degrees of freedom.

The future behavior of the system will be determined by the instantaneous values of these n generalized coördinates and by the instantaneous values of the corresponding n generalized velocities $\dot\phi_1\,\dot\phi_2\,\dot\phi_3\,\ldots\,\dot\phi_n$, the dot being used in general to indicate differentiation with respect to time. If the system is a conservative one, the equations of motion can be written in the remarkably symmetrical Hamiltonian form

$$\begin{aligned}\frac{\partial H}{\partial \psi_1} &= \dot\phi_1 \quad \frac{\partial H}{\partial \psi_2} = \dot\phi_2 \quad \frac{\partial H}{\partial \psi_3} = \dot\phi_3 \ldots \\ \frac{\partial H}{\partial \phi_1} &= -\dot\psi_1 \quad \frac{\partial H}{\partial \phi_2} = -\dot\psi_2 \quad \frac{\partial H}{\partial \phi_3} = -\dot\psi_3 \ldots\end{aligned} \qquad (13)$$

where the new quantities, $\psi_1\,\psi_2\,\psi_3\,\ldots\,\psi_n$, are known as the generalized momenta for the system and are themselves functions of the ϕ's and $\dot\phi$'s, and H, the so-called Hamiltonian function, is the energy of the system E expressed as a function of the generalized coördinates and momenta.

$$H = E\,(\phi_1\,\phi_2\,\ldots\,\phi_n\,\psi_1\,\psi_2\,\ldots\,\psi_n). \qquad (14)$$

2. Geometrical Representation.—The state of our system at any instant will be completely determined by the specification of the $2n$ variables, $\phi_1\,\phi_2\,\ldots\,\phi_n\,\psi_1\,\psi_2\,\ldots\,\psi_n$. We shall find it convenient to think of the state of the system as represented by the position of a point in a $2n$ dimensional space.

Suppose now we have a great many systems of the same structure but differing in state. Then for each system we shall have a point in our $2n$ dimensional space, and if the systems are left to themselves these points will describe stream lines in accordance with the equations of motion (13).

3. **The Maintenance of Uniform Density.**—Suppose now that the points representing the states of the different systems are originally distributed with the uniform density ρ throughout the $2n$ dimensional space. Then it is a necessary consequence of the equations of motion that the density will remain uniform. For the rate at which the density would increase at any point we can obviously write

$$\frac{d\rho}{dt} = \rho\left(\frac{\partial\dot{\phi}_1}{\partial\phi_1} + \frac{\partial\dot{\phi}_2}{\partial\phi_2} + \ldots + \frac{\partial\dot{\psi}_1}{\partial\psi_1} + \frac{\partial\dot{\psi}_2}{\partial\psi_2} + \ldots\right)$$

and since the equations of motion (13) evidently necessitate the relations

$$\frac{\partial\dot{\phi}_1}{\partial\phi_1} + \frac{\partial\dot{\psi}_1}{\partial\psi_1} = 0, \quad \frac{\partial\dot{\phi}_2}{\partial\phi_2} + \frac{\partial\dot{\psi}_2}{\partial\psi_2} = 0, \quad \text{etc.},$$

we conclude that the original uniform density will not change.

This maintenance of uniform density is a very important result. It means that there is no tendency for the representative points to crowd into any particular portion of the $2n$ dimensional space. For this reason if we start some one isolated system going and plot its state in our $2n$ dimensional space, we shall assume that after an indefinite lapse of time its representative point is equally liable to be in any one of the infinitesimal elements of equal volume ($d\phi_1\, d\phi_2 \ldots d\phi_n\, d\psi_1\, d\psi_2 \ldots d\psi_n$) into which we can divide our space, provided this elementary region corresponds to the energy content of the system.

4. **Probability of a Given Microscopic State.**—As a convenient nomenclature, we shall say that the *microscopic state* of a system is specified by a statement of the particular element of volume ($d\phi_1\, d\phi_2 \ldots d\phi_n\, d\psi_1\, d\psi_2 \ldots d\psi_n$) in which the representative point for the system falls. On the basis of the conclusion reached in the last paragraph we shall state the important principle that *all the different microscopic states of a system have the same probability.*

5. **Probability of a Given Statistical State.**—Let us suppose that our system is a chemical one composed of a large number of identical elements such as atoms, molecules, modes of electromagnetic vibration, etc. Let A, B, C, etc., be the number of elements of each of the various kinds which go to make up the complete system, and let us consider that our $2n$ generalized coördinates and momenta can be assigned to the individual elements of the system.

For a chemical system of this kind, we shall be particularly interested in the number of elements of any particular kind A which have coördinates and momenta falling in any given infinitesimal range,

$$d\sigma_A = d\phi_{A_1}\, d\phi_{A_2} \dots d\psi_{A_1}\, d\psi_{A_2} \dots \qquad (15)$$

where $\phi_{A_1}, \phi_{A_2} \dots \psi_{A_1}\, \psi_{A_2} \dots$ are generalized coördinates and momenta of the kind that are assigned to one of the elements of the kind A. We shall specify the *statistical state* of our system by stating the number of elements of the various kinds A, B, C, etc., which fall in the different possible infinitesimal ranges $d\sigma$.

A specification of the *microscopic state* of the system determines the coördinates and momenta for each individual element of which the system is composed. The *statistical state* merely determines the number of elements of each of the different kinds which have coördinates and momenta of a particular magnitude, without attempting to make any distinction as to which particular elements are taken to supply the quota. We thus see that corresponding to a given statistical state there will be a large number of different microscopic states which can be obtained by the intertransposition of elements of a given kind from one region $d\sigma$ to another without disturbing the total number in each region. Since we have already concluded that all microscopic states are equally probable, we may now conclude that *the probability of any given statistical state is proportional to the number of microscopic states to which it corresponds.*

Let us specify a given statistical state by stating that $A_1A_2A_3 \dots B_1B_2B_3 \dots C_1C_2C_3 \dots$, etc., are the number of elements of each of the kinds which have coördinates and momenta falling in the particular infinitesimal ranges Nos. 1A, 2A, 3A..., 1B, 2B, 3B, ... etc.

Then it is evident from the principles of permutation that the number of microscopic states corresponding to this statistical state will be

$$W = \frac{\underline{|A}\;\underline{|B}\;\underline{|C}}{\underline{|A_1}\;\underline{|A_2}\;\underline{|A_3} \dots \underline{|B_1}\;\underline{|B_2}\;\underline{|B_3} \dots \underline{|C_1}\;\underline{|C_2}\;\underline{|C_3} \dots} \qquad (16)$$

where A, B, C, etc., are the total number of elements of each of the kinds. We shall call W the probability of the given statistical state, without introducing any proportionality factor.

Let us now assume that each of the numbers $A\ A_1\ A_2 \dots B\ B_1\ B_2 \dots$, etc., is large enough so that we may apply Stirling formula for factorial N,

$$\underline{|N} = \sqrt{2\pi N}(N/\epsilon)^N. \qquad (17)$$

Substituting in Equation 16, taking the logarithm of W for greater convenience and omitting negligible terms, we obtain

$$\begin{aligned} \log W = {} & A \log A + B \log B + C \log C + \dots \\ & - A_1 \log A_1 - A_2 \log A_2 - A_3 \log A_3 - \dots \\ & - B_1 \log B_1 - B_2 \log B_2 - B_3 \log B_3 - \dots \\ & - C_1 \log C_1, - \text{etc.} \end{aligned} \qquad (18)$$

which can be rewritten in the form

$$\log W = \mathrm{A}\log\mathrm{A} + \mathrm{B}\log\mathrm{B} + \mathrm{C}\log\mathrm{C} + \dots \\ - \Sigma\mathrm{A}_i\log\mathrm{A}_i - \Sigma\mathrm{B}_j\log\mathrm{B}_j - \Sigma\mathrm{C}_k\log\mathrm{C}_k - \dots \qquad (18a)$$

where the summation Σ is to be taken over all the infinitesimal regions, $i = 1, 2, 3, \dots j = 1, 2, 3 \dots k = 1, 2, 3 \dots$ etc.

6. Statistical State of Maximum Probability.—We shall be specially interested in the statistical state of maximum probability with a system having a given energy content. The condition for maximum probability will evidently be

$$\delta\log W = -\Sigma(\log\mathrm{A}_i + 1)\delta\mathrm{A}_i - \Sigma(\log\mathrm{B}_j + 1)\delta\mathrm{B}_j - \dots = 0 \qquad (19)$$

The variation δ however cannot be carried out entirely arbitrarily since the total number of elements of any kind A, B, C, etc., will not be taken as subject to variation, and the total energy of the system will be taken as constant.

For the total number of elements of each kind we may write

$$\mathrm{A} = \Sigma\mathrm{A}_i \quad \mathrm{B} = \Sigma\mathrm{B}_j \quad \mathrm{C} = \Sigma\mathrm{C}_k, \text{ etc.,}$$

and since these totals are not to vary we obtain

$$\Sigma\delta\mathrm{A}_i = 0, \quad \Sigma\delta\mathrm{B}_j = 0, \quad \Sigma\delta\mathrm{C}_k = 0, \text{ etc.} \qquad (20)$$

For the total energy of the system we may write,[1]

$$E = \Sigma\mathrm{A}_iE_i + \Sigma\mathrm{B}_jE_j + \Sigma\mathrm{C}_kE_k + \dots$$

where E_i is the energy of an element of kind A in the i'th region, etc. Since the total energy is to remain constant during the variation, we obtain

$$\delta E = \Sigma E_i\delta\mathrm{A}_i + \Sigma E_j\delta\mathrm{B}_j + \Sigma E_k\delta\mathrm{C}_k + \dots = 0. \qquad (21)$$

The simultaneous Equations 19, 20 and 21 may be combined by the method of undetermined multipliers giving us

$$\begin{aligned} &\Sigma(\log\mathrm{A}_i + 1 + \lambda_\mathrm{A} + \mu E_i)\delta\mathrm{A}_i \\ &+ \Sigma(\log\mathrm{B}_j + 1 + \lambda_\mathrm{B} + \mu E_j)\delta\mathrm{B}_j \\ &+ \Sigma(\log\mathrm{C}_k + \dots \text{etc.} \qquad = 0 \end{aligned} \qquad (22)$$

where the quantities $\lambda_\mathrm{A}\ \lambda_\mathrm{B} \dots$ and μ are undetermined multipliers. The introduction of these undetermined multipliers now makes the variations $\delta\mathrm{A}_i$, etc., entirely arbitrary, so that Equation 22 may be solved in the form

$$\begin{aligned} &\log\mathrm{A}_i + 1 + \lambda_\mathrm{A} + \mu E_i = 0 \\ &\log\mathrm{B}_j + 1 + \lambda_\mathrm{B} + \mu E_j = 0 \\ &\log\mathrm{C}_k +, \text{etc.} \end{aligned} \qquad (23)$$

These relations may be rewritten in the form

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[1] We introduce at this point the tacit assumption that no error will be introduced in to the discussion, if we take the energy of an element as independent of the state of other elements of the sytsem.

$$\begin{aligned} A_i &= \alpha_A \epsilon^{-\mu E_i} \\ B_j &= \alpha_B \epsilon^{-\mu E_j} \qquad (23a) \\ &\text{etc.} \end{aligned}$$

where α_A, α_B, etc., correspond to the original undetermined multipliers, λ_A, λ_B, etc., and ϵ is the base of the natural system of logarithms. It should be specially noticed that α_A, α_B, etc., are dependent on the kind of element in question, but that the quantity μ occurring in Equations 23 and 23*a* is the same for elements of any kind.

7. **Introduction of a Continuous Variable.**—Let us now express the information contained in Equations 23*a* in a slightly different form. The quantity A_i occurring in Equations 23*a* is the number of elements of the kind A in the *i*'th region $d\sigma_i = (d\phi_{A_1} d\phi_{A_2} \ldots d\psi_{A_1} d\psi_{A_2} \ldots)$ when we have the distribution of maximum probability, and this quantity A_i is as we see determined solely by the kind of element involved and the energy of an element in the *i*'th region. Now A_i/A will be the chance that an element of kind A will be in the *i*'th infinitesimal region when we have the distribution of greatest probability, let us write A_i/A proportional to the volume of the infinitesimal region, we have

$$\frac{A_i}{A} = w_i d\sigma_i$$

where w_i is the chance per unit generalized volume that an element of kind A will have coördinates and momenta of the specified magnitude. w_i will evidently depend as does A_i solely on the kind of element involved and on the energy of an element in the particular region $d\sigma$ involved. It is evident from Equation 23*a* that we can then write as an expression for the chance that the coördinates and momenta of an element will fall in a particular infinitesimal region $d\sigma$,

$$\begin{aligned} w_A d\sigma_A &= a_A \epsilon^{-\mu E_A} d\sigma_A, \\ w_B d\sigma_B &= a_B \epsilon^{-\mu E_B} d\sigma_B, \\ &\text{etc.} \end{aligned}$$

where the quantities a_A, a_B, etc., correspond to the original undetermined multipliers, λ_A, λ_B, etc., and hence depend on the kind of element involved and where μ is the same for all kinds of elements.

Now it is well known that for a perfect monatomic gas μ has the value $1/kT$ where T is the absolute temperature and k is the gas constant R divided by Avogadro's number N, for the number of molecules in a gram molecule. Since part of our system could always be a dilute indifferent monatomic gas without influencing any phenomena, we may write in general as our final expressions for the chance that an element of a given kind will have coördinates and momenta falling in a given infinitesimal region,

$$
\begin{aligned}
w_A d\sigma_A &= a_A \epsilon^{-E_A/kT}\, d\sigma_A = a_A \epsilon^{-E_A/kT}\, d\phi_{A_1} d\phi_{A_2} \ldots d\psi_{A_1} d\psi_{A_2} \ldots \\
w_B d\sigma_B &= a_B \epsilon^{-E_B/kT}\, d\sigma_B = a_B \epsilon^{-E_B/kT}\, d\phi_{B_1} d\phi_{B_2} \ldots d\psi_{B_1} d\psi_{B_2} \ldots \\
w_C d\sigma_C &= \text{etc.} \qquad (24)
\end{aligned}
$$

Or, in general,

$$w d\sigma = a\epsilon^{-E/kT}\, d\sigma = a\epsilon^{-E/kT}\, d\phi_1 d\phi_2 \ldots d\psi_1 d\psi_2 \ldots$$

This may be called the generalized Maxwell's distribution law.

8. Three Fundamental Equations of Statistical Mechanics.—Since the probability that a given element has some value for its generalized coördinates is unity we may write

$$\not\int a\epsilon^{-E/kT} d\sigma = \not\int \ldots \not\int a\epsilon^{-E/kT} d\phi_1 d\phi_2 \ldots d\psi_1 d\psi_2 \ldots = 1 \qquad (25)$$

where the symbol $\not\int$ indicates that the integration is to be carried out over the whole region of the generalized space involved. This equation may be regarded as determining the quantity a, which is seen to be a function of the temperature.

Since $a\epsilon^{-E/kT} d\sigma$ is the chance that an element will be found in the region $d\sigma$ it is evident that the average value of any property P of the elements will be given by the equation

$$\overline{P} = \int a\epsilon^{-E/kT}\, P d\sigma = \int \ldots \int a\epsilon^{-E/kT}\, P d\phi_1 d\phi_2 \ldots d\psi_1 d\psi_2 \ldots \qquad (26)$$

where P is to be regarded as a function of the coördinates and momenta and where the integration is to be taken over the whole or a part of the generalized space, according as the average of P is desired for all or a part of the elements.

Equations 25 and 26 will permit us to obtain important information as to the multiplier a. If we differentiate Equation 25 with respect to the temperature T we obtain

$$\not\int da/dT\, \epsilon^{-E/kT}\, d\sigma + \not\int a\epsilon^{-E/kT}\, E/kT^2\, d\sigma = 0.$$

Dividing the first term of this equation by $\not\int a\epsilon^{-E/kT}\, d\sigma = 1$, and noting that the second term in accordance with Equation 26 is the average value of E/kT^2 for all the elements of the kind in question we obtain

$$\frac{\not\int da/dT\, \epsilon^{-E/kT}\, d\sigma}{\not\int a\epsilon^{-E/kT}\, d\sigma} = -\frac{\overline{E}}{kT^2} \qquad (27)$$

or

$$\frac{d\, ln\, a}{dT} = -\frac{\overline{E}}{kT^2}$$

where we have used the symbol $\overline{E}$ to indicate the average value of E. We shall find later use for this important equation.

IV. Application of Statistical Mechanics to Rate of Chemical Reaction.

It is evident that statistical mechanics is a much more powerful, although more complicated, tool for the treatment of chemical problems than is thermodynamics. It is more powerful because it is based on a consideration of the behavior of the ultimate elements of which the system is composed.

1. **Nature of Systems to be Considered.**—In the present article we shall apply statistical mechanics to a consideration of the rate of chemical reaction in gaseous systems, and shall make a number of restrictions as to the nature of these systems.

(*a*) In the first place, we shall assume that the reactions which we consider do not proceed with explosive violence, but at a slow and measurable rate. We shall assume this rate slow enough, so that we can assume that the elements of our system at any instant of time are in the statistical state of maximum probability. The instantaneous rate of chemical reaction will then be determined by the characteristics of this particular statistical state concerning which we have already obtained important information.

(*b*) We shall further assume for the sake of simplicity that the reactions which we are considering consist of a single molecular change of the general type

$$a\mathrm{A} + b\mathrm{B} \longrightarrow \text{Products.}$$

In practice, there are of course many reactions which take place in steps, with the formation of intermediate compounds which later react again, or with the formation of temporary compounds with some substance which acts as a catalyst. Since, however, the total process can be thought of as analyzed into a series of simple steps of the above type we shall confine our immediate theoretical treatment to a consideration of single molecular changes.

(*c*) We shall assume our gaseous mixtures dilute enough so that the gas laws hold for each of the reactants and each of the products of the reaction, and dilute enough so that the specific reaction rate for the forward reaction k_1 and for the reverse reaction k_2 are independent of concentration. This assumption that the gases are dilute entails several important consequencies.

Since the gases are dilute enough to obey the perfect gas laws, van't Hoff's equation for the equilibrium constant will be exactly true, namely,

$$\frac{\mathrm{d}\,ln\,K}{\mathrm{d}T} = \frac{\Delta E}{RT^2}, \qquad (28)$$

where K is the (concentration) equilibrium constant, ΔE, is the energy change accompanying the reaction at constant temperature and volume and R and T have their customary significance.

As a further consequence of the dilution we shall have as an exact relation,

$$K = k_1/k_2, \qquad (29)$$

and hence our theory of rate of reaction must lead exactly to the relation,

$$\frac{d\,ln\,k_1}{dT} - \frac{d\,ln\,k_2}{dT} = \frac{\Delta E}{RT^2}. \qquad (30)$$

As a final consequence of the dilution assumed, we are led to the conclusion that radiant energy takes a *necessary* part in the mechanism of the chemical change. If reactions take place only between "activated" molecules which have considerably more energy than the average, it is evident that in order to maintain a steady rate of chemical change, there must be some source from which molecules may receive the necessary "energy of activation." The source of the "energy of activation" must either be molecular collision or the bath of radiant energy in which the molecules are immersed. If our gases are assumed dilute enough so that further dilution leads to no change in the specific reaction rate, we must conclude, since dilution decreases the number of molecular collisions, that radiant energy is the source of the energy of activation and hence takes an essential part in the chemical change.

2. Thermal Rate of a Monomolecular Reaction.—Let us first consider monomolecular reactions, which might consist either in a decomposition of the molecules or in the formation of an isomer. The decomposition of nitrogen pentoxide, which has been studied in this laboratory by Daniels, is the most satisfactory example of a gaseous monomolecular reaction.

In the case of monomolecular reactions, we may conceive of the reaction taking place as soon as the molecule has received its energy of activation. This differs from the case of di-, and poly-molecular reactions, where we shall expect cases in which the molecules exist for an appreciable length of time in the activated state and then react upon collision.

The chance that a molecule will react, *i. e.*, will pick up the necessary energy of activation from its bath of radiant energy, will be determined in the first place by the state of the molecule itself, and this means of course by the values of the generalized coördinates and momenta which describe the condition of the molecule. If C_A is the number of molecules in unit volume of the reacting gas, then by Equation 24,

$$A_i = C_A a_A \epsilon^{-E_i/kT} d\sigma_i, \qquad (31)$$

is the number of molecules whose coördinates and momenta fall in the small region $d\sigma_i$, provided we assume that the molecules are distributed in the statistical state of maximum probability. This latter assumption cannot of course, be exactly true, since some of the regions $d\sigma_A$ correspond to an activated condition of the molecule and hence one which immediately leads to a destructon of the molecule. Since, however, we shall find that the energy E_i is very large for activated molecules, the number of such molecules, even without reaction, would be negligibly small. As to the re-establishment of the statistical state of maximum probability, as molecules are removed by reaction, we have already assumed the reaction slow enough to permit of this adjustment.

The chance that a molecule will take up the necessary energy of activation will depend not only on the condition of the molecule but also on the condition of the surrounding bath of radiant energy. If the electromagnetic disturbances in a hohlraum be analyzed into periodic disturbances by the methods of Fourier's series, it can be shown that the number of modes of vibration per unit volume having a frequency between ν and $\nu + d\nu$ is equal to

$$N = \frac{8\pi\nu^2}{c^3}\,d\nu \tag{32}$$

where c is the velocity of light. The complicated derivation of Equation 32 need not detain us here. It is sufficient to note that except for the magnitude of the factor 8π, Equation 32 is a necessary consequence of the theory of dimensional homogeneity, since N must have the dimensions of a number per unit volume.

The electromagnetic condition in which a given mode of vibration finds itself will be determined by a specification that certain generalized coordinates and momenta fall in a particular infinitesimal region $d\sigma_k$. If we have the statistical state of maximum probability the number of modes of vibration per unit volume having frequencies in the range $d\nu_j$ and coordinates and momenta in the region $d\sigma_\nu$ will be in accordance with Equations 24 and 32,

$$\nu_{jk} = \frac{8\pi\nu^2}{c_3}\,d\nu_j a_\nu \epsilon^{-E_k/kT}\,d\sigma_k. \tag{33}$$

Let s_{ijk} be the chance per unit time that a molecule in state $d\sigma_i$ will undergo its monomolecular chemical change when it is surrounded by unit density of modes of electromagnetic vibration in state $d\sigma_k$. Then for the total number of molecules which react in unit time, we may write in accordance with Equations 31 and 33,

$$-\frac{dC_A}{dt} = \Sigma s_{ijk} C_A a_A\,\epsilon^{-E_i/kT}\,d\sigma_i\,\frac{8\pi\nu^2}{C^3}\,d\nu_j a_\nu\,\epsilon^{-E_k/kT}\,d\sigma_k, \tag{34}$$

where the summation Σ is to be carried out for all frequencies and for all possible regions i and k. Dividing through by C_A and replacing the summation by the integration form, we obtain

$$-\frac{1}{C_A}\frac{dC_A}{dt} = k_1 = \oint\oint\oint s a_A\,\epsilon^{-E_A/kT}\,\frac{8\pi\nu^2}{c^3} a_\nu\,\epsilon^{-E_\nu/kT}\,d\sigma_A d\nu d\sigma_\nu \tag{35}$$

as an expression for the specific rate k_1 of our reaction.

In order to have a complete understanding of the significance of Equation 35 we may note that σ_A, ν, σ_ν and T are to be regarded as independent variables. The other quantities on the right hand side of Equation 35 are functionally dependent on these variables as follows:

$$
\begin{aligned}
s &= s(\sigma_{\mathrm{A}}, \nu, \sigma_\nu)^1 \\
a_{\mathrm{A}} &= a_{\mathrm{A}}(T) \\
E_{\mathrm{A}} &= E_{\mathrm{A}}(\sigma_{\mathrm{A}}) \\
a_\nu &= a_\nu(\nu, T) \\
E_\nu &= E_\nu(\sigma_\nu)
\end{aligned}
\qquad (36)
$$

A complete knowledge of these functional relations would permit an exact prediction of the specific reaction rate, and this must be regarded as an ultimate problem of chemical kinetics.

In the meantime, we can get important further information from Equation 35 without any knowledge of these functional relations.

3. Temperature Coefficient for Monomolecular Reaction Rate.—If we differentiate Equation 35 with the temperature, we shall obtain a derivation of the Arrhenius expression for the temperature coefficient of specific reaction rate, which will give a real insight into the meaning of that equation. Differentiating Equation 35, dividing by k_1, and noting in accordance with Equation 27 that

$$
\begin{aligned}
\frac{\mathrm{d}a_{\mathrm{A}}}{\mathrm{d}T} &= a_{\mathrm{A}} \frac{\mathrm{d}\, ln\, a_{\mathrm{A}}}{\mathrm{d}T} = -\, a_{\mathrm{A}} \frac{\bar{\bar{E}}_{\mathrm{A}}}{kT^2} \\
\frac{\mathrm{d}a_\nu}{\mathrm{d}T} &= a_\nu \frac{\mathrm{d}\, ln\, a_\nu}{\mathrm{d}T} = -\, a_\nu \frac{\bar{\bar{E}}_\nu}{kT^2}
\end{aligned}
$$

we obtain

$$
\begin{aligned}
\frac{1}{k_1}\frac{\mathrm{d}k_1}{\mathrm{d}T} = \frac{\mathrm{d}\, ln\, k_1}{\mathrm{d}T} = \frac{1}{k_1} & \int\int\int -\frac{\bar{\bar{E}}_{\mathrm{A}}}{kT^2} s a_{\mathrm{A}} \epsilon^{-E_{\mathrm{A}}/kT} \frac{8\pi\nu^2}{c^3} a_\nu \epsilon^{-E_\nu/kT} \mathrm{d}\sigma_{\mathrm{A}} \mathrm{d}\nu \mathrm{d}\sigma_\nu \\
&+ \frac{1}{k_1} \int\int\int \frac{E_{\mathrm{A}}}{kT^2} s a_{\mathrm{A}} \epsilon^{-E_{\mathrm{A}}/kT} \frac{8\pi\nu^2}{c^3} a_\nu \epsilon^{-E_\nu/kT} \mathrm{d}\sigma_{\mathrm{A}} \mathrm{d}\nu \mathrm{d}\sigma_\nu \\
&+ \frac{1}{k_1} \int\int\int -\frac{\bar{\bar{E}}_\nu}{kT^2} s a_{\mathrm{A}} \epsilon^{-E_{\mathrm{A}}/kT} \frac{8\pi\nu^2}{c^3} a_\nu \epsilon^{-E_\nu/kT} \mathrm{d}\sigma_{\mathrm{A}} \mathrm{d}\nu \mathrm{d}\sigma_\nu \\
&+ \frac{1}{k_1} \int\int\int \frac{E_\nu}{kT^2} s a_{\mathrm{A}} \epsilon^{-E_{\mathrm{A}}/kT} \frac{8\pi\nu^2}{c^3} a_\nu \epsilon^{-E_\nu/kT} \mathrm{d}\sigma_{\mathrm{A}} \mathrm{d}\nu \mathrm{d}\sigma_\nu,
\end{aligned}
\qquad (37)
$$

Examining this equation in the light of Equation 35 itself, it will be found that each of the terms on the right hand side is the average value of some property of the molecules or of the modes of vibration that enter into the reaction, we obtain

$$
\frac{\mathrm{d}\, ln\, k_1}{\mathrm{d}T} = \frac{\bar{\bar{E}}_{\mathrm{A}} - \bar{E}_{\mathrm{A}} + \bar{\bar{E}}_R - E_R}{kT^2} \qquad (38)
$$

where $\bar{\bar{E}}_{\mathrm{A}}$ is the average energy of the molecules which actually enter into the reaction, $\bar{E}_{\mathrm{A}}$ is the average energy of all the molecules of this kind in the system, $\bar{\bar{E}}_R$ is the average radiant energy of the modes of vibration

---

[1] Since σ_i must vary when ν varies, the introduction of ν into this equation is not essential, although informing.

upon participation in the reaction, and $\overline{E}_R$ is the average radiant energy of such modes of vibration whether or not they are in a reactive condition.

Equation 38 may be written in the form

$$\frac{\mathrm{d}\, ln\, k_1}{\mathrm{d}T} = \frac{E_{\text{activated}} - E_{\text{average}}}{RT^2} = \frac{E_c}{RT^2} \tag{39}$$

where $E_{\text{activated}}$ is the energy entering into the decomposition of one mol of molecules through their interaction with one "mol" of modes of vibration. E_{average} is the average energy of these elements, and their difference is E_c, which may be called the critical increment.

In obtaining Equation 39 we have completed our derivation of the Arrhenius expression for the temperature coefficient of reaction velocity, for the special case of monomolecular reactions. It should be noted that the quantity E_c, is one which will not vary much with the temperature, since neither the energy of the activated molecules and modes of vibration, nor their average energy will change rapidly with the temperature. This approximate constancy of E_c agrees with the experimental facts, as determined for example, by Daniels, for the monomolecular decomposition of nitrogen pentoxide.

4. Photochemical Rate of a Monomolecular Reaction.—In the foregoing development we have regarded a thermal monomolecular reaction essentially as a photochemical reaction, in which the activating light has its energy distributed among the different frequencies in accordance with the normal distribution in a hohlraum which has come to thermal equilibrium. By a photochemical reaction in the narrower sense we mean one in which we have monochromatic illumination. Our method of treatment will permit us to obtain important information as to the effect of monochromatic light.

Returning to Equation 35, we have as an expression for the thermal specific reaction rate,

$$k_1 = \int\int\int s a_{\mathrm{A}}\, \epsilon^{-E_{\mathrm{A}}/kT}\, \frac{8\pi\nu^2}{c^3}\, a_\nu\, \epsilon^{-E_\nu/kT}\, \mathrm{d}\sigma_{\mathrm{A}} \mathrm{d}\nu \mathrm{d}\sigma_\nu. \tag{35}$$

It is evident that for the part of the reaction which is due to frequencies between ν and $\nu + \mathrm{d}\nu$ we may write the reaction rate

$$k' = \frac{8\pi\nu^2}{c^3}\, \mathrm{d}\nu \int\int s a_{\mathrm{A}}\, \epsilon^{-E_{\mathrm{A}}/kT}\, a_\nu\, \epsilon^{-E_\nu/kT}\, \mathrm{d}\sigma_{\mathrm{A}} \mathrm{d}\sigma_\nu. \tag{40}$$

Furthermore, in accordance with measurements which have been made on black body radiation, we may write for the density of radiant energy having frequencies between ν and $\nu + \mathrm{d}\nu$,

$$\mathrm{d}u = \frac{8\pi\nu^2}{c^3}\, \frac{h\nu}{\epsilon^{h\nu/kT} - 1}\, \mathrm{d}\nu. \tag{41}$$

If then we assume, in accordance with the available experimental data, that the rate of a photochemical reaction is proportional to the intensity of illumination, we may divide Equation 40 by Equation 41 and write as an expression for *photochemical specific reaction rate*

$$k_\nu = \frac{\epsilon^{h\nu/kT} - 1}{h\nu} \int\int s a_A \, \epsilon^{-E_A/kT} \, a_\nu \epsilon^{-E_\nu/kT} \, d\sigma_A d\sigma_\nu. \qquad (42)$$

This expression is important, since k_ν is a quantity which can be determined experimentally by measuring the rate of reaction under a known intensity of illumination with monochromatic light of frequency ν. Having determined the value of k_ν over the complete range of active frequencies we may then predict the thermal reaction rate by a process of integration. This will afford a valuable check of the soundness of the theory.

We have from Equations 42 and 35

$$\int \frac{8\pi\nu^2}{c^3} \frac{h\nu}{\epsilon^{h\nu/kT} - 1} k_\nu d\nu = k_1. \qquad (43)$$

Hence the value of k_1 can be predicted from a complete knowledge of k_ν. It is hoped that quantitative photochemical experiments will be made on the decomposition of N_2O_5 suitable for testing Equation 43.

If there were only one narrow range of activating frequencies as assumed by Perrin, then it would be possible to carry out the inverse process of predicting k_ν from k_1, but in general this does not seem to be true. In the case of the decomposition of nitrogen pentoxide, Daniels predicts, on the basis of Perrin's theory, that light of wave length $1150\mu\mu$ should be photochemically active, but finds experimentally that this is not the case.

5. **Temperature Coefficient for Monomolecular Photochemical Reaction Rate.**—By the temperature coefficient of a photochemical reaction, we shall understand the change in rate produced when the temperature of the gas is raised but the nature of the monochromatic illumination is kept constant. Referring again to Equation 42, we have for the reaction rate under the influence of monochromatic illumination of frequency ν and unit energy density

$$k_\nu = \frac{\epsilon^{h\nu/kT} - 1}{h\nu} \int\int s a_A \epsilon^{-E_A/kT} \, a_\nu \epsilon^{-E_\nu/kT} \, d\sigma_A d\sigma_\nu. \qquad (42)$$

If we raise the temperature of the gas, but hold our artificially produced illumination constant, we shall vary the quantity $a_A \epsilon^{-E_A/kT} d\sigma_A$, which determines the distribution of the molecules in the different regions $d\sigma_A$, but shall leave the other quantities unaffected. We may thus obtain

$$\frac{1}{k_\nu} \frac{dk_\nu}{dT} = \frac{1}{k_\nu} \frac{\epsilon^{h\nu/kT} - 1}{h\nu} \int\int \frac{d \, ln \, a_A}{dT} s a_A \, \epsilon^{-E_A/kT} \, a_\nu \epsilon^{-E_\nu/kT} \, d\sigma_A d\sigma_\nu$$

$$+ \frac{1}{k_\nu} \frac{\epsilon^{h\nu/kT} - 1}{h\nu} \int\int \frac{E_A}{kT^2} s a_A \, \epsilon^{-E_A/RT} \, a_\nu \epsilon^{-E_\nu/RT} \, d\sigma_A d\sigma_\nu.$$

Applying the same considerations and symbols used in connection with Equation 38, we obtain as an expression for the temperature coefficient of a monomolecular photochemical reaction,

$$\frac{\mathrm{d}\, ln\, k_\nu}{\mathrm{d}T} = \frac{\bar{\bar{E}}_A - \bar{E}_A}{kT^2}. \tag{44}$$

In other words, the temperature coefficient of the photochemical reaction rate is proportional to the difference between the energy of the molecules which actually react and the average energy of all the molecules of that kind. It will be remembered that the temperature coefficient of the thermal reaction rate was proportional to the energy of the molecules *and* modes of vibration that entered into the reaction minus the average energy of these molecules and modes of vibration. Hence it does not surprise us to learn experimentally that photochemical reactions actually have in general a small temperature coefficient compared with thermal reactions. We conclude that the ability of the molecules of a substance to take up radiant energy is *on the average* but slightly affected by rise in temperature.

As far as the author knows, this is the first theoretical treatment of the temperature coefficient of photochemical reactions.

6. Di- and Poly-molecular Reactions.—Our considerations up to this point have concerned themselves strictly with the monomolecular reactions of dilute gases, although the extension to more complicated reactions and even to non-gaseous systems will in many cases be obvious.

The case of polymolecular reactions in dilute gases is somewhat different from that of monomolecular reactions. We may distinguish two steps in the process; first, the actual interaction of the molecules, which will at least in many reactions occur only between specially "activated" molecules containing more than the average amount of internal energy, and second, the continuous re-establishment of the statistical state of maximum probability for the remaining molecules as those of high internal energy are removed by the progress of the reaction.

In the case of dilute enough gases, since the number of molecular collisions can be made as small as desired by increasing dilution, it is evident that the maintenance of statistical equlibrium for the molecules of the reactants will be mainly the business of the bath of radiant energy in which they are immersed. The interaction between molecules which come into contact may conceivably take place either with or without the intervention of radiant energy.

Consider our expression for the mechanism of a chemical reaction,

$$a\mathrm{A} + b\mathrm{B} \ldots \longrightarrow c\mathrm{C} + d\mathrm{D} + \ldots \tag{1}$$

To make our considerations as general as possible let us assume that this reaction may take place with the interaction of radiant energy simultaneously from any number of modes of vibration of any frequency. Employing the same considerations that led to Equation 34, it will be found that we may write for the rate of reaction

$$\frac{-dC_A}{dT} = \Sigma\left\{s_{ijklmn}\ldots \times C_A a_A \epsilon^{-E_i/kT}\, d\sigma_i \times C_A a_A \epsilon^{-E_j/kT}\, d\sigma_j \ldots \right.$$
$$\times\, C_B a_B \epsilon^{-E_k/kT}\, d\sigma_k \times C_B a_B \epsilon^{-E_l/kT}\, d\sigma_l \ldots \times \ldots \qquad (45)$$
$$\left. \times\, \frac{8\pi\nu^2}{c^3}\, d\nu_m a_\nu \epsilon^{-E_n/kT}\, d\sigma_n \times \frac{8\pi\nu^2}{c^3}\, d\nu_o a_\nu \epsilon^{-E_p/kT}\, d\sigma_p \ldots\right\}.$$

C_A, C_B, etc., are the instantaneous concentrations of the reacting substances. The product of the factors of the type $C_A a_A \epsilon^{-E/kT} d\sigma$ is continued a times where a is the number of molecules of kind A that enter into the reaction; similarly there are b factors for molecules of Type B, etc. There are as many factors of the type $\frac{8\pi\nu^2}{c^3}\, da_\nu \epsilon^{-E_\nu/kT}\, d\sigma_\nu$ as are necessary to take care of the fact that quantities of radiant energy of more than one frequency might be drawn simultaneously into the reaction. $s_{ijklmn}\ldots$ is the chance per unit time that the indicated chemical change will occur when there is one molecule of the Type A in region $d\sigma_i$, one of Type A in region $d\sigma_j$, etc., similar considerations applying to molecules of Type B, etc., and to the modes of vibration of different frequencies. The summation is to be considered as taken for all possible regions $i\ j\ k\ l\ m\ n \ldots$, for which $s_{ijklmn}\cdots$ has an appreciable value. Cases in which no radiant energy enters into the reaction will, of course, be included if they exist. Their existence is improbable in the case of monomolecular reactions. In the case of many polymolecular reactions the interaction of radiant energy may be entirely unnecessary for the actual chemical change, although the interplay of radiant energy is necessary as we have already shown for the maintenance of the statistical state of maximum probability.

Equation 45 may be rewritten in the integral form

$$-\frac{1}{C_A^a C_B^b}\cdots\frac{dC_A}{dT} = k_1 = \int\ldots\int s(a_A\epsilon^{-E_A/kT}\, d\sigma_A)^a$$
$$(a_B\epsilon^{-E_B/kT}\, d\sigma_B)^b \ldots \left(\frac{8\pi\nu^2}{c^3}\, d\nu a_\nu \epsilon^{-E_\nu/kT}\, d\sigma_\nu\right)^n \qquad (46)$$

where the meaning of the symbolism is evident. It should be noticed that our earlier Equation 35 for specific reaction rate is merely a special example of Equation 46 for the particular case of a monomolecular reaction taking place with the inter-action of radiant energy from a single mode of vibration.

By differentiating Equation 46 with respect to the temperature, we may obtain in the same way that we derived Equation 39, a general expression for the temperature coefficient of specific reaction rate,

$$\frac{d\, ln\, k_1}{dT} = \frac{E_{\text{activated}} - E_{\text{average}}}{RT^2} = \frac{E_\epsilon}{RT^2} \tag{47}$$

where $E_{\text{activated}}$ is the actual energy of the molecules and modes of vibration which enter into the reaction of *a* mols of A with *b* mols of B, etc., and E_{average} is the average energy of these elements.

We have thus obtained equations for thermal reaction rate and for the temperature coefficient of thermal reaction rate entirely analogous to those for monomolecular reactions.

As to the photochemical reaction rate for a polymolecular reaction, we cannot make such definite statements as in the case of monomolecular reactions. Since we have come to the conclusion that the state of maximum statistical probability is maintained by the interaction of radiant energy, we are of course forced to the conclusion that all reactions are photochemical. If we illuminate a reacting gas with radiation other than that corresponding to the temperature of the enclosure, there will certainly be some frequencies which will increase the proportion of "activated" molecules over the normal and hence increase the reaction rate. More specific statements on this point, however, do not now seem possible.

7. Conditions at Equilibrium.—If we consider again our expression for the mechanism of a chemical change,

$$aA + bB + \ldots = cC + dD + \ldots \tag{1}$$

we may write in accordance with Equation 40, for the temperature coefficient of the specific reaction rate in the forward direction

$$\frac{d\, ln\, k_1}{dT} = \frac{E_{1\, \text{activated}} - E_{1\, \text{average}}}{RT^2} \tag{48}$$

and for the temperature coefficient of the specific reaction rate in the reverse reaction

$$\frac{d\, ln\, k_2}{dT} = \frac{E_{2\, \text{activated}} - E_{2\, \text{average}}}{RT^2}. \tag{49}$$

$E_{1\, \text{activated}}$ is the energy that enters into the reaction when *a* mols of A combine with *b* mols of B, etc., and $E_{2\, \text{activated}}$ is the energy that enters into the reaction when *c* mols of C combine with *d* mols of D, etc. Now it is evident that when the concentrations are such that equilibrium is maintained, *a* mols of A will combine with *b* mols of B, etc., in exactly the same time interval that it takes for *c* mols of C to combine with *d* mols of D, etc., to reform A, B, etc. Since there will be no transfer of energy to or from the system at equilibrium, it is then evident that the following equation must be true,

$$E_{1\, \text{activated}} = E_{2\, \text{activated}}. \tag{50}$$

It is also to be noted that at equilibrium we may write

$$K = k_1/k_2 \tag{51}$$

where K is the equilibrium constant. Combining Equations 48, 49, 50 and 51, we obtain

$$\frac{\mathrm{d}\,ln\,k_1}{\mathrm{d}T} - \frac{\mathrm{d}\,ln\,k_2}{\mathrm{d}T} = \frac{\mathrm{d}\,ln\,K}{\mathrm{d}T} = \frac{E_{2\,\text{average}} - E_{1\,\text{average}}}{RT^2}.$$

It is evident, however, that we may write

$$\Delta E = E_{2\,\text{average}} - E_{1\,\text{average}}$$

where ΔE is the internal energy change accompanying the reaction. We obtain

$$\frac{\mathrm{d}\,ln\,K}{\mathrm{d}T} = \frac{\Delta E}{RT^2} \tag{53}$$

and have thus deduced the well known van't Hoff equation from the principles of statistical mechanics. This is an important test of the correctness of our development.

V. Further Developments.

The foregoing development has been valuable in providing a derivation of the Arrhenius equation for the temperature coefficient of reaction rate, in providing information as to the relation between thermal reaction rate and photochemical reaction rate, in providing an expression for the temperature coefficient of photochemical reactions and generally in leading to more specific ideas as to the mechanism of chemical reactions. The work, however, has provided no method of predicting the actual magnitude of any individual reaction rate, and this must be regarded as the most important task which chemical kinetics must yet solve.

Some progress towards the solution of the problem is possible in the case of polymolecular reactions. Let us consider for example, the dimolecular reaction

$$\mathrm{A} + \mathrm{B} \longrightarrow \text{Products}. \tag{54}$$

Let us now assume that radiant energy, although necessary for the maintenance of the statistical state of maximum probability, does not enter into the actual chemical change involved in the reaction. Then, in accordance with our general Equation 46, we can write for the specific reaction rate of the above chemical change

$$k_1 = \oint\oint s a_{\mathrm{A}}\epsilon^{-E_{\mathrm{A}}/kT} a_{\mathrm{B}}\epsilon^{-E_{\mathrm{B}}/kT}\,\mathrm{d}\sigma_{\mathrm{A}}\mathrm{d}\sigma_{\mathrm{B}}. \tag{55}$$

If now we had sufficient knowledge of the quantities involved in Equation 55, it is evident that we could predict the reaction rate. The dependent and independent variables in Equation 55 are functionally related, as follows:

$$\begin{aligned} s &= s(\sigma_{\mathrm{A}},\sigma_{\mathrm{B}}) \\ a_{\mathrm{A}} &= a_{\mathrm{A}}(T) \\ E_{\mathrm{A}} &= E_{\mathrm{A}}(\sigma_{\mathrm{A}}) \\ a_{\mathrm{B}} &= a_{\mathrm{B}}(T) \\ E_{\mathrm{B}} &= E_{\mathrm{B}}(\sigma_{\mathrm{B}}) \end{aligned}$$

As to s, it is obvious that s is zero when σ_A and σ_B have such values that the molecules involved are far apart. We might further assume that s has the value unity (*i. e.*, reaction is sure to occur) when the values of σ_A and σ_B are such that the molecules have certain minimum energy contents and such that they have come into contact in the sense of the kinetic theory. Hypotheses of this type have led to useful considerations in the hands of Trautz and W. C. M. Lewis.[1] Any really satisfying solution of the problem, however, would necessitate much more information than we now have as to the nature of the functional relationships of the type

$$E_A = E_A(\sigma_A)$$

connecting the energy of a molecule with its coördinates and momenta. Such information will become available as our knowledge of atomic structure increases, and this is a field where great advances may be expected in the near future. As to the functional relationships of the type $a_A = a_A(T)$, these can be obtained with the help of Equation 25 as soon as the nature of the relationships $E_A = E_A(\sigma_A)$ is known.

In conclusion, although the considerations of this paper have dealt solely with reactions in dilute gases, the general nature of their extension to concentrated gases, non-gaseous systems, and even non-homogeneous systems, will be evident even if exact mathematical treatments are not now possible.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF AMHERST COLLEGE.]

THE STANDARDIZATION OF WEIGHTS.

BY A. J. HOPKINS, J. B. ZINN AND HARRIET ROGERS.

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In order that the student beginning quantitative analysis should acquire, at the very first, a thorough manipulative knowledge of the balance, it has been our custom to provide, as a first exercise, the standardization of his box of weights. This has proved in the past an excellent method of accomplishing the result indicated and in addition he has obtained a knowledge of the relative values of his weights.

During the progress of such a standardization, from the fractional denominations to the 50 g. weight, any error, however slight, is multiplied until at the end a not inconsiderable but factitious correction is accumulated. Richards, in his excellent and well known contribution,[2] has given us a method of redistributing this error according to the relative values of the weights. This method of calculation is now in general use.

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[1] *Loc. cit.*

[2] THIS JOURNAL, 22, 144 (1900).

The present paper suggests a slight modification now being followed by students in the Amherst College laboratory, consisting of the introduction of checks at fixed intervals in the progress of the work.

Three considerations have influenced the authors to this result. In the first place, a system of checks by converting the long process into a series of short exercises, makes it possible to use single hours—an advantage when the student's time is not so continuous as one could wish.

The second consideration is the fact that the method of redistribution overlooks the possibility of compensation of errors occurring more often in the extended process, so that a 10 g. weight (*e. g.*,) upon which there should be no correction might be assigned by the redistribution a positive or negative "correction" to which it is not entitled.

The last point is a pedagogic one, namely that the division of the long process into separate exercises results in a simplification, so that this method has been found in the past few years much easier for the student to understand than any of the older methods.

In this modification, the essential thing is the use of a small box of auxiliary weights, standardized by the Bureau of Standards, and used only for checking. Our box of standards, marked "S," contains 5 weights—100 mg., 1 g., 5 g., 50 g. and 500 g.—of which only the first 4 are called into use in standardizing the ordinary box of weights. The class, after 2, or at most 3, weeks has completed its use of the little box of standards and shortly after this these 5 weights are sent to Washington for restandardization. The charges for this are very small.

By consulting the accompanying chart, which gives the series of weighings from 100 mg. to 1 g., it will be seen that each group of weighings (Col. I) corresponds to the tare maintained upon the right-hand balance pan during the weighings of that group. In Col. II are found the weights used successively on the left-hand balance pan. Differences found between weights in the same group are expressed in milligrams (by dividing the differences in "centers"—Col. IV—by the sensitivity) as given in Col. V; and from these the true values of the weights are found by algebraic addition, as given in Col. VI.

The work begins by placing a 100 mg. tare on the right-hand pan and the 100 mg. Bureau of Standards weight on the left-hand pan and finding the center of oscillation. Since the value of this weight (marked "S") is known, the center thus found is used as the unit for comparison in the next 3 weighings, (*b*), (*c*) and (*d*). A 200 mg. weight, as tare, is then placed on the right-hand pan and Group II is carried through in the same way. At the end of Group IV, a second standard weight is reached—the one g. weight of the Bureau, and here it is desirable to break the progress of the successive weighings long enough to check the final weighing, which contains all accumulated errors, against the new standard weight. In the illustration, this amounts to +0.79 mg.

CHART I.

Name B.................... Balance No. I........ S = 2.1....

I. Group.	II. Denominations.	III. Centers.	IV. Diff's.	V. Mg.	VI. Values.	VII. Corr. values.
I.	(*a*) 100 mg. (S)............	+1.15	......	......	100,10	100,10
	(*b*) 100′..................	+1.05	+0.10	—0.05	100,05	99,96
	(*c*) 100′..................	+1′.01	—0.14	—0.07	100,03	99,94
	(*d*) 50 + 20 + 10′ + 10″+ R.....................	+1.05	—0.10	—0.05	100,05	99,96
II.	(*a*) 100 (S) + 100′.........	—0.25	......	......	200,15	200,06
	(*b*) 200...................	—0.02	+0.23	+0.11	200,26	200,08
III.	(*a*) 200 + 100′ + 100″ + 100(S).................	—0.67	......	......	500,44	500,09
	(*b*) 500...................	—0.73	—0.06	—0.03	500,41	500,01
IV.	(*a*) III (*a*) + III (*b*).......	+0.70	......	......	1.000,85	1.000,06
	(*b*) 1 g. (S)...............	+0.45	—0.25	—0.12	1.000,73	999,94
		Check: True value, 1 g. (S) =			0.999,94	999,94
					Error = + 0,79	

On passing on to that portion of the standardization which runs from one g. to 5 g., as given on the succeeding Chart II (furnished to the student, but not shown here) this error is automatically discarded, for here the work begins by making the "center" found for the standard one g. the new unit of reference for all weighings of Chart II. The weighings of this chart may be checked in the same way at the end, against the third standard weight which is the 5 g. weight, of the Bureau. Chart III, which completes the work up to 50 g., is covered in a similar manner.

Returning now to Chart I, it will be evident that it would be possible to distribute the total error by subtracting from the value given in Column VI aliquots of the total positive error, or by adding, in case the error is negative. The correction for each 100 mg. will be $^1/_9$ of the total error (*i. e.*, 0.088 mg. in the illustration) rather than $^1/_{10}$, since the standard 100 mg. weight does not share in this distribution. The result of this process is exhibited in Column VII.

The illustration chosen shows a portion of the work of a student finding a rather large final error. This has been selected in order that the process of redistribution as shown in Column VII may be made clearer. By careful checking the final error should be less than 0.1 mg.

Charts II and III have not been presented in this paper, since they are arranged in the same way as Chart I. The sequence of weighings and the method of checking is essentially the same.

It may be unnecessary to add that there is no advantage claimed for the use of standards, as absolute. It will be apparent, however, that in a system of checks it is necessary to use standards. The theoretical objective is, of course, solely to have the weights accurately compared *inter se*. But there is also the desideratum, when the exercise is given to students who are using the balance for the first time, that the method should appeal to them as simple and easy to grasp.

AMHERST, MASS.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA.]

HYDROLYSIS OF ZIRCONYL CHLORIDE AND SULFATE AT ZERO AND TWENTY DEGREES.

BY F. P. VENABLE AND D. H. JACKSON.

Received September 17, 1920.

The hydrolysis of zirconyl chloride has been measured at room and higher temperatures by Ruer[1] and a partial table given by Ruer and Levin[2] for zirconyl sulfate at room temperature. It was thought desirable to repeat these for varying dilutions and to determine both the progress and extent of hydrolysis. To throw further light, if possible, upon the reaction, experiments were carried out with a precipitant, iodic acid, which forms a practically insoluble compound with a portion of the combined zirconyl radical and carries down with it the fully hydrolyzed zirconyl hydroxide. At least this is one explanation of its action.

The 2 stable salts, zirconyl chloride and zirconium sulfate, were chosen for the purposes of the investigation. The latter is readily hydrolyzed to the zirconyl sulfate on the addition of water. These salts were freshly prepared and their purity carefully tested. The hydrolysis depends upon 3 factors—concentration, temperature, and time. In these experiments the temperature was held constant and separate series were carried out for each degree of dilution.

The apparatus used in making the conductivity measurements consisted of a modification of the Arrhenius conductivity cell, a Wheatstone bridge, and a small induction coil with telephone receiver. The measurements were made with 0.2, 0.1 and 0.01 *M* solutions for the sulfate and chloride. Readings were taken at 5-minute intervals when the hydrolysis was fairly rapid, and at increasing intervals as it slowed down. The first reading was taken immediately after solution. At the expiration of 3 or 4 hours the changes were so slight that the readings were stopped, since it was difficult to maintain the constant temperature for many hours or days. The relative conductivity is given in reciprocal ohms.

It will be noticed that at both 0° and 20°, and especially at the higher concentration, there is a brief period of temperature adjustment. This

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[1] Ruer, *Z. anorg. Chem.*, 43, 282 (1905).

[2] Ruer and Levin, *ibid.*, 46, 449 (1905).

is more pronounced at 0° and is doubtless due to the heat of solution. After expiration of 3 to 4 hours the change in conductivity is so slow as to amount almost to an equilibrium in the reaction. This may be due to the reversing influence of the liberated acid or to the formation of some definite product of hydrolysis which is more resistant to the action of water. These results corroborate those of Ruer, who found that further notable increase in hydrolysis was brought about only after many hours or on heating to boiling. On standing for some time after boiling the resistance increased to a slight extent, showing a reversal of the reaction or partial removal of the free acid.

TABLE I.—EXPERIMENTS WITH $ZrOCl_2$.

Time elapsed in minutes.	0°. 35.50 g. in l.	0°. 17.75 g. in l.	0°. 1.775 g. in l.	20°. 35.50 g. in l.	20°. 17.75 g. in l.	20°. 1.775 g. in l.
First reading.	0.11307	0.05194	0.01014	0.16700	0.10799	0.01215
5	0.08877	0.04929	0.01008	0.16072	0.11055	0.01213
10	0.08500	0.04920	0.01009	0.15957	0.11292	0.01218
15	0.08383	0.05010	0.01014	0.15905	0.11545	0.01227
25	0.08356	0.05153	0.01027	0.16191	0.11672	0.01241
35	0.08469	0.05250	0.01041	0.16500	0.12220	0.01252
45	0.08500	0.05331	0.01055	0.16734	0.12472	0.01264
55	0.08560	0.05413	0.01066	0.17129	0.12806	0.01285
75	0.08681	0.05451	0.01080	0.17261	0.13057	0.01299
95	0.08763	0.05619	0.01090	0.17360	0.13251	0.01311
115	0.09053	0.05641	0.01096	0.17492	0.13392	0.01321
145	0.09245	0.05719	0.01103	0.17558	0.13586	0.01328
175	0.09282	0.05729	0.01104	0.17558	0.13670	0.01333
205	0.09436	....	....	....	0.13670	0.01333

TABLE II.—HYDROLYSIS OF ZIRCONYL SULFATE, $ZrOSO_4$.

Time elapsed in minutes.	0°. $ZrOSO_4 = 20.26$ in 1000 cc.	0°. $ZrOSO_4 = 2.026$ in 1000 cc.	20°. $ZrOSO_4 = 40.52$ in 1000 cc.	20°. $ZrOSO_4 = 20.26$ in 1000 cc.	20°. $ZrOSO_4 = 2.026$ in 1000 cc.
First reading.	0.10067	0.01275	0.24800	0.13178	0.01389
5	0.10000	0.01263	0.24550	0.13108	0.01385
10	0.10000	0.01272	0.24550	0.13190	0.01385
15	0.10044	0.01313	0.24700	0.13322	0.01389
25	0.10209	0.01328	0.24875	0.13553	0.01408
35	0.10297	0.01353	0.25167	0.13678	0.01430
45	0.10418	0.01376	0.25500	0.13822	0.01449
55	0.10528	0.01397	0.25750	0.13982	0.01469
75	0.10682	0.01401	0.26167	0.14107	0.01481
95	0.10803	0.01408	0.26582	0.14196	0.01495
115	0.10880	0.01414	0.26822	0.14232	0.01507
145	0.10935	0.01421	0.27166	0.14286	0.01511
175	0.11011	0.01423	0.27332	0.14335	0.01514
205	0.11011	0.01425	0.27332	0.14335	0.01514

Zirconium sulfate, $Zr(SO_4)_2$, was used for the next series of experiments. It has been shown that on the addition of water this immediately hydrolyzes, forming a crystalline substance. The reaction is $Zr(SO_4)_2 + 4H_2O \longrightarrow ZrOSO_4.H_2SO_4.3H_2O$. This appears in the older literature as $Zr(SO_4)_2.4H_2O$. As the sulfate is less soluble than the chloride, it was found impossible to make a 0.2 *M* solution at 0°. In this series the temperature adjustment is noticed again but is slighter. The equilibrium is reached after the same lapse of time.

Precipitation with Iodic Acid.

These experiments were carried out with zirconyl chloride only. Solutions of known strength were prepared and 25-cc. portions were withdrawn at definite time intervals. In these the iodic acid solution was added from a buret until a drop gave no further precipitate. This does not give the end-point with great accuracy, but sufficient to mark the change of ratio of the iodic acid to the zirconyl radical present. The results obtained give an indication of the extent of the hydrolysis.

TABLE III.—PRECIPITATION WITH IODIC ACID.

Time elapsed in minutes.	0°. ZrO=0.5330.		0°. ZrO=0.2665.		0°. ZrO=0.02665.		20°. ZrO=0.5330.		20°. ZrO=0.2665.	
	IO_3.	ZrO/IO_3.	IO_3.	ZrO/IO_3.	IO_3.	ZrO/IO_3.	IO_3.	ZrO/IO_3.	IO_3.	ZrO/IO_3
1st measure	1.242	0.421	0.752	0.353	0.192	0.134	0.875	0.609	0.542	0.492
10	1.189	0.448	0.664	0.400	0.175	0.152	0.664	0.803	0.472	0.564
20	1.101	0.483	0.577	0.462	0.158	0.169	0.612	0.871	0.437	0.609
30	1.066	0.500	0.560	0.476	0.140	0.190	0.577	0.923	0.402	0.663
50	1.031	0.517	0.542	0.492	0.123	0.216	0.551	0.966	0.367	0.726
70	0.997	0.534	0.533	0.500	0.114	0.233	0.525	1.011	0.350	0.757
90	0.979	0.544	0.525	0.511	0.105	0.253	0.508	1.049	0.341	0.775
120	0.962	0.554	0.507	0.525	0.105	0.253	0.491	1.081	0.338	0.788
150	0.962	0.554	0.498	0.535	.....	.....	0.483	1.106	.....	.....

It is noteworthy that there is here also indication of the initial effect of temperature adjustment and that there is a decrease in the amount of iodic acid necessary for precipitation until at the expiration of about 3 hours the change becomes very slight. The iodic acid forms a compound with the zirconyl radical, liberating the hydrochloric acid. This compound is practically insoluble in water or weak mineral acids. When precipitated this carries with it such of the colloidal zirconyl hydroxide as may have been formed by hydrolysis. It has been shown by Venable and Smithey[1] that when this precipitate is treated with hot or cold water much of the iodic acid may be washed out. It is interesting to note that after the lapse of 2 or 3 hours a practical equilibrium or period of slow change is reached in all 3 dilutions. When the rate of change per minute is examined it will be found that there are fluctuations. Sometimes these show a reversal from increase to decrease, and again the opposite is indicated. This is true both of the resistance and extent changes.

In examining Table V the recurrence of certain ratios will be observed,

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[1] Venable and Smithey, THIS JOURNAL, 41, 1722 (1919).

for instance, the end-points in the first 2-ratio columns and the ratios between 0.450 and 0.480. Some light is thrown on these by the experiments of Venable and Smithey. The ratio 0.456 would correspond to a hydrolyzed product $ZrO(OH)_2.2ZrO(IO_3)_2$, or to a zirconyl iodate in which $^1/_3$ of the molecules had undergone hydrolysis. Such a product was obtained by these investigators when the precipitation was made in cold, concentrated solutions and the precipitate was freed from the filtrate by suction without washing. The ratio 0.533 corresponds to a product $3ZrO(OH)_2.4ZrO(IO_3)_2$, in which 3 out of 7 molecules had been hydrolyzed. This was obtained when the precipitate was formed from dilute solutions and washed with a limited amount of water at room temperature. The ratio 0.914 corresponds in the same way to $2ZrO(OH)_2.ZrO(IO_3)_2$, in which 2 out of 3 molecules have been hydrolyzed. Here the precipitate was washed with hot water in increased amount. A ratio 1.218, corresponding to $3ZrO(OH)_2.2ZrO(IO_3)_2$, where 3 out of 4 molecules had been hydrolyzed, was obtained after prolonged washing with hot water.

Summary.

1. The hydrolysis of zirconyl sulfate and chloride has been examined both by relative conductivity and by a precipitation method. The temperatures were 0° and 20°, respectively. Three different dilutions were used and the effect of the time factor noted.

2. There appears to be an initial temperature adjustment on dissolving the salts. Afterwards there is a decrease in the resistance until after about 3 hours an equilibrium or period of very slow change is reached.

3. In the experiments with iodic acid there is also indication of an initial adjustment. The extent of the hydrolysis is indicated. The equilibrium or period of slow change is reached in 2 to 3 hours.

Chapel Hill, N. C.

[Contribution from the Kent Chemical Laboratory of the University of Chicago.]

SURFACE TENSION AND MOLECULAR ATTRACTION: ON THE ADHESIONAL WORK BETWEEN MERCURY AND ORGANIC LIQUIDS.[1]

By William D. Harkins and E. H. Grafton.

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Most of the papers on molecular attraction make use of one of the equations of state in order to calculate the internal pressure of pure substances in the liquid state. It is evident that such equations give a very uncertain basis for the determination of results which represent more

[1] Published in abstract in *Proc. Nat. Acad. Sci.*, **5**, 569–73 (1919). For similar work with water and organic liquids see Hardy, *Proc. Roy. Soc. London* (A) **88**, 303–33 (1913); Harkins, Brown and Davies, This Journal, **39**, 354–64 (1917); and Harkins, Clark, and Roberts, *ibid.*, **42**, 700–12 (1920).

than an approximation. Moreover, they give no indication at all of the magnitude of the attraction between 2 liquids made up of molecules which are unlike. In studying the attraction between 2 dissimilar liquids use will be made of equations which are not only applicable to such a case but are also entirely accurate, since they are based upon thermodynamics alone. The first of these is the equation of Dupré,

$$W_A = -\Delta\gamma = \gamma_1 + \gamma_2 - \gamma_{1,2}$$

where γ_1 and γ_2 represent the free surface energies per square centimeter of the 2 liquids, $\gamma_{1,2}$, the free surface energy of their interface, and $-\Delta\gamma$ is the decrease of free energy when the surfaces of the two liquids come together to form an interface. The work done is represented by W_A which represents the amount of work done by the molecular attraction between the 2 surfaces. An equation which is more closely related to the molecular attraction is that derived in an earlier paper from this laboratory,

$$E_A = -\Delta E_s = (\gamma_1 + l_1) + (\gamma_2 + l_2) - (\gamma_{1,2} + l_{1,2}),$$

where l represents the latent heat of a surface, E_s the total surface energy, and $-\Delta E_s$ the total decrease in surface energy per square centimeter when the two surfaces come together. This equation may be put in the form

$$E_A = E_{s_1} + E_{s_2} - Es_{s_{1,2}} = \int_{s_0}^{\infty} F ds$$

or the integral of the molecular surface attraction is equal to the change in the total surface energy.

This paper will present data from which the adhesional *work* between organic liquids and mercury may be calculated, and the paper which follows will deal with the total adhesional *energy*. Both papers will give extensive data on the surface and interfacial tension and energy relations of mercury.

Experimental Procedure.

The surface and interfacial tension measurements were made in an apparatus somewhat similar to that used for work on surface tension by Morgan, but in the modified form designed by Harkins and Brown.[1] However, it was found necessary to allow the drop to hang from the inside instead of the outside edge of the capillary tip. The apparatus will be described in the second paper, but some mention will be made here of the experimental difficulties of the work, which are not inconsiderable.

The surface tension was in all cases calculated by the use of the correction curve determined experimentally by Harkins and Brown.[2]

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[1] THIS JOURNAL, 37, 1656–76 (1915).

[2] *Ibid.*, 41, 499–524 (1919).

Surface Tension of Mercury in Air at 20°.

In order to illustrate the character of the results obtained by the method, the data obtained in air are given in Table I. A small constriction was made in the capillary of the tip such that with from one to 1.5 cm. head of mercury the natural period of fall per drop was 30 minutes. In order to shorten this time suction was applied for 0.5 minute, after which it took from 40 to 180 seconds for the drop to fall. The experiments (B), (C), (D), were made 2 months after Experiment A.

TABLE I.—SURFACE TENSION OF MERCURY IN AIR AT 20°.

	Diam. tip cm.	Drop wt. G.	$f\left(\frac{r}{V^{1/3}}\right)$.	Surface tension dynes.
A..........	0.12524	0.1345	0.7289	459.4
B..........	0.12524	0.1359	0.7290	464.3
C..........	0.1369	0.1475	0.7218	465.8
D..........	0.1438	0.1519	0.7157	464.6

TABLE II.—SURFACE TENSION OF MERCURY IN WATER.

					Corrected wt. drop.
A..........	0.12524	0.1179	0.7234	375.4	0.1092
B..........	0.12524	0.1176	0.7234	375.6	0.1091
C..........	0.14375	0.1317	0.7076	374.5	0.1221
			Average =	374.8	

It will be noted that in spite of the fact that tips of different diameters were used, and that in both tables determinations were made 2 months apart, there is very good agreement between the results.

Table III gives similar results for other liquids. The ether which was used had been standing over sodium for several months, was then distilled off from fresh sodium, allowed to stand over mercury, distilled again, and stored over mercury. On long standing a black residue formed, similar to that formed when ordinary ether is placed over mercury. The ether was redistilled before using. A similar black residue formed in nitro-ethane on long standing in contact with mercury. The liquids used were carefully purified.

TABLE III.—SURFACE TENSION OF MERCURY IN DIFFERENT LIQUIDS AT 20°.

	Density.	Diam. tip. cm.	Drop weight. G.	Corrected drop wt. G.	$f\left(\frac{r}{V^{1/3}}\right)$.	Surface tension dynes.	
			In Ethyl Alcohol.				
A.......	0.7893	0.12524	0.1120	0.1054	0.7214	364.6	.....
B.......	......	0.14375	0.1255	0.1182	0.7049	364.0	364.3
			In Ethyl Ether.				
A.......	0.7119	0.12524	0.1165	0.1104	0.7228	398.3	.....
			In Octyl Alcohol.				
A.......	0.8252	0.12524	0.1083	0.1016	0.7197	351.7	.....
			In Nitro-ethane.				
A.......	1.0528	0.14375	0.1338	0.1234	0.7084	378.2	.....

TABLE III (*continued*).

	Density.	Diam. tip, cm.	Drop weight. G.	Corrected drop wt. G.	$\left(\frac{r}{V^{1/3}}\right)$.	Surface tension dynes.	
In Nitrobenzene.							
A.......	1.185	0.14375	0.1240	0.1131	0.7005	350.5	.....
In Carbon Disulfide.							
A.......	1.262	0.12524	0.10538	0.09555	0.7178	339.3	.....
In Carbon Tetrachloride.							
A.......	1.593	0.12524	0.1197	0.1054	0.7249	362.2	.....
In Chloroform.							
A.......	1.485	0.12524	0.1163	0.1034	0.7233	356.6	.....
In Methylene Chloride.							
After standing over mercury for 4 weeks.							
A.......	1.337	0.14375	0.1225	0.1104	0.7035	340.7	.....
In Ethylidene Chloride.							
A.......	1.175	0.12524	0.1063	0.0971	0.7181	336.8	.....
In Ethylene Dibromide.							
A.......	2.178	0.12524	0.1124	0.0934	0.7205	326.0	.....
In Acetylene Tetrabromide.							
Before being placed over mercury.							
A.......	2.97	0.12524	0.1192	0.0931	0.7240	320.3	.....
After standing over mercury for 4 weeks.							
B.......	......	0.14375	0.1229	0.0959	0.7038	293.3	....
In Methyl Iodide distilled from silver foil.							
A.......	2.2786	0.12524	0.1051	0.0874	0.7176	304.1	....
After standing over mercury for 6 weeks.							
B.......	......	0.14375	0.1026	0.0854	0.6933	266.6	....
Distilled from Mercury.							
C.......	......	0.14375	0.1149	0.0956	0.7000	296.4	....
In Ethyl Iodide distilled from silver foil.							
A.......	1.9375	0.12524	0.1089	0.0929	0.7192	321.7	.....
After standing over mercury for 6 weeks.							
B.......	......	0.14375	0.1056	0.0905	0.6950	282.7	.....
Distilled over mercury.							
C.......	......	0.14375	0.1180	0.1011	0.7103	312.9	.....
In Benzene.							
A.......	0.8784	0.12524	0.1092	0.1021	0.7197	353.2	.....
In Hexane.							
A.......	0.6630	0.12524	0.1133	0.1077	0.7220	371.53	.....
In Octane.							
A.......	0.7022	0.12524	0.1092	0.1035	0.7201	357.9	.....

It will be noted that when the interfacial tension of mercury was determined in acetylene tetrabromide, methyl iodide, or ethyl iodide, which had been standing for some weeks over mercury, the values were in all cases considerably lower than those obtained before such a treatment. This seemed to be due to the fact that these liquids acted slowly on mercury forming halides, which dissolved to some extent in the organic liquid and was adsorbed by the mercury surface. Similar results were obtained with fresh liquids on adding a mercury halide.

The above tables are summarized in Table IV, which gives in addition the values for the adhesional work.

TABLE IV.—THE SURFACE TENSION OF MERCURY AND ITS INTERFACIAL TENSION AND ADHESIONAL WORK IN DIFFERENT ORGANIC LIQUIDS AT 20°.(a)

	Density.	Wt. Hg. in drop. G.	Tip.	f.	γ liquid.	γ interface.	W_A.
Air	......	0.1359	1	0.7290	.....	464.35	......
Air	......	0.1475	2	......	.....	465.8	......
Air	......	0.1519	3	......	.....	464.6	......
Hexane	0.6630	0.1092	1	0.7220	19.24	378.1	121.71
Octane	0.7022	0.1092	1	0.7201	21.52	374.6	131.0
Nitro-ethane	1.0528	0.1338	3	0.7084	32.52	378.2	139.2
Ethyl Alcohol	0.7893	0.1120	1	0.7214	21.7	364.38	142.3
Ethyl Alcohol	0.7893	0.1255	3	0.7049	21.7	364.00	142.7
Carbon Tetrachloride	1.593	0.1197	1	0.7247	26.95	362.2	149.75
Chloroform	1.485	0.1163	1	0.7233	26.51	356.6	154.91
Benzene	0.8789	0.1092	1	0.7197	28.9	362.8	150.3
Octyl Alcohol	0.8252	0.1083	1	0.7196	27.51	351.7	160.8
Methylene Chloride	1.337	0.1098	1	0.7199	26.52	340.7	170.82
Methylene Chloride	1.337	0.1225	5	0.7035	26.52	342.5	168.00
Ethylidene Chloride	1.175	0.1063	1	0.7181	25.71	336.8	173.91
Nitro Benzene	1.185	0.1240	3	0.7005	43.55	350.5	178.05
Carbon Disulfide	1.262	0.1054	1	0.7220	34.49	339.3	180.19
Water	0.9982	0.1179	1	0.7234	72.8	374.8	183.00
Water	0.9982	0.1317	3	0.7076	72.8	375.6	182.20
Ethyl Iodide	1.937	0.1089	1	0.7192	31.79	321.7	195.09
Ethyl Iodide	1.937	0.1056	3	0.6950	31.79	282.7	234.09
Ethyl Iodide	1.937	0.1180	3	0.7013	31.79	312.9	204.89
Ethylene Bromide	2.178	0.1124	1	0.7205	37.89	326.00	196.89
Methyl Iodide	2.278	0.1051	1	0.7176	30.39	304.1	211.29
Methyl Iodide	2.278	0.1026	3	0.6933	30.39	266.6	248.79
Methyl Iodide	2.278	0.1149	3	0.7000	30.39	296.4	219.99
Acetylene Tetrabromide	2.97	0.1192	1	0.7240	48.21	320.3	212.91
Acetylene Tetrabromide	2.97	0.1229	3	0.7038	48.21	293.3	229.91

(a) When several values are given for one liquid, Table III should be consulted for an explanation of the apparent discrepancy.

The above table represents the preliminary results obtained. A more complete table and a discussion of the results, will be found in the paper which follows.

CHICAGO, ILL.

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

THE SURFACE ENERGY OF MERCURY AND THE ENERGY RELATIONS AT THE INTERFACE BETWEEN MERCURY AND OTHER LIQUIDS.[1]

BY WILLIAM D. HARKINS AND WARREN W. EWING.

Received September 24, 1920.

Introduction.

The measurement of interfacial tension offers a convenient method for determining the energy relations—free energy, latent heat, total energy of surface formation, and work of adhesion—between liquids insoluble, or slightly soluble, in each other. While considerable is known concerning these relations in the case of liquids, but little is known about the energy relations existing between solids and liquids at their interface. Such knowledge would be of special value in connection with problems concerning lubrication and the flotation of ores. It is difficult to measure either the force or the work of adhesion between a solid metal and a liquid, but the adhesional work may be determined from measurements of surface tension provided the metal is in the liquid state. Among the metallic elements mercury and gallium[2] have freezing points lower than the boiling points of ordinary liquids. Some of the low melting alloys also possess this characteristic.

This paper gives the energy relations obtained by measuring the surface tension of mercury at various temperatures, the interfacial surface tension between mercury and various liquids and vapors at 20°, and the interfacial surface tension between mercury and 4 organic liquids at different temperatures between 0° and 60°.

Surface Energy Relations of Mercury in a Vacuum.

Since the values found in the literature[3] vary by a hundred ergs per square centimeter, it was thought best to make a new determination of the surface tension of mercury in a vacuum. Also it is necessary to know the surface tension of mercury at several temperatures if the total energy relations at the interfaces is to be calculated.

A new form of apparatus was constructed for measuring the surface tension of mercury *in vacuo*. Fig. 1 represents the final form of the apparatus used.

The carefully purified mercury was distilled from Flask A into Reser-

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[1] A similar paper on the energy relations at the interface between water and organic liquids will be presented in THIS JOURNAL by Harkins and Cheng. For the preliminary work on mercury see the preceding paper by Harkins and Grafton.

[2] We hope to work on the surface energy relations of both liquid and solid gallium in this laboratory.

[3] Cenac, *Ann. chim.*, [VIII] 29, 298 (1913).

voir B after the system had been evacuated by means of a mercury condensation pump, with the pump still running. The spirals C, C′ permitted the reservoir to be raised so that the mercury flowed over and dropped from the tip T. The height of B was adjusted so that a drop formed in 2 minutes. Determinations were made in which the time of formation of the drop was varied between one and five minutes and it was found that the weight of the drop is independent of the time whenever the period is greater than 1.5 minutes. When 10 drops had fallen into D, the tube was sealed off and another 10 drops collected. The sealed portions of the tube containing the mercury were broken and the mercury weighed in a weighing bottle. A constriction was made in the capillary tube at E to control the speed of drop formation. In the diagram F represents a ground glass joint and G a mercury seal. It was found necessary to have the portion of the capillary tube above the tip perfectly smooth and clean. Any roughness of the glass or the presence of a particle of dust caused the mercury column to break apart at that point, so that many tubes had to be tried before a satisfactory one was found. A 2-stage mercury condensation pump was used in producing the vacuum, and the system was evacuated for 2 hours before starting the collection of drops. The pressure was so low that no pressure could be detected by the use of a McLeod gage. The results obtained are given in Table I. The surface tensions, Col. 2, are calculated from the equation $\gamma = mg/2\pi\tau\psi(\tau/v^{1/3})$ and the latent heats from the Clapeyron equation $l = -T\,\Delta\gamma/\Delta T$.

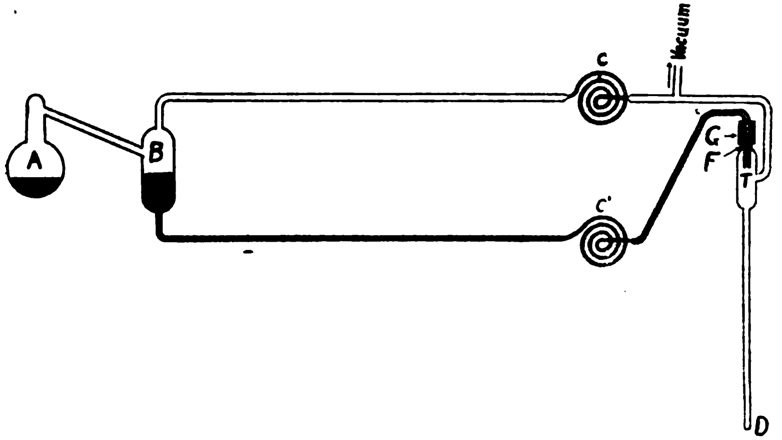

Fig. 1.—Apparatus for the determination of the surface tension of mercury in a vacuum produced by a mercury diffusion pump.

The following results indicate that the Ramsay-Shields constant is 0.96 instead of the normal 2.12 for mercury, or the entropy of surface formation for the area occupied by a molecule is 0.0135×10^{-14} ergs.

TABLE I.—THE FREE ENERGY, LATENT HEAT, AND TOTAL ENERGY OF SURFACE FORMATION OF MERCURY *in Vacuo*.[a]

(All values in ergs per sq. cm.)

Entropy of surface formation = 0.22 ergs per degree per cm^2.

1. Temp. ° C.	2. Free energy of surface formation.	3. Latent heat of surface formation.	4. Total energy of surface formation.	5. $\frac{\Delta\gamma/\Delta T}{\gamma_0}$.
0	480.3	60.1	540.4	0.00046
10	478.3	62.3	540.6	......
20	476.1	64.5	540.6	......
30	474.2	66.7	540.9	......
40	471.3	68.9	540.2	......
50	469.4	71.1	540.5	......
60	467.1	73.3	540.4	......

[a] Instead of the value 480.3 dynes at 0° as given here, Cenac found 460 or 467, according as the correction used was that determined by calculations by Lohnstein or by the experiments of Rayleigh. Cenac, Cantor (*Wied. Ann.*, 1894, p. 423) and Siedentopf (*Diss.* Göttingen, 1897) obtained the value 0.0005 for $\frac{\Delta\gamma/\Delta T}{\gamma_0}$ instead of 0.00046 as given above.

Apparatus and Experimental Procedure.

The interfacial tensions were measured by means of the drop-weight apparatus devised in this laboratory for measuring the surface tension of liquids in air, but in a slightly modified form. Since mercury does not wet glass, the drops form and fall from the circumference of the bore and not from the circumference of the tube. Also, because of the high density of mercury, it is not possible to cause the drops to form slowly enough if the mercury siphons through the tube under the influence of gravity. A third difficulty, not met with in making similar measurements with water, is that the mercury surface adsorbs very readily any water in the organic liquid, the dry organic liquid dissolving enough moisture from the air in a few minutes to appreciably change the interfacial surface tension.

To overcome the first of these difficulties a tip made from a metal which mercury wets was first tried, but it was found that with a metal such as platinum enough of the metal dissolved in the mercury to change its surface tension. Glass tips were, therefore, used in all measurements recorded. To insure a sharp edge to the bore of the tube at the end where the drop broke off, the bore was filled with Woods metal before grinding. All the tips used had a diameter of 1.2 mm. to 1.4 mm., and this was accurately measured.

To control the speed of flow of mercury, a very small constriction (B, Fig. 2) was made in the siphon. After considerable practise it was found possible to make a constriction so small that with a head of mercury of 2 centimeters in the reservoir A, a drop weighing one g. would take 5 minutes to form at the end of the tip C. In practise suction was applied at D until the drop was so large that it would fall in about one minute after the suction was released. The constriction was so small that sulfuric acid could be forced through under pressure only very slowly, and so small, too, that a small particle of dust was found to clog the bore completely, thus ruining the tube for further use.

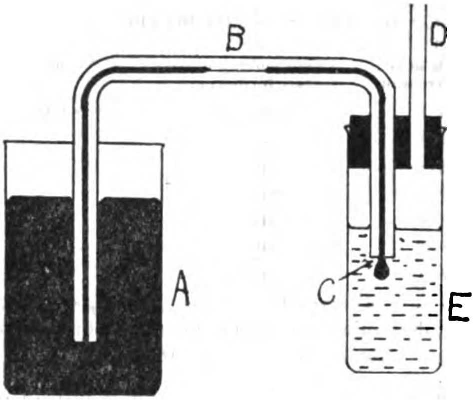

Fig. 2.—Glass parts of apparatus for the determination of the surface tension (interfacial tension) between other liquids and mercury. For a figure showing the metal parts see This Journal, 37, 1656–76 (1915).

In purifying the liquids used great care was exercised both in drying the liquids and in keeping them from contact with moist air during the experiment. It was found that the same portion of liquid could not be used for running a second set of drops, since in changing the liquid from the weighing bottle (Fig. 2, E) to another weighing bottle, in order to remove the mercury, enough moisture was taken up from the air to change the interfacial surface tension markedly.

Purification of Liquids.

The liquids used were purified by the methods given below.

Mercury.—Commercial mercury was distilled and this was then purified by electrolysis and repeated distillations according to the method recommended by the Bureau of Standards.[1]

The alcohols were treated with freshly burned quicklime for several days, distilled off, fractionally distilled and dried over metallic calcium for 2 weeks.

The **hydrocarbons** and also alcohol-free **ether** were purified by heating for several hours, in a flask containing mercury and fitted with a reflux condenser, until the black precipitate which appeared at first no longer formed. They were then fractionally distilled and dried over metallic sodium for 2 weeks.

Oleic and undecylinic acids were distilled *in vacuo*.

Carbon disulfide and di-amyl amine were fractionally distilled and the distillates dried over freshly fused potassium hydroxide.

Aniline was fractionally distilled 2 times, finally with zinc dust and hydrogen, and the colorless product was dried over potassium hydroxide.

Acetone was fractionally distilled and dried over calcium chloride.

The *halogen compounds* were distilled and kept over mercury, redistilled and always used immediately after the redistillation.

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[1] Bur. Standards, *Bull.* 4, 10 (1907).

Carefully purified aromatic hydrocarbons and ether contained an impurity, presumably a sulfur compound, which caused a black precipitate to form in the presence of mercury. After refluxing several hours with mercury, this impurity was removed.

The Interfacial Tensions at the Phase Boundary Between Mercury and Another Liquid.

TABLE II.—THE INTERFACIAL TENSION AND ADHESION BETWEEN MERCURY AND ORGANIC ACIDS.

(Liquids arranged in order of adhesional work against mercury.)

(Values in ergs per sq. cm. Temperature 20°.)

1.	2. Free surface energy of liquid. γl.	3. Free interfacial energy against mercury. γi.	4. Adhesional work against mercury (W_A) $\gamma Hg+\gamma l-\gamma i$.	5. Cohesional work against itself. (Wc) $2\gamma l$.	6. Difference. (4)—(5) S W_A-W_C.	7. Adhesional work against water. $\gamma H_2O+\gamma l-\gamma i$	8. Difference. (4)—(7) $W_{A_{Hg}}-W_{A_{H_2O}}$
Acetone	26.1	390	112	52.2	60	.....	...
Hexane	18.4	378	116	36.9	79	40	76
Ethyl ether	21.8	379	119	43.6	75	73	46
Octane	21.7	375	123	43.5	79	44	79
Di-amyl Amine	24.6	371	130	49.2	81	.....	...
Propyl alcohol	23.7	368	132	47.4	85	96	36
Nitro-ethane	34.9	378	133	69.8	63	.....	...
Ethyl alcohol (G)	22.4	364	134	44.8	89	85	39
Secondary octyl alcohol	27.0	359	144	54.0	90	.....	...
Carbon tetrachloride (G)	26.6	362	146	53.3	93	56	90
Toluene	29.0	359	147	58.0	89	67	80
Benzene	28.8	357	148	57.6	90	67	81
m-Xylene	29.0	357	148	38.0	90	64	84
o-Xylene	29.0	359	149	58.0	91	67	82
p-Xylene	27.0	361	151	54.0	97	64	87
Chloroform (G)	27.1	357	151	54.3	97	67	84
Undecylinic acid	30.6	353	154	61.2	93	103	51
iso-Butyl alcohol	22.8	343	156	45.6	110	94	62
Octyl alcohol (G)	27.5	352	157	55.0	102	92	65
Methylene chloride (G)	26.5	341	165	53.0	112	71	94
Nitrobenzene..(G)	43.4	350	169	86.8	82	91	78
Ethylidene chloride (G)	24.6	337	170	49.2	121	.....	...
Carbon disulfide	31.4	336	171	62.8	108	56	115
Aniline	42.6	341	177	85.2	92	110	67
Water (G)	72.8	375	178	145.6	32	145.6	32
Oleic acid	32.5	322	187	65.0	122	90	97
Ethyl iodide (G)	28.2	322	191	56.4	135	63	128
Ethylene bromide (G)	38.7	326	193	77.4	116	75	118
Methyl iodide (G)	35	304	207	70	137	.....	...
Acetylene tetrabromide (G)	49.6	320	213	99.3	114	84	129
Mercury	476.0	...	(952)	952	...	178	774

Values marked (G) obtained by Dr. E. H. Grafton.

Adsorption of Vapors on a Mercury Surface.

Preliminary experiments were made on the surface tension of mercury in air saturated with vapors of volatile liquids. The results are only approximate as the only precaution taken to control the concentration of the vapor was to let the apparatus stand for an hour at 20° ±0.1 with a few drops of the liquid in the bottom of the weighing bottle (Fig. 2, E). In benzene vapor the surface tension was found to be about 394, in ether vapor about 389 and in carbon disulfide vapor about 370 ergs per sq. cm. This shows a lowering of the free-surface energy of mercury of 80 to 100 ergs per sq. cm. and gives values approximating those found in liquids. This indicates a *strong positive adsorption* of these vapors on a mercury surface.

An attempt was made to measure the adsorption of nonylic acid in water solution by mercury but the results were not concordant. The solution could not be kept from creeping up into the tube and thus displacing the mercury. The same difficulty was met with in the case of some of the organic liquids. Monochloro-acetone in particular would displace the mercury for a distance up into the tube of from 1 to 2 cm. This is probably caused by the attractive forces between the liquid and glass being stronger than the forces keeping the mercury in contact with the glass. The interfacial tension against benzaldehyde could not be determined because in it a white skin formed about the mercury drop and supported the drop until it became abnormally large. The skin then broke letting the drop fall through.

Accuracy of the Experimental Work.

As has been stated, in all of this work the mercury was dropped down from the sharp inside edge of the capillary tube, or from what is called an open tip. This method, as was found by Harkins and Brown, is not so accurate as that in which what is termed a closed tip is used, so the results should not be expected to attain the precision better than 0.1% such as was obtained in work on water and other liquids in their work. The precision attained in the present work seemed to be of the order of 1%—that is, results on the same liquid agreed to within 1% even after long periods of standing, provided the liquid was kept carefully sealed in the interim, though opening the bulb to the ordinary air of the laboratory would often allow enough moisture to be absorbed to cause a lowering of several per cent. in the interfacial tension. However, such manipulation as this is inexcusable.

Two important sources of error have been mentioned in the previous section. First, the organic liquid may creep up the capillary tip between the mercury and the wall of the glass capillary, as was the case with monochloro-acetone, and with an aqueous solution of nonylic acid. However, in such cases the results obtained were altogether irregular and erratic, with a variation as large as 25%. The very regular results obtained in connection with the data presented here give a reasonable basis to the assumption that this error was avoided. In order to do this, however, it was necessary to use a small tip, with a diameter less than 2 mm. in order to give a bulging drop, so that the mechanical forces would cause the mercury to press tightly against the edge of the tip. Second, there was no evidence of the formation of a quasi-solid film except with benzaldehyde, where the results were *entirely erratic* and *abnormally high*, and in the case of the halogen derivatives, which gave very consistent and low results. In all other cases the mercury remained extremely bright, and consistent results were obtained. Attempts to obtain the interfacial tension by dropping the liquid upward through the mercury failed, since with the experimental arrangements at hand it was found impossible to control the drop sufficiently well. The results obtained *in vacuo* are believed to be the most accurate thus far obtained with mercury. Any small differences noted in the data of the preceding and of the present paper are not due to the drop weight method as employed, but to the later removal of impurities, small traces of which may change the values greatly.

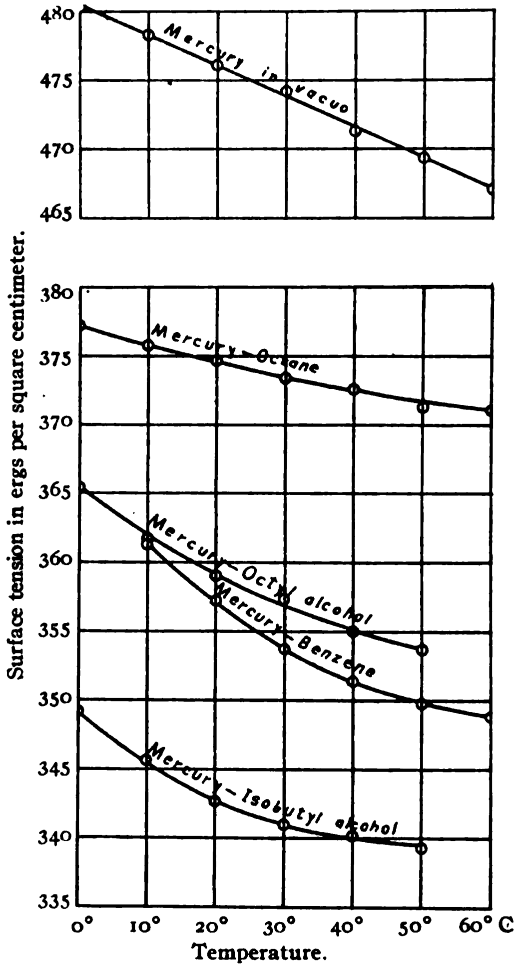

Fig. 3.—The free surface energy (or surface tension) of mercury *in vacuo* and at the interface with other liquids.

Discussion of Results.

The data presented in the tables of this and of the preceding paper indicate that the adhesional work between a mercury surface and the surface of an organic liquid is always greater than that between the organic

TABLE III.—THE ADHESIONAL WORK AND ENERGY AND THE SURFACE TENSION AT THE INTERFACE BETWEEN MERCURY AND VARIOUS ORGANIC LIQUIDS.

1. Temp. °C.	2. Free surface energy of mercury. γHg.	3. Free surface energy of organic liquid. γ_l.	4. Free interfacial energy against mercury. γ_i.	5. Adhesional work against mercury. $\gamma\text{Hg}+\gamma_l-\gamma_i$.	6. Cohesional work against itself. $2\gamma_l$.	7. Difference (5)—(6) W_A-W_C.	8. Adhesional work against water. $\gamma\text{H}_2\text{O}+\gamma_l-\gamma_i$.	9. Difference (5)—(8) $W_A\text{Hg}-W_A\text{H}_2\text{O}$.	10. Free interfacial surface per degree. $\left(\frac{\Delta\gamma}{\Delta T}\right)_i$.	11. Latent heat of interfacial surface formation. $l_i=T\frac{\Delta\gamma}{\Delta T}$.	12. Total energy of interfacial surface formation. $E_i=\gamma_i+l_i$.	13. Total adhesional energy, $E_a=\gamma\text{Hg}+\text{Hg}+\gamma_l+l_l-(\gamma_i+l_i)$.
						iso-Butyl Alcohol.						
0	480	24.3	349.1	155	49	106	....	..	0.48	130	479	106
10	478	23.5	345.6	156	47	109	....	..	0.31	87	433	153
20	476	22.7	342.7	156	45	111	....	..	0.21	62	405	184
30	474	22.0	341.0	155	44	111	....	..	0.14	42	383	206
40	471	21.3	340.2	152	43	109	....	..	0.09	28	368	217
50	469	20.5	339.3	151	41	110	....	..	0.05	16	355	230
						Secondary Octyl Alcohol.						
0	480	27.9	365.4	143	56	87	95.4	48	0.38	104	469	93
10	478	27.2	361.7	143	54	89	92.7	50	0.33	93	455	108
20	476	26.3	359.0	143	53	90	89.9	53	0.25	73	432	132
30	474	25.5	357.3	143	51	92	87.2	56	0.20	61	418	147
40	471	24.7	355.0	141	49	92	84.5	56	0.13	41	396	170
50	469	23.8	353.6	140	147	93	81.8	58	0.10	32	386	181
						Octane.						
0	480	23.7	377.2	127	47	81	48.0	79	0.16	44	421	145
10	478	22.7	375.8	126	45	81	46.1	80	0.14	40	416	151
20	476	21.8	374.7	123	44	79	43.8	79	0.12	35	410	158
30	474	20.8	373.4	121	42	79	41.9	79	0.11	33	406	163
40	471	19.8	327.6	118	40	78	40.0	78	0.09	28	401	169
50	469	18.8	371.3	117	38	79	38.2	79	0.08	26	397	174
60	467	17.9	371.1	114	36	78	36.2	78	0.06	20	391	181
						Benzene.						
10	478	30.4	361.3	147	61	86	69.1	78	0.50	142	503	106
20	476	28.9	357.2	148	58	90	66.7	81	0.37	108	465	144
30	474	27.6	353.7	148	55	93	64.6	83	0.26	79	433	177
40	471	26.3	351.4	146	53	93	62.2	84	0.16	50	401	208
50	469	24.9	349.8	144	50	94	59.7	84	0.14	45	395	214
60	467	23.6	348.8	142	47	95	57.2	85	0.09	30	379	230

[1] NOTE.—The derived values given in Cols. 10 to 13 inclusive, should not be expected to represent more than an approximation, since their calculation involves a differential. The values given in these columns are presented in order to represent only the general order of magnitude of the quantities involved. On the other hand, the data of Cols. 2 to 9, are, it is believed, quite accurate, probably within 1 or 2% in the case of the larger numbers.

[illegible] entropy of interface formation.

substance and water, and also greater than that between the organic liquid and itself, or the cohesional surface work. A second point of interest is that for about half of the substances investigated, the *difference* between the adhesional work against mercury and that against water is nearly constant, and between 80 and 90 ergs. This is true for such liquids as the paraffin hydrocarbons, benzene, toluene, and xylenes, carbon tetrachloride, chloroform, and nitrobenzene, so the *work of attraction is by no means entirely specific.* On the other hand the adhesional work is specifically high toward water in the case of the alcohols, water itself, organic acids, acetone and ether, while that toward mercury is very high in the case of the compounds containing iodine, bromine, and sulfur, and somewhat high for oleic acid, which indicates that the specific effects are very marked.

The values for $W_A - W_C$ or of S, the *spreading coefficient*, are all large, which would indicate that if what may be termed the Neuman triangle principle is applicable to spreading all of these liquids should spread on a *pure* mercury surface. That they often do not spread is not surprising, when it is considered that a mercury surface in ordinary air is always covered by a film of water and other vapors, as may be seen by consulting the preceding section of this paper. It will be seen that this spreading coefficient *increases* with the temperature for *iso*-butyl alcohol, *secondary* octyl alcohol, and benzene, but *decreases* for octane.

Table III shows that the *adhesional work decreases* rapidly with increase of temperature, while the *total adhesional energy increases.*[1] The latent heat of the interface between mercury and another liquid decreases rapidly as the temperature increases, while the latent heat of most ordinary surfaces increases with the temperature, and the total energy of interface formation also decreases, though not so rapidly.

Since the halogen and sulfur atoms in organic compounds show a specifically high attraction for the mercury surface, it is to be expected that at such an interface the molecules should be oriented in such a way that the halogen or sulfur atoms are turned toward the mercury.

CHICAGO, ILL.

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[1] It is evident that at higher temperatures the adhesional energy must also decrease.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF McGILL UNIVERSITY.

THE PROPERTIES OF PURE HYDROGEN PEROXIDE. I.

BY O. MAASS AND W. H. HATCHER.

Received September 25, 1920.

There are few chemicals which have found a greater variety of uses than hydrogen peroxide. Every year the literature becomes enriched with papers dealing with reactions in which hydrogen peroxide in dilute solution plays an important part. On the other hand, the properties, both physical and chemical, of pure hydrogen peroxide are for the greater part unknown and the accuracy of those properties which have been tabulated is subject to doubt. The present paper deals with the preparation of pure anhydrous hydrogen peroxide and the determination of some of its properties.

To treat hydrogen peroxide historically and describe its multitudinous reactions in dilute solution would fill several volumes and would not come within the scope of this paper. It will therefore be most convenient in the following account of the various steps in which hydrogen peroxide was purified and its properties investigated, to refer at each stage to any previously published work which suggests similarity to that being discussed.

What might be termed the "raw product" from which the pure hydrogen peroxide was to be derived consisted of a 3% solution prepared from commercial barium peroxide in the ordinary way. The principal impurities were sodium sulfate, phosphoric, sulfuric and hydrochloric acids and traces of several inorganic salts. This 3% solution was concentrated to 30% by means of the sulfuric acid concentrator[1] described in another paper, a yield of 95% being obtained. The details of various yields obtained under different conditions of temperature and pressure are of no particular scientific interest but may be made the subject of a separate paper in an industrial journal.

Subsequent purification of the hydrogen peroxide from the 30% solution was effected in 3 stages: (1) distillation to remove non-volatile impurities; (2) concentration of the 30% solution (now pure) to 90%; (3) separation of pure hydrogen peroxide out of this concentrated solution by fractional crystallization.

The first stage required considerable development as the 30% solution was found to be very unstable. This was due to the fact that all the impurities had been concentrated as well as the hydrogen peroxide. Generally, the decomposition at room temperature was found to average 1% per day so that, up to the moment when they were to be distilled, the solutions were kept at 0°, at which temperature the rate of decomposi-

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[1] THIS JOURNAL, 42, 2571 (1920).

tion is much less. A sulfuric acid pump[1] was used in the distillation in order that during this process the pressure might be kept at a minimum.

Fig. 1 is drawn to scale, and shows the relative sizes of Distilling Flask B, Receiver G and barrel of sulfuric acid Pump M. The volume of the latter is some 6 liters, this being more than 3 times the volume of all the rest of the apparatus to be evacuated. The sulfuric acid pump is regulated by a control valve[2] leading to J, O being connected to a Geissler water-pump, O N acting as a sulfuric acid seal. The reservoir K is filled with commercial sulfuric acid (95%), one filling being sufficient for innumerable distillations. D is a water condenser and is connected to a spiral, F, and a receiver, G, both of which are placed in vessels filled with ice. The tubing H connecting the receiver G to the sulfuric acid pump is about one cm. in diameter, the height of H being the barometric height in terms of sulfuric acid. A manometer, E, indicates the pressure at any moment. The distilling flask, B, with ground glass neck, has a volume of about 300 cc. and is heated by means of a water-bath. In the first experiments, 200 cc. of the 30% solution was placed directly in this flask at one time. The apparatus was constructed wholly out of glass tubing.

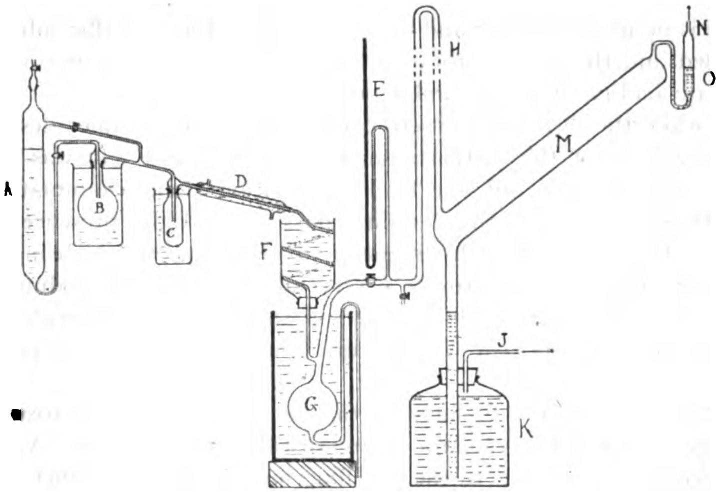

Fig. 1.

The sulfuric acid pump works automatically, going through one cycle in less than one minute with the aid of a small electric pre-evacuator connected through the valve to J. The water-bath is heated to about 60° so that this is the maximum temperature reached by the hydrogen

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[1] O. Maass, This Journal, 41, 53 (1919).

[2] *Ibid.*

peroxide solution during the distillation. At first the distillation takes place without a great loss of hydrogen peroxide due to decomposition. The solution gradually becomes more concentrated, the impurities concentrating more rapidly than the hydrogen peroxide, which, at the temperature of the distillation and under a pressure of one cm., vaporizes with the water and is condensed in the receiver. Towards the last, the impurities are concentrated to such an extent that they are precipitated in the solid form along the sides of the distilling flask. Then a certain amount of decomposition takes place. It is here that the value of the sulfuric acid pump becomes evident for it is possible to keep the pressure below one cm. of mercury in spite of the oxygen liberated. Any oxygen liberated is in an active form and mercury or any other metallic substance is corroded and the oil of a rotary pump thickens—another reason why the sulfuric acid pump is a desirable one to use.

For a while the distillations were carried out in the manner described above. Analysis of the distillate showed a 60% yield. It was found that the 40% loss was not due to decomposition alone, examination of the gelatinous residue in the distilling flask showed the presence there of a fairly large amount of hydrogen peroxide, suspected of being held in the form of hydrogen peroxide of crystallization by the sodium sulfate. It was found impossible to drive off this hydrogen peroxide without having to heat it to a temperature where vigorous decomposition resulted.

An attempt was made to increase the yield of hydrogen peroxide by what may be termed a vacuum steam distillation. A vessel, A, filled with water, was connected to the distilling flask B in the manner shown in the diagram. During the latter part of a distillation, when the solution had become very concentrated, the proper tap was opened slightly. The water entering the distilling flask was immediately vaporized, as the pressure in the apparatus was below the vapor pressure of water. Consequently a stream of water vapor was bubbled through the solution, the object being to displace the hydrogen peroxide. A fair measure of success attended this innovation, and the yields rose to 75%.

A further improvement was made by heating the empty distilling flask, B, to 65° and placing the hydrogen peroxide solution in A from which it was admitted into the heated flask drop by drop at the rate at which it evaporated. Thus the major portion of the distillate was kept cool during the greater part of the time of distillation. The yield was increased considerably, being over 90% in many cases. Three hours are required for the distillation of half a liter. Furthermore, it was found advisable to place a trap between distilling flask and the water condenser. This trap (C in Fig. 1), a thin-walled wash-bottle, was heated continuously to a temperature of 70°. This temperature, somewhat higher than that in the distilling flask, prevented the condensation of any hydrogen peroxide. The function of the trap is of course to catch any small drops of liquid which might be carried along during the distillation.

A few further particulars of the precautions taken to insure the absolute purity of the hydrogen peroxide solution may be in place. The tap leading from A to the distilling flask B (by means of which the speed of entry of the hydrogen peroxide was regulated) was not greased. The same applies to the ground glass joints fitting into the tops of Flasks B and C. The latter were immersed in the heating water to such an extent that the ground glass joints were below the surface. The leak from the outside was negligible, as especially well-fitting joints had been chosen; the slight quantity of water working through was also distilled over, but the absence of tap-grease made certain that no organic impurity would find its way into the distillate. The bottom of Receiver G was connected to a glass tube as shown in the diagram, the end of the tube being sealed off before the distillation. After the distillation, this end of the tube was filed off and the peroxide forced out of the receiver by air pressure into the vessel in which it was to be stored. Thus, at no time during the distillation, or afterwards, was the peroxide brought into contact with any material except glass. Previous to a distillation, the whole apparatus was filled with chromic acid cleaning mixture by suction. The cleaning solution was removed after a few hours and the whole apparatus flushed out with distilled water until it was certain that no trace of the cleaning mixture remained.

A qualitative analysis of the distillate showed the absence of all nonvolatile impurities. Sulfuric acid was also shown to be absent, but, in those cases where the original peroxide solutions contained large amounts of chloride, a small amount of hydrochloric acid was invariably present in the distillate. In order to prevent this, the concentrated peroxide solution was made slightly alkaline with sodium hydroxide before submitting it to distillation. This procedure removed the last impurity; it was found that the distillate was now absolutely pure, although the yield was cut down considerably.

The first stage in the purification of hydrogen peroxide may be summed up by saying that if the experimental methods described above are followed, it is possible to distil 30% impure peroxide solutions, the distillate being absolutely pure and corresponding to an 85% yield.

The second stage in the process of reaching 100% hydrogen peroxide is carried out as follows. The smaller of the 2 flasks in the sulfuric acid concentrator[1] was reserved for the concentration of the pure solutions. This flask had been especially cleaned with a hot chromic acid solution and had then been scrupulously washed out with distilled water. The

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[1] THIS JOURNAL, 42, 2571 (1920).

concentration of *pure* hydrogen peroxide solutions can be carried out by means of the sulfuric concentrator without any loss whatever due to decomposition because concentrations can be rapidly carried out at low temperatures; attention was drawn to this factor in the description of the pump.

There is, however, an inevitable loss of hydrogen peroxide due to evaporation. As the solution becomes more concentrated in hydrogen peroxide, the partial vapor pressure of the peroxide itself, relative to the water-vapor pressure, becomes appreciable and, therefore, a portion finds its way into the sulfuric acid together with the water vapor. But this source of loss is also dependent on the temperature of concentration and therefore pressure. The lower the temperature, the greater is the difference, apparently, between the relative vapor pressures of water and hydrogen peroxide.

At this stage it might be well to refer to Wolffenstein,[1] who was the first to concentrate hydrogen peroxide by means of vacuum evaporation. Wolffenstein reported fairly large losses when concentrations were carried out to a high percentage concentration of peroxide in the concentration of pure solutions. Thus he obtained only a 28.3% yield when he concentrated 802 g. of 4.5% peroxide to 66.6%. The following example, taken at random from our experiments, shows in comparison what the sulfuric acid concentrator can do. 582 g. of 24.3% hydrogen peroxide was concentrated to 91.1%, 102 g. of this solution corresponding to a 65% yield being obtained. Thus, starting with a much larger quantity of peroxide (a solution containing 141 g. as compared to Wolffenstein's solution which contained 36 g.) 2.5 times the yield was obtained and the peroxide concentrated to a higher degree (91% as compared to 66%). The time required for the concentration in the example cited above was 4 hours, the temperature of the solution remaining below 0°.

The above is a typical example of the results obtained during this stage. The 30% pure peroxide solutions are concentrated to 90%, a yield of 65% being obtained. It is not advisable to try to concentrate the peroxide above this point as the loss becomes enormous. Around 98% the proportion of peroxide lost due to evaporation approaches the amount of water driven off, so that no gain is made. Apparently it is impossible in this way to dehydrate hydrogen peroxide completely.

There now remains a discussion of the last stage, which bears a similarity to a method employed by Ahrle[2] for obtaining strong concentrated solutions. Ahrle concentrated perhydrol (30% solution) to 85%, and some 50 g. of this solution was cooled to a temperature where the hydrogen peroxide crystallized out, the supernatant liquid was removed, the

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[1] Wolffenstein, *Ber.*, 27, 3307 (1894).

[2] Ahrle, *J. prakt. Chem.*, 79, 129 (1909).

remaining crystals melted, and they were then subjected again to this same process. The quantity remaining was taken as being pure, and probably was sufficiently so for the purpose for which it was made, namely, the preparation of Caro's acid. Outside of the preparation of this acid, no further experiments were carried out by Ahrle with the hydrogen peroxide, and in view of the experiments to be described, it is doubtful if the hydrogen peroxide obtained in the above cited investigation was absolutely anhydrous.

After many attempts to obtain pure hydrogen peroxide from the 90% solution by crystallization, the following technique was devised. 100 g. of solution was placed in a large tube which was itself placed in a cooling mixture in a Dewar flask. A continuous stream of dried air was sent through a glass tube of small diameter leading through its cooling mixture to the bottom of the solution. The latter was thus kept stirred. The temperature indicated by a thermometer was then regulated to be one degree below the freezing point of the solution.[1] The latter was then inoculated with a crystal of hydrogen peroxide, and the temperature of the cooling bath was lowered until half the solution had solidified; the solution being stirred vigorously during this procedure. The crystals were finally allowed to settle, the supernatant liquid poured off, and the crystals and absorbed liquid transferred to another glass tube perforated by fine holes in the bottom. The transference was effected in a few seconds, crystals adhering to the side of the first test-tube having been melted by the warmth of the hand. The crystals were pulled out by a glass rod with a hook at the end.

A larger tube constituted an outer jacket for the perforated tube to which suction was applied by means of a side arm. Dried air entered the inner tube and carried the liquid adhering to the crystals into the outer jacket. The crystals meanwhile were pressed down by means of a glass rod flattened out at the bottom. The whole apparatus previous to the admission of the crystals was cooled in an ice-bath.

Vessel A, with the crystals, was then removed from B and was suspended in a beaker, and the crystals allowed to melt. The first few drops were added to the liquid collected in B to which was also added the supernatant liquid poured off from the crystals. The tube containing the melting crystals and the beaker into which they were melting were enclosed by a large bell jar containing also a desiccating agent; this precaution being necessary to prevent the solution from taking up moisture from the air during the time required for the crystals to melt.

The solution was thus separated into 2 portions—one concentrated and the other dilute. One might have expected that the concentrated solu-

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[1] See freezing-point curve. O. Maass and O. W. Herzberg, THIS JOURNAL 42, 2569 (1920).

tion, formed from the dry melted crystals, would approach 100%, but when carried out under the conditions described above, the concentration was only of the order of 4%, the solution having increased in concentration from 90 to 94%. This degree of concentration was still less without the precautions described above. The stirring of the solution during crystal formation was essential.

A number of results obtained may be worth while giving as showing the stepping up of the concentration of the solution.

% H_2O_2 in solution.	% H_2O_2 in melted crystals.	% H_2O_2 in mother liquor.
91.1	95.3	86.9
86.9	92.0	81.9
88.2	93.4	82.0
93.4	97.4	88.2
92.0	96.8	88.0
95.0	98.3	91.9
96.8	99.0	94.0
98.7	99.9	93.0

A systematic fractional crystallization was devised to utilize all available stock to obtain the highest percentage. Starting with 100 g. of 90% solution, 50 g. of 94% and 50 g. of 85% are obtained. This is repeated with another 100 g. of 90% solution. The 2 portions of 50 g. each of the 85% solution are united, and by crystallization 50 g. of 82% and 50 g. of 90% solution are obtained. The 2 portions of 94% are also united and give 50 g. of 97% and 50 g. of 90%, and so on. Thus 400 g. of 90% solution gave 50 g. of 100%, 50 g. of 97%, 50 g. of 94%, 50 g. of 90%, 50 g. of 86% and 150 g. of 82%. After having obtained these solutions, a fresh portion of 90% is separated completely into 2 end products 100% and 82%.

In practise, of course, the crystallizations are not controlled with the exactitude which the diagram would indicate, but a variation takes place due to the variation in relative amount of crystal and solution. However, the various solutions are united according to the scheme described above, which in the end results in the same thing.

Any impurities which may have found their way into the hydrogen peroxide will accumulate in the 82% solution. After a certain amount of this solution has been collected, it is distilled and then reconcentrated. There is no real loss in hydrogen peroxide during this third stage of the process except that sticking to the sides of the glass vessels.

Now that the various stages in the preparation of the anhydrous hydrogen peroxide have been described, it is possible to discuss the process as a whole. The limits of the various stages are not chosen in a haphazard manner, but were chosen with the object of obtaining the optimum yield, the time factor being taken into account. First, the impure 3% solutions are concentrated to 30%. If this concentration is carried further, say to 50%, the impurities are concentrated to such an extent that a rapid decomposition sets in during the last part of the concentration. On the other hand, it is essential to have as small a bulk as possible when it comes to the actual distillation. If concentration is stopped at 10% instead of 30%, the time of distillation is increased and the decomposition during the distillation is tripled. It pays to carry out the first concentration to just about 30%. From the freezing-point curve it is evident that the concentration must be carried out to at least 80% before the crystallization procedure will give any results at all, and since it is the most cumbersome it is best to start crystallizing with solutions as highly concentrated as possible. On the other hand, concentrating a hydrogen peroxide solution above 90% is attended by high losses due to the vapor pressure of hydrogen peroxide itself so that 90% is perhaps the best concentration with which to end the concentration *in vacuo*.

The time required for the process is an important factor. The concentration of a liter of 3% solution requires 3 hours. The product of 4 such concentrations is distilled at one time, the distillation requiring about 3 hours. About 500 g. of the pure distillate is concentrated to 90%, 5 hours being allowed for the actual concentration. The crystallization is the most tedious, 4 or 5 sets of apparatus as described being required, so that several crystallizations may be carried out at once. The time for each crystallization may be put at 4 hours, the crystals taking a long time to melt completely.

The need of great cleanliness is essential throughout the work. The hydrogen peroxide solutions are allowed to come in contact only with glass. This glass, be it the receiver in the still or the thermometer used during crystallization, is treated with hot chromic acid solutions with subsequent washing with distilled water.

As regards the methods of analysis used, a few words may be in place. The silver test for chloride works in the presence of excess of nitric acid, the latter preventing the formation of silver oxide. The barium test can be used for the detection of sulfuric acid. Another qualitative test which is applied is the evaporation of the solution to dryness in a platinum evaporating dish to see if a non-volatile residue remains.

The amount of acid present in hydrogen peroxide solutions can be measured in the ordinary way with phenolphthalein as indicator, the hydrogen peroxide having no effect on the end-point up to 20% concentration.

The strength of hydrogen peroxide was measured by means of potassium permanganate solutions, carefully standardized by means of several samples of potassium tetra-oxalate of known purity. The use of potassium permanganate is objectionable in the presence of foreign substances, but gives perfect results in the case of pure aqueous solutions.

The experiments dealing with anhydrous hydrogen peroxide which will be described later on were carried out with a sample which had been obtained after many crystallizations as described above. The analysis of the final product, about 200 g., was carried out in this fashion. Portions weighing between 0.2 and 0.5 g. were transferred to a carefully weighed weighing bottle. This was weighed to 0.1 mg., the contents diluted with water and then transferred into an Erlenmeyer flask. The weighing bottle was washed out a number of times, the solution diluted to some 500 cc. and the requisite amount of sulfuric acid added. The permanganate solution was then added to the end-point, obtained under the same conditions as the conditions of standardization. One cc. of permanganate solution corresponded to 0.005070 g. of hydrogen peroxide, and hence the concentration could be determined to one part in 3000. The following percentages of hydrogen peroxide were obtained when the end product of all the crystallizations was analyzed: 100.02%, 99.89%, 99.91%, 99.90% and 99.94%. It may be stated here that it was the above sample which was used in the determination of the physical constants as will be described further on.

Brühl,[1] chiefly interested in determining its refractive index, prepared hydrogen peroxide by concentration alone (that is, continued evaporation *in vacuo*); his best sample, he claimed, showed 99.2% peroxide. Apart from the great losses attending this method, it is doubtful whether complete separation from water based on a fractional distillation method is possible; one need only draw attention to the futility of attempting to prepare anhydrous ethyl alcohol or anhydrous sulfuric acid by distillation. Brühl determined the refractive index, density and freezing point. These were the only properties of pure hydrogen peroxide known up to the present to which any reliability whatever could be attached, and the values obtained by Brühl will be referred to later on in comparison with those obtained by the authors.

The work described so far may be summed up as follows. Starting with commercial 3% hydrogen peroxide solutions, containing many impurities, it has been shown how the pure hydrogen peroxide can be isolated. The methods present several novel features, and a 50% yield of pure hydrogen peroxide is possible. In view of what has been said it is probable that the end product obtained was purer than any previous preparation.

Properties.

Freezing Point.—Brühl had found that the freezing point of his peroxide was —2.0°. The value found by the authors was 0.3° higher, namely, —1.70°. The determination was made by means of a Beckmann thermometer which was directly immersed in some of the pure peroxide

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[1] Brühl, *Ber.*, **28**, 2854 (1895).

placed in a test-tube. The proximity of the freezing point of hydrogen peroxide to the freezing point of water made the calibration of the Beckmann thermometer a simple matter.

The freezing point of a 96.7% peroxide solution was also determined, and found to be —4.00°. Inserting these 2 values in the freezing-point curve, determined in a former piece of work,[1] it will be seen that *dt/dc* decreases with increased concentration.

Hydrogen peroxide can be supercooled more readily than water; a temperature of —30° has been reached before the solid phase separated out.

Density.—The density of liquid hydrogen peroxide was determined by the dilatometer method. A bulb having a capacity of about 10 cc. was blown at the end of a capillary tube which was graduated in mm. One cm. length of this capillary tube was found to correspond to a volume of 0.09627 cc. It was therefore easy to calibrate the volume of one part in 10,000. The position of a meniscus between two millimeter marks was found by means of a microscope with a scale and cross hair in the eye-piece, with an accuracy of one part in 20. The bulb and stem were immersed in a glass-walled thermostat whose temperature could be regulated to 0.1°. The reading of the meniscus was naturally taken while the bulb was immersed in the thermostat.

The calibration was carried out with water after the bulb had been well seasoned. Water was deemed preferable to mercury because of the exact similarity of its meniscus to that of hydrogen peroxide, thus making unnecessary any corrections. The bulb could be easily filled with liquid by means of a glass tube drawn out into a fine capillary.

The densities tabulated below were corrected to a vacuum. The total weight of the liquid in the bulb was 15.2575 g.

Temperature. °C.	Volume. Cc.	Density.
—12.13	10.3272	1.4774
— 9.80	10.3436	1.4751
— 8.38	10.3561	1.4733
— 6.23	10.3754	1.4705
— 2.85	10.3973	1.4674
— 0.53	10.4235	1.4638
+ 0.10	10.4295	1.4631
1.20	10.4379	1.4617
3.00	10.4523	1.4597
5.55	10.4716	1.4570
8.30	10.4928	1.4541
12.60	10.5294	1.4496
15.30	10.5476	1.4465
19.90	10.5814	1.4419

The graph (Fig. 2) shows the variation of the density with the temperature, the decrease in density per degree rise being 0.001075 on the

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[1] See graph. O. Maass and O. W. Herzberg, THIS JOURNAL 42, 2570 (1920).

average. It is evident that the temperature coefficient is very large when compared to that of water. The possible source of error which at once suggests itself is a slight decomposition during the course of the measurement, the resulting bubbles of oxygen adhering to the sides of the tube. In the first place, not the smallest sign of such a bubble was visible. A large number of the density determinations were made at successive lower temperatures and a slight decomposition would result in a temperature coefficient smaller than the true one being found. The value at +0.1° was obtained first, and, after the other densities had been determined, the temperature was readjusted to the proximate temperature —0.53°. As is seen from the values of the 2 densities at these 2 temperatures no possible change in volume could have been caused by decomposition during the course of the experiments.

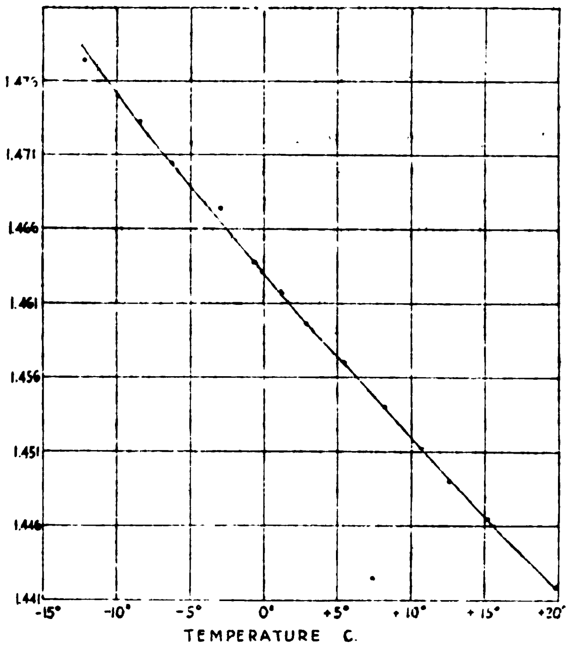

Fig. 2.

As was mentioned above, Brühl determined the density of his hydrogen peroxide. His value at 0° of 1.4584 is the closest to those obtained above, *viz.*, 1.4632 at 0°. His other determinations are obviously inexact.

Brühl's values.

Temperature. ° C.	Density.
0	1.4584
14	1.3955
18.7	1.4262
19.6	1.4392
20.4	1.4371

It might be well to insert here the values for the densities of hydrogen peroxide—water mixtures; determined at a much later date with freshly prepared samples of hydrogen peroxide. The densities were determined at 2 temperatures, 0° and 18°, the method employed being the same as the one described above.

H_2O_2, %.	Density. 0°.	Density. 18°.	Temperature coefficient.
0.00	0.99987	0.99862	0.00007
10.57	1.0419	1.0372	0.000268
22.33	1.0894	1.0815	0.000437
40.14	1.1655	1.1552	0.000573
56.70	1.2404	1.2270	0.000744
61.20	1.2610	1.2465	0.000815
73.44	1.3235	1.3071	0.000921
84.86	1.3839	1.3662	0.000980
90.42	1.4144	1.3955	0.001050
98.89	1.4596	1.4404	0.001067

In Fig. 3 these results are shown graphically.

These data are of value in checking up the value for the density of 100% hydrogen peroxide for a calculation shows that 1.4633 at 0° and 1.4442 at 18° are the value for the anhydrous peroxide. It is seen also how the temperature coefficient increases uniformly from that of pure water 0.00007 to that of the pure peroxide 0.001075.

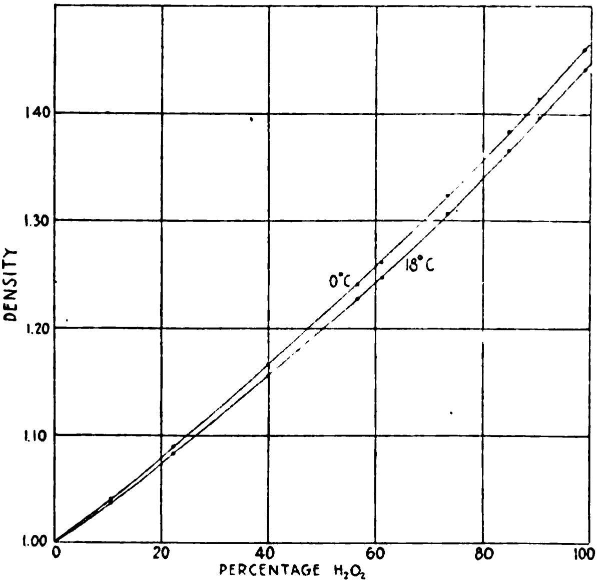

Fig. 3.

Density of Solid Hydrogen Peroxide.—Crystals of hydrogen peroxide sink to the bottom when formed in the liquid, and give the impression of being much denser than the liquid. The actual density of the solid determined as follows. The hydrogen peroxide in the dilatometer bulb was cooled until crystals formed. Most of these were allowed to melt and then the bottom of the bulb was gradually immersed in a freezing mixture kept at a constant temperature several degrees below the freezing point of the peroxide. The rate of immersion was timed to equal the rate of solid formation until all the bulb and a portion of the capillary were immersed in the freezing mixture. This insures the complete solidification without strain of the hydrogen peroxide in the bulb. The bulb was kept in the freezing mixture for one hour, the height to which the solid came in the capillary and the position of the meniscus of the liquid portion in the capillary being carefully measured. The mean temperature of this liquid portion being known, its weight can be calculated because the volume it occupies in the capillary is known. The weight of that portion of the hydrogen peroxide which is in the solid form (by far the largest portion) is then found by difference, and as its volume is also known by the position of the top of the solid in the capillary, the density of the solid follows directly. The determinations were made *ab initio* at 2 temperatures of the freezing mixture.

Temperature of solid. ° C.	Density of solid.
—4.45	1.6434
—7.45	1.6437

There is, therefore, a contraction of about 11% on solidification.

Viscosity.—The impression seems to prevail that highly concentrated solutions of hydrogen peroxide are thick, viscous, syrupy liquids, although no measurements of viscosity had been made. It was therefore rather surprising to note the results obtained when the viscosity of pure hydrogen peroxide was measured with the aid of an Ostwald viscosimeter.

The values of viscosity tabulated below are given in absolute units.

Temperature. ° C.	Viscosity.
0.04	0.01828
11.90	0.01456
12.20	0.01447
19.60	0.01272

The graph, Fig. 4, shows the variation of viscosity with the temperature. For purposes of comparison, the viscosity curve for water is plotted alongside that for hydrogen peroxide. At 0° the viscosity of hydrogen peroxide differs only slightly from that of water.

The viscosities of hydrogen-peroxide-water mixtures were also determined at a later date with the samples with which the densities of these mixtures had been determined. From the values obtained, it was seen that 0.01828 at 0° and 0.01307 at 18° were the correct values of 100% peroxide.

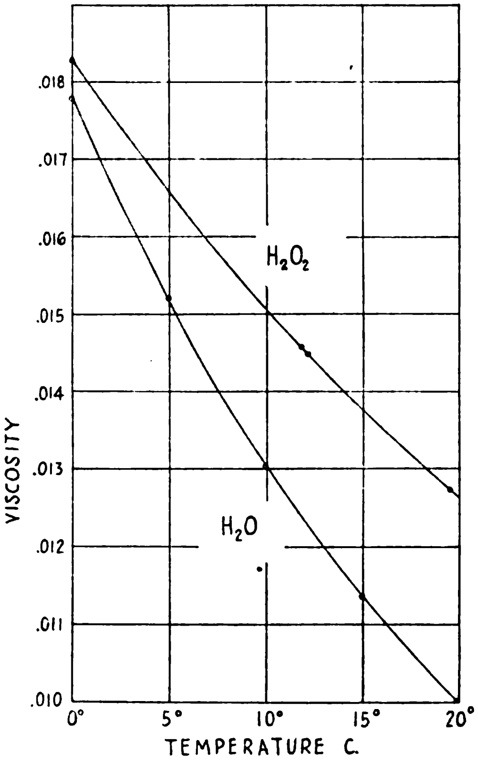

Fig. 4.—Viscosity-temperature curves for hydrogen peroxide and water.

H_2O_2. %.	Viscosity.	
	0°.	18°.
0.00	0.01778	0.01054
5.71	0.01762	0.01061
11.21	0.01740	0.01066
14.98	0.01734	0.01072
22.33	0.01758	0.01105
34.05	0.01805	0.01157
44.83	0.01846	0.01204
52.49	0.01876	0.01235
59.62	0.01900	0.01266
68.50	0.01938	0.01285
75.03	0.01929	0.01292
83.15	0.01909	0.01300
89.47	0.01873	0.01301
98.89	0.01828	....

Fig. 5 shows these results graphically. It will be seen that at 0° there is a marked minimum at 15% and a maximum at 70%. At a higher temperature, this maximum and minimum degenerate into discontinuities. The molecular compound $2H_2O.H_2O_2$ has been shown to exist[1] but this corresponds to a 48.6% concentration. Certainly a study of binary mixtures does not seem to have established that a maximum or minimum in the viscosity curve indicates the existence of a compound of the composition indicated. The viscosity-concentration curve of *iso*-amyl alcohol-formamide[2] is an example of a system showing a similarity to the hydrogen-peroxide-water curve at 0°.

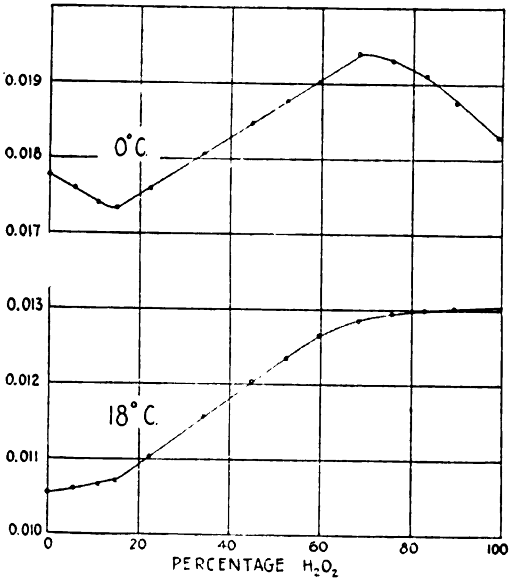

Fig. 5.

Surface Tension.—The principal interest attached to the determination of the surface tension of a substance in the past was not in the absolute value of this constant, but rather in its variation with the temperature in order that some clue might be found as to the molecular complexity of the liquid molecules. Recently some doubt has been thrown on the validity of this conception.

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[1] O. Maass and O. W. Herzberg, This Journal 42, 2570 (1910).

[2] Z. Drucker, *Z. physik. Chem.*, 76, 371 (1911).

The surface tension of hydrogen peroxide was measured by means of the capillary rise method, an apparatus being used similiar to the one described by Richards.[1] The wide arm of the tube was only 2.5 cm. in diameter so it was considered best to calibrate the capillary by measuring the surface tension of water. The angle of contact which hydrogen peroxide makes is very small; as far as could be judged by means of a microscope, the angle is zero.

Temperature. ° C.	Density.	Surface tension in dynes.
0.2	1.4630	78.73
6.2	1.4564	77.79
11.0	1.4512	77.51
13.9	1.4481	76.47
18.2	1.4434	75.94

The variations of surface tension with the temperature are plotted graphically (Fig. 6). For purposes of comparison, the surface tension of water and its variation with the temperature is plotted alongside.

On the assumptions made by Ramsay and Shields, the association of hydrogen peroxide would then be given by the following equation

$$\frac{78.73\left(\frac{34.02}{1.4630}\right)^{2/3} - 75.94\left(\frac{34.02}{1.4434}\right)^{2/3}}{18.2^\circ - 0.2^\circ} = 0.923.$$

x, the association of hydrogen peroxide is therefore $\left(\frac{2.12}{0.923}\right)^{3/2} = 3.48$. The value for water is 3.58.

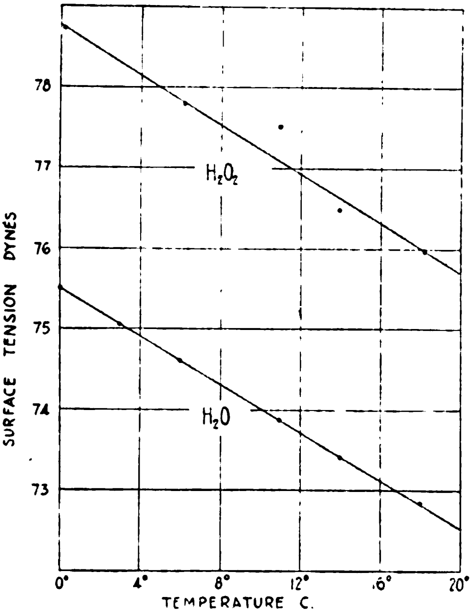

Fig. 6.

The surface tension of hydrogen peroxide is therefore, slightly greater than that of water and the association as calculated from the variation of surface tension with temperature is slightly less.

The similarity between the surface tensions of pure hydrogen peroxide and water has a certain significance in the light of recent work on surface tension by Langmuir[2] and Harkins.[3] Evidently the peroxide and water molecules are orientated in exactly the same way at the surface, and

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[1] T. W. Richards and L. B. Coombs. This Journal, 37, 1656 (1915).

[2] I. Langmuir, *ibid.*, 39, 1848 (1917).

[3] W. D. Harkins, E. C. H. Davies and G. L. Clark, *ibid.*, 39, 541 (1917).

from that point of view also it might have been predicted, when their composition is taken into account, that pure hydrogen peroxide would have a slightly greater surface tension then water.

As a means of checking up the surface tension of pure hydrogen peroxide, the surface tensions of various concentrations were measured at 2 temperatures.

	H_2O_2. %	Surface tension (dynes).
At 0°............	0.00	75.49
	12.54	75.91
	18.17	76.04
	27.22	76.26
	34.58	76.55
	56.06	77.31
	59.27	77.38
	86.31	78.30
At 18°...........	0.00	72.82
	12.78	73.22
	23.70	73.51
	28.14	73.67
	44.31	74.13
	59.27	74.67
	60.83	74.73
	79.01	75.29
	90.66	75.67

As Fig. 7 shows, the surface tensions vary in a regular expected manner, confirming the values of 78.76 dynes at 0° and 75.99 dynes at 18°, obtained from the pure 100% peroxide.

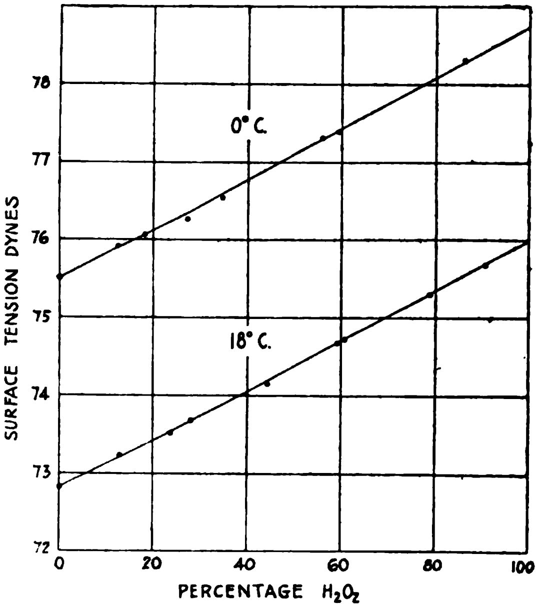

Fig. 7.—Surface tension curves for aqueous H_2O_2.

Specific Heat of Liquid Hydrogen Peroxide. Specific Heat of Solid Hydrogen Peroxide. Latent Heat of Fusion of Hydrogen Peroxide.—The measurement of the above constants of hydrogen peroxide presented certain experimental difficulties. Its chemical nature is such that it must not be allowed to come in contact with anything except glass. It was therefore decided to use the following method. A bulb, B (Fig. 8), was sealed at the end of a long glass tube, A, of small diameter, and, by means of a long drawn-out capillary, some 10 g. of peroxide was transferred into the bulb and weighed accurately. The bulb and a definite portion of the stem was then cooled to a known temperature by placing it in a metal Tube R, which latter was placed in a constant temperature mixture, H. Some phosphorus pentoxide placed at E and separated by a gauze frqm the bulb, B, presented the deposition of moisture on B. When sufficient time had elapsed for thermal equilibrium to set in, the bulb was quickly transferred into the inner vessel of a Richards' adiabatic calorimeter and the temperature changes measured in the usual way. It was considered advisable not to seal the hydrogen peroxide into a bulb so that if by chance any decomposition should occur, an explosion would be avoided.

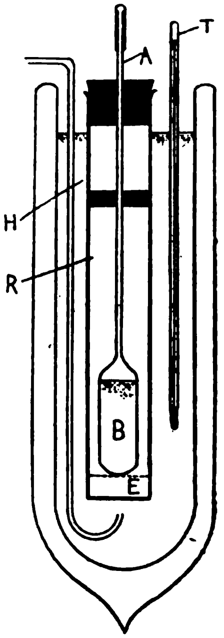

Fig. 8.

If H is the heat given by the calorimeter

$$H = ms(t - t') + k(t - t')$$

where s is the specific heat of the hydrogen peroxide, m its mass, t' the initial and t the final temperature, and k a constant involving the specific heat of the glass bulb and the mass of glass immersed in the calorimeter. The constant k was determined in 2 separate experiments by going through the procedure described above with the bulb empty. This value of k was also determined by filling the bulb with a substance having a known specific heat (water). All the values of k agreed to within a few per cent., the mean value coming out to be 2.19. Then finally to test the accuracy of the method a weighed quantity of water was frozen in the bulb and the latter placed in a carbon dioxide-ether bath (—78.2°). Taking the latent heat of ice as being 80 calories, the specific heat of ice came out to be 0.460, which is in fairly good agreement with the value 0.470 obtained by others for the specific heat of ice in that temperature range.

The values found for the specific heat of the liquid are given below.

Temperature range. ° C.	Lowering of temperature in calorimeter. ° C.	Specific heat.
0.0 to 18.5	0.3520	0.5730
0.0 to 18.5	0.3565	0.5841
—32.0 to 18.0	0.9480	0.5697

The figures for the lowering of the temperature in the calorimeter are given in order that the accuracy of the method may be judged. Evidently the experimental error is about 2%. In determining the last value given above the hydrogen peroxide was carefully cooled down in order to prevent it from freezing. As constant temperature-bath, there was employed an ether-bath described elsewhere.[1]

The specific heat of the solid and latent heat of fusion of hydrogen peroxide were determined by means of the same apparatus. The hydrogen peroxide was first of all frozen and then kept for a long time at a constant temperature well below its freezing point. By varying this initial temperature, at which the frozen peroxide was kept, in a number of experiments it was possible to determine both specific heat and latent heat by combining the results of these several experiments.

The relation between the heat H given up by the calorimeter and the various factors governing the absorption of this heat by the bulb and contents is given by the following expression:

$$H = ms(t - t') + mL + ms'(t' - t'') + k(t' - t''),$$

where m is the weight of hydrogen peroxide in the bulb (8.995 g.)

s the specific heat of the liquid (0.579),
t the final temperature,
t' the melting point of hydrogen peroxide (—1.7°),
s' the specific heat of the solid,
k the constant of the bulb (2.19),
t'' the initial temperature at which the frozen hydrogen peroxide had been kept.

Number.	t''. °C.	t. °C.	Lowering of temperature in calorimeter. °C.	S'.	L.
1	—9.0	16.87	2.124	0.4636	74.28
2	—9.0	18.87	2.109	0.4767	73.55
3	—57.2	16.07	2.909	......	.....
4	—30.5	16.47	2.556	......	.....

By combining Experiments 1 and 3 and Experiments 2 and 4, two values of each of the constants S' and L can be calculated from the experimental data. The specific heat of the liquid is 0.579, that of the solid 0.470, and the latent heat of fusion 74 calories. These last 2 values are probably correct to within 4%.

Refractive Index.—The refractive index of the pure hydrogen peroxide was determined last of all. Analysis of the purity of the sample showed that it was 99.91% pure. The method employed was the measurement of the "angle of least deviation."

For this purpose a special hollow prism was made. A thick-walled glass tube about 3 cm. long, 1.5 cm. diameter was rounded off at the bottom and 2 sides were ground out of the walls making an angle of about

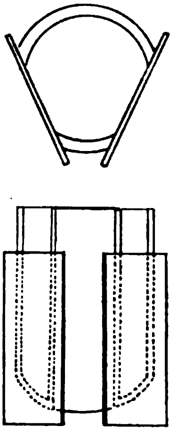

Fig. 9.

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[1] McIntosh and Maass, This Journal, 35, 536 (1913).

60°. Two plates of optical glass edges were cemented on the outside so that the hydrogen peroxide did not come in contact with the cement. The accompanying diagram (Fig. 9) gives an idea of the prism when viewed from the top and the front (plan and elevation). Sodium light was used throughout the measurements.

Substance.	Temperature. °C.	Prism angle.	Angle of minimum deviation.	Refractive index.
Hydrogen peroxide.........	22	57° 54′	27° 54′	1.4140
Hydrogen peroxide.........	22	57° 54′	27° 53′	1.4138
Solution of hydrogen peroxide 96.81%................	24	$56^\circ\ 58\frac{1}{2}'$	$27^\circ\ 4^{3}/_{4}'$	1.4043
Water....................	25	$56^\circ\ 58^{1}/_{2}'$	$21^\circ\ 55^{1}/_{2}'$	1.3330

The prism was taken apart and cleaned after the first 2 experiments described above had been made; hence the slight change in the prism angle. The refractive index of water was measured in order that the accuracy of the measurements might be tested. The value 1.3330 obtained is in excellent agreement with the recognized value.

The refractive index was one of the few measurements which Brühl undertook to make; as a matter of fact, this measurement was really the sole object of his research. The values he obtained range from 1.4005 to 1.4069, indicating that his purest sample may have been only 98% at the time of measurement.

The interest in the refractive index lies principally in the fact that this physical property is both a constitutive and an additive one for atoms. That is, the property depends both on the atom and the nature of its linkages to other atoms. For purposes of comparison, the molecular refractive power of a substance is calculated by means of the Lorenz-Lorentz formula

$$R = \frac{n^2 - 1}{n^2 + 2}\,\frac{m}{d}$$

where R is the molecular refractive power, m the molecular weight, d the density and n the refractive index.

Substance.	Density.	Refractive index.	R.
Hydrogen peroxide.........	1.4403	1.4139	5.900
Water....................	0.9973	1.3330	3.715

Brühl of course obtained a lower value for R.

Following Brühl's reasoning in determining the constitution of hydrogen peroxide, but using the figures obtained by the author:

R for water, H.OH is 3.715
R for hydrogen, H is 1.050

R for hydroxyl, OH is 2.665

Hence, if hydrogen peroxide had the constitution given by

HO — OH

R for hydrogen peroxide would be 5.33. The fact that the experimental value is higher, points to unsaturation. Hence Brühl proposed the constitutional formula

$$HO \equiv OH$$

in which there are 2 quadrivalent oxygen atoms. Now, the value for the molecular refractive power of quadrivalent oxygen has been measured by Miss Homfray[1] in a number of salts of pyrone where oxygen is supposed to be quadrivalent. Miss Homfray's value for quadrivalent oxygen, R is 2.55 and, if this value is correct, the molecular refractive power of hydrogen peroxide containing 2 quadrivalent oxygen atoms would be much larger than the experimental value obtained.

Miscellaneous Facts about Anhydrous Peroxide.—An attempt was made to determine the crystal form of hydrogen peroxide. The crystals in contact with air take up moisture even at a temperature of —10°, so that a special apparatus is being built which will make it possible to measure the angles between 2 faces of a "growing" crystal.

The dielectric constant for hydrogen peroxide has been extrapolated by Calvert[2] from a value determined for a 45% solution. The accuracy of this extrapolation is very doubtful and the dielectric constant of the pure hydrogen peroxide is now being measured. An apparatus has also been devised by means of which the conductivity of pure hydrogen peroxide and of solutions of salts in hydrogen peroxide can be measured.

The impression seems to prevail that hydrogen peroxide is very soluble in ether and ether extraction has been used as a method of concentration. Brühl in his paper refers to his non-success in making use of this method of concentration. In this connection the interesting observation was made by the authors that apparently pure hydrogen peroxide and anhydrous ether are only slightly soluble in one another. In an experiment, a small amount of hydrogen peroxide was shaken up with a larger volume of ether without an appreciable visible change in the relative volumes.

Pure hydrogen peroxide dissolves various neutral salts readily, and at high temperatures it apparently acts on glass with resulting decomposition, this fact rendering the direct measurement of the boiling point impossible until a suitable container has been found.

Pure hydrogen peroxide coming in contact with wood decomposes. The presence of even a small amount of acid in the hydrogen peroxide causes this action to become so violent that the wood catches fire. Hydrogen peroxide also decomposes when brought in contact with most metals; the pure hydrogen peroxide does not do so explosively. However, a small piece of metallic sodium caused an "intense" explosion when brought in contact with a few drops of pure hydrogen peroxide.

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[1] Miss Homfray, *J. Chem. Soc.*, **87**, 1443 (1905).

[2] Calvert, *Ann. chim. phys.*, **4**, 483 (1900).

Other observers have mentioned the effect of strong hydrogen peroxide solutions on the skin. The following observations were made when a drop of pure hydrogen peroxide was brought in contact with the skin of the hand. A violent decomposition of the peroxide occurred, and the skin became absolutely white. No blister was formed, but the skin had the appearance of being loose. No pain at all was felt although dilute solutions give burns accompanied by the sensation of pricking needles. But the most remarkable feature of all was that after 3 or 4 hours not a mark was left on the spot where the hydrogen peroxide had been applied, although, immediately after application, the appearance of the skin was sickening. Apparently the living tissue had not been hurt in the slightest. On the other hand, dead tissue is destroyed and removed by the pure peroxide.

As regards the decomposition of hydrogen peroxide solutions, experience has shown that pure aqueous solutions in a suitable container will keep indefinitely. Decomposition is caused by foreign substances getting into the solution and stronger solutions seem to be capable of destroying, in many cases, such impurities before they start the decomposition; hence, the stronger a solution is the better it "keeps." A "neutral" salt such as chemically pure sodium chloride does not in itself cause the slightest decomposition, but its presence seems to augment any decomposition caused by a second impurity. A salt consisting of a strong base and weak acid, or *vice versa,* causes decomposition to take place and the mechanism of many so-called catalyzers can be traced back to this cause. Anti-catalyzers were investigated and found to consist in every case of catalyzer-destroyers; that is, pure hydrogen peroxide does not decompose and the function of anti-catalyzers consists solely in destroying or rendering catalyzers innocuous.

Pure anhydrous hydrogen peroxide does not decompose when kept at 0°. Strong solutions even had the reputation of being highly explosive, but the apparent stability of the anhydrous substance soon caused the precautions which were initially taken to be relaxed. It must be stated, however, that in spite of the apparent stability of the pure hydrogen peroxide, all precautions are well worth taking.

An investigation of the chemical properties of anhydrous peroxide and of the physical properties indicated in the last few paragraphs is being carried out at the present time, and a discussion of the probable constitution of hydrogen peroxide had better be left until this investigation has been completed. In this paper the method of preparing absolute peroxide has been described and in conclusion, the peroxide's properties so far determined, compared to the corresponding ones of water, are tabulated.

Physical constant.	Hydrogen peroxide.	Water.
Freezing point	—1.70°	0°
Density of liquid at 0°	1.4633	0.99987
Mean coefficient of expansion —10° to +20°	0.00107	0.00000
Density of solid	1.644	0.9167
Specific heat of liquid	0.579	1.0
Latent heat of fusion	74 calories	80 calories
Specific heat of solid	0.470	0.472
Surface tension 0°	78.7 dynes	75.5 dynes
Association (Ramsay and Young) at 0°	3.48	3.58
Viscosity 0°	0.01828	0.01778
Refractive index (D) 22°	1.4139	1.3330
Molecular refractive power (D)	5.90	3.715

MONTREAL, CANADA.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF McGILL UNIVERSITY.]

THE PROPERTIES OF PURE HYDROGEN PEROXIDE. II.

BY O. MAASS AND O. W. HERZBERG.

Received September 25, 1920.

This second paper deals solely with the freezing-point curve of solutions of hydrogen peroxide and water. These solutions were prepared by concentrating 3% hydrogen peroxide and purifying the resultant concentrated solution by means of a distillation. As the only volatile impurity contained by the original solution consisted of a trace of hydrochloric acid, the final product may be looked upon as having been pure except for a trace of this acid which found its way into the distillate. In this way an 86% solution was obtained.

In order to obtain the freezing points of hydrogen peroxide-water mixtures a weighed amount of this 86% peroxide solution was placed in a test-tube. A platinum thermometer, reading to 0.1°, was immersed in it. The temperature was lowered by means of a suitable freezing mixture until crystals formed. All but a few of these were allowed to melt and then the temperature was slightly lowered until crystallization again set in, the liquid in the meantime being vigorously stirred. The solution was then allowed to warm up slowly, the freezing point being taken as the temperature at which the last crystals melted under vigorous stirring. The solution was analyzed; an adequate amount of water, sufficient to dilute the solution a few per cent. was added, and then the whole procedure repeated. In this way the freezing points at various concentrations were determined.

The solutions between the concentrations 40% and 60% hydrogen peroxide had a tendency to supercool into a thick viscous mass, but when allowed to stand at a temperature of —90°[1] crystallization started after some time.

[1] Carbon dioxide-ether under a vacuum was used as freezing mixture in this case.

Hydrogen peroxide. %.	Freezing point of solution. ° C.
86.0	—14.0
80.45	—22.7
74.0	—32.5
69.2	—39.0
67.4	—41.5
65.4	—45.5
63.05	—50.0
61.14	—52.5
58.8	—54.5
56.2	—54.3
55.06	—53.6
53.7	—52.5
49.8	—51.7
47.0	—50.8
46.21	—51.8
42.02	—46.25
37.80	—38.0
36.47	—35.7
31.96	—28.5
27.72	—23.4
22.50	—17.0
15.91	—11.1
9.96	— 6.1
4.9	— 3.4

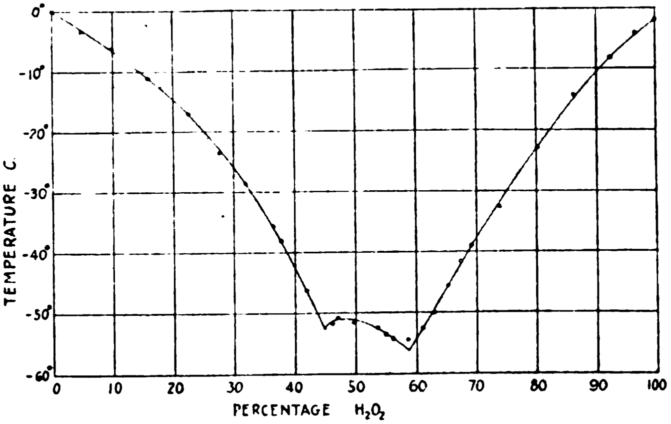

Fig. 1.

The graph (Fig. 1) of these results gives a good idea of the variation of the freezing point with concentration. It is seen that a molecular compound $2H_2O$-H_2O_2 is formed corresponding to a composition 48.6% of hydrogen peroxide.

Wolffenstein[1] had cooled down concentrated solutions of hydrogen peroxide and analyzed the crystals formed. He came to the conclusion that 2 compounds existed, represented by the formulas—$H_2O_2.H_2O$ and $H_2O_2.2H_2O$. The freezing point curve gives no evidence for the existence of the former, and it is probable that the belief in its existence was due to the difficulty of separating the solution completely from the hydrogen peroxide crystals at low temperatures. This phenomenon was considered in the first paper on hydrogen peroxide.

Summing up: the freezing point curve of hydrogen peroxide-water has been determined, and one molecular compound, namely, $H_2O_2.2H_2O$, with a melting point of —51°, has been shown to exist.

MONTREAL, CANADA.

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[1] Wolffenstein, *Ber.*, 27, 3307 (1894).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF McGILL UNIVERSITY.]

SULFURIC ACID CONCENTRATOR AND VACUUM PUMP.

BY O. MAASS.

Received September 25, 1920.

The sulfuric acid pump here described has been designed for vacuum distillation, and is particularly adapted to the special case where the liquid to be distilled is an aqueous solution which is to be freed, partly or completely, from its water content. When large quantities of solution have to be dealt with, and especially in the case where the formation of appreciable amounts of non-condensible, or of a corrosive gas occurs, the apparatus described in this paper will be found to be very efficient.

The idea occurred to the writer to use the sulfuric acid both as absorbent and evacuating medium, employing the apparatus represented by Fig. 1. The part at the left of O is drawn on a much larger scale and shows how the control which regulates the sulfuric acid pump is connected through Tube O to the latter. A detailed description of the control will be found elsewhere.[1] A′ and A are flasks which act as the containers of the liquid to be concentrated or evaporated. One or both are half filled by suction, the inlet tubes then being sealed off, or closed with ground glass stoppers. G is the sulfuric acid reservoir, and is filled to level "a;" the inlet tube to G is then also closed up. M and F lead to ordinary Geissler suction pumps. The whole system is then pre-evacuated by the Geissler pump leading to F, and when the pressure has fallen to that which the Geissler pump can conveniently establish, the control is started and admits atmospheric pressure to the space above the sulfuric acid in G. The sulfuric acid rushes up through N into B and C, reaching the level "d" in the latter, and driving all the air in D out through the capillary tube at the top of D into E. Finally a portion of the sulfuric acid itself enters E and acts as a seal; then the downward stroke takes place. The control shuts off access of atmospheric pressure to B so that the sulfuric acid is drawn back into G, out of C and D. The weight of the column of sulfuric acid between levels "*b*" and "*e*" is greater than the pressure maintained in E by the Geissler pump. Hence, the sulfuric acid "breaks" at the top of D, and in D there is therefore a perfect vacuum, which is filled with gas and vapor from C, as soon as the sulfuric acid has been lowered into N. C is filled with glass rods, about 3 mm. apart from one another, so that a large surface of sulfuric acid is left in C and absorbs any water vapor coming from A, the non-absorbable gases passing on into D. The next up-stroke of the pump forces these out of D and at the same time renews the surface of sulfuric acid on the rods in C.

Now the following feature of the sulfuric acid pump needs special em-

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[1] O. Maass, THIS JOURNAL, 41, 53 (1919).

phasis. Any water vapor which gets into D together with non-absorbable gas is absorbed in the sulfuric acid, while the non-absorbable gas is driven out. When mercury is used, the latter will drive out the gas,

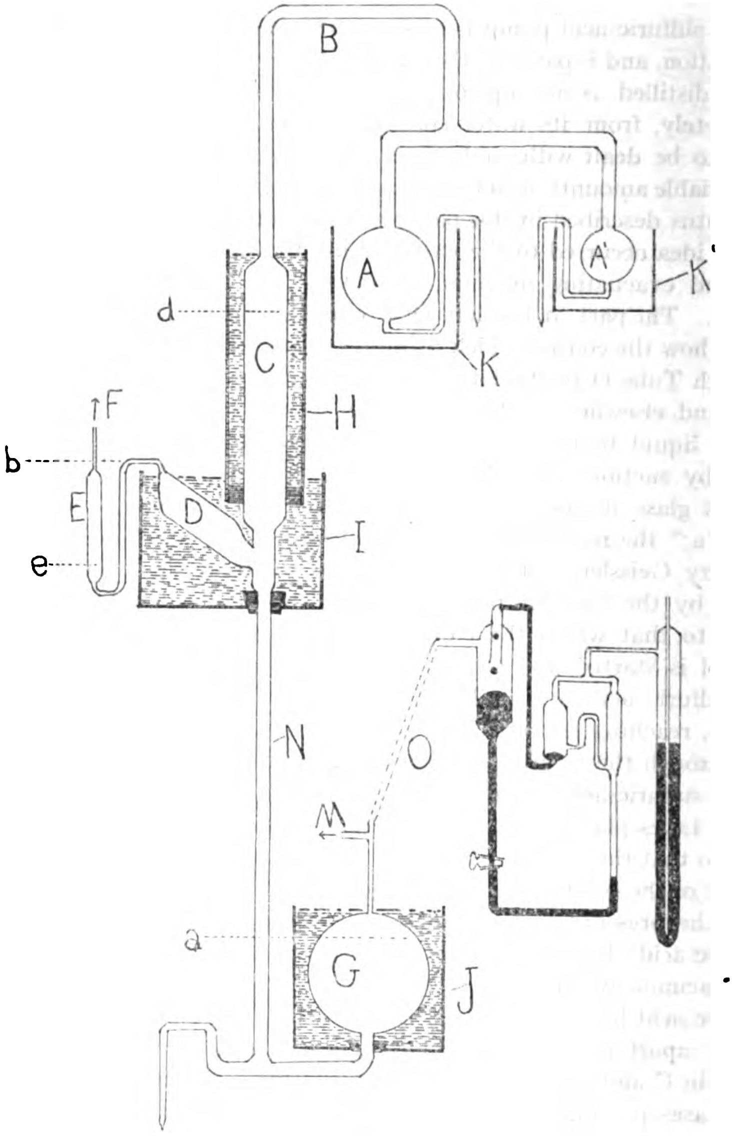

Fig. 1.

but the water vapor condenses during the up-stroke between the walls and the mercury and this water is then vaporized on the down-stroke so that in time the gas pressure in the apparatus will be that of water vapor at the temperature of the pump. In the case of the sulfuric acid, the pressure will never be greater than that of the vapor pressure of sulfuric acid itself.

C, D and G are water-jacketted to prevent the temperature of the sulfuric acid from rising on account of its water absorption. The circulation of the sulfuric acid is such as to make this quite easy. The acid coming from C is dilute and therefore lighter than that remaining in G, and hence, on entering G, rises to the top. On the next up-stroke the denser acid in G, being at the bottom, enters C first, so that the sulfuric acid is kept thoroughly mixed throughout.

The height of C and D above G can be varied anywhere between 3 and 5.5 meters, the latter being approximately the barometric height in terms of sulfuric acid. The maximum height to which the acid rises is, of course, regulated by the control. The apparatus works automatically so that after being filled and the control having been started, it requires no further attention.

The above suffices to explain the mechanism of the pump, and the next important question to consider is the relation between the temperature at which the concentration is carried out, the time it takes and the amount of acid used up.

In the first pump which was built, Flask A had a volume of 2 liters and was filled with one liter of solution to be concentrated. Sulfuric acid, Reservoir G had a column of 2.5 liters and was filled with 1.5 liters of 95% commercial sulfuric acid. Heat for the evaporation was supplied by the water-bath K, which was heated by a Bunsen burner. As soon as a vacuum was established and the sulfuric acid pump in action, the solution boiled so rapidly that when the temperature of the water-bath was kept at 30°, the temperature of the solution did not rise above 15°.

It was possible, with the aid of the sulfuric acid pump of the small dimensions quoted, to evaporate a liter of water at a temperature of 20° in 3 hours, 1.5 liters of commercial sulfuric acid being required.

Concentrations can be carried out at lower temperatures than 20°; water at 0° boils vigorously. This proved invaluable when highly concentrated hydrogen peroxide solutions were further concentrated, because the low temperature at which it was possible to do so and the small time required prevented any loss due to decomposition.

The following facts may be worth mentioning. When water is placed in A and the pump started without heating the water, the latter supercools and then freezes. The ice formed continues to evaporate and "supercools" itself several degrees below the freezing point. If the pump is stopped and the acid withdrawn into the reservoir and the ice melted, the vacuum above it being maintained during this procedure, then on restarting the pump, the water can be supercooled to an extraordinary degree before it freezes. After repeating this a number of times, the water is de-aerated to such an extent that it evaporates without boiling, the surface remaining absolutely at rest. When freezing finally begins under these conditions, if by chance ice formation starts in the center, beautiful designs appear on the surface. At times the surface is divided into regular hexagons 5 cm. in diameter. Occasionally the water has been supercooled to such an extent that $^3/_4$ of the volume solidified immediately when crystallization started. In no case was the flask broken during the ice formation.

It has been found advantageous to use another form of sulfuric acid pump as a source of vacuum in distillations when the products of the distillation were to be collected. In this case, Portion C (Fig. 1) is dispensed with, as the primary object of the sulfuric acid is to create a vacuum and not to absorb the distillate. The distilling flask is connected to a condensing coil and receiver surrounded by a freezing mixture, a tube of medium diameter replaces C and is connected to the receiver.

In the case where the distillate consists of an aqueous solution, all that has been previously said about the sulfuric acid pump holds; for instance, any vapor getting past the receiver into the body of the pump is absorbed, and therefore does not lower the efficiency of the vacuum. The relatively small density of the sulfuric acid when compared to the density of mercury, makes it possible to make the volume of the body of the pump of such a size that its capacity is comparable to the best rotary pump.

In the case of a larger sized pump, the latter is best constructed out of lead, and the Geissler pump used for "driving purposes" replaced by an electric pre-evacuator.

In some recent work on tar sands carried out by Dr. Krieble and Mr. Seyer at McGill University, it was found that in the fractional distillation of oil extracted from tar sands cracking could only be avoided by distilling under as low and as constant a vacuum as possible. Various vacuum pumps which were tried, failed to give the desired result principally because part of the oil consisted of volatile constituents which found their way past cooling coils and reduced the efficiency of the particular pump used. The sulfuric acid pump proved adequate, as the volatile portions were absorbed by the sulfuric acid without a change in the vacuum being noticeable and the vacuum could invariably be maintained for any length of time desirable.

The preparation of pure hydrogen peroxide on a large enough scale was rendered possible only by the sulfuric acid concentrator and the sulfuric acid pump described above.

MONTREAL, CANADA

[CONTRIBUTION FROM THE MELLON INSTITUTE OF INDUSTRIAL RESEARCH, UNIVERSITY OF PITTSBURGH.]

THE HYDROLYSIS OF THE SILICATES OF SODIUM.[1]

BY ROBERT HERMAN BOGUE.[2]

Received September 25, 1920.

Introduction.

An investigation of the electrical conductivity of solutions of sodium silicates was made by Kohlrausch[3] in 1893. He studied especially compounds of the formulas Na_2SiO_3 and $Na_2O.3.4SiO_2$, and also a solution of sodium hydroxide to which was added increasing amounts of silicic acid. He found that in dilute solution the metasilicate conducted the current very readily while that same compound in concentrated solution was a very poor conductor. This was also true of the more acid silicate. Kohlrausch furthermore found that if a solution of silicic acid were added to one of equivalent concentration of sodium hydroxide, the conductivity decreased constantly until the ratio $Na_2O:2SiO_2$ was attained, beyond which point no further changes were observed. The conclusions which he draws from these experiments are that in concentrated solutions the extent of hydrolytic or of ionic dissociation is very slight, while in dilute solutions hydrolysis has taken place to a very great extent. He also infers that, except in very dilute solutions, a compound of the formula $Na_2Si_2O_5$ is present.

Kahlenberg and Lincoln[4] a few years later urged that while Kohlrausch was probably correct in his conclusions yet his procedure of experimentation did not prove that the increased conductivity obtained upon dilution was due to hydrolytic rather than to ionic dissociation, and that his results were not quantitative. They accordingly proceeded to examine compounds of the compositions Na_2SiO_3, $NaHSiO_3$ and $Na_2Si_5O_{11}$ (also the potassium, lithium, rubidium and cesium salts of the corresponding acids) from the data obtained by freezing-point determinations. Their conclusions confirm those of Kohlrausch, *e. g.*, that "in solutions of sodium silicates these salts are hydrolytically decomposed into sodium hydroxide and colloidal silicic acid." They further assert that "silicates of the general formulas M_2SiO_3 and $MHSiO_3$ are practically completely hydrolytically dissociated when one gram molecule is contained in 48 liters. Silicates of the general formula $M_2Si_5O_{11}$ are practically completely decomposed by water when one gram molecule is present in 128 liters."

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[1] Presented at the 60th General Meeting of the American Chemical Society, Chicago, Ill., September 6–10, 1920.

[2] Industrial Fellow, Mellon Institute of Industrial Research, Pittsburgh, Pa.

[3] Kohlrausch, *Z. physik. Chem.*, **12**, 773 (1893).

[4] Kahlenberg and Lincoln, *J. Phys. Chem.*, **2**, 77 (1898).

A year earlier Loomis[1] had also reported that the metasilicate Na_2SiO_3 gave a greater molecular depression in freezing-point determinations than would accord with the hypothesis of ionic dissociation alone.

In the course of an investigation upon hydrogen-ion concentrations by the author it seemed that such a method applied to a study of the hydrolysis of the silicates of sodium might throw further light upon this question.

Experimental.

The apparatus used in making the measurements of hydrogen-ion concentration was as follows.

Standard Half Cells.—The standard cells consisted of 0.1 *N* calomel cells made up with the utmost care. The mercury was washed in nitric acid and 3 times redistilled. The potassium chloride was several times recrystallized from conductivity water. Redistilled hydrochloric acid was allowed to act upon an excess of the purified mercury, and the precipitated calomel washed by decantation with conductivity water for a week, then several times with 0.1 *N* potassium chloride solution, and finally made up in the latter solution for the cells. These cells were tested against standard cells and solutions of known hydrogen-ion concentration and found to be accurate to about 0.1 millivolt.

Hydrogen Cell.—The hydrogen cell was of the type suggested by Clark.[2] The platinum electrode was platinized by the method described by Findlay.[3] Electrolytic contact was made through a saturated solution of potassium chloride. The hydrogen was supplied from a commercial tank, the gas being passed through, first, an alkaline solution of potassium permanganate, second, conc. sulfuric acid, and third, water containing a little barium chloride.

Thermostat.—All of the above apparatus was enclosed in an air thermostat which was set to a temperature of 30° and the average deviation during measurements was not greater than 0.02°.

Potentiometer.—Measurements were made upon a Leeds and Northrup Type K potentiometer, the current being supplied by a single accumulator cell which was set just before and after each reading against a Weston cell which had been recently calibrated by the U. S. Bureau of Standards. Rough adjustment of the current was made by a simple pointer galvanometer, and the final adjustment by a very sensitive Type R reflecting galvanometer.

The silicates[4] which were studied consisted of 7 of various compositions, as follows:

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[1] Loomis, *Ann. Phys. Chem.*, **60**, 523 (1897).

[2] Clark, *J. Biol. Chem.*, **23**, 475 (1915).

[3] Findlay, "Practical Physical Chemistry," 1911, p. 150.

[4] The author is indebted to the Philadelphia Quartz Company for the silicates experimented upon. The analyses of these samples were furnished by William Stericker, of the Mellon Institute of Industrial Research.

Number.	Na_2O. %.	SiO_2. %.	H_2O. %.	Approximate molecular structure. Na_2O.	SiO_2.	H_2O.
1	7.0	26.9	66.1	1	4	33
2	8.98	30.3	60.72	1	$3\frac{1}{2}$	23
3	11.0	31.2	57.8	1	3	18
4	13.7	32.9	53.4	1	$2\frac{1}{2}$	13
5	17.83	36.45	45.72	1	2	9
6	24.2	38.3	37.5	1	$1\frac{1}{2}$	5
7	26.95	28.85	44.2	1	1	6

Number 7, the metasilicate, was in the form of clear well-defined crystals, and was unquestionably the pure compound Na_2SiO_3. The others were all in the form of liquid glasses. These glasses, according to Stericker,[1] probably contain various amounts of compounds of the formulas Na_2SiO_3, $NaHSiO_3$, $Na_2Si_2O_5$, in addition to colloidal silica, and sodium hydroxide. Foreign impurities are, however, practically absent.

The 7 silicates were each made up in 5 different concentrations, the number of liters containing one gram molecule of the several silicates being 3.3, 10, 20, 50 and 100 respectively. These were each examined in the hydrogen gas cell previously described, and their P_H value calculated according to the well-known formula of Nernst: $E = E_o + RT/nF \log_e C$ where E is the electrode potential corresponding to ionic concentration C, E_o is the electrolytic potential (electrode potential at molar concentration), R is the gas constant (8.32 joules per degree), T is the absolute temperature, n is the valence of the ion, F is the faraday constant (96,500 coulombs), and C is the ionic concentration of the solution. Using the value 0.337, obtained by Auerbach,[2] as the electromotive force of a normal hydrogen electrode against a 0.1 N potassium chloride-calomel electrode, and calculating for a temperature of 30°, the working formula becomes $P_H = E - 0.337/0.0601$. The corresponding values for hydroxyl-ion concentration were taken from the tables of Schmidt and Hoagland.[3]

Assuming that, first, if there were no hydrolytic dissociation whatever, the hydroxyl-ion concentration would be identical with that of pure water at the same temperature (according to Michaelis[4] 1.37×10^{-7} at 30°), and second, if the silicate had suffered complete hydrolysis the hydroxyl-ion concentration would be identical with that of an equivalent solution of sodium hydroxide at the same temperature, and if we may assume further that the hydroxyl-ion concentration is a straight-line function of the degree of hydrolysis, then it becomes an easy matter to calculate the degree of hydrolytic dissociation which the several silicates at their sev-

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[1] Stericker, personal communication.

[2] Auerbach, *Z. Elektrochem.*, **18,** 13 (1912).

[3] Schmidt and Hoagland, University of California, *Pub. Physiology,* **5,** No. **4,** 23-69 (1919).

[4] Michaelis, "Die Wasserstoffionenkonzentration," **1914,** p. 8.

eral dilutions have undergone. In doing this the degree of ionization of the sodium hydroxide at the several concentrations was taken directly, or extrapolated, from A. A. Noyes' publications[1] as follows:

Concentration, M.	Ionization, %.	(OH)⁻ion concentration.
0.66	77	5080×10^{-4}
0.2	85	1700×10^{-4}
0.1	88	880×10^{-4}
0.04	93	372×10^{-4}
0.02	95	190×10^{-4}

If $n \times 10^{-7}$ = observed hydroxyl-ion concentration of the silicate solution, $m \times 10^{-7}$ = calculated hydroxyl-ion concentration of sodium hydroxide at the same equivalent concentration, and 1.37×10^{-7} is the hydroxyl-ion concentration of water, then $n - 1.37/m - 1.37$ = degree of hydrolysis (h). The values of both n and m are so great in comparison with the corresponding value for water that the latter may be eliminated from the equation without error and the equation becomes $n/m = h$. This equation was accordingly used in calculating h.

The hydrolytic-dissociation constant was calculated according to the equation $h^2/(1-h)v = K_H$, where v = the number of liters in which one gram molecule is dissolved. The ionization constants for the hypothetical silicic acids were calculated from the equation: $K_A = K_W/K_H$, K_W being the water constant which according to Michaelis[2] is 1.89×10^{-14} at 30°.

The following tables present the data obtained.

Discussion.

An examination of the data brings out several points which are of interest. Most important, perhaps, is the relatively small values obtained for the percentage of hydrolytic dissociation, when contrasted with the high values obtained by the conductivity and freezing-point methods of Kohlrausch and of Kahlenberg and Lincoln.[2] This discrepancy leads one to look more closely to the several methods employed, to the assumptions made, and to an explanation for the differences observed.

A questionable assumption in the work of Kohlrausch was that his increased conductivity was due entirely to hydrolytic rather than to ionic dissociation. But in order to account for this increased conductivity on the ground of ionic dissociation would, as Kahlenberg and Lincoln emphasized, necessitate the assumption that the ion $SiO_3^{=}$ possessed a mobility exceeding that of the chlorine ion by about 70%. This reasoning has indeed led most of the older investigators to a rejection of the ionic theory in favor of the hydrolytic dissociation hypothesis as an explanation

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[1] A. A. Noyes, *Carnegie Inst. Pub.*, 63, 177, 340 (1908).

[2] *Loc. cit.*

TABLE I.—VALUES OBTAINED FOR EACH SILICATE AT VARIOUS DILUTIONS.

v.	E.	P_H.	$C_{OH} \times 10^{-4}$.	100h.	$K_H = \frac{h^2}{(1-h)v}$.	$K_A = \frac{K_W}{K_H}$
Silicate No. 1. $Na_2O.4SiO_2$.						
3.3	0.9980	11.01	10.2	0.20	1.38×10^{-6}	13.70×10^{-9}
10	0.9859	10.80	6.4	0.38	1.45×10^{-6}	13.00×10^{-9}
20	0.9837	10.77	6.0	0.68	2.33×10^{-6}	8.12×10^{-9}
50	0.9748	10.61	4.13	1.11	2.51×10^{-6}	7.52×10^{-9}
100	0.9669	10.48	3.00	1.58	2.54×10^{-6}	7.44×10^{-9}
Silicate No. 2. $Na_2O.3.5SiO_2$.						
3.3	1.0020	11.08	12.1	0.24	1.93×10^{-6}	9.80×10^{-9}
10	0.9921	10.90	8.2	0.49	2.41×10^{-6}	7.84×10^{-9}
20	0.9877	10.82	6.6	0.75	2.83×10^{-6}	6.67×10^{-9}
50	0.9773	10.67	4.76	1.28	3.32×10^{-6}	5.70×10^{-9}
100	0.9692	10.52	3.36	1.77	3.20×10^{-6}	5.90×10^{-9}
Silicate No. 3. $Na_2O.3SiO_2$.						
3.3	1.0120	11.23	17.6	0.35	4.07×10^{-6}	4.64×10^{-9}
10	1.0019	11.08	12.0	0.71	5.21×10^{-6}	3.63×10^{-9}
20	0.9930	10.92	8.4	0.95	4.55×10^{-6}	4.15×10^{-9}
50	0.9831	10.77	5.95	1.60	4.32×10^{-6}	4.37×10^{-9}
100	0.9715	10.57	3.72	1.96	3.92×10^{-6}	4.82×10^{-9}
Silicate No. 4. $Na_2O.2.5SiO_2$.						
3.3	1.0191	11.36	23.4	0.46	7.10×10^{-6}	2.68×10^{-9}
10	1.0070	11.16	14.5	0.85	7.28×10^{-6}	2.60×10^{-9}
20	0.9996	11.02	10.8	1.23	7.69×10^{-6}	2.46×10^{-9}
50	0.9892	10.84	6.95	1.87	7.15×10^{-6}	2.65×10^{-9}
100	0.9791	10.69	4.94	2.60	6.96×10^{-6}	2.71×10^{-9}
Silicate No. 5. $Na_2O.2SiO_2$.						
3.3	1.0421	11.74	54.8	1.08	3.91×10^{-5}	4.83×10^{-10}
10	1.0279	11.50	32.0	1.88	3.62×10^{-5}	5.22×10^{-10}
20	1.0029	11.25	18.0	2.04	2.12×10^{-5}	8.91×10^{-10}
50	0.9937	10.93	8.8	2.37	1.15×10^{-5}	16.40×10^{-10}
100	0.9828	10.77	6.0	3.15	1.03×10^{-5}	18.30×10^{-10}
Silicate No. 6. $Na_2O.1.5SiO_2$.						
3.3	1.0678	12.18	155.0	3.05	3.20×10^{-4}	5.90×10^{-11}
10	1.0552	11.95	90.0	5.29	2.98×10^{-4}	6.34×10^{-11}
20	1.0361	11.63	53.5	6.08	1.97×10^{-4}	5.59×10^{-11}
50	1.0230	11.42	26.8	7.21	1.12×10^{-4}	16.90×10^{-11}
100	1.0121	11.24	17.6	9.27	0.95×10^{-4}	19.90×10^{-11}
Silicate No. 7. $Na_2O.SiO_2$.						
3.3	1.0992	12.69	504.0	9.92	3.64×10^{-3}	5.20×10^{-12}
10	1.0944	12.43	275.0	16.18	3.12×10^{-3}	6.05×10^{-12}
20	1.0710	12.21	162.0	18.40	2.08×10^{-3}	9.08×10^{-12}
50	1.0533	11.93	85.0	22.81	1.35×10^{-3}	14.00×10^{-12}
100	1.0422	11.73	54.0	28.43	1.13×10^{-3}	16.70×10^{-12}

of the case in hand. McBain and has collaborators[1] have, however, recently shown that in such solutions as sodium silicate[2] colloidal electrolytes are

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[1] See especially, McBain and Salmon, THIS JOURNAL, 42, 426 (1920).

[2] *Ibid.*, p. 427, line 7.

present which, in the words of the authors are "salts in which an ion has been replaced by a heavily hydrated polyvalent micelle that carries an equivalent sum-total of electrical charges and conducts electricity just as well or even better than the simple ion it replaces."[1] This new discovery renders valueless deductions which have been made upon the assumption of an especially low conductivity for solutions of sodium silicate, *per se*.

Kahlenberg and Lincoln considered that it was more probable that the mobile hydroxyl-ion was the dominating influence, and their work apparently confirms that probability. It is permissible to point out, however, that the data obtained by the above mentioned investigators do not provide conclusive evidence in favor of a high hydrolytic dissociation. To illustrate: in the compound Na_2SiO_3, if ionization only had taken place, the apparent molecular weight would be $^1/_3$ of 121.58 or 40.53. If hydrolysis only had taken place, and the resulting sodium hydroxide were completely dissociated, the apparent molecular weight would be $^1/_4$ of 121.58 or 30.39. Thus a degree of hydrolysis from 0 to 100% would be revealed by variations in the apparent molecular weight of only 10 points. As a matter of fact, the authors obtain values at dilutions from 8 to 64 ranging from 41.3 to 32.6. It is suggested that those data may not warrant the all-conclusiveness of the deductions which have been drawn from them by the authors. And the function of the micelle in freezing-point determinations of silicates is still an unknown factor.

In the present investigation 3 assumptions have been made, and 2 of these are open to question. The first, namely, that if no hydrolytic dissociation had occurred, the hydroxyl-ion concentration would be the same as that of water at the same temperature, is undoubtedly justified. The second, that if hydrolytic dissociation had proceeded to completion, the hydroxyl-ion concentration would be the same as in an equivalent solution of sodium hydroxide, at first seemed entirely warranted. The third, that the hydroxyl-ion concentration is a straight-line function of the degree of hydrolysis, also seems warranted, and has often been made in previous investigations upon hydrolysis. But if the work of previous investigators, which has long been accepted, is to be taken as authoritative it follows that one of the above assumptions is not well made. The second, only will be considered. If hydrolytic dissociation has proceeded to completion at finite dilution, will the hydroxyl-ion concentration be the same as in an equivalent solution of sodium hydroxide? In order that the question may be answered in the affirmative, it is necessary to admit, first, the non-existence of any ionizable silicic acid,[2] and second, the absence of any influence of the colloidal or otherwise dispersed silica upon

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[1] THIS JOURNAL, p. 426.

[2] Stericker (*Loc. cit.*) and others have maintained the non-existence of silicic acids, *per se*.

the hydroxyl-ions. This latter assumption seems more open to question than any other. It seems indeed altogether possible that the particles of colloidal silica may either adsorb the ions upon their surface, or exert such a retarding influence upon their movements, that a numerical measurement of the latter would reveal an apparent ion concentration far below the actual or effective value. On the other hand, such a measurement might accurately represent the ionic condition of the *dispersed phase* of the solution. But if it be assumed that no such adsorption or other retarding influence is exerted upon the ions by the colloidal silica, then it would seem that the high values which have previously been obtained for the hydrolytic dissociation of the silicates of sodium have been erroneous. The several methods are in agreement in that the metasilicate, Na_2SiO_3, shows the greatest hydrolysis, while as the ratio of silica to soda increases, the degree of hydrolysis decreases.

The values for K_H and K_A have been inserted, as they are instructive. It is observed that the values for these constants at the several dilutions are not in all cases constant, but there is no great discrepancy in any instance. Indeed the values are in as close agreement as many that have been reported upon much better understood compounds. This can only mean, *if* the silica plays the role of an adsorbing or retarding agent upon the ions in solution, that the law governing the degree of adsorption or retardation is very similar to that which accounts for the hydrolytic dissociation constant, which is, in fact, the widely used "dilution law" of Ostwald.

Conclusions.

1. *If* the conclusions reached by earlier investigators to the effect that dilute solutions of sodium silicates are very highly dissociated hydrolytically may be accepted as authoritative, then it follows from data herein presented that the electrometric hydrogen-ion method is unsuitable as a means of measuring such dissociation. The reason for this appears to be in a possible ability of the colloidal silica to adsorb or retard or otherwise destroy the effect of a certain proportion of the hydroxyl-ions in the solution. The effect of the dilution upon this adsorptive or retarding influence follows closely the same laws as the effect of dilution upon hydrolytic dissociation. The hydroxyl-ion determination may serve, however, as a measure of the actual alkalinity of the dispersed phase.

2. The deductions put forward by earlier investigators are based upon data which, although expressive of a high degree of probability, are not, however, altogether conclusive evidence in favor of the much higher degree of hydrolysis which they report.

3. If the assumptions made in this report *are* found to be entirely justified, then it follows that the hydrolytic dissociation of the silicates

of sodium is much lower in dilute solutions than has been thought to be the case, ranging from 1.58 to 28.43% at a dilution of 100 liters per gram molecule in the silicates which vary respectively in their $Na_2O:SiO_2$ ratio of from 1:4 to 1:1.

4. The findings of earlier investigators, that the metasilicate, Na_2SiO_3, was most completely hydrolyzed, and that as more silica was added to the molecule the degree of hydrolysis decreased, have been confirmed.

PITTSBURGH, PA.

[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY OF THE CARNEGIE INSTITUTION, OF WASHINGTON.]

THE SYSTEM CUPRIC OXIDE, CUPROUS OXIDE, OXYGEN.

BY F. HASTINGS SMYTH AND HOWARD S. ROBERTS.

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1. Previous Work on the System.

The system cupric oxide, cuprous oxide, oxygen has been studied by L. Wöhler.[1] The results of this investigation led to the conclusion that cupric and cuprous oxides form a continuous series of solid solutions. That is, if cupric oxide was heated *in vacuo* to a temperature such that it began to lose oxygen according to the reaction

$$4CuO(s) \rightleftarrows 2Cu_2O(s) + O_2,$$

this action was not accompanied by the formation of a second solid phase. The 2-component system remained in 2 phases, solid solution of the 2 oxides and gas, until all oxygen required by the reaction had been removed and pure cuprous oxide remained. If the temperature of the charge was held constant and successive quantities of oxygen were removed, the equilibrium pressure varied continuously from that of pure cupric oxide to that of pure cuprous oxide. The true dissociation pressure of cupric oxide was not determined directly by Wöhler, since some oxygen was always lost from the charge used, in order to fill the apparatus with oxygen at the pressure corresponding to the initial temperature of each experiment. The volume of the apparatus used is not given, nor are the successive quantities of oxygen removed in any experiment indicated and it is impossible to follow the composition of the solid phase. All the results are therefore qualitative. However, using the same apparatus, with varying charges and with removal of varying quantities of oxygen, different equilibrium pressures of oxygen were obtained at identical temperatures. There are given in Table I a few of the results, which are typical.

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[1] L. Wöhler, *Z. Elecktrochem.*, 12, 781 (1906).

TABLE I.

Wöhler's Data on Dissociation of Cupric Oxide.

Charge: Pure cupric oxide.

Temperature, ° C.	Pressure, mm. mercury.
1000	103, 100, 111, 95, 91
1020	149, 145, 136, 126
1040	210, 216, 184, 179, 175, 163
1084	502, 478, 473

A dissociation pressure-temperature curve obtained by using an initial mixed charge of 50% each of cuprous and cupric oxides, gave values uniformly lower than those obtained with an initial charge of pure cupric oxide, as shown in Table II. It was remarked by Wöhler that the charges, when removed from the apparatus, appeared to be homogeneous, though apparently a microscopic examination was not made.

TABLE II.

Wöhler's Data on Dissociation of Mixed Copper Oxides.

Temperature, ° C.	Pressure, mm. mercury,	
	50% CuO; 50% Cu_2O.	Pure CuO.
960	31	51
1000	65	103
1030	108	177
1060	164	290

On the other hand, Foote and Smith[1] obtained identical values for dissociation pressures, at various temperatures, of mixed charges of the 2 oxides in various proportions, which would indicate that solid solution does not occur.

2. Purpose of the Present Investigation.

The original purpose of the present work was to confirm, if possible, the results of Wöhler and to determine accurately the compositions of solid solutions of cupric and cuprous oxides corresponding to a series of pressures at a number of different temperatures, and to find the true equilibrium pressure of the reaction

$$4CuO(s) \rightleftarrows 2Cu_2O(s \text{ solution in } CuO) + O_2(g)$$

with as nearly pure cupric oxide as possible.

It may be said at the outset, however, that the results of our experiments are not in agreement with those obtained by Wöhler, and that we have been unable to prove the existence of any solid solutions of cuprous oxide in cupric oxide. When cupric oxide loses oxygen, a second solid phase appears at once. This consists of small ruby-colored crystals, readily seen under a small glass, throughout the cooled charge of partially dissociated oxide. These are probably crystals of pure cuprous oxide, although our results do not entirely exclude the possibility of their containing a very small quantity of cupric oxide. However, it will develop

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[1] Foote and Smith, THIS JOURNAL, 30, 1344 (1908).

that the cupric oxide content of these crystals must be very small, if it exists at all. The composition of this second solid phase certainly does not vary sufficiently to make its effect felt in the general form of the dissociation pressure-temperature curve of cupric oxide, and in the present paper this phase is treated as pure cuprous oxide.

This investigation then resolved itself into a determination of the equilibrium constant of the reaction

$$4CuO(s) \rightleftarrows 2Cu_2O(s) + O_2(g) - \Delta H_1 \qquad (I)$$

both throughout the temperature range where cupric and cuprous oxides remain solids, and also above the melting point of the eutectic of the 2 oxides where the possible reactions are:

$$4CuO(s) \rightleftarrows 2Cu_2O(l \text{ solution in } CuO) + O_2(g) - \Delta H_2 \qquad (II)$$

and

$$4CuO(l \text{ solution in } Cu_2O) \rightleftarrows 2Cu_2O(s) + O_2(g) - \Delta H_3 \qquad (III)$$

ΔH_1, ΔH_2, and ΔH_3 are the heats absorbed in the several reactions.

3. Theoretical Discussion.

The form of the melting diagram for mixtures of cuprous and cupric oxides at various temperatures under equilibrium pressures of oxygen gas is not known. Excluding the possibility of the formation of compounds, and of solid solutions between the 2 oxides, we may assume, for the purpose of this discussion, a diagram like that of Fig. 1.

If a large quantity of cupric oxide be heated in a system of small volume to a temperature, t, above the eutectic point, the pressure being allowed to vary, the composition of the melt formed after dissociation has begun will be given by the point D (Fig. 1), and the 3 phases present will be solid cupric oxide, a liquid solution of cuprous oxide in cupric oxide, and oxygen gas. That is, Reaction II will take place. With increasing temperature the proportion of cupric oxide to cuprous oxide in the liquid in general becomes larger.

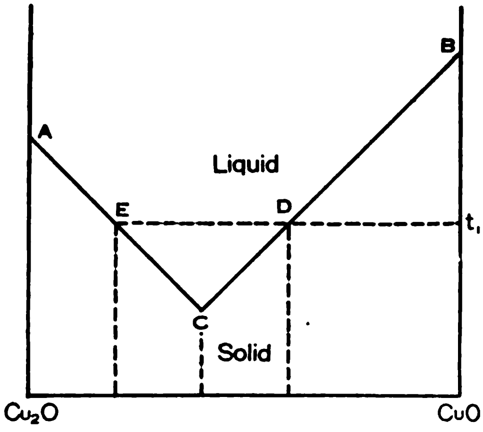

Fig. 1.—Arbitrary melting-point diagram, system; CuO, Cu_2O.

On the other hand, if a large amount of oxygen be allowed to escape from the charge of cupric oxide or if the original charge consist largely of cuprous oxide, the composition of the melt at the temperature t, will be given by the point E on the diagram, and the 3 phases present will then be solid cuprous oxide, liquid solution of cupric oxide in cuprous oxide, and oxygen gas. Reaction III will take place and with increasing temperature the proportion of cuprous oxide in the melt becomes greater.

At the eutectic point C, 4 phases exist at equilibrium, both solid oxides, liquid, and oxygen gas. Since the system is one of 2 components, the point C is invariant. On the other hand, along the lines CA and CB the system is monovariant, and the temperature may be adjusted at will if the oxygen pressure is allowed to vary.

At any temperature below the eutectic point Reaction I takes place, and the system at equilibrium consists of 3 phases, solid cupric and cuprous oxides and oxygen gas. This system is also monovariant.

The pressure-temperature curves for the monovariant Reactions I, II and III can be followed by means of the Clapeyron equation

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta H}{T\Delta V}. \tag{1}$$

Since both ΔH and ΔV can in general be divided into a number of more fundamental effects, we may write

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta H_1 + \Delta H'}{\Delta V_g + \Delta V'} \cdot \frac{1}{T}, \tag{2}$$

where ΔH_1 is the heat of dissociation, *i. e.*, the heat absorbed in Reaction I at constant pressure, and $\Delta H'$ is the summation of all other heat effects for the particular Reactions I, II, III; V_g is the volume of one mol of oxygen gas under equilibrium conditions; $\Delta V'$ the combined change in the volume of the solid or liquid phases.

As has already been stated, however, no compound has been found between cupric oxide and cuprous oxide, and also for Reaction I, at least, solid solution of small amounts of cuprous oxide in cupric oxide does not occur. Also we have found no evidence of solid solution of cupric oxide in cuprous oxide.

Reaction I. $4CuO\,(s) \rightleftarrows 2Cu_2O(s) — O_2(g)$.

As neither fusion nor solidification takes place in this reaction, we shall, for the moment, assume that ΔH_1 is constant over the range investigated. Then, ignoring the possibility of solid solution and changes in specific heats of the reacting substances, $\Delta H'$ is negligible. Since the pressure along this curve has remained less than 400 mm., we may also neglect $\Delta V'$ in comparison with V_g. Making these assumptions, Equation 2 becomes

$$\frac{\mathrm{d}p}{\mathrm{d}t} = \frac{\Delta H_1}{TV_g}. \tag{3}$$

Replacing V_g by RT/p and integrating, we obtain

$$ln\ p = -\frac{\Delta H_1}{RT} + \text{Const.} \tag{4}$$

the usual integrated form of the van't Hoff equation. The fact that within the limits of experimental error, our data satisfy Equation 4 (cf. Fig. 7), shows that the assumptions made above are justified.

Reaction II. $4CuO(s) \rightleftarrows 2Cu_2O(l \text{ solution in } CuO) + O_2(g)$.

Here dissociation is accompanied by fusion, not only of 2 mols of cuprous oxide formed, but of additional cupric oxide in order to form a liquid sufficiently rich in cupric oxide to be in equilibrium with the solid phase. As the temperature is raised, the melt requires increasingly more cupric oxide per mol of cuprous oxide (cf. Fig. 1, line CB). Consequently $\Delta H'$, which includes heats of fusion and dilution must increase. For the same reason $\Delta V'$ is negligible only at points at a distance from the melting point of pure cupric oxide, and at low pressures. For the lower temperatures, Equation 2 becomes

$$\frac{dp}{dT} = \frac{\Delta H_1 + \Delta H'}{TV_g}. \tag{5}$$

As $\Delta H'$ is positive, the slope of this curve is always greater than that of the extrapolation of the curve in the case of Reaction I, and it increases with rising temperature.

As we pass along the line CB (Fig. 1) and approach the melting point of cupric oxide, continuously larger quantities of cupric oxide must melt to dissolve the 2 mols of cuprous oxide formed in Reaction II. At the limit which is the melting point of pure cupric oxide, we can consider that an infinite amount of cupric oxide must melt to dissolve the cuprous oxide formed. As this point is approached, the solid and liquid phases approach the same composition and $\Delta H'$ and $\Delta V'$ increase without limit. ΔH_1 and V_g can then be neglected and we obtain as the limit is approached

$$\frac{dp}{dT} = \frac{\Delta H'}{T\Delta V'}. \tag{6}$$

Now since $\Delta H'$ is the heat required to melt a very large, though definite quantity of cupric oxide, and $\Delta V'$ is the volume change of the same quantity of oxide on melting, Equation 6 is the equation of the pressure-temperature curve for the condensed system CuO(s),CuO(l). The dissociation-pressure curve then becomes tangent to the melting-point pressure curve for pure cupric oxide at the temperature corresponding to the dissociation pressure of pure cupric oxide at its melting point.

Reaction III. $4CuO(l \text{ solution in } Cu_2O) \rightleftarrows 2Cu_2O(s) + O_2(g)$.

Here dissociation is accompanied by solidification; consequently $\Delta H'$ is negative, and, since $\Delta V'$ can again be neglected except near the melting point of cuprous oxide, the slope of the curve dp/dT must be less than that of the extrapolation of the curve in the case of Reaction I. Again $\Delta H'$ increases, numerically, without limit as the temperature is raised (cf. Fig. 1, line CA). Consequently the algebraic sum $\Delta H_1 + \Delta H'$ becomes less until the point is reached where $\Delta H_1 + \Delta H' = 0$, which is a maximum on the pressure-temperature curve. This point, it should be noted, may or may not lie on a stable part of the curve, because at the point C (Fig. 1) the amount of liquid cuprous oxide necessary to dissolve 4 mols of cupric oxide may already be large, and sufficient to give to $\Delta H'$ a numerical value greater than that of ΔH_1. As soon as the value of $\Delta H'$ does become greater than that of ΔH_1, the slope of dp/dT of the curve becomes negative.

For most substances, fusion is accompanied by an increase in volume. $\Delta V'$ is therefore probably negative and as its numerical value increases also without limit on approaching the melting point of cuprous oxide, the algebraic sum $V_g + \Delta V'$ must at some point become zero. Here the slope of the curve is negatively infinite.

Finally, as we approach the melting point of cuprous oxide, the slope of the curve is again given by Equation 6, but in this case both numerator and denominator of the second member of the equation have negative values. As in the case of Reaction II, therefore, the end of the curve has a positive slope and is tangent at the melting point of cuprous oxide to the pressure-temperature curve for the condensed system $Cu_2O(s),Cu_2O(l)$, at a temperature which corresponds to the dissociation pressure of pure cupric oxide at its melting point.

The value of dp/dT for the system $Cu_2O(s),[CuO,Cu_2O](l),O_2(g)$ therefore has at first a positive value, passes through zero, and becomes negative. Its negative value increases to infinity and toward the very end of the curve the slope again becomes positive. This end of the curve also may not lie in a region in which the system is stable, because as the pressure is lowered, the cuprous oxide present may itself start to dissociate with the appearance of a possible new phase, liquid or solid, and giving a system whose equilibrium pressure again increases with rising temperature. However, the dissociation pressure of cuprous oxide in the neighborhood of its melting point (1210°) is known to be less than 5 mm. of mercury.[1]

The principal fact which develops from this discussion is that the oxygen equilibrium pressure for Reaction III in general falls with rising temperature, with the exception of the small regions at the beginning of the curve where the numerical value of $\Delta H'$ is less than that of ΔH_1 and at the end of the curve where both total heat and volume changes for Reaction III are negative.

It remains to be noted that since the eutectic point is a quadruple point for the system $CuO(s),Cu_2O(s),O_2(g),[Cu_2O,CuO](l)$, all three of the above dissociation-pressure curves intersect at that point.

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[1] Slade and Farrow, *Proc. Roy. Soc.* [A,] 87, 524 (1912).

In the above discussion, heats of dilution of one liquid oxide in the other have been considered as negligible as compared with the heats of fusion involved.

4. Apparatus and Materials.

(*a*) Apparatus for Moderate Pressures.—The apparatus used is shown diagrammatically in Fig. 2, and consisted essentially of a reaction chamber of silica glass, 50 cm. long and 12 mm. internal diameter, closed at the lower end and attached through a ground joint to a glass cap 20 cm. long and of the same diameter as the tube itself through which were sealed the thermo-element connections. The manometer used for measuring equilibrium pressures was that which has already been used and described by Day and Clement[1] in gas thermometric work.

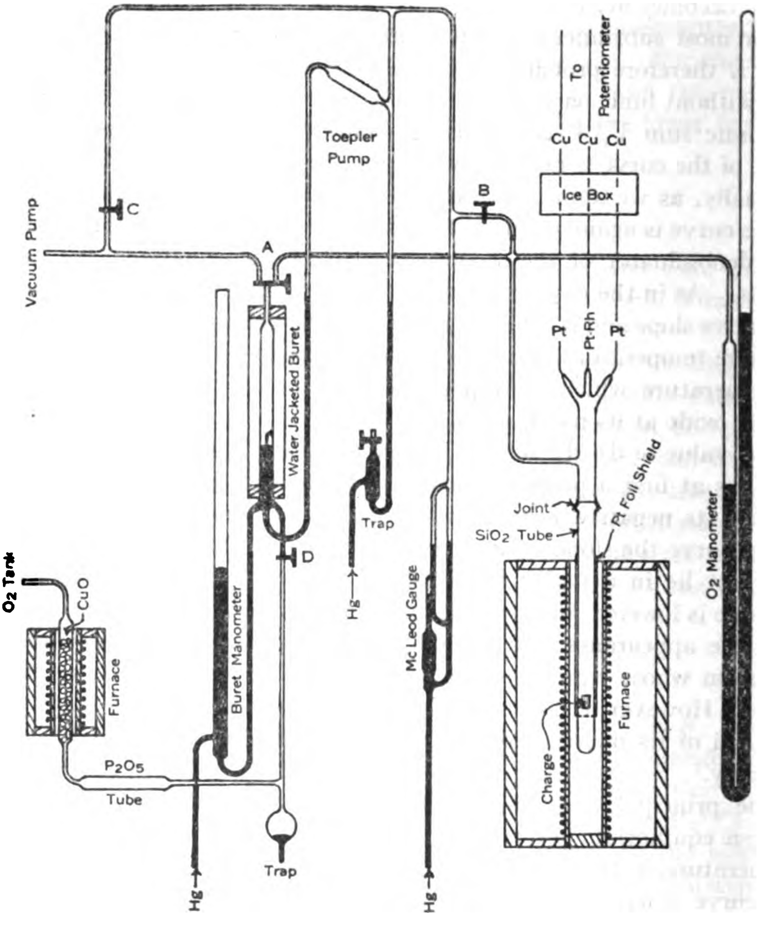

Fig. 2.—Apparatus used for measurements of pressures less than 3 atmospheres.

[1] Day and Clement, *Am. J. Sci.*, 24, 415 (1908).

A water-jacketted buret, of constant and known volume, was arranged so that quantities of oxygen either admitted or withdrawn from the system could be accurately measured. This was accomplished by adjusting a mercury column in the buret, so that the meniscus came to a glass point shown in the figure, and reading the level of the other meniscus in the buret manometer by means of a telescope cathetometer, which could be read to 0.1 mm. Fresh oxygen was admitted to the buret through the cock D, from a cylinder of electrolytic oxygen. On the other hand; oxygen from the system was withdrawn by means of a Toepler pump, the capillary of which discharged into the bottom of the buret. When pressures in the apparatus were sufficiently high, oxygen could be withdrawn directly into the buret through the 2-way Cock A, but with low pressures, readily measurable amounts of oxygen had to be pumped out.

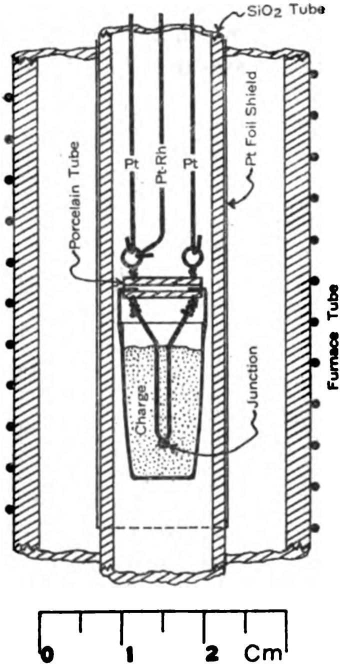

Fig. 3.—Section through low-pressure furnace showing method of supporting charge and arrangement of thermoelements.

The McLeod gage in the system served simply to determine when evacuation was complete, or to test for leaks.

The furnace used had a platinum wound alundum tube, 45 cm. long, and of 3 cm. internal diameter, insulated with magnesia. It was arranged on a sliding frame, so that it could be readily lowered away from the reaction tube, to allow the walls of the latter to be quickly cooled by spraying them with water. Exploration of this furnace with a thermoelement showed a range of at least 5 mm. through which the temperature within the charge did not vary more than 0.1° at 1100°. The height of the furnace in each experiment was adjusted so that this constant temperature region surrounded the charge of oxides.

Details of the way in which the charge was suspended are shown in Fig. 3. A small platinum crucible, about 10 mm. in diameter, was used to hold the charge. The crucible was lined with a thin coating of sintered magnesia,[1] and the thermoelement tip was also protected in this way. These magnesia coatings were not acted on by the copper oxides,

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[1] Magnesia coating prepared by applying a paste made from finely ground magnesia moistened with water saturated with magnesium nitrate. After painting this paste on the walls of the crucible it was slowly dried and then ignited by raising its temperature slowly to about 1600°.

as long as the latter remained solid. Above the fusion temperatures, however, no lining was found which would not react with the charge, and the platinum crucible was used unlined. The liberation of oxygen, however, due to absorption of copper by the platinum, is slow, compared to the rate at which dissociation equilibrium is accomplished, and is not a disturbing factor in the presence of cuprous oxide.

The thermoelement used for measuring the temperature of the charge was within the charge as shown. The crucible was suspended by platinum hooks from a small piece of capillary porcelain tube (Fig. 3). This piece of tube also carried and insulated the thermoelement tip, which was renewed before each experiment. Another thermoelement junction placed immediately above the crucible outside the charge, was used in certain cases to follow absorption or evolution of heat by the charge itself, using the differential method.[1] The platinum and platinum-10% rhodium alloy wires used for these elements were calibrated at the gold point (1062.6°). Thermoelement potentials were read with a Wolff potentiometer. The whole potentiometer system was shielded,[2] a platinum foil shield being placed around the quartz reaction tube.

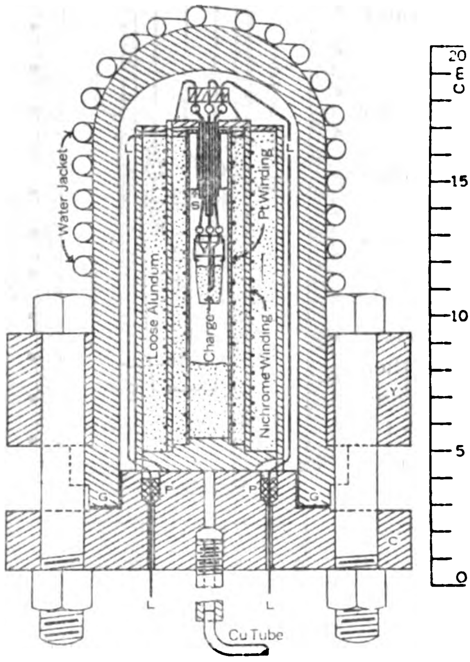

Fig. 4.—Section through bomb-furnace for measuring pressures higher than 3 atmospheres.

(*b*) **Apparatus for High Pressures.** — For pressures greater than 2000 mm. of mercury the furnace shown in Fig. 4 was used. This was a small, wire-wound, cascade furnace built into an inverted bronze autoclave. The furnace proper was made with alundum tubing and alundum end rings, and a fireclay base. Loose, granular alundum was used for insulation rather than magnesia because of the tendency of the latter to be blown out of the furnace when the gas pressure was released.

As in the case of the furnace used for low pressures, 2 thermocouples of platinum-platinrhodium were employed, one located in the middle

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[1] C. N. Fenner, *Am. J. Sci.*, 36, 361 (1913).

[2] W. P. White, "Leakage Prevention by Shielding," THIS JOURNAL, 36, 2011 (1914).

of the charge itself and the other directly above the crucible. From these, the 3 thermocouple lead wires passed through porcelain capillaries to the top of the furnace where they were hooked over loops supported by the porcelain block B. A circular platinum diaphragm, S, was supported by a platinum sleeve around the porcelain tubes, which in turn was connected by a wire, not shown in the figure, to the potentiometer shield. The electrical leads, L, of which there were 6, passed through holes in the cover of the autoclave, made gas-tight with soapstone plugs, P, which were spread into the holes under sufficiently heavy pressure to upset the soapstone and stretch the surrounding bronze.[1]

Connection to the oxygen tank and pressure gage was made through a fine copper tube. All the joints in this line were soft soldered to prevent leaks.

The autoclave was cooled by circulating water through a jacket of copper tubing, soldered in place, and through holes drilled in the cover C and the yoke Y. These holes are not shown in the figure.

Packing was provided at G in the form of a lead gasket. This was compressed by means of 6 bolts. The whole was supported on a bracket beneath the cover, so that the bottom was accessible.

Since organic matter in the presence of oxygen under pressure is apt to explode, the furnace was carefully heated all over to redness, and the inside of the autoclave washed with carbon tetrachloride before it was used.

The oxygen pressures in this furnace were read on a Bourdon gage reading up to 1000 pounds per square inch and previously calibrated in this laboratory.

Electric current for both furnaces was supplied by storage batteries, which gave practically an unvarying potential and allowed very constant temperature regulation.

(*c*) **Volume of Moderate Pressure System.**—To avoid calculations involving temperature gradients in the gas contained in the apparatus between the heated furnace portion and the tubes at room temperature, the quantity of oxygen contained by the apparatus at various furnace temperatures was determined empirically.

With the furnace in place, and heated to a definite temperature, but with no charge in the apparatus, a measured quantity of oxygen was admitted from the buret, and the resulting pressure in the apparatus was read on the manometer. Assuming that the temperature of the entire quantity of admitted gas remained at room temperature, and that the ordinary pressure-volume relations still applied to the partially heated system, what may be called an "apparent volume" of the apparatus was calculated. From this value the oxygen contained in the system at other

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[1] A modification of the seal used by Adams, Williamson and Johnston, THIS JOURNAL, 41, 18 (1919).

pressures, the furnace temperature being kept constant, could be closely estimated.

Furthermore, the change in the value of this "apparent volume" was not great with a variation of furnace temperature between 700° and 1100°, being 165.3 cc. at 1065° and 172.6 cc. at 725°. The assumption is therefore further made here that this value is a linear function of the temperature of the furnace within this range. The actual volume of the apparatus at the uniform temperature of 22° was 201.7 cc.

The quantities of oxygen lost by a charge when heated in the previously evacuated apparatus, are calculated in the following experiments from the values obtained in the manner predicted above. It will develop later that these values need not be very accurately known.

(*d*) **Preparation of Copper Oxides.**—The cupric oxide used in all experiments was prepared from C. P. "copper drops cooled in hydrogen" of the lot previously used as a melting-point standard in gas thermometric work in this laboratory.[1] The metallic copper was heated in an electric muffle furnace at low red heat for several days, in the presence of gentle air circulation. The resulting mass containing cupric and cuprous oxides and unoxidized copper was then removed from the furnace and ground in an agate mortar. That portion of the fines which passed a 150-mesh sieve was again heated in a porcelain boat in a tube combustion furnace at about 800° in a current of dry air for 3 or 4 days and until the boat and its contents ceased to gain weight during a heating period of 24 hours. When examined under a microscope,[2] the resulting cupric oxide appeared to be homogeneous and to contain opaque black particles only. It is a significant fact that until such time as the oxide ceased to gain weight while heated in the air current, the microscope always disclosed small ruby-colored crystals of cuprous oxide scattered throughout the mass as a separate solid phase. A sufficient quantity of oxide for all the following work was thus prepared, ground in an agate mortar to pass a 200-mesh sieve, mixed thoroughly, and kept as a stock, to assure uniform material for each experiment.

Cuprous oxide was prepared from the cupric oxide described above, by heating a portion of it in a porcelain boat at 900°, and pumping off oxygen at 5 mm. pressure, until the material ceased to lose in weight and until microscopic examination showed no black cupric oxide present as a separate phase.

(*e*) **Oxygen.**—The oxygen gas used was from a cylinder of compressed electrolytic oxygen, analysis of which showed the presence of less than 0.1% of gas which could not be absorbed in dilute ammonia solution in

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[1] E. T. Allen, in paper by Day and Clement, *Am. J. Sci.*, [4], 26, 456 (1908), finds 0.0083% total impurities in it.

[2] Microscope work by H. E. Merwin.

the presence of metallic copper. It was freed from hydrogen by passing over heated cupric oxide and dried in a tube containing phosphorus pentoxide.

5. Experimental Results. I. Absence of Solid Solutions and the Equilibrium Pressures of the System CuO(s), Cu_2O(s), O_2(g).

Experiment 1.—A charge of pure cupric oxide was placed in the apparatus, and the system was pumped down to 0.01 mm. mercury pressure, with the charge and furnace tube heated to about 300°. The temperature was then raised to about 984°. The initial manometer pressure was read after equilibrium was reached. Successive quantities of oxygen were then removed. After each removal of oxygen the temperature was brought back to 984° and the pressure was again recorded when it reached a constant value. Each recorded pressure reading was approached several times from temperatures both above and below 984°. The results are given in Table III. In Table III arrows after pressure values indicate whether pressure was reached from above or below the equilibrium pressure. That is, an upward pointed arrow indicates that the recorded pressure was reached from a lower value, and by dissociation.

Table III.

Dissociation Pressures of Cupric Oxide.

Weight of charge 2.8206 g. = 0.0355 mol cupric oxide.

Mol fraction CuO in charge.	Temperature. ° C.	Pressure. Mm. of mercury.	$\frac{1}{T(\text{abs.})}$
0.021 g. of O_2 to fill apparatus, equivalent to loss of 0.00192 mol of CuO.			
	983.5	68.21 ↑	0.0007959
0.975	998.5	93.22 ↑	0.0007868
	983.6	68.99 ↓	0.0007958
Removed 0.02165 g. of O_2 = 0.00271 mol of CuO.			
0.930	983.5	68.25 ↑	0.0007959
Removed 0.05105 g. of O_2 = 0.00640 mol of CuO.			
0.817	983.6	67.91 ↑	0.0007958
Charge left overnight at about 900°.			
	983.4	68.29 ↑	0.0007959
Removed 0.04937 g. of O_2 = 0.00616 mol of CuO.			
0.707	983.7	68.07 ↑	0.0007958
Removed 0.06492 g. of O_2 = 0.00812 mol of CuO.			
0.447	983.6	67.91 ↑	0.0007958
	983.7	67.73 ↑	0.0007959
	983.7	67.85 ↑	0.0007958

Charge quickly cooled. Apparatus evacuated cold.
0.0105 g. of O_2 removed during evacuation.
Total oxygen removed = 0.198 g.
Loss in weight of charge after cooling = 0.191 g.

After the experiment the charge was quickly cooled and the crucible removed and weighed. The loss in weight (0.191 g.) corresponds fairly closely to the calculated weight of oxygen removed during the experiments.

It was not possible to quench the charge rapidly enough to avoid the absorption of some oxygen during cooling. The total quantity of oxygen available from 2.8206 g. of cupric oxide, assuming the reaction: $4CuO \longrightarrow 2Cu_2O + O_2$, is 0.283 g. From this we calculate that 69% by weight of cupric oxide was converted into cuprous oxide during the experiment. Microscopic examination of the cooled charge showed it to be about $^2/_3$ converted into cuprous oxide which appeared as entirely distinct red crystals separate from the remaining black particles of cupric oxide. This result strongly indicates the absence of solid solutions at 984°. With the idea that high initial pressures (obtained by previous investigators) might be due to the giving off of adsorbed nitrogen by the charge of cupric oxide under certain conditions, the following experiment was tried.

Experiment 2.—A charge of pure cupric oxide was placed in the apparatus and pumped to 0.01 mm. pressure at room temperature. The charge was then treated as in Experiment 1. The results are given in Table IV. During this experiment the behavior of the temperature of

TABLE IV.

Dissociation Pressures of Cupric Oxide.

Charge: 2.7822 g of cupric oxide.

Temperature. ° C.	Pressure. Mm. of mercury.	Behavior of temperature of charge on removal of oxygen.
	Oxygen required to fill apparatus = 0.021 g.	
983.7	81.22 ↑	....
983.0	77.31 ↓	....
982.7	75.88 ↓	....
	Removed 0.0011 g. of O_2.	
982.7	74.10 ↑	Drop 2°
	Removed 0.0597 g. of O_2.	
982.7	71.08 ↑	Drop 3°
	Removed 0.0720 g. of O_2.	Drop 4°
	Furnace cooled overnight to room temperature. Pressure dropped to zero. Gas completely re-absorbed.	
982.7	71.26 ↑	
	Removed 0.0752 g. of O_2.	
982.6	68.44 ↑	Drop 4°
	Removed 0.0305 g. of O_2.	
982.6	67.12 ↑	Drop 2°
	Removed 0.0166 g. of O_2.	
982.3	57.14 (Stationary)	Drop 2°
	Removed unmeasured quantity of O_2	
982.3	16.94 (Stationary)	Stationary
	Removed unmeasured quantity of O_2.	
982.1	2.68 (Stationary)	Stationary

Last pressure rose about 0.2 mm. in 30 minutes, possibly indicating initial dissociation of cuprous oxide.

Total oxygen removed to point where pressure did not react to temperature = 0.276 g.

Theoretical amount of oxygen required to give pure cuprous oxide = 0.280 g.

the charge during the removal of oxygen from the system was carefully watched. The slightest amount of dissociation was immediately noticeable by the temperature drop in the charge which it caused.

The above results show a continual decrease in the apparent equilibrium pressure of about 8 mm. between the point at which the charge is practically pure cupric oxide and the point at which it is nearly converted into cuprous oxide.

After the removal of about 0.07 g. of oxygen the equilibrium pressure fell about 5 mm. and was practically unchanged by the further removal of 0.147 g. On the further removal of 0.0305 g. of oxygen, dissociation was nearly complete, cuprous oxide was present in excess, and the equilibrium pressure was adjusting itself very slowly.

From what we know of the effect on dissociation pressures of the formation of solid solutions, the pressure changes indicated in Table IV are hardly sufficiently great to be attributed to this cause. Sosman and Hostetter[1] found that in the case of the solid solutions of ferroferric oxide in ferric oxide, the dissociation pressure dropped about 50% of its initial value at 1200°, while the ferrous oxide content of the charge increased from zero to 13%. No such parallel behavior of the pressure can be noted in the present experiment where the initial pressure dropped only 6% of its original value on removal of less than 3% of the total available oxygen, and then remained practically unchanged until dissociation of the cupric oxide was complete.

As each quantity of oxygen was removed, the temperature of the charge dropped from 2° to 4°, until the pressure became 57.14 mm. This pressure was not sensitive to slight temperature changes, and further removal of oxygen gave a manometer reading of 16.94 mm. without any effect on the charge temperature due to further dissociation. This shows that when dissociation is complete, the equilibrium pressure drops abruptly, subsequent pressures being insensitive to temperature change, and removal of oxygen from the system causing no temperature reaction in the charge. The slightly high initial pressure, therefore, obtained in this experiment is probably due to the liberation of nitrogen adsorbed by the cupric oxide during cooling in air.

The following experiment shows that cupric oxide does retain adsorbed gas very tenaciously.

Experiment 3.—A charge of about 3 g. of cupric oxide was heated slowly from room temperature, during which time the system was evacuated continuously by means of the diffusion pump. Readings of pressure and temperature are plotted against time in Fig. 5. The pressure curve (P in the figure) passes through a maximum at about 365°; an extrapolation of the right-hand portion of the curve reaches about 0.01

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[1] Sosman and Hostetter, THIS JOURNAL, 38, 832 (1916).

mm. at 365° as shown by the dotted line. This is presumably about the pressure that would be developed by the cupric oxide if no gas were adsorbed by it at this temperature.

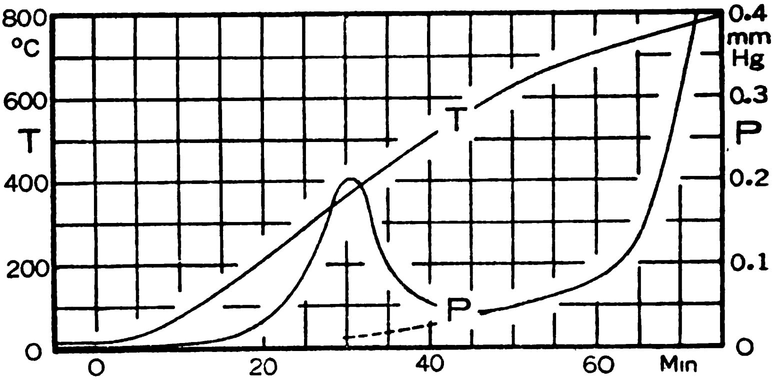

Fig. 5.—Pressure over charge during evacuation and simultaneous heating.

With another charge of cupric oxide the temperature was raised through a period of 40 minutes to 330°, running the pump continuously as before. The furnace was then allowed to cool slowly, reaching 249°, when the pressure had fallen to 0.008 mm. The furnace was lowered away from the reaction chamber and the system pumped down to 0.001 mm. at 50° and shut off from the pump. The charge was then heated rapidly to 1055° when a 300 cc. bulb, which had been connected to the system, was sealed off. After absorbing the oxygen in the bulb with an ammoniacal copper solution, 0.08 cc. of gas remained. This quantity of gas would have been sufficient to raise the pressure in the system by about 0.4 mm. Thus even after pumping out a charge of cupric oxide at 330° an appreciable amount of nitrogen remains which is driven out at higher temperatures. The results of this experiment, taken in conjunction with the high initial pressures of Expt. 2, indicate that when charges of cupric oxide, cooled in air, are heated in a closed system, misleading pressure values will almost certainly be obtained through the liberation of adsorbed nitrogen at high temperatures.

Experiment 4.—The equilibrium pressure of oxygen over practically pure cupric oxide was determined as follows. A charge of cupric oxide was pumped down at 200°. Oxygen was then run into the apparatus at a pressure of 228.65 mm. and the temperature was raised to about 984°. Oxygen was then removed in very small amounts, until a pressure was reached where further withdrawal of oxygen caused a drop in the temperature of the charge, and a pressure adjustment took place. The results are given in Table V.

TABLE V.

Dissociation Pressures of Cupric Oxide.

Charge 2.2490 g. of CuO.

Temp. °C.	Time elapsed between successive removals of oxygen. Min.	Pressure on removal of oxygen. Mm. of mercury.	Time to reach constant pressure. Min.	Final constant pressure. Mm. of mercury.	Oxygen removed. G.		Temperature drop on removal of oxygen. microvolts.
		......	..	228.65			
					Undet'd.	0.0175 g.	None
983.2		219.11	10	219.00			
	11				Undet'd.		None
983.3		209.67	16	209.93			
	18				Undet'd.		None
983.5		199.88	6	199.82			
	9				Undet'd.		None
983.6		189.30	5	189.20			
	12				Undet'd.		None
983.4		179.33	5	179.35			
	12				Undet'd.		None
983.5		168.00	26	168.11			
	31				Undet'd.		None
983.5		157.51	5	157.47			
	10				Undet'd.	0.0210 g.	None
983.3		151.17	15	151.25			
	19				Undet'd.		None
983.4		140.45	3	140.39			
	10				Undet'd.		None
983.4		129.38	5	129.26			
	12				Undet'd.		None
983.3		118.25	3	118.27			
	10				Undet'd.		None
983.3		107.52	4	107.44			
	9				Undet'd.		None
983.4		99.77	48	99.91			
	52				Undet'd.		None
983.3		93.70	4	93.58			
	7				Undet'd.		None
983.3		82.97	5	82.97			
	12				Undet'd.		None
983.3		72.76	5	72.79			
	10				Undet'd.		None
983.3		68.85	4	68.83			
	9				Undet'd.		8 m.v.
983.4		63.24	5	68.66↑			

Left overnight at about 850°. Pressure dropped to 60.87 mm. Temp. raised again to 983.6° on following day, and held constant for 3 hrs.

983.6		.....	3 hrs.	71.26↑		
	20 hrs.				0.0152	20 m.v.
983.6		62.96	40 min.	70.26↑		
	43 min.				0.0053	17 m.v.
983.6		64.22	31 min.	69.82↑		

An examination of this table shows that the charge did not begin to dissociate at 983.3° until the pressure had dropped to 63.24 mm. At this point an immediate drop of temperature was evident in the charge, and the pressure rose again to 68.66 mm. when the temperature was restored to 983.3°. After leaving this charge for 17 hours at 850°, the pressure again rose to 71.26 mm., after holding the temperature once more for 3 hours at 983.3°. Further removal of oxygen from the system did not effect a material change in the equilibrium pressure. These results agree with those obtained in Expt. 1. That the final pressure (about 70 mm. of mercury) was indeed the equilibrium pressure at 983.3°, was further demonstrated by twice again approaching this equilibrium temperature from 2 directions, with the results shown in Table VI.

Table VI.
Dissociation Pressures of Cupric Oxide.
Charge: Same as that of Table V.

Temperature. ° C.	Pressure. Mm. of mercury.
983.5	70.62↓
983.3	70.50↑

Arrows indicate whether pressure was falling or rising at time of final reading.

The conclusion can safely be drawn that solid solutions of cuprous oxide in cupric oxide do not exist at 983°, and therefore probably at no temperature at which both oxides remain solid.

It remains, therefore, to determine the form of the oxygen equilibrium pressure curve for the reaction $4CuO \rightleftarrows 2Cu_2O + O_2$.

As pointed out above, the curve will have 3 branches which will be treated separately: (1) when there are present oxygen gas and cupric and cuprous oxides as solid phases; (2) solid cupric oxide, liquid solution of cuprous oxide in cupric oxide, and oxygen gas; (3) solid cuprous oxide, liquid solution of cupric oxide in cuprous oxide, and oxygen gas.

One point on the first curve has been determined above in the search for solid solutions. At the conclusion of Expt. 4 the temperature of the charge was raised to determine 2 additional points, given in Table VII.

Table VII.
Dissociation Pressures of Cupric Oxide.
Charge: Same as that of Table IV.

Temperature. ° C.	Pressure. Mm. of mercury.
1017.7	135.31↑
1043.3	214.61↑
1043.2	214.61↓
1043.1	214.85↑

The arrows again indicate whether pressure was approached from above or below the equilibrium point. Microscopic examination of the cooled charge removed after this experiment, showed the presence of considerable cuprous oxide.

Experiment 5.—A mixed charge of 0.7647 g. of cuprous oxide and

2.1616 g. of cupric oxide was heated to about 750°, the apparatus having been evacuated cold. The pressure rose to about 3.9 mm. The charge was again cooled and the residual gas was pumped out to a pressure of 0.001 mm. The charge was then heated to a series of temperatures. The results are given in Table VIII.

TABLE VIII.

Dissociation Pressures Obtained with a Charge of Mixed Oxides.

Charge: 0.7647 g. Cu_2O
2.1616 g. CuO.

Temperature. ° C.	Pressure. Mm. of mercury.	Time between readings. Min.
956.0	40.24	
		22
956.0	40.46	
		82
956.0	40.56	
		30
956.1	40.82	
		30
956.2	41.06	
1001.0	97.07	
		14
1000.7	96.87	
		12
1000.5	96.65	
		12
1000.6	96.77	
		7
1000.6	96.77	
		9
1000.6	96.79	
1038.6	193.26	
		9
1038.8	194.50	
		7
1038.8	194.72	
		10
1038.8	194.66	
	Small quantity of oxygen added.	
1041.9	209.00	
		16
1038.9	196.33	
		9
1038.9	195.58	
		8
1038.9	195.48	
		7
1038.9	195.40	
		8
1038.9	195.48	

TABLE VIII (*continued*).

Temperature. ° C.	Pressure. Mm. of mercury.	Time between readings. Min.
1058.3	236.09	
		18
1059.0	277.47	
		8
1059.1	277.55	
		6
1059.1	278.53	
		3
1059.2	279.07	
		8
1059.2	279.07	
		6
1059.1	278.97	
		3
1059.1	278.91	
	Small quantity of oxygen added.	
1061.6	293.10	
		2
1060.0	287.10	
		8
1059.2	280.15	
		4
1059.1	279.93	
		22
1059.1	279.71	

These results with a mixed charge are given in full in order to show that long periods were allowed at each temperature to approach equilibrium from both sides, and that the pressure changes rather slowly in the immediate neighborhood of the equilibrium point. The pressure is also very sensitive to exceedingly small temperature fluctuations, but Table VIII shows that the temperature was fairly well controlled.

Final equilibrium pressures from the above experiments, with certain additional points determined in a similar manner, are tabulated in Table IX, together with the reciprocals of the absolute temperatures, and the logarithms of the pressures.

The data of Table IX are plotted in Figs. 7 and 9. Previous results obtained by Foote and Smith are also shown, and our own values obtained with charges of mixed oxides are indicated by vertical lines.

The best curve which can be drawn through the points determined by the figures of Cols. 3 and 5 of Table IX, below the eutectic point, is a straight line (Fig. 7). All equilibrium points obtained, whether over pure cupric oxide, partially dissociated charges, or charges previously mixed, lie on this line within the limits of experimental error. This proves conclusively that the heat effect of Reaction I is substantially constant, and that solid solution between the 2 oxides cannot take place to an appreciable extent.

TABLE IX.

Equilibrium Pressures for the System CuO (s), Cu_2O (s), O_2 (g).

Summary of results of Experiments 1 to 4, inclusive, with some additional points on the pressure-temperature curve.

Temperature. ° C.	Temperature. ° Absolute.	$\frac{1}{T} \times 10^3$.	Pressure. Mm. of mercury.	Log_{10} p.
838.8	1111.8	0.8994	4.62	0.66464
905.0	1178.0	0.8488	14.92	1.17377
915.6	1188.6	0.8413	17.20	1.23553
956.2	1229.2	0.8135	41.06[a]	1.61342
956.1	1229.1	0.8136	40.82	1.61087
983.5	1256.5	0.7958	68.50	1.83569
983.3	1256.3	0.7959	70.50	1.84819
983.5	1256.5	0.7958	70.60[b]	1.84880
1000.6	1273.6	0.7851	96.77[a]	1.98574
1017.7	1290.7	0.7747	135.31	2.13133
1038.8	1311.8	0.7623	195.00[a]	2.29003
1043.1	1316.1	0.7598	214.85	2.33213
1059.1	1332.1	0.7506	279.00[a]	2.44560

[a] Charge of mixed oxides.

[b] Charge of pure cupric oxide (average value).

All other points obtained with partially dissociated charges.

6. Experimental Results. II: System CuO(s), [CuO,Cu_2O](l), O_2(g).

In order to determine points on the equilibrium curve for this system, 2 methods were employed, both of which are somewhat subject to error due to the difficulty of temperature control and measurement when the charge starts to melt. These consisted first in heating a charge of pure cupric oxide in an excess pressure of oxygen to a given temperature and then removing oxygen slowly, as in Expt. 4 above, until the pressure returned to a constant value; and second, in heating pure cupric oxide in a high pressure of oxygen until dissociation took place. This last point was evident from the shape of the heating curve, because when dissociation began at a temperature above the eutectic point, fusion occurred at once.

The difficulty with both these methods lay in the fact that the temperature of the charge was always very erratic when fusion took place, because of the complicated changes which occurred. Between the eutectic point and the melting point of pure cupric oxide, fusion must be preceded by dissociation, and addition of heat causes a continuation of the process, which always seems to cause sudden local temperature changes throughout the charge. These were plainly registered by the thermoelement.

However, the sudden irregularities in temperature were themselves indications that dissociation and fusion were taking place, and smooth curves drawn through the irregular parts of the actual heating curves obtained indicate the true temperature, it is thought, certainly within a degree. In Fig. 6 is shown a typical heating curve for a charge of cupric oxide under a pressure of 6700 mm. of mercury. 1171° is chosen as the corresponding temperature.

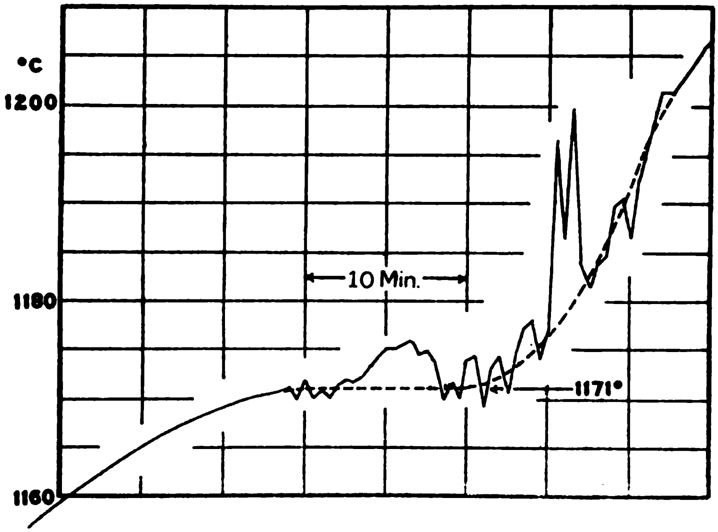

Fig. 6.—Typical time-temperature curve for melting cupric oxide with simultaneous dissociation.

Dissociation pressures up to 2000 mm. were determined in the quartz-tube apparatus, the pressures being read on the mercury manometer. Higher pressures were determined in the bomb-furnace, and were read on the Bourdon gage. Results are given in Table X.

TABLE X.

Dissociation Pressures of Cupric Oxide.

System CuO (s) — $Cu_2O.CuO$ (l) — O_2 (g).

Temperature. ° C.	$\frac{1}{T} \times 10^3$.	Pressure. Mm. of mercury.	$\log_{10} p$.
1083.8	0.7370	450	2.6532
1088.7	0.7345	512	2.7093
1092.6	0.7322	601	2.7789
1096.4	0.7302	671	2.8267
1097.2	0.7298	722	2.8585
1105.7	0.7253	939	2.9727
1119.0	0.7184	1258	3.0997
1130.0	0.7128	1716	3.2345
1135.8	0.7098	2020	3.3053
1171.0	0.6925	6700	3.8211
1204.4	0.6769	16090	4.2063
1210.6	0.6740	21450	4.3314
1232.5	0.6642	44700	4.6503

An examination of Table X shows a rapid rise of equilibrium pressure with temperature. But even at the highest pressure and temperature recorded, the melting point of pure cupric oxide without dissociation has not been reached. This is apparent from the logarithmic plot of these data (Fig. 7), in which the equilibrium curve does not yet show a tendency to become nearly vertical as would be predicted at the melting point of pure cupric oxide. It is shown more definitely by the fact that all the charges, when cooled, showed the presence of considerable cuprous oxide when examined under the microscope.

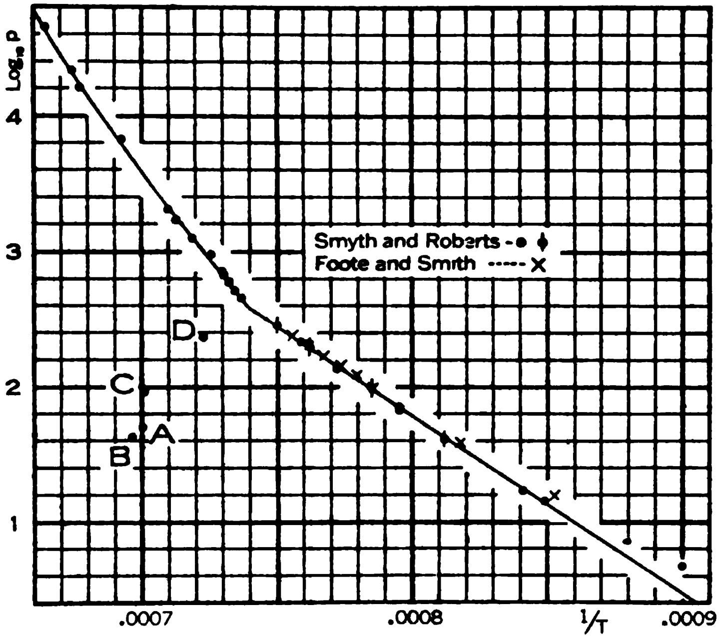

Fig. 7.—Plot of $\log_{10} p$ vs. $1/T$ abs. for the dissociation of cupric oxide.

7. Experimental Results. III: System $Cu_2O(s)$, $[CuO,Cu_2O](l)$,$O_2(g)$.

Charges of pure cuprous oxide were heated in the evacuated apparatus (Fig. 2) to temperatures above the eutectic point and oxygen was admitted in small quantities until it was absorbed by the charge and the pressure readily responded to slight temperature changes. That pressure adjustment appeared very rapid is shown on the accompanying plot (Fig. 8) in which pressures in mm. of mercury are plotted vertically and centigrade temperatures horizontally, the points representing readings 30 seconds apart, while the temperature of the charge was slowly raised and lowered. The ascending and descending curves lie very close to each other, indicating a slight lag of pressure adjustment behind the temperature but showing in a striking way how the pressure values vary in a manner the reverse of the temperature changes. Points lying in the center of pressure temperature loops thus obtained might be considered as representing equilibrium points. The two points A and B (Figs. 7 and 9) are shown with corresponding letters on the plots together with 2 other points obtained from independent experiments. This method of experimentation has, however, led to discordant results, and many points determined in this manner do not lie on any smooth curve which can be drawn through them and the eutectic point.

We hope later to show the cause of these variations, but for the present cannot show the true equilibrium values for this part of the system. These preliminary results are here given as showing the main fact that the behavior of the pressure with the temperature is in accord with the prediction, and the general direction of the pressure temperature curve is indicated.

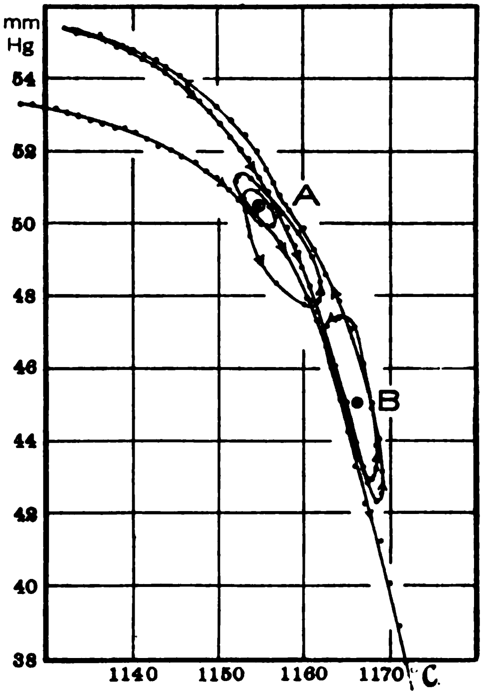

Fig. 8.—Showing behavior of pressure with temperature when the phases present are cuprous oxide, liquid mixture of cupric and cuprous oxides, and oxygen gas.

The Eutectic Point.—It has been found impractical to make a direct determination of the eutectic point, which is also the quadruple point of the system, by taking either heating or cooling curves on charges of mixed oxides. This is due to the fact that the temperature changes at this point become too erratic to interpret, even in the manner described above, in determining dissociation pressures at higher temperatures. The best value which can be given is therefore obtained by extrapolating the curves drawn through the accurately determined points to their intersection, which gives for the eutectic point a value of 390 mm. pressure and 1080.2° (Fig. 7). This point is also a point on the curve for the system, $Cu_2O(s),[Cu_2O,CuO](l),O_2(g)$.

Values of pressures in millimeters of mercury at temperature intervals of 20°, as taken from the logarithmic plot (Fig. 7), are given in Table XI.

TABLE XI.

Oxygen equilibrium pressures for the systems:

$$4CuO\ (s) \rightleftarrows 2Cu_2O\ (s) + O_2\ (g).$$
$$4CuO\ (s) \rightleftarrows [2Cu_2O,xCuO]\ (l) + O_2\ (g).$$

At even temperatures from 900° to 1240°.

Temperature. ° C.	Pressure. Mm. of mercury.	Pressure. Atmospheres.
900	12.5	....
920	19.2	....
940	29.2	....
960	43.9	....
980	65.0	....
1000	95.3	....
1020	137.7	....
1040	196.0	....
1060	278.0	....
1080	388.0	....
(1080.2 : eutectic point	390.0)	....
1100	724.0	0.95
1120	1328.	1.75
1140	2440.	3.21
1160	4470.	5.87
1180	8180.	10.8
1200	15150.	19.9
1220	29000.	38.1
1240	57500.	75.7

Fig. 9 shows the curve which the points of Table XI determine up to a pressure of 2000 mm., together with the points experimentally found over this same pressure range.

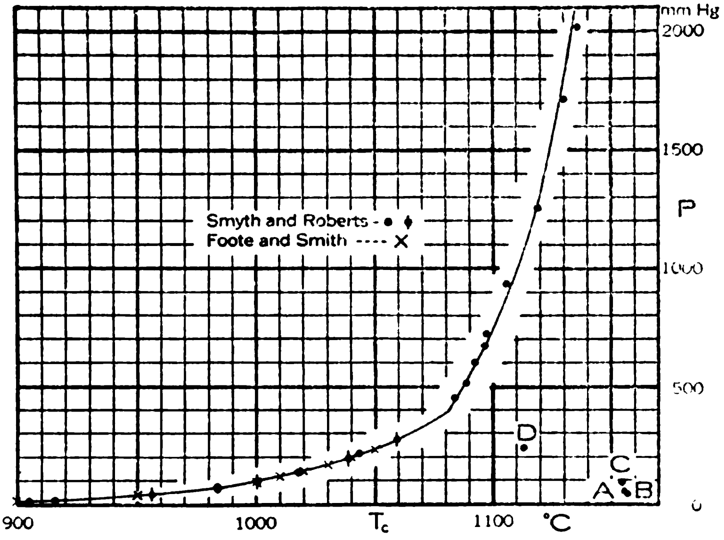

Fig. 9.—Dissociation pressure curve of cupric oxide.

8. Calculation of Energy Changes.

Over that part of the temperature range above 900° in which no liquid phase appears the integrated form of the van't Hoff equation

$$2.303 \log_{10} p(\text{mm.}) = -\frac{\Delta H_1}{RT} + \text{const.}$$

may be directly applied.

Solving for the constants of this equation, applying the method of least squares to the data of Table IX, we obtain

$$\log_{10} p(\text{mm.}) = \frac{-13216}{T} + 12.35$$

as the equation connecting the dissociation pressure of cupric oxide with the absolute temperature for the range 900° to 1082° (the eutectic point).

From this we calculate

$$\Delta H_1 = 60{,}568 \text{ calories}$$

for the change

$$4\text{CuO(s)} \longrightarrow 2\text{Cu}_2\text{O(s)} + \text{O}_2\text{(g)}$$

or

$$(\Delta H_{1000^\circ}): \text{CuO(s)} \longrightarrow {}^1/_2\text{Cu}_2\text{O(s)} + {}^1/_4\text{O}_2\text{(g)} - 15{,}142 \text{ cal.}$$

Previously determined values for the last quantity are 17,500 calories,[1] 18,100 calories,[2] and 16,755 calories.[3]

Again for the change:

$$4\text{CuO(s)} \rightleftarrows 2\text{Cu}_2\text{O(s)} + \text{O}_2\text{(g 1 atm.)}$$

the corresponding free energy decrease is

$$-\Delta F = 2.303\, RT \log_{10} \frac{p(\text{mm.})}{760} = -60568 + 43.38T.$$

In making the foregoing calculations, only data lying between 900° and the eutectic point have been used. A reference to Fig. 7 will show that the first point of Table IX with a pressure of 4.62 mm. at 838.8°, is not in agreement with the rest of the data, and shows too high a pressure value. It is thought that the pressure data at this low temperature are unreliable both because of the fact that small amounts of adsorbed gases cause a large percentage error in pressure readings, and because equilibrium is obtained very much more slowly as the temperature drops below 900°. For these reasons we believe better values of equilibrium pressures at low temperatures may be obtained by extrapolation of the logarithmic curve than by direct measurement.

9. Summary of Results.

1. It has been shown that solid solution of cuprous oxide in cupric oxide does not take place in the temperature range where both oxides

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[1] Dulong, *Compt. rend.*, **7**, 871 (1838).

[2] Andrews, *Phil. Mag.* [3], **32**, 321 (1848).

[3] J. Thomsen, "Thermochemistry," **1908**, p. 268.

remain solid. Previous results indicating such solution may probably be explained by lack of careful temperature control, and by possible adsorption of nitrogen in solid cupric oxide giving high initial pressures. Results below the eutectic point are in agreement with those of Foote and Smith.[1]

2. The pressure-temperature equilibrium curves for the system CuO, Cu_2O,O_2 have been established over the range (1), in which the oxides remain solid, below the eutectic point, and (2) above the eutectic point where cupric oxide remains the solid phase, up to 1233°.

3. The pressure and temperature of the quadruple (eutectic) point for the system have been established from the intersection of these 2 curves. The quadruple point lies at 1080.2° and 390 mm. pressure.

4. The general direction of the equilibrium curve has been indicated for the system when cuprous oxide remains the only solid phase, and it has been proved that, in accordance with theory, the equilibrium pressure drops in this case with rise in temperature.

5. It has been shown that pure cupric oxide does not melt without dissociation below 1233°.

The foregoing investigation was begun by one of us at the Research Laboratory of Physical Chemistry of the Massachusetts Institute of Technology. The work was interrupted at the declaration of war and has been continued in this Laboratory.

WASHINGTON, D. C.

THE DIELECTRIC CONSTANT OF SELENIUM OXYCHLORIDE.

BY JAMES E. WILDISH.

Received October 16, 1920.

Selenium oxychloride was prepared by bringing together molecular proportions of selenium dioxide and selenium tetrachloride. The dioxide was prepared according to Lenher.[2] The selenium tetrachloride was prepared in the usual manner by treating selenium with an excess of dry chlorine. This was accomplished by allowing finely powdered selenium[3] to fall through an atmosphere of dry chlorine. The operation was carried out in the apparatus shown in Fig. 1. A glass tube, A, about 45 cm. long and 38 mm. in diameter, was tightly fitted into a 4-liter flask, B. A glass tube, C, about 25 mm. in diameter and 91 cm. long, was tightly fitted into Tube A. The whole apparatus was made perpendicular by suspending a small weight from the center of the top of the tube. The dry chlorine was passed in at D, until the whole apparatus was filled with

[1] *Loc. cit.*

[2] Lenher, THIS JOURNAL, 20, 555 (1898).

[3] The selenium used in this work was obtained through the courtesy of the Baltimore Copper Smelting and Refining Company.

chlorine. The selenium was then slowly and at short intervals dropped into the top of the tube through a Gooch crucible. Between the intervals, the tube was covered with a crucible lid. At first, the main part of the reaction takes place near the top of the tube, but the selenium was added at such a rate that most of the reaction took place in A and the lower part of C.

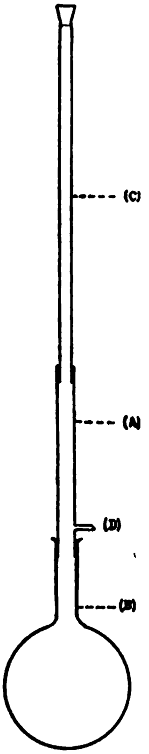

Fig. 1.

The major portion of the selenium tetrachloride falls directly into the flask. If formed too high in the tube some of it is driven out by the heat of the reaction and the larger part is always mixed with diselenium dichloride. If the main part of the reaction occurs in Tube A some of the material will sublime on the sides of the tube. This may be pushed down into the flask. If the main part of the reaction is allowed to take place in the large flask there is insufficient chlorine for the reaction and the dichloride is formed.

When sufficient tetrachloride had been formed, the chlorine supply was shut off and the small tube, C, which contains a small amount of tetrachloride, mixed with the dichloride, is removed. Any tetrachloride formed in Tube A could then be forced down into the flask. Tube A was thereupon removed and the tetrachloride corked up tightly.

By knowing the weight of the flask, the weight of the tetrachloride is easily calculated. Selenium dioxide is then added in molecular proportions and the flask gently heated to form selenium oxychloride. This, when distilled 3 times, had a constant boiling point of 179.4° (at 745.44 mm.), and a conductivity of about $^1/_{10}$ that of conductivity water.

The apparatus used for the determination of the dielectric constant was that of Drude as modified by Schmidt.[1]

Three cells of somewhat different electric capacities were used. These were standardized with acetone distilled over fused calcium chloride and 4 solutions of this purified acetone and water, 2 of which had dielectric constants below that of selenium oxychloride and the other 2 had dielectric constants above it. The data for these solutions were taken from Drude.[2] The water used was that prepared for conductivity work.

Ten readings were taken for each cell for each solution; of these, 5 were taken by each of 2 observers. By plotting the scale readings against the dielectric constants a curve was thus obtained for each cell, and the value of the dielectric constant for selenium oxychloride was deduced from

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[1] W. Schmidt, *Ann. Phys.*, 9, 919 (1902).

[2] Drude, *ibid.*, 8, 336(1902).

the scale. The unusally high value of the dielectric constant thus obtained is of interest.

The following results were obtained.

TABLE I.—DIELECTRIC CONSTANT OF SELENIUM OXYCHLORIDE.

	At 20°.	At 10°.	Solid at 0°.
Cell 1	46.50	.....	.....
Cell 2	47.10	51.30	13.80
Cell 3	44.20	50.70	18.80

Liquid selenium oxychloride has a dielectric constant of 46.2 ± 1 at 20°, 51.00 ± 0.5 at 10° and a temperature coefficient of 1.04%.

Solid selenium oxychloride has a dielectric constant of 16.8 ± 2 at 0°.

This work was suggested by Dr. Herman Schlundt of the Department of Chemistry. His valuable assistance, in every way, is hereby acknowledged.

CHEMICAL LABORATORY,
COLUMBIA, MO.

VOLATILIZATION LOSSES OF PHOSPHORUS DURING EVAPORATIONS OF PHOSPHATES WITH SULFURIC ACID OR FUSIONS WITH PYROSULFATE.[1]

BY W. F. HILLEBRAND AND G. E. F. LUNDELL.

Received October 22, 1920.

I. Introduction.

Little has been written as to the possibility of volatilization losses of phosphoric acid during operations involving evaporation of phosphates with sulfuric acid or fusion with pyrosulfate, although these questions are of prime importance in the determination of phosphorus in rocks, ores, metallurgical products and many other materials. The experiments to be described were therefore undertaken with a view to determining whether any appreciable volatilization takes place, and in case of evidence of volatilization, to discovering contributing causes and preventive measures.

Rose[2] says in speaking of the treatment of phosphates with sulfuric acid, "Erhitzt man bis zum Verdampfen der Schwefelsäure so kann sich eine Spur Phosphorsäure verflüchtigen."

One of us[3] has repeatedly called attention to the fact that the possibility of loss of phosphorus pentoxide by volatilization during a pyrosulfate fusion or evaporation with sulfuric acid must be borne in mind.

Fresenius-Cohn[4] discuss losses of phosphorus pentoxide by volatiliza-

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[1] Published by permission of the Director of the Bureau of Standards.

[2] H. Rose, "Handbook of Quantitative Analysis," Finkener Ed., 2, 575 (1871).

[3] W. F. Hillebrand, "The Analysis of Silicate and Carbonate Rocks," U. S. Geol. Surv., *Bull.* 700, p. 116; and earlier editions.

[4] Fresenius-Cohn, "Quantitative Chemical Analysis," J. Wiley and Sons, 1, pp. 444–445 (1904).

tion as follows: "Bunce's[1] statement that phosphoric acid volatilizes when a phosphate is evaporated to dryness with hydrochloric or nitric acid and the residue heated a little, is quite erroneous. But, on the other hand, it must be borne in mind that orthophosphoric acid under these circumstances changes, not indeed at 100° C., but at a temperature still below 150°, to pyrophosphoric acid; thus, for instance, upon evaporating common hydrogen sodium phosphate with hydrochloric acid in excess, and drying the residue at 150°, we obtain $2NaCl + Na_2H_2P_2O_7$." Fresenius makes no mention of the behavior of a phosphate upon fuming with sulfuric acid or during a fusion with pyrosulfate.

II. Sources of Losses of Phosphorus Pentoxide.

A. Manipulation Losses.

Losses due to faulty manipulation are easily avoidable. Care must, of course, be taken during evaporation lest there be undue effervescence before the actual fuming of the sulfuric acid. Spattering during pyrosulfate fusions can be entirely avoided through the use of a properly prepared pyrosulfate,[2] a low initial flame, and only sufficient heat to keep the fusion molten.

B. Conversion Losses.

1. **Preliminary Remarks.**—Losses due to change of composition are occasioned by the conversion, under certain conditions of evaporation or fusion, of orthophosphoric acid into pyro- or metaphosphoric acids. These acids cannot be determined by any of the methods used for orthophosphoric acid, and hence failure to reconvert them into orthophosphoric acid may entail serious errors. The following reconversion procedures are quoted from Fresenius-Cohn:[3] "(1) In the dry way by protracted fusion with Na_2CO_3. This method is applicable only in case of alkali meta- and pyrophosphates, and of those metallic meta- or pyrophosphates which are completely decomposed by fusion with alkali carbonates; it fails with the salts of the alkaline earth metals, magnesium excepted. (2) In the wet way by heating with strong acid, best with concentrated sulfuric acid. This method leads to the attainment of only approximate results, in the case of all salts whose basic radicals form soluble salts of the acid added, because in these cases the meta- or pyrophosphoric acid is never completely liberated; but the desired result may be fully attained by the use of any acid which forms insoluble salt compounds with the basic radicals present. Respecting the partial conversion in the former case, I have found that it approaches the nearer to completeness the greater the quantity of free acid added, and that the ebullition must be long continued."

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[1] J. B. Bunce, *Am. J. Sci. Arts* [2] 11, 403–5 (1851).

[2] W. F. Hillebrand, *loc. cit.*, p. 116.

[3] Fresenius-Cohn, *ibid.*

TABLE I.—CONVERSION LOSSES.

Substance.	Treatment.	Precipitation conditions.	P_2O_5 calculated on basis of ignited phosphate obtained from.		Error, G.	Reconversion Treatment.
			Converted aliquot. G.	Reconverted aliquot. G.		
H_3PO_4 (sp. gr. 1.88)	Heated for 2 hours at 240-265° in a platinum dish.	Double precipitation with magnesia mixture	0.1304	0.4990	—0.3686	Boiled with 10% H_2SO_4 for 2 hrs.
	Evaporated to cessation of fumes with 20 cc. of H_2SO_4 (sp. gr. 1.84)		0.1135	0.2449	—0.1314	
	Evaporated with 20 cc. H_2SO_4 (sp. gr. 1.84) for 2.75 hours, 10 cc. of H_2SO_4 evaporated		0.0713	0.0713	0.0000	
$NaNH_4HPO_4$	Evaporated to dryness with 4 successive 5 cc. portions of H_2SO_4 (sp. gr. 1.84)	Single precipitation	0.3192	0.3353	—0.0161	Fused with Na_2CO_3
	As above	Double precipitation	0.3148	0.3353	—0.0205	
	Evaporated to dryness with 2 cc. H_2SO_4 (sp. gr. 1.84)		0.0193	0.0291	—0.0098	
Na_2HPO_4	Evaporated for 3 hours with excess concentrated H_2SO_4 always present		0.1219	0.1222	—0.0003	Boiled with 10% H_2SO_4 for 2 hours
$4Al_2O_3.3P_2O_5$[a]	Evaporated to cessation of fumes with 12 cc. of H_2SO_4 (sp. gr. 1.84)	Precipitation as phosphomolybdate and then twice with magnesia mixture	0.0585[b]	0.0585	0.0000	Boiled with 10% H_2SO_4 and HNO_3 for 5 hours
$NaNH_4HPO$	Fused with 20 g. of $K_2S_2O_7$ at faint dull red for 2.25 hours	Double precipitation	0.0420	0.0638	—0.0218	
$4Al_2O_3.3P_2O_5$[a]	Fused with 10 g. of $K_2S_2O_7$ at a low temperature for 1.5 hours	Precipitation as phosphomolybdate and then twice with magnesia mixture	0.1285[b]	0.1286	—0.0001	
$6Fe_2O_3.P_2O_5$[a]	Fused with 5 g. of $K_2S_2O_7$ at a dull red for 2 hours		0.0067	0.0073	—0.0006	
$6Fe_2O_3.P_2O_5$[a]	Fused with 10 g. of $K_2S_2O_7$ at a dull red for 2 hours		0.0045	0.0054	—0.0009	

[a] Mixture artificially prepared.

[b] The classification "Unconverted" does not strictly apply here, since a certain amount of heating with acid was required to obtain perfect solution of the treated material.

2. **Experimental.**—In the experiments listed in Table I, phosphoric acid or phosphates were either evaporated with sulfuric acid or fused with pyrosulfate and then dissolved under conditions giving as little reconversion as possible. These solutions were then diluted to definite volume and aliquot portions taken for analysis with or without preliminary reconversion treatment. Double precipitations were usually carried out by first precipitating with magnesia mixture in excess, filtering without washing, dissolving the precipitate in a small amount of hydrochloric acid, reprecipitating in small volume after the addition of a few drops of magnesia mixture[1] and final washing with 10% by volume ammonium hydroxide solution. It was found that this procedure in addition to being more accurate than a single precipitation afforded a test for converted phosphates since these invariably caused a marked precipitation in the second filtrate and washings when excess magnesia mixture was added and the solution was allowed to stand for 12 hours. This precipitation is due to the fact that magnesium pyro- and metaphosphates are more soluble than the ortho-compounds. Consequently if pyro- or meta- compounds are present the addition of an excess of magnesia mixture in the first precipitation results in a more complete deposition than takes place in the second precipitation where the precipitant is present in very slight excess. In addition to this, the thorough washing of the second precipitate with 10% (by volume) ammonium hydroxide results in a partial solution of the pyro- and meta- compounds which are then again precipitated in the filtrate upon standing. The data in Table I demonstrate that: (1) orthophosphoric acid and secondary (presumably also primary) phosphates suffer marked conversion upon evaporation to dryness with sulfuric acid, and serious errors will ensue in these cases if phosphate determinations are subsequently carried out without reconversion treatment; (2) no conversion need be feared in evaporations involving the continuous presence of excess sulfuric acid; (3) secondary (and presumably also primary) orthophosphates suffer partial conversion during fusions with pyrosulfate and require reconversion treatment before precipitation by ordinary methods. Basic orthophosphates may suffer conversion.

In the light of the experiments performed, it is apparent that all phosphate-bearing residues obtained through evaporation with sulfuric acid to cessation of fumes, and all pyrosulfate fusions of phosphate material should be boiled with acid, preferably 10% sulfuric acid, for at least 2 hours before precipitation as phosphomolybdate or magnesium ammonium phosphate.

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[1] F. A. Gooch and M. Austin, *Am. J. Sci.*, [4] 7, 187–198 (1899), state that the first phosphate precipitate should be filtered off, dissolved in hydrochloric acid and reprecipitated by ammonia without further addition of magnesia mixture. This statement, which has been copied in several texts, is wrong, since this procedure is sure to lead to an incomplete final precipitation.

C. Volatilization Losses.

1. Upon Evaporation with Sulfuric Acid.—Since phosphorus compounds begin to volatilize from phosphoric acid at temperatures near 270°, losses are to be expected when sulfuric acid solutions of phosphates are evaporated at temperatures near this point. Sulfuric acid may, however, be volatilized at temperatures much lower than this and therefore the experiments listed in Table II were carried out to ascertain the extent of the losses which might be expected when phosphate solutions were evaporated at low temperatures (just fuming) with excess of conc. sulfuric acid, as compared with the losses experienced in evaporations carried on at higher temperatures and to the partial or complete expulsion of all sulfuric acid. Solutions of phosphoric acid, secondary phosphates and basic phosphates were accordingly evaporated with sulfuric acid under conditions specified in Table II, in platinum dishes placed in a "radiator."[1] The solutions or residues were then subjected to reconversion treatments and analyzed for their phosphorus pentoxide content.

TABLE II.—EVAPORATION OF SULFURIC ACID SOLUTIONS OF PHOSPHATES.

Compound taken.	H_2SO_4. Cc.	Treatment		H_2SO_4 volatilized. Cc.	P_2O_5 taken. G.	P_2O_5 found. G.	Error. G.
		Temp. ° C.	Time. hrs.				
H_3PO_4	20	135–145	2.25	7	0.0714	0.0714	0.0000
	20	145–155	2.75	10	0.0714	0.0713	−0.0001
	20	200+	4.00	20	0.0714	0.0612	−0.0102
$NaNH_4HPO_4$	20 in 4–5 cc. portions	.....	5.75	20	0.3510	0.3399	−0.0111
	20	.....	5.75	20	0.3510	0.3475	−0.0035
Na_2HPO_4	20	low gradual fuming	3	5	0.0043	0.0041	−0.0002
$4Al_2O_3.3P_2O_5$[a]	12	150	1.5	3	0.1366	0.1366	0.0000
	12	165	3	5	0.1366	0.1348	−0.0018
	12	165+	3	12	0.1366	0.1170	−0.0196
	20	150	3	3	0.0057	0.0057	0.0000
$4Al_2O_3.3P_2O_5$	5 drops of H_2O, 5 drops of 1 : 1 H_2SO_4, 5 cc. of HF, volatilized at lowest possible temp. in a platinum crucible, then ignited, and finally dissolved.[b]				0.0057	0.0057	0.0000
Na_2HPO_4					0.0045	0.0045	0.0000

[a] See Table I.

[b] To imitate the conditions obtaining when an impure silica containing phosphates, such as titanium or zirconium phosphates, is treated with HF and H_2SO_4.

The data in Table II demonstrate that: (1) volatilization losses of phosphorus pentoxide will surely ensue when phosphoric acid or phosphates are evaporated with sulfuric acid to complete expulsion of fumes; (2)

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[1] W. F. Hillebrand, *loc. cit.*, p. 33.

losses will occur if evaporation takes place at elevated temperatures even though sulfuric acid is continuously present in excess; (3) slight losses may occur upon prolonged evaporation with conc. sulfuric acid at temperatures near 150°; (4) no losses need be feared when solutions of phosphates are slowly evaporated with sulfuric acid (preferably in a radiator and not over a free flame) to the first appearance of fumes; (5) no losses need be feared in a hydrofluoric-sulfuric acid treatment of a silica contaminated by phosphorus pentoxide, provided a slight excess only of sulfuric acid is used and the evaporation is carried on slowly in a radiator. Losses will occur if excessive amounts of sulfuric acid are used. That the losses listed were true volatilization losses and not losses due to failure in reconversion, was definitely established by qualitative and quantitative tests which showed the presence of phosphorus pentoxide in the vapors given off during the evaporations which resulted in low phosphorus pentoxide values.

The experiments listed in Table II were carried out by the junior author. Many years ago, and again more recently, the senior author obtained losses, when treating sodium phosphate, that were much greater than any of those above reported. Presumably the volatilization was much more forced than in the present series of tests.

2. Upon Fusion with Pyrosulfate.—The question as to volatilization losses during pyrosulfate fusions is important, since many precipitates obtained by ammonium hydroxide in rock analyses carry phosphorus pentoxide and it is often desirable to determine the amount after fusion with pyrosulfate. The experiments listed in Table III were carried out in covered platinum crucibles at temperatures ranging from the very dull red of ordinary fusions, to the higher temperatures which analysts sometimes vainly employ in an attempt to "force" a fusion. The cooled fusions were dissolved, treated to effect reconversion and then finally precipitated twice with magnesia mixture. The experiments in Table III indicate that: (1) pyrosulfate fusions of secondary phosphates result in decided losses of phosphorus pentoxide by volatilization; (2) fusions of basic phosphates (comparable with most of the fusions carried on in most

TABLE III.—FUSION OF PHOSPHATES WITH PYROSULFATE.

The heating was to dull redness in all experiments.

Compound used.	$K_2S_2O_7$ taken. G.	Duration of fusion. hrs.	P_2O_5 taken. G.	P_2O_5 found. G.	Error. G.
$NaNH_4HPO_4$	10	2.5	0.0700	0.0680	−0.0020
	20	2.25	0.0700	0.0638	−0.0062
	5	2	0.0045	0.0039	−0.0006
$4Al_2O_3.3P_2O_5$[a]	5	1	0.1749	0.1748	−0.0001
	5	2	0.0057	0.0057	0.0000
$6Fe_2O_3.P_2O_5$[a]	10	2	0.0055	0.0054	−0.0001
	5	2	0.0078	0.0075	−0.0003

[a] See Table I.

analyses) in covered platinum crucibles at low temperatures, do not ordinarily occasion serious losses. Since losses may occur in such fusions, they should be avoided when accurate determinations of phosphorus pentoxide are desired.

Qualitative and quantitative tests of the vapors given off during special fusions in Gooch tubulated crucibles demonstrated that the phosphorus pentoxide losses were true volatilization losses and were not due to incomplete reconversion treatments.

III. Summary.

1. No volatilization losses of phosphorus occur during evaporations of sulfuric acid solutions of phosphates, provided the evaporations are carried on at temperatures below 150° and stopped when fumes appear. Such evaporations are best performed over "radiators."

2. Volatilization losses during evaporation of sulfuric acid solutions of phosphates are occasioned by (1) evaporation to complete expulsion of sulfuric acid; (2) evaporation at high temperatures such as 200–260°; and (3) unduly prolonged evaporation at temperatures above 150°. Evaporations involving only a drop or two of sulfuric acid, such as apply in silica treatments, do not cause measurable losses.

3. Fusions with pyrosulfate in *covered* crucibles and at dull red temperatures result in appreciable losses in the case of secondary (and presumably primary) phosphates, and may result in slight losses in the case of basic phosphates.

4. Orthophosphoric acid and primary and secondary orthophosphates suffer conversion to pyro- and metaphosphoric acid or phosphates when evaporated to dryness with sulfuric acid or fused with pyrosulfate; such "converted" compounds must be subjected to "reconversion" treatments before precipitation with molybdic acid or magnesia mixture.

WASHINGTON, D C.

NOTE.

Correction.—In the articles "Adsorption by Charcoal," I and II, appearing in the July number of THIS JOURNAL, mention of the fact that the work was made possible by a grant from the "Elizabeth Thompson Science Fund" was overlooked. We would like at this time to express our thanks publicly for that assistance.

G. A. HULETT AND H. H. LOWRY.

THE PREPARATION OF CERTAIN DERIVATIVES OF CYCLOHEXANE.

By A. E. Osterberg and E. C. Kendall.

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Many methods for the preparation of cyclohexane derivatives have previously been employed.[1] The method described herewith for the preparation of cyclohexane and cyclohexanol, embodying Ipatiew's principle of high pressure, offers a simple procedure for the manufacture of these materials on a large laboratory scale with easily accessible materials.

The substance to be reduced, together with a metal oxide catalyst, is placed in a suitably constructed bomb which can be filled at intervals with hydrogen under pressure of 115 to 120 atmospheres, and the whole subjected to a temperature of approximately 250° until reduction is complete. The higher temperature and pressure tend to counteract the decreased activity of a partially poisoned catalyst. The process requires very little attention other than periodic filling and emptying of the bomb. The reaction proceeds to completion with a catalyst much less reactive than that necessary to obtain any reduction by the Sabatier method. The high pressure needed is obtained by use of commercial hydrogen sold in tanks at a pressure of 1800 pounds per square inch. Without materially slowing up the reaction the hydrogen tanks may be used without replacement until the pressure is decreased to approximately 1000 pounds.

During the past year in connection with work on the production of hydroheterocyclic compounds it was necessary to prepare considerable quantities of cyclohexane, cyclohexanol, and some of their derivatives. These are not procurable on the market, although the first two mentioned have been articles of commerce.

In seeking a method which could be standardized for the preparation of cyclohexane and cyclohexanol, we have used that of Ipatiew, for reasons given above. By this process about 30 kg. of hexahydrophenol have been prepared, the method being found very satisfactory. Nothing new is offered in the preparation of these compounds, but as they are the necessary starting materials for the production of a series of new substances, the procedure found most satisfactory for the preparation of cyclohexane, cyclohexanol, cyclohexylamine, cyclohexene and the more simple, well-

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[1] Aschan, *Ber.*, **24**, 1864, 2617 (1891); Einhorn and Meyenberg, *ibid.*, **27**, 2466, 2829 (1894); Baeyer, *ibid.*, **19**, 1797 (1886); **26**, 229 (1893); *Ann.*, **278**, 88 (1894); Paal and Amberger, *Ber.*, **38**, 1406 (1905); **40**, 2201 (1907); Paal and Gerum, *ibid.*, **40**, 2209 (1907); **42**, 1553 (1909); Paal and Roth, *ibid.*, **42**, 1541 (1909); Sabatier and Mailhe, *Ann. chim. Phys.*, **10** (s. 8), 527 (1907); *ibid.*, **16** (s. 8), 70 (1909); Sabatier and Murat, *Compt. rend.*, **154**, 928 (1912); Sabatier and Senderens, *ibid.*, **133**, 321 (1901); *Ann. chim. phys.*, [8] **4**, 319 (1905); Skita, *Ber.*, **48**, 1486, 1685 (1915); Senderens, *Compt. rend.*, **154**, 1168 (1912); Ipatiew, *Ber.*, **37**, 2961, 2986 (1904); **40**, 1270, 1281 (1907); **41**, 991, 993 (1908); Ipatiew, Jakowlen and Rakitin, *ibid.*, **41**, 996 (1908).

known members of this series will be outlined, since even after a careful perusal of the literature one is in doubt as to which method to follow.

A study of *o*-disubstituted derivatives of cyclohexane offers many opportunities in determining the effects of one group on the activity of the other, since these compounds lie intermediate to aliphatic and aromatic substances. Studies of *o*-disubstituted derivatives of the cyclohexane series are relatively few and these are confined mainly to compounds in which the groups are similar, such as the dibromo and dichloro prepared from cyclohexene. A few compounds in which the *ortho* groups are dissimilar have brief mention in the literature, for example, *o*-iodochloro-cyclohexane,[1] *o*-iodo-cyclohexanol,[2] *o*-iodobromo-cyclohexane and *o*-cyano-iodo-cyclohexane.[3] In addition the preparation of *o*-amino-cyclohexanol, *o*-chloro-cyclohexylamine and *o*-bromo-cyclohexylamine, together with some of their derivatives, will be described.

Experimental.

Preparation of Catalyst.—Metallic nickel was used almost exclusively. Pure nickel nitrate is calcined at a dull red heat for an hour, cooled, and very finely ground. It may be heated again to a red heat to insure complete decomposition of the nitrate. The powdered nickel oxide is then reduced in a stream of hydrogen at 250° for several hours. It is allowed to cool overnight in an atmosphere of hydrogen and is placed in a tightly stoppered flask until used. This catalyst used in the proportion of one part catalyst to 10 of substance remains in an active state for 5 or 6 reductions. If the reduction is proceeding too slowly it is best to replace the old by fresh unused nickel.

Cyclohexane.—Three hundred g. of purified benzene free from thiophene by the isatin test and 30 g. of nickel catalyst are placed in the bomb and shaken well to obtain a good distribution of the nickel. The bomb is placed in an electrically heated hot air oven at 250° and filled with hydrogen at 1800 pounds pressure; at intervals of 2 hours during the day more hydrogen is introduced to replace that which has reacted. At night the bomb is not refilled but is allowed to remain in the oven. At the end of 48 hours the reaction is complete. The bomb is then removed, cooled, and the contents poured into a distilling flask and distilled. The fraction boiling between 80° and 85° is collected and is sufficiently pure for synthetic work. The nickel remaining in the flask is washed back into the bomb with the next run and used again. Yield of cyclohexane, 275 g. or 85% of the theoretical amount.

Cyclohexanol.—Three hundred g. of redistilled U. S. P. phenol is melted and poured into the bomb with 30 g. of nickel. The reduction is

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[1] Brunel, *Zentralbl.*, **1903**, pp. 233, 711.

[2] Brunel, *Compt. rend.*, **135**, 1055–1057 (1902).

[3] Brunel, *Zentralbl.*, **1905**, ii, 1337–1339.

carried out precisely as given for benzene. When completed the reaction product is fractionated, the fraction boiling at 158° at 730 mm. being practically pure cyclohexanol. A small amount of cyclohexane and water is formed and is collected in the lower fraction, boiling between 80° and 110°. If the reduction has not proceeded to completion a fraction boiling above 158° is obtained. This may be returned to the bomb with the next run and the reduction is completed. The nickel is also returned. Yield, 255 g. or 80%.

Cyclohexanone.—Baeyer[1] prepared this substance by the oxidation of cyclohexanol with Beckman's chromic acid mixture and proved its identity with the ketohexamethylene obtained by Perkin, Jr., from calcium pimelate.[2] Baeyer used a proportion of 2 g. of cyclohexanol to 27 g. of the chromic acid mixture. The method used by us is essentially the same, modified slightly to keep the volumes down when dealing with 100-g. portions.

One hundred g. of cyclohexanol and 150 cc. of water are placed in a one-liter flask and cooled in ice water. To this is added gradually 35 cc. of conc. sulfuric acid. One hundred g. of sodium dichromate ($Na_2Cr_2O_7$-$2H_2O$) is dissolved in a solution of 35 cc. of conc. sulfuric acid in 150 cc. of water. The chromic acid solution is added to the cyclohexanol mixture in 10 cc. portions over a period of 2 hours, and the solution is shaken well after each addition. To complete the reaction the mixture is heated in a water-bath for 2 hours, cooled, and ether extracted, the extract dried with potassium carbonate and the ether distilled off. The cyclohexanone boils constantly at 155°. Yield, 83 g. or 85%.

o-**Chloro-cyclohexanone.**—This may be prepared by a method similar to that used by Kotz[3] for the corresponding bromine compound. Chlorine is bubbled through a mixture of 20 g. of cyclohexanone, 15 g. of calcium carbonate, and 50 cc. of water in a flask immersed in cold water, until the reaction is complete. The oil is extracted with ether, dried, and the ether removed. The oil does not distil *in vacuo* without decomposition and is difficult to obtain pure and free from chlorine.

Attempts to form an aminoketone invariably led to condensation products, and secondary and tertiary amines.

Cyclohexanone Oxime.—Baeyer[4] obtained the oxime in theoretical yield, by allowing the ketone to react with hydroxylamine hydrochloride and excess sodium hydrogen carbonate in alcohol at water-bath temperature, extracting the residue with ether and recrystallizing the residue from petroleum ether. It may also be obtained with equal facility and in theoretical yield in water solution by the following method.

[1] A. Baeyer, *Ann.*, 278, 88–116 (1894).

[2] W. N. Perkin, Jr., *Ber.*, 18, 3245–3252 (1885).

[3] Kotz, *Ann.*, 358, 194–208 (1907).

[4] Baeyer, *ibid.*, 278, 88–116 (1894).

Eight and four-tenths g. of hydroxylamine sulfate in 60 cc. of water is added in small portions to a mixture of 10 g. of cyclohexanone and 50 cc. of water containing 4.1 g. of sodium hydroxide or excess of bicarbonate. The reaction flask should be continually shaken and cooled under tap water. When nearly all the hydroxylamine has been added the oxime separates as a crystalline solid and is filtered immediately, washed with water, and dried. If the reaction mixture is not cooled a red color is developed and the yield decreased. The dried product recrystallized from boiling ligroin melts at 88°.

Cyclohexylamine.—Many attempts to prepare cyclohexylamine by direct catalytic reduction of aniline have at the best resulted in very poor yields. By Paal's method a yield of 10% has been obtained in 80 hours.[1] The use of Sabatier's and Senderens' method results in destruction and numerous side reactions. Ipatiew[2] reports a yield by his method of from 40 to 50%, with nickel oxide as a catalyst and a pressure of 115 to 120 atmospheres. We have attempted to use Ipatiew's method with a nickel catalyst, but it has invariably resulted in such great destruction and production of side reactions as to cause its abandonment.

Cyclohexylamine may be obtained in good yield by reduction of ketohexamethylene oxime by either the method of Sabatier and Senderens[3] or that of Baeyer.[4]

In Baeyer's method 5 g. of the oxime is dissolved in 200 cc. of absolute alcohol and added to 25 g. of sodium. It is best to dissolve all the oxime in a small amount of alcohol, and add the solution to the sodium. Additional alcohol is then poured through the reflux condenser. In this way all the oxime is present during the entire reaction.

Ten g. of cyclohexanone oxime in 30 cc. of absolute alcohol is added through a reflux condenser to 50 g. of sodium strips, followed by an additional 400 cc. of absolute alcohol. When the reaction is complete the alcohol is distilled from a water-bath, water is added, and the solution made acid with hydrochloric acid. The acid solution is evaporated to dryness on a water-bath with the help of an air blast. A small amount of water is added (20 cc.), and an excess of solid potassium hydroxide. The oil which separates is extracted with ether, dried, and distilled, after removal of the ether; b. p., 133°. It distills with some decomposition and takes up carbon dioxide very rapidly, and consequently is best distilled in a stream of hydrogen as Baeyer recommends. However, this is not necessary if the receiver is protected with a soda-lime tube. The melting point of the carbonate is 110°, the hydrobromide 195°, the hydrochloride 204°, the acetate 147°, and the acetyl derivative 99°.

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[1] Willstätter and Hatt, 45, 1471–1481 (1912).

[2] Ipatiew, *Ber.*, 41, 991–3 (1908).

[3] Amouroux, *Chem.-Ztg.*, 35, 192 (1911).

[4] Baeyer, *Ann.*, 278, 88–116 (1894).

Cyclohexene.—Many methods have been proposed for the production of cyclohexene from cyclohexanol, using various dehydrating agents. It is also frequently made by treating monohalide cyclohexanes with alkalies, such as calcium oxide[1] and quinoline. Among the dehydrating agents may be mentioned particularly oxalic acid,[2] iodine,[3] sulfuric acid,[4] dimethyl sulfate,[5] and potassium hydrogen sulfate.[6]

Zelinsky, using one part of cyclohexanol to 5 parts of anhydrous oxalic acid at 100° to 110°, obtained cyclohexene. In using this method it has been found that this proportion may be considerably increased and good yields obtained. The process may be made continuous by addition of cyclohexanol as the tetrahydrobenzene and water distil over, and with occasional addition of anhydrous oxalic acid to replace that which is destroyed or distils over as the ester of cyclohexanol.

The objection to using dimethyl sulfate is of course obvious; calcium oxide requires a temperature of 350° and special apparatus, and potassium hydrogen sulfate gives poor yields due to formation of cyclohexyl ether. The catalytic sulfuric acid method described by Senderens is easy of application and gives practically a 90% yield. The procedure followed is precisely that of Senderens.

One hundred g. of cyclohexanol and 2 cc. of conc. sulfuric acid are slowly distilled until white fumes are evolved and the odor of sulfur dioxide is apparent. The water and cyclohexene in the distillate are separated, the cyclohexene dried with potassium carbonate and redistilled. Sixty g. of pure cyclohexene, boiling 82° to 84°, is obtained, and 16 g. of a higher boiling fraction, consisting of a mixture of unacted-on cyclohexanol and cyclohexene. Yield of pure cyclohexene, 73%. This may be increased to approximately 90% by retreating the higher fraction with the next run.

In searching for other agents which would serve to dehydrate cyclohexanol to cyclohexene, phosphorus trichloride has been found to be fairly efficient. Its disadvantage lies in the amount of phosphorus trichloride necessary to be used and in the mechanical losses of cyclohexene which occur. About one kg. of cyclohexene has been prepared by the following method.

Two hundred and seventy-four g. of phosphorus trichloride is added slowly through a dropping funnel to 300 g. of cyclohexanol in a one-liter flask fitted with a reflux condenser. The temperature is maintained at

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[1] Schmidt, Hochschwender and Eichler, U. S. Patent 1,221,382. *C. A.* **11,** 1885 (1917).

[2] Zelinsky and Zelikow, *Ber.*, **34,** 3249–3256 (1901).

[3] Hibbert, Brit. Pat. 5,408; *C. A.* **9,** 2291 (1915); THIS JOURNAL, **38,** 1748 (1915).

[4] Senderens *Compt. rend.*, **154,** 1168–1170 (1912).

[5] Chavonne and van Roelen, *Bull. soc. belge. chim.*, **22,** 410–413 (1908).

[6] Brunel, *Bull. soc. chim.*, [3] **33,** 270–271 (1905).

70° by immersion in a water-bath. Addition of the first mole (137 g.) of phosphorus trichloride produces a vigorous reaction, but the second may be added more rapidly. When all the phosphorus trichloride has been added the product is refluxed for 4 hours and then distilled from the phosphorus oxide. One hundred and fifty cc. of water is added to the distillate through a reflux condenser and the mixture is refluxed for a short time to decompose all excess phosphorus trichloride. The cyclohexene is separated from the aqueous layer, dried, and distilled. Yield of cyclohexene, 65% of the theoretical amount, or 160 g. of tetrahydrobenzene boiling between 82° and 87°, and 30 g. of a fraction boiling between 87° and 160°.

It is necessary to have the cyclohexanol warm when the trichloride is added as otherwise considerable chloro-cyclohexane is formed, which is not broken down by subsequent treatment and may be obtained in the final distillation as the fraction boiling at 143°.

***o*-Chloro-cyclohexanol.**—This substance, described by Fortey,[1] was made by shaking tetrahydrobenzene with a dilute hypochlorous acid solution, the hypochlorous acid being made by passing chlorine into water containing freshly precipitated mercuric oxide. Fortey described it as a yellowish oil distilling with decomposition and having a characteristic odor. Prepared by the following method it is a water-white oil possessing a characteristic odor, distilling in atmospheric pressure with only slight decomposition.

One hundred cc. of cyclohexene (about 3 times the calculated quantity) is shaken with 1700 to 1800 cc. of a 2% hypochlorous acid solution; the acid is added in 200 cc. portions and the mixture shaken until it is decolorized before the addition of more. When all hypochlorous acid has been added the mixture is shaken until one cc. gives only a faint or no yellow color with potassium iodide solution. The hypochlorous acid has always been made by bubbling carbon dioxide through a suspension of bleaching powder in water and filtering off the calcium carbonate. The reaction product is saturated with salt and steam distilled. The distillate is saturated with salt, and the upper layer of cyclohexene and *o*-chloro-cyclohexanol removed and fractionated. The first fraction boiling below 90° at 20 mm. is a mixture of water, unacted-on cyclohexene and some *o*-chloro-cyclohexanol, which may be used again. The *o*-chloro-cyclohexanol boils, at 92° under pressure of 10 mm. Yield, 85 g.

Subs., 0.1236: AgCl, 0.1298.
Calc. for $C_6H_{11}OCl$: Cl, 26.35. Found: 25.99.

***o*-Amino-cyclohexanol.**—No mention of *o*-amino-cyclohexanol can be found in the literature although it is easily prepared from *o*-chloro-cyclohexanol and alcoholic ammonia, the chlorine being substituted by the

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[1] Fortey, *J. Chem. Soc.*, 23, 948 (1898).

amino group. In aqueous solutions secondary and tertiary amines are the chief products, but if sufficient strength of alcohol is used to maintain a clear solution the primary amine is the chief product.

For the preparation of the free amine the following has been found to be the best procedure. 26.8 g. ($^1/_5$ mole) of *o*-chloro-cyclohexanol is placed in a pressure bottle (the ordinary citrate of magnesia bottle fitted with a rubber stopper which can be clamped down is satisfactory) and 100 cc. of a strong solution of ammonia in 50% alcohol is added. If the solution is not clear, a higher per cent. of alcohol is used. The bottle is shaken well and is then heated in a steam-bath for one hour. The contents of 5 such bottles after cooling are poured into a one-liter distilling flask, 60 g. of anhydrous sodium carbonate is added and the alcohol and water distilled off; the temperature should be allowed to rise to 110° and maintained there until the greater portion of water is removed. Two hundred cc. of alcohol is added. The salts are removed by filtering the hot solution with suction, washing the precipitate well with alcohol. The alcohol is removed by distillation and the residue fractionated *in vacuo*, using the side neck of the flask as a condenser and immersing the receiver flask in ice water.

The fraction distilling up to 120° at 7 mm. pressure is redistilled at atmospheric pressure. The pure *o*-amino-cyclohexanol boils at 104° at 7 mm. pressure and at 212° at atmospheric pressure. It crystallizes in the receiver in rosets which melt at 65°. Yield, 70 g.

Subs., 0.0100: Amino nitrogen, 2.19 cc. (21° and 734 mm.).
Calc. for $C_6H_{13}ON$: N, 12.17. Found: 12.00.

Melting point of salts made from the corresponding acid and an ether solution of the amine: hydrochloride, 175°; hydro-iodide, 187°; hydrobromide, 191°; carbonate, 139°; sulfate not melted at 250°.

***o*-Chloro-cyclohexylamine.**—In attempting to prepare an *ortho* halogen cyclohexylamine, *o*-amino-cyclohexanol was treated with fuming hydriodic acid in a sealed tube at temperatures from 100° to 150°. It was found that the iodine did not replace the hydroxy group at a temperature below 130°, while at a higher temperature there was a deep-seated decomposition, with the separation of ammonium iodide. Hydrobromic acid also failed to substitute. Thionyl chloride does not replace the hydroxy group even when refluxed at the boiling point. Phosphorus trichloride does not substitute the hydroxy group with chlorine, producing instead an ester of a phosphorus acid. The great resistance of the hydroxy group suggested the necessity of using phosphorus pentachloride. When this was tried in chloroform a very poor yield of *o*-chloro-cyclohexylamine was obtained. Further investigations showed that phosphorus oxychloride readily reacts with *o*-amino-cyclohexanol in chloroform even at a temperature of 0°, apparently forming the phosphoric acid ester. If, however, the hydrochloride of *o*-amino-cyclohexanol is suspended in chloroform the reaction with phosphorus oxychloride is practically suppressed. Phosphorus pentachloride, even at 0°, reacts vigorously with the hydrochloride of *o*-amino-cyclohexanol.

The reaction product dissolved in water after the treatment with phosphorus pentachloride in chloroform is made alkaline with sodium hydroxide, extracted with ether, the ether removed, and the residue consisting of *o*-chloro-cyclohexylamine distilled *in vacuo.* Boiling point 85°, at 15 mm. pressure.

Fifty-seven and one-half g. ($^1/_2$ mole) of *o*-amino-cyclohexanol is dissolved in 300 cc. of anhydrous and alcohol-free chloroform. The chloroform solution is placed in a one-liter Erlenmeyer flask, with side neck, and fitted with a one-hole rubber stopper. A few milligrams of methyl orange is added and dry hydrogen chloride led in through a glass tube until the reaction is distinctly acid, indicating complete formation of the hydrochloride. The flask is cooled in ice-water. One hundred and fifty g. of phosphorus pentachloride, ground in a dry mortar to a fine powder, and about 300 cc. of purified chloroform are placed in a one-quart Mason fruit jar, which is packed in an ice- and salt-mixture. To this suspension, which is stirred mechanically and maintained below 0°, is added the mixture of *o*-amino-cyclohexanol hydrochloride and chloroform. This will require approximately one hour. The solution may then be filtered. The hydrochloride of the *o*-chloro-cyclohexylamine is quite soluble in chloroform, but a considerable portion will separate at 0°. The chloroform solution is placed in a one-liter distilling flask. One hundred cc. of water is added and the flask placed under a reflux condenser. Occasional shaking will start the reaction, decomposing the phosphorus oxychloride. After the vigorous reaction has subsided it is refluxed in a water-bath for not less than 90 minutes in order to decompose the last traces of phosphorus oxychloride. The chloroform is then distilled and the residue placed in a tall jar. The volume of the residue should be between 100 and 200 cc. This is packed in ice and salt, and a saturated solution of sodium hydroxide in water is added. The solution is stirred with a mechanical stirrer until it becomes very thick. Ether is then added and sufficient sodium hydroxide to make the solution distinctly alkaline. Solid sodium hydroxide is now added, and about 500 to 600 cc. of ether. The salt separates in solid, dry form and is readily extracted with ether. Three extractions are generally sufficient. The ether is dried over solid sodium hydroxide, removed by distillation, and the *o*-chloro-cyclohexylamine distilled *in vacuo*. The yield depends on the extent to which water is excluded and may reach 70 to 80%. If water is not completely excluded the yield may drop as low as 50%. The *o*-chloro-cyclohexylamine is a colorless oil of characteristic odor, which does not solidify at —10°.

Subs., 0.1412: AgCl, 0.1510.
Calc. for $C_6H_{12}NCl$: Cl, 26.55. Found: 26.45.

Hydro-anilides from *o*-amino-cyclohexanol and *o*-chloro-cyclohexylamine may be quantitatively prepared by the usual methods in an indifferent solvent, such as chloroform. As examples, the preparation of the acetyl and chloro-acetyl derivatives is given.

Acetyl-*o*-chloro-cyclohexylamine, $\underline{CH_2CH_2CH_2CH_2CHClCH}.NHCO.CH_3$.—To 13.4 g. of *o*-chloro-cyclohexylamine dissolved in 50 cc. of anhydrous chloroform and immersed in ice-water is added a solution of 12 g. (1.5 times of the theoretical amount) of acetyl chloride in chloroform. When all is added the solution is refluxed for about 2 hours. A small amount of alcohol is added to decompose the excess acetyl chloride, and the chloroform distilled off on a water-bath. The residue may be recrystallized by dissolving it in 90% alcohol and diluting this solution with water; m. p. 88°.

Chloro-acetyl-*o*-chloro-cyclohexylamine, $\underline{CH_2CH_2CH_2CH_2CHClCH}.NH.CO.CH_2Cl$.—This is prepared by a procedure identical with that given for the acetyl, using 1.5 times the calculated amount of chloro-acetyl chloride. It is recrystallized from the alcohol by the addition of water. It is soluble in hot water, one part in 220; in cold water, one part in 2,000. The chloro-acetyl-*o*-chloro-cyclohexylamine melts at 111°.

Subs., 0.0882: AgCl, 0.1192.
Calc. for $C_8H_{13}ONCl_2$: Cl, 33.76. Found: 33.43.

Cyano-acetyl-*o*-chloro-cyclohexylamine, $\underline{CH_2CH_2CH_2CH_2CHClCH}.NH.CO.CH_2CN$.—The chloro-acetyl-*o*-chloro-cyclohexylamine may be treated with large excesses of sodium cyanide in water at the boiling point for a short time with substitution taking place only on the side chain. The yield, however, is not particularly good, since boiling with alkalies decomposes the nitrile present to some extent.

A mixture of 4 g. of chloro-acetyl-*o*-chloro-cyclohexylamine and 4 g. sodium cyanide in 400 cc. of water is boiled for 10 minutes. The solution is then quickly made acid to methyl orange by addition of about 15 cc. of conc. hydrochloric acid diluted 1 : 1. The cyano-acetyl-*o*-chloro-cyclohexylamine crystallized on cooling. Yield, 2.3 g. It may be purified by recrystallizing from hot water; m. p. 139°.

Subs., 0.1357: AgCl, 0.0965.
Calc. for $C_9H_{13}ON_2Cl$: Cl, 17.59. Found: 17.59.

***o*-Chloro-hexahydro Anilide of Malonic Acid,** $\underline{CH_2CH_2CH_2CH_2CHClC}$-

$CH.NH.CO.CH_2COOH$.—This may be obtained by converting the corresponding cyano compound first to the ester, and then hydrolyzing the ester to the sodium salt with an aqueous solution of sodium hydroxide.

Four g. of the cyano-acetyl-*o*-chloro-cyclohexylamine is dissolved in 75 cc. of alcohol, which is then saturated with dry hydrogen chloride. It is refluxed for one hour while passing a stream of dry hydrogen chloride through the solution. The solution is concentrated to $^1/_2$ the original volume, the ammonium chloride removed by filtering, and the remainder of the alcohol distilled off *in vacuo*. The residue is taken up in water, 5 cc. of 30% sodium hydroxide added, and the product shaken until the saponification is complete. The alkaline solution is then acidified with hydrochloric acid and allowed to stand. The free acid crystallizes slowly; m. p., 132°.

Subs., 0.1598: AgCl, 0.1046.
Calc. for $C_9H_{14}O_3NCl$: Cl, 16.14. Found: 16.17.

o-**Bromo-cyclohexylamine**, $\underline{CH_2CH_2CH_2CH_2CHBrCH}.NH_2$.—This may be obtained in a manner similar to that given for the *o*-chloro-cyclohexylamine. It is not necessary, however, to maintain as low a temperature during the reaction.

Fifty-seven and one-half g. of *o*-amino-cyclohexanol is precipitated as the hydrochloride salt in anhydrous chloroform, as described for the preparation of the corresponding chlorine derivative. This suspension is added to a suspension of phosphorus pentabromide in anhydrous chloroform. The phosphorus pentabromide is prepared by adding 70 cc. of dry bromine to 17 g. of yellow phosphorus in 150 cc. of chloroform, cooling the jar in ice-water, and stirring mechanically. During the addition of the *o*-amino-cyclohexanol hydrochloride it is not necessary to cool the reaction mixture as the temperature does not rise above 35° or 40°. When the mixture becomes clear the chloroform is removed by distillation on a water-bath. About 300 cc. of toluene is then added and the solution cooled. The crystals which separate are filtered off, washed well with toluene, and dried.

Purification is effected by dissolving the crystals in a small amount of water, making this solution strongly alkaline with a 30% solution of sodium hydroxide, and extracting this product a few times with toluene. The toluene is dried for not more than one hour over stick sodium hydroxide and the amine is then precipitated as the hydrochloride salt with hydrogen chloride, in the form of needles, melting at 168°. Yield, 75 g. or 70%.

Subs., 0.0732: AgHal., 0.1142.
Calc. for $C_6H_{13}NBrCl$: Halogen, 54.04. Found: 53.89.

Acetyl-*o*-bromo-cyclohexylamine, $\underline{CH_2CH_2CH_2CH_2CHBrCH}.NH.CO$-

CH_3.—To 21.4 g. of *o*-bromo-cyclohexylamine hydrochloride in toluene is added 10 cc. of acetyl chloride and the mixture is refluxed for several hours. When the reaction is completed the toluene is removed *in vacuo.* The solid residue is dissolved in a small amount of warm alcohol and ice-water added. An oil separates, which crystallizes in a short while. M. p. of the acetyl derivative, 103–104°. Yield, 13.5 g. or 61%.

Subs., 0.1516: AgBr, 0.1312.
Calc. for $C_8H_{14}ONBr$: Br, 36.32. Found: 36.81.

Attempts to prepare *o*-iodo-cyclohexylamine in a manner analogous to the preparation of the chlorine and bromine compounds, using phosphorus tri-iodide in chloroform, were unsuccessful. Invariably the main products were esters of *o*-amino-cyclohexanol.

Substitution of bromine for iodine in *o*-bromo-cyclohexylamine, using potassium iodide in aqueous or alcoholic solution, has given 50% substitution, but the product is too impure for definite identification.

Summary.

Methods for obtaining cyclohexane derivatives by direct reduction of the corresponding benzene compounds have been reviewed. The method of Ipatiew for the reduction of benzene and phenol has been particularly applied.

Methods, with some modifications which are most applicable for the laboratory production of cyclohexane, cyclohexanol, cyclohexanone and its oxime, cyclohexylamine, and cyclohexene, are described.

Methods for obtaining the following *ortho* substituted cyclohexane compounds in which the *ortho* groups are dissimilar, chloro-cyclohexanone, chloro-cyclohexanol, amino-cyclohexanol, chloro-cyclohexylamine and bromo-cyclohexylamine, with certain of their derivatives, are given.

Work in this series is being continued.

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FRACTIONATION OF CHAULMOOGRA OIL.

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The material known commercially as chaulmoogra oil has assumed considerable importance in recent years. For many years, perhaps for centuries, this oil has been used in India as a palliative in leprosy. In more recent times it has had more or less use in all countries where leprosy occurs. Taken by way of the mouth its administration is frequently attended by amelioration of the disease, although the intolerance exhibited by many persons limits its usefulness, and at best the action is slow.

New interest was aroused by the results obtained by intramuscular injections of this oil fluxed with olive oil, a line of experimentation to which the work of Heiser was especially stimulating. Leprologists believed that although chaulmoogra oil had by no means been proven a specific in leprosy, it was the most promising drug known in combating the disease.

The statements in the older literature dealing with the origin and composition of chaulmoogra oil are conflicting and unreliable. It was frequently stated to be the product of *Gynocardia odorata* and to contain "gynocardic acid" as its characteristic constituent. The true origin and nature of the oil was elucidated by Power and his collaborators in a series of papers from the Wellcome Chemical Research Laboratories.[1]

These authors showed that the true chaulmoogra oil is derived from the seeds of *Taraktogenos Kurzii* and that the oils from 2 closely related species of *Hydnocarpus* were practically identical. The oil from *Gynocardia odorata*, however, is wholly different. The outstanding feature of their work was the discovery of a new type of fatty acid present in *Taraktogenos* and *Hydnocarpus* oils. These acids are strongly dextro-rotatory and the study of their consitution indicated that they contain a 5-membered carbon ring with side chains of different length. Two acids of this series were isolated and studied; chaulmoogric acid, $C_{17}H_{31}.COOH$, and hydnocarpic acid, $C_{15}H_{27}.COOH$. Chaulmoogric acid melts at 68°, has an iodine value of 90.1, and shows a specific rotation of +56°; hydnocarpic acid melts at 59°, possesses an iodine value of 100.2, and gives a specific rotation of + 68.1°. Structural formulas believed to be consistent with their experimental results were proposed.

Brill,[2] in a series of papers from Manila, confirmed the work of Power and his collaborators by isolating both chaulmoogric and hydnocarpic acids and extended our knowledge of their distribution in several species of plants related to those examined by Power.

The following tabular statement shows some of he essential facts concerning these oils.

	Taraktogenos[a] Kurzii.	Hyndo. carpus[a] Wightiana.	Hydnocarpus[a] anthelminticus.	Hydnocarpus[b] venenata.	Hydnocarpus[b] alcalae.	Pangium[b] edule.
Melting point......	22	22	24	20	32	Cloudy at 2°
Specific gravity....	0.951 (24°)	0.958 (25°)	0.953 (25°)	0.948 (30°)	0.9502 (30°)	0.9049
Specific rotation....	+52.0°	+57.7°	+52.5°	+52.03°	+49.6°	+4.28°
Iodine value.......	103.2	101.3	86.4	99.1	93.1	113.1
Chaulmoogric acid..	+	+	+	+	(90%) +	?
Hydnocarpic acid..	+	+	+	+	—	?

[a] Power, *et al.*

[b] Brill.

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[1] Power and Gornall, *J. Chem. Soc.*, 85, 838, 851 (1904); Power and Barrowcliff, *ibid.*, 87, 884 (1905); Barrowcliff and Power, *ibid.*, 91, 557 (1907).

[2] H. C. Brill, *Philippine J. Sci.*, Section A, 11, 75 (1916); 12, 37 (1917); Brill and Williams, *Philippine J. Sci.*, Section A, 12, 207 (1917).

Goulding and Akers[1] showed that the oil from the seeds of *Oncoba cs'uinata*, an African plant belonging to the same family as *Taraktogenos* and *Hydnocarpus*, yielded chaulmoogric acid to the extent of 87.5% of its fatty acids.

It is therefore well established that optically active oils containing esters of acids of the chaulmoogric acid series are quite widely distributed in the seeds of members of the order *Flacourtiaceae*.

The injection of chaulmoogra oil rendered more liquid by admixture with about an equal volume of olive oil and combined with other drugs was tried at the Kalihi Leprosy Hospital in Honolulu by officers of the United States Public Health Service. The results led them to believe that there might be real value in such administration and in the fall of 1915 they came to the chemical laboratory of the College of Hawaii for assistance. On the assumption that there was some therapeutic value in the oil, the most obvious line of experimentation was that directed to the isolation of the active agent or agents and the preparation of liquids more suitable for intramuscular or intravenous injections.

Since there was no method of testing for the curative principle except the results of injections, the plan proposed was to split the oil up into fractions, test these and follow the clues which their clinical application might furnish. The form of material for administration presented some difficulties. The mixed fatty acids from chaulmoogra oil are solid at ordinary temperatures. The physicians were adverse to using the soluble salts for intravenous injections for fear of haemolysis. On making the ethyl esters of the fatty acids we found them thin liquids and experiment showed that they were readily absorbed from intramuscular injections.

Leprosy is a slow disease and improvement, when it occurs, is a matter of months and even years. After several years' experience with ethyl esters of the fatty acids of chaulmoogra oil the working hypothesis appeared justified that the fatty acids of the chaulmoogric acid series are specific in leprosy.

Reports of the earlier part of the clinical work have been published[2] and a later report will soon appear. In brief it may be said that a considerable number of patients improved to the point of becoming clinically and bacteriologically free from leprosy and that it was impossible to identify this effect with any one of the 4 fractions of fatty acids used.

It seemed important to test out the hypothesis stated above by placing groups of lepers on treatment with the pure ethyl esters of chaulmoogric acid and hydnocarpic acid. This necessitated the preparation of con-

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[1] Goulding and Akers, *Proc. Chem. Soc.*, 29, 197 (1913).

[2] Hollmann and Dean, *J. Cutaneous Diseases*, 37, 367. McDonald and Dean, *U. S. Public Health Repts.*, Aug. 20, 1920.

siderable quantities of the pure acids and led to the following study of methods of fractionating chaulmoogra oil.

Experimental Part.

Separation of Fatty Acids by Crystallization from Alcohol.—Five hundred g. of the mixed fatty acids from chaulmoogra oil was dissolved by warming with 1125 cc. of 92% alcohol and allowed to crystallize over night in the refrigerator, which gave an approximately 30% yield of a semi-crystalline material which, after repeated recrystallization from alcohol, gave about 18 g. of chaulmoogric acid melting at 68°.

By concentrating the mother liquors resulting from the above operations further yields of less crystalline material were obtained which on extended recrystallization from alcohol gave a few grams more of pure chaulmoogric acid, but no hydnocarpic acid. It was found that this semi-crystalline material, which may have represented a eutectic mixture of chaulmoogric and hydnocarpic acids, on recrystallization from alcohol rapidly improved in melting point until the range of 48–52° was reached, after which repeated crystallization had little effect beyond the separation of very small first crops melting at 52–54° which, if saved and combined with others of similar melting point and then recrystallized several times from alcohol, would afford fractions of a gram of pure chaulmoogric acid.

To determine whether or not a slower rate of crystallization than that obtained in the refrigerator would effect a more clean-cut separation of chaulmoogric acid and perhaps furnish the means for isolating hydnocarpic acid, the following experiment was tried.

Four hundred and seventy-nine g. of mixed fatty acids was dissolved in 1000 cc. of hot 92% alcohol, the resulting solution cooled to room temperature and slowly evaporated in a current of air from an electric fan, during which the temperature remained between 20° and 23°. As evaporation and precipitation progressed the following fractions were removed:

Fraction.	Time required to precipitate. Hours.	Yield. G.	Melting point. °C.
1...........	3	57	43–44
2...........	1	79	42–46
3...........	3	63	43–47
4...........	Overnight	139	43–45
5...........	....	40	25–35
6...........	....	100	Below 25

The fourth fraction appeared to contain a small amount of oil occluded in the solid material.

To the small amount of mother liquor from this fourth fraction water was added, which caused precipitation at first, then separation into aqueous and oily layers. The oil was taken up in ether, washed free from alcohol and dried. On evaporating the ether an oily mass was obtained which was separated, by pressing, into about 40 g. of low melting solids and 100 g. of oil which were designated as the fifth and sixth fractions, respectively.

The first and second fractions were combined and recrystallized from 92% alcohol, which gave 35 g. of semi-crystalline material melting at 44–45°, and the mother liquor which was evaporated to dryness and combined with the original third, fourth and fifth fractions. These combined materials were recrystallized from alcohol but gave low melting solids and mother liquors from which oily materials were obtained. On account of this, and the failure of the 2 fractions to give a crystalline material of appreciably improved melting point on recrystallization, this method was abandoned.

Separation of Fatty Acids by Means of Barium Acetate.—The following experiment was undertaken to determine whether chaulmoogric and hydnocarpic acids could be obtained on the large scale from chaulmoogra oil by the barium acetate method which enabled Power and Barrowcliff to isolate hydnocarpic acid from chaulmoogra oil[1] and which they used successfully in preparing this acid from the oil derived from the seeds of *Hydnocarpus Wightiana.*[2]

Four hundred and seventy-eight g. of the mixed fatty acids from chaulmoogra oil was dissolved in one liter of 93.5% alcohol, and boiled with animal charcoal for 1.5 hours to remove the resinous matter which imparted a yellow color to the solution. After filtering off the animal charcoal, which left the solution much lighter in color, another liter of alcohol was added and the solution warmed. To this was added, with constant stirring, 62 g. of barium acetate monohydrate dissolved in the least possible quantity of hot water, this being a slight excess over the calculated amount of barium acetate necessary to precipitate $^1/_4$ of the fatty acids, figured in terms of chaulmoogric acid, $C_{17}H_{31}.COOH$. A pasty mass was immediately precipitated which did not entirely dissolve on heating. When the solution was cool, a large flocculent precipitate separated which was filtered off. To the resulting mother liquor a second and third 62-g. portion of barium acetate were added, which furnished the second and third fractions of barium salts respectively; also a final mother liquor from which the alcohol was evaporated, leaving a pasty non-crystalline mass.

The 3 fractions of barium salts were warmed with an excess of dil. sulfuric acid which caused precipitation of barium sulfate and liberation of free fatty acids which were liquid at the temperature employed and rose to the top of the aqueous layer in the form of a reddish-brown oil.

This treatment with dil. sulfuric acid had to be repeated several times,

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[1] *J. Chem. Soc.*, 87, 896 (1905).

[2] *Ibid.*, 87, 888 (1905).

as it was found to be difficult to remove the last of the barium salts from the oily layer. During this process the discoloration of the fatty acids increased, due probably to slight charring, in spite of the fact that the sulfuric acid used was quite dilute.

Fractions 1 and 2 were combined, dissolved in 93.5% alcohol and boiled with animal charcoal to remove charred matter, after which the solution was filtered and allowed to crystallize. The resulting material was small in amount and melted at 61°. After several recrystallizations it melted at 67–68°, and as this remained unchanged on recrystallization from a variety of solvents the material was apparently chaulmoogric acid. The yield was less than 10 g.

The third fraction and the residue from the final mother liquor were combined and treated in a similar manner. After 2 crystallizations the material melted at 62°; after 4 crystallizations it melted at 58° and after 2 more crystallizations it melted at 60°. As the yield at this point was only a little over 0.2 g., it was not practicable to recrystallize it again to determine whether the melting point had become stationary, but since a little of this material mixed with an equal part of the chaulmoogric acid obtained from the first 2 fractions melted at 55°, it was assumed that this was hydnocarpic acid rather than an impure chaulmoogric acid.

While the yields of both chaulmoogric and hydnocarpic acids could undoubtedly be increased by improved manipulation, this method was abandoned as unsuitable for producing these acids in sufficiently large quantities.

Fractional Distillation of Ethyl Esters Under High Vacuum.—The mixed ethyl esters of the acids in chaulmoogra oil were prepared by passing dry hydrogen chloride into a mixture of equal volumes of dry alcohol and the mixed, free fatty acids. The resulting esters, after being washed and dried, had a specific gravity of 0.891 at 15.5° and were reddish-brown in color. By titration it was found that they contained about 5% of uncombined acids.

The apparatus used for the distillation of these esters consisted of a 500 cc. Kjeldahl flask with a fractioning column in the neck, composed of glass beads supported by a tight roll of wire gauze placed at the bottom of the neck. This roll of gauze also served the purpose of preventing frothing over. The flask was provided with a cork stopper through which ran a thermometer, a dropping funnel and a delivery tube. The delivery tube was constructed from a meter length of ordinary glass tubing by making an approximately 80° bend in it sufficiently near one end so that the short arm would just reach through the cork.

Considerable difficulty was experienced in obtaining an air-tight joint at this point. The use of rubber stoppers was prohibited on account of the softening effect of the hot vapors. The best results were obtained by cutting a special cork on a turning lathe so that it could penetrate the neck of the flask about $1^1/_2$ inches, making a good contact with the glass all the way, and yet be prevented from going too far by means of a shoulder left on the top of the cork. A coat of shellac over this made a fairly effective seal.

At the far end of this delivery tube, which on account of its length also acted as a condenser, was connected, by means of a short length of pressure tubing, a 3-way stopcock through which the distillate could be directed into either of 2 graduated receivers. Beyond these receivers, and connected to them by short lengths of glass tubing, was a 4-way stopcock by means of which either receiver could be connected with the outer air to release its vacuum while the other receiver was connected through a manometer to a powerful motor-driven vacuum pump. By means of this apparatus the fraction which had been collected in one of the receivers could be removed while the distillate was caught in the other, without the vacuum or the rate of distillation being disturbed.

Two 350-cc. portions of the mixed ethyl esters were subjected to fractional distillation in this apparatus, the results of which are given in tabulated form below.

Distillation of Two 350 cc. Portions of Mixed Esters Under Pressure of 3 to 4 mm.

Fraction.	Temp. range. ° C.	No. 1. Cc.	No. 2. Cc.
A-1	Below 185	90	90
A-2	185–190	80	155
A-3	190–195	90	40
A-4	Above 195	70	45
Total vol. recovered		330	330

As both portions of ethyl esters were from the same lot, it was assumed that fractions of approximately equal volume would be obtained in each case, when these were collected over the same temperature range. It will be noted, however, that there is a wide discrepancy between the volumes of fractions Nos. A-2, A-3 and A-4 obtained from these duplicate operations. This is accounted for by the fact that under the high vacuum employed here, slight variations in pressure, with the consequent changes in the rate of heating necessary to maintain a fairly even rate of distillation, cause variation of 6° to 8° in the temperature recorded by the thermometer in the neck of the flask.

The corresponding fractions from these duplicate operations were combined and redistilled, introducing each combined fraction into the distilling flask through the dropping funnel, as soon as the previous fraction had nearly all distilled over.

The products of this operation were classified into 4 fractions according to the temperature at which they had distilled over. The results were as follows.

Fraction.	Volume. Cc.	Temperature range. ° C.
B-1	150	Below 185
B-2	290	185–190
B-3	60	190–195
B-4	50	Above 195
Total	550	

One-g. portions of each of the above fractions were saponified, and the melting points of the free acids taken with the following results.

Fraction.	Melting point. ° C.
B-1	51–53
B-2	50–52
B-3	43–48
B-4	56–57

These 4 fractions were redistilled in the manner just described except that the pressure was reduced from 3–4 mm. to one mm. by the use of a more suitable grade of oil in the vacuum pump.

The yields and temperature ranges of the 4 fractions obtained are given herewith.

Fraction.	Volume. Cc.	Temperature ranges. ° C.
C-1	70	Below 175
C-2	340	175–180
C-3	50	180–185
C-4	70	Above 185
Total volume	530	

The results of this and the preceding distillation illustrate the wide difference in boiling-point range caused by a slight difference in the pressure.

One-g. portions from each of the above fractions were saponified and the melting points of the free acids taken, which were as follows.

Fraction.	Melting point. ° C.
C-1	50–53
C-2	52–54
C-3	55–57
C-4	59–62

These 4 fractions were redistilled once more in the same manner as described above with the following results.

Fraction.	Volume. Cc.	Temperature range. ° C.
D-1	260	Below 175
D-2	160	175–180
D-3	40	180–185
D-4	40	Above 185
Total volume	500	

The esters comprising these 4 fractions were saponified by heating with an excess of alcoholic potash and the resulting soaps decomposed with hydrochloric acid. The yields of free fatty acids and their melting points were as follows.

Fraction.	G.	Melting point. ° C.
D-1	197.3	50–53
D-2	118.8	43–47
D-3	21.7	56–60
D-4	20.2	63–65
Total volume	358.0	

It was thought from the above results that the isolation of pure chaulmoogric and hydnocarpic acids simply by distillation of their mixed ethyl esters is not practicable, as the improvement in melting point between the fractions resulting from the second distillation and these resulting from the fourth distillation was so small. When, however, these fractions were recrystallized from alcohol it was at once apparent that a partial separation had been effected. The results were as follows.

	First crystallization from alcohol.		Recrystallization from alcohol.		Second recrystallization from alcohol.	
Fraction.	G.	° C.	G.	° C.	G.	° C.
D-1	50.4	55–56	32	58	21.2	58.5–59.5
D-2	74.2	48–51	61.5	48–51	20	48–51
D-3	13.1	67–68	10	67–68	9.8	67.5–68
D-4	13.8	66–67	6	67–67.5	4.4	67.5–68

The 21.2 g. from Fraction D-1 melting at 58.5–59.5°, on being recrystallized from petroleum ether, benzene, and alcohol, respectively, gave small transparent plates melting at 59–60°, and this melting point did not change upon subsequent recrystallization. It is evident that this material was almost pure hydnocarpic acid.

Fractions D-3 and D-4 which furnished 14.2 g. of acids melting at 67.5 to 68° proved to be almost pure chaulmoogric acid, as on recrystallizing once more this material came down in the form of glistening plates melting at 68° and this melting point did not change on subsequent recrystallization.

This method was abandoned in favor of the more satisfactory method of direct fractional distillation of the fatty acids themselves, but the ester distillation method is thought to be a very promising one and will be investigated further.

Fractional Distillation of Fatty Acids.—For the distillation *in vacuo* of the fatty acids themselves, which are solid at ordinary temperatures, it was necessary to modify the apparatus used in distilling the ethyl esters described above.

The delivery tube was shortened to 35 cm. in order that the distillate could pass through hot, and not tend to solidify. The end of the delivery tube reached through a No. 10 2-hole stopper, through the other hole of which extended a short piece of glass tubing which was connected with the vacuum line through a 3-way stopcock.

This large 2-hole stopper was inserted into a wide mouthed dropping funnel, the stem of which was cut off 5 cm. below the valve, and inserted into one of the 2 openings of a No. 11 2-hole stopper which fitted into a graduated receiver. Through the other hole of this stopper was a short piece of glass tubing which was connected to a 3-way stopcock, one branch of which communicated with the outer air, the other being connected with the 3-way stopcock in the vacuum line to which reference is made above.

By means of this apparatus, when a fraction of the desired size had collected in the graduated receiver, the valve in the stem of the dropping funnel above the receiver could be closed, the vacuum could be communicated to the connection in the dropping funnel, while air could be allowed to enter the graduated receiver through the 3-way stopcock connected to it. In this way the receiver could be removed, while the distillate meanwhile was collecting in the dropping funnel under a vacuum which had not been disturbed. Having replaced the graduated receiver and evacuated it, the one-way stopcock above it could be opened and the small amount of distillate in the dropping funnel allowed to flow down into the graduated receiver. The principle of this receiving apparatus was the same as that of the special receiver shown in Fig. 2, which was designed later to eliminate the difficulties encountered in operating this improvised apparatus, the worst of which were air leaks in the rubber connections, and clogging up of the small bores of the stopcock by condensed fatty acids.

Three hundred and fifty cc. of mixed fatty acids from chaulmoogra oil was distilled in this apparatus under a pressure of 1.5 mm. which increased to 3 mm. when the distillation was about half completed, due to an air leak. The results are given in tabulated form herewith.

Fraction.	Volume. Cc.	Temperature range. ° C.	Melting point of crude distillate. ° C.	Melting point distillate crystallized from alcohol. ° C.
1	40	174–199	48–49	54–55
2	100	199–204	49–52	54–56
3	100	204–211	47–49	48–49
4	50	211–212	42–46	67–68

Total volume....290

Thus 290 cc. was recovered, the first 2 fractions of which, amounting to 140 cc., on being recrystallized from 93.5% alcohol 3 times gave approximately 15 g. of pure hydnocarpic acid melting at 59–60°, and the last fraction, amounting to 50 cc., on being recrystallized twice, gave approximately 25 g. of pure chaulmoogric acid melting at 68°.

The third fraction, which melted at 47–49°, did not improve in melting point to any appreciable extent. It is thought to be a eutectic mixture of chaulmoogric and hydnocarpic acids.

Three separate portions of mixed fatty acids from the same lot, consisting in each case of 300 g. (325 cc.) were distilled *in vacuo*, the results of which are given below. As in the case of the ethyl esters, there is a wide discrepancy in temperature-range of the vapor for corresponding fractions, due to slight variations in the pressure and rate of heating.

		First Portion.		Second Portion.		Third Portion.	
Fraction.	Volume. Cc.	Temp. range. ° C.	Av. pres. Mm.	Temp. range. ° C.	Av. pres. Mm.	Temp. range. ° C.	Av. pres. Mm.
A-1	20	178–190	2.5	186–193	2.5	186–190	1.5
A-2	100	190–197	2.5	193–196	2.5	190–192	1.5
A-3	100	197–199	2.5	196–203	2.5	192–201	1.5
A-4	70	199–209	2.5	203–208.5	2.5	201–210	1.5

To try the effect of redistillation the corresponding fractions from these distillations were combined and redistilled, adding each fraction through the small dropping funnel in the top of the distilling flask when the previous fraction was nearly all distilled over.

The results of this redistillation and the melting points of the crude distillates, and the small portions thereof crystallized from alcohol, were as follows.

				M. p. of distillates.	
Fraction.	Volume. Cc.	Temp. range. ° C.	Average Pressure. Mm.	Crude. ° C.	Recrystallized. ° C.
B-1	100	160–192	3	45–47	48–51
B-2	300	186–193[a]	1.25	40.5–42.5	48–51
B-3	160	193–197	1.5	40–41	55–57
B-4	240	197–202.5	1.5	50–52	64–66

[a] Shut down overnight between fractions Nos. B-1 and B-2.

These 4 fractions of Series B were redistilled in the same way, cutting into 6 fractions.

				M. p. of distillates.	
Fraction.	Volume. Cc.	Temp. range. ° C.	Average Pressure. Mm.	Crude. ° C.	Recrystallized. ° C.
C-1	70	196–199.5	2	42–46	46–50
C-2	40	199.5–204	2.5	42–46	54–55
C-3	190	204–208.5	2.5	45–47	55–56
C-4	150	199–206.5[b]	2.5	43–45	48–50
C-5	250	206.5–216	2.5	47–49	65–66
C-6	25	216–218	4	55–56.5	65.5–66.5

[b] Shut down overnight between fractions Nos. C-3 and C-4.

Fractions C-2 and C-3, and C-5 and C-6, were combined, necessitating a new designation of the series as follows.

Fraction C-1 becomes Fraction C-*a*
Fraction C-2 and C-3, becomes Fraction C-*b*
Fraction C-4 becomes Fraction C-*c*
Fraction C-5 and C-6, becomes Fraction C-*d*

Each of these 4 resulting fractions was redistilled independently, dividing the distillate from each into fractions when necessary. The results are given herewith in tabulated form.

Fraction distilled.	Volume. Cc.	Fraction received.	Volume. Cc.	Temp. range. ° C.	Press. Mm.	Melting points of distillates.	
						Crude. ° C.	Recrystallized from alcohol. ° C.
C-*a*...........	70	D-1	60	164–178	1.25	43–45	45–47
C-*b*...........	230	D-2	150	165–177	1	47–49	53–55
		D-3	60	177–180	1	47–49	52–54
C-*c*...........	150	D-4	100	174–178	1	45–48	51–53
		D-5	40	178–188	1	41–43	57–59
C-*d*...........	275	D-6	100	174–192	1	39–42	55–59
		D-7	160	192–199	1.25	51–53	63–65

In order to combine fractions of similar melting point and reduce the total number, Fraction D-1 was kept separate and designated as D-a; Fractions D-2, D-3 and D-4 were combined and designated as D-*b*; Fractions D-5 and D-6 were combined and designated as D-*c*; Fraction D-7 was kept separate and designated as D-*d*.

Fraction.	Wt. G.	Wt. obtained. G.	Substance.	M. p. ° C.
D-*a*	59	0.6	hydnocarpic acid	59–60
		1.4	material	62–63
		21.0	material	45–53
		31.0	oily material	.....
D-*b*	287	82	hydnocarpic acid	59–60
		112.5	material	45–53
		65	oily material	.....
D-*c*	130	18.4	chaulmoogric acid	67–68
		54	material	45–53
		45	oily material	.....
D-*d*	168	59.6	chaulmoogric acid	67–68
		25.4	material	45–53
		68	oily material	.....
Total for the entire 4 fractions of:				
		78	chaulmoogric acid	67–68
		1.4	unknown acid	62–63
		82.6	hydnocarpic acid	59–60
		212.9	material	45–63
		209	oily material	.....
		583.9		

Each of these resulting 4 fractions was subjected to an extended fractional crystallization from alcohol, involving from 25 to 33 recrystallizations in each case. Work was continued on each of the 4 fractions until nothing remained but pure chaulmoogric or hydnocarpic acids, or oily material, or solids which did not improve in melting point on further crystallization.

The results are briefly summarized in the preceding table.

It was found that the 212 g. of miscellaneous material from all 4 fractions, melting between 45–53°, could in each case be purified by recrystallization from alcohol until its melting point became approximately 48–52°, after which further recrystallization had little effect.

In order to determine whether this was a lower homologue of chaulmoogric and hydnocarpic acids, or a eutectic mixture of the two, 139 g. of this material melting at 48–52° was subjected to further distillation *in vacuo.* During the distillation the temperature fluctuated between 188° and 195° and the pressure between 1.5 and 3 mm. The distillate was cut into four 30-cc. fractions, on which the following data was gathered.

	1.		2.		3.		4.	
Fraction.	G.	° C.	G.	° C.	G.	° C.	G.	° C.
Melting points of crude distillates	27	49–51	27	50.5–52	27	50.5–52	27	50–51.5
Cryst. from alcohol..........	25	46–49	16	49.5–52	20	49.5–52	19.5	50–53
Recrystallized from alcohol..	21	49.5–52	4.3	57–58	18.5	51–53	11.2	53–55
Recryst. again from alcohol..	14.5	49.5–52	2.4	59–60	17	56–57	9	53–55
Recryst. again from alcohol..	....	.....	...	....	6.5	58.5–59.5	....	.....
Recryst. from P. ether........	4	56–57	...	....	...	....	2	57–58

While these results are rather indeterminate, they indicate a material which approximates a eutectic mixture which neither the fractional distillation nor crystallization could separate effectively.

From the foregoing, it is apparent that the original experiment on direct fractional distillation of the mixed fatty acids, which gave 4 fractions melting at 54–55°, 54–56°, 48–49°, and 67–68° respectively, after one crystallization from alcohol, effected a separation of chaulmoogric and hydnocarpic acids which was as good, if not better, than the one just described, which involved 3 redistillations of the fractions obtained by distilling once, and gave 6 fractions melting, after one crystallization from alcohol, at 45–47°, 53–55°, 52–54°, 51–53°, 57–59°, 55–59° and 63–65° respectively. It was therefore decided to distill the mixed fatty acids only once, and to attempt to get larger yields of pure acids by making that one distillation more efficient by means of improved apparatus and by cutting into fractions at the most advantageous points.

In order to determine the best possible points for cutting fractions a new vacuum distillation was run on a 300-g. portion of mixed fatty acids, and the distillate cut into fifteen 20-cc. fractions. The melting point of each of these fractions was taken and the fraction then crystallized from alcohol, in such a manner as to give a first crop, second crop and residue of approximately equal weights. The melting points of these 3 crops were taken and are given in graphic form herewith, together with the melting points of the crude distillates. (Fig. 1.)

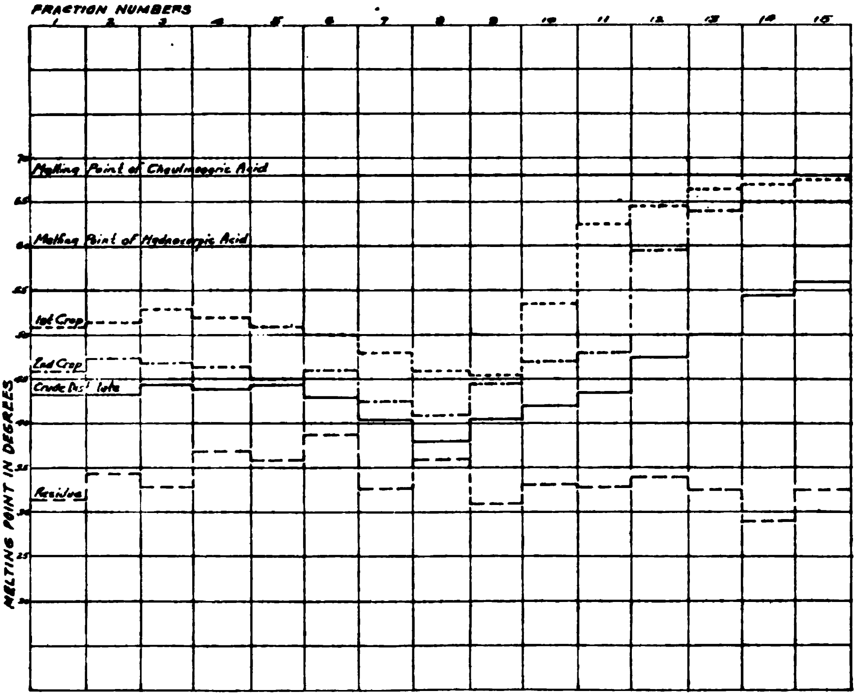

Fig. 1.

On the strength of the above melting-point diagram, Fractions 1–6 inclusive were combined and worked for hydnocarpic acid, of which they furnished 20 g. Fractions 12–15 inclusive were worked for chaulmoogric acid, of which they furnished 32 g. Fractions 7–11 inclusive were combined and crystallized from alcohol, but it was found that the melting point quickly rose to the 48–52° range, after which repeated recrystallization had little effect. This was apparently a eutectic mixture of hydnocarpic and chaulmoogric acids.

From this time up to the present the work has been severely handicapped by a radical lowering in the quality of the chaulmoogra oil coming on the American market. In place of the clear amber colored oil obtainable in the fall of 1919, it is now necessary to continue investigation on a dark reddish-brown oil which is about 70% by volume solid matter. This inferior product has nearly the normal amount of chaulmoogric acid in it, but the hydnocarpic acid content is only about one-third as great as in previous lots.

An improved apparatus, which was first employed in making the fractional distillation next to be described, was identical with that shown in Fig. 2, except that it had a 2-liter side neck flask of the Claisen type with a fractionating column of glass beads and short lengths of glass tubing about 12.5 cm. high in the side neck.

The large capacity of this flask permitted the vacuum distillations in kilogram lots of mixed acids, and up to the present time these flasks, which were made of heavy Pyrex glass, have shown no tendency to collapse under high vacuum, the only weak points being the junctures of the side and main neck, and of the side neck and delivery tube.

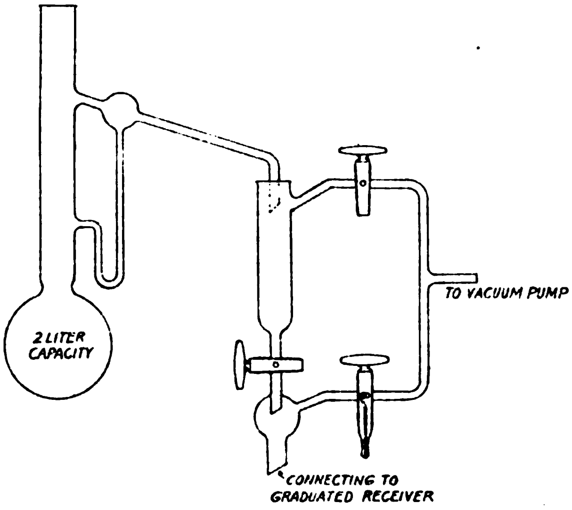

Fig. 2.

In order to throw more light on the character of the mixed acids from chaulmoogra oil, 1000 g. of the mixed acids (1084 cc.) was distilled and

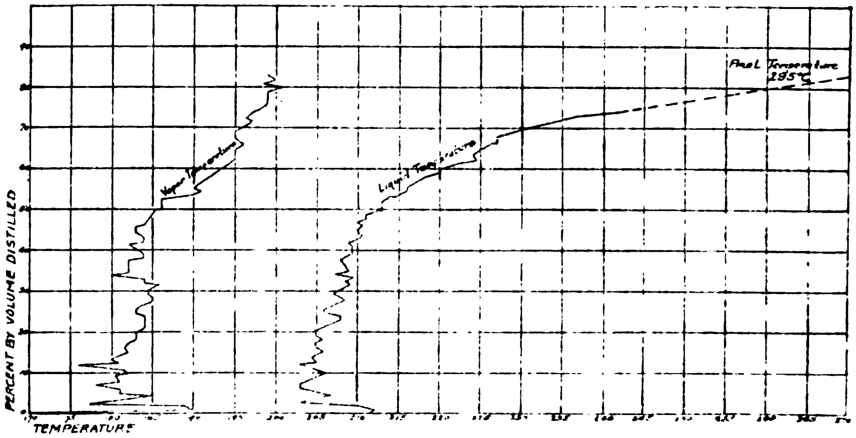

Fig. 3.

cut into 18 fractions of 50 cc. each. The temperature curves of the vapor and of the liquid in the distilling flask are given in Fig. 3. The melting points, indices of refraction, iodine numbers, specific rotations, and apparent molecular weights for each of the 18 fractions are given in Fig. 4.

Interpretation of Results.—An inspection of the data presented shows that the distillation is not effective in segregating any liquid fatty acids which may be present since all fractions solidify on cooling and require temperatures of at least 40° to liquefy them.

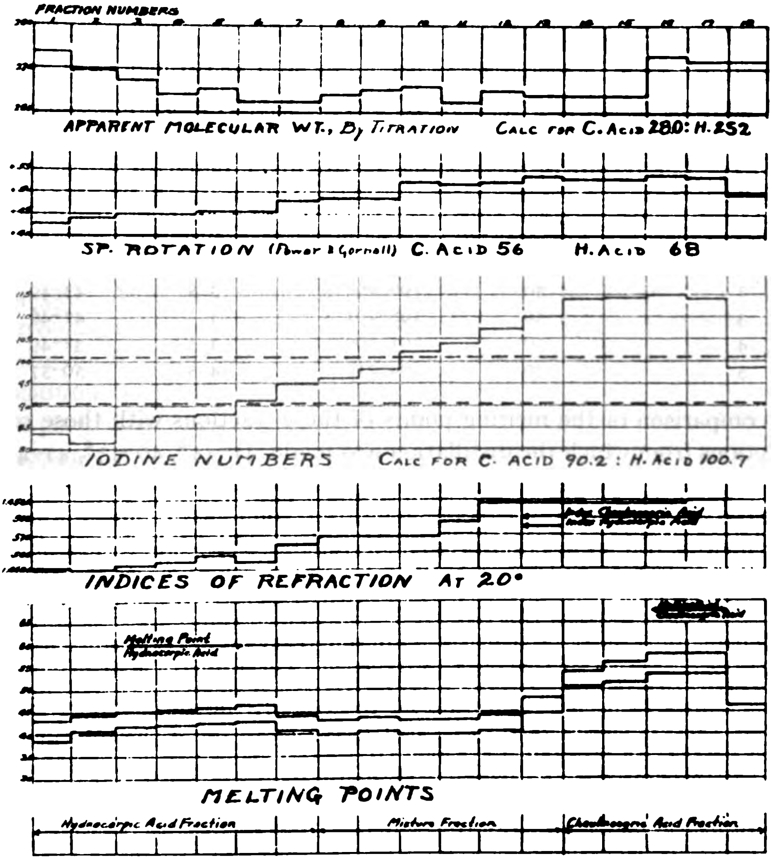

Fig. 4.

The higher boiling fractions give evidence of being much nearer to pure chaulmoogric acid than the lower fractions to hydnocarpic. Evidently the lower fractions contain material of higher molecular weight, lower or no rotatory power, lower iodine absorption, and lower indices of refraction. Oleic and palmitic acids, both of which were identified by Power in chaulmoogra oil, would have the effects indicated. With the chaulmoogric acid fractions there appears to be relatively little optically inactive material, but some materials which raise both the iodine value and the indices of refraction, indicative of more highly unsaturated acids.

No evidence of any members of the chaulmoogric series below hydnocarpic acid nor above chaulmoogric appears.

After a careful consideration of the probable composition of each of the 18 fractions, based on data shown in Fig. 4, Fractions 1–6 inclusive were combined and worked for hydnocarpic acid, of which they gave 48 g.; Fractions 14–18 inclusive were combined and worked for chaulmoogric acid, of which they gave 110 g.

Fractions 7–13 inclusive were combined and redistilled to determine whether this would afford a separation of the hydnocarpic and chaulmoogric acids which they were thought to contain in the form of a eutectic mixture. The results of this distillation are given herewith.

Fraction.	Volume. Cc.	Temp. range of vapor. ° C.	Average pressure. Mm.	Melting points of distillates. ° C.
1	50	186–196	3.25	43–49
2	50	196–198.5	3.5	43–49
3	50	198–201.5	4	42–46
4	50	201–209	4.5	32–49
5	30	209–210	4.5	50–57

A comparison of the melting points of these fractions with those of the 7 fractions from which the distillation was made, 41–44°, 40–43°, 41–43.5°, 40–43°, 40–43°, 41–44° and 45–48° respectively, shows very plainly that a partial separation was effected by this second distillation. This was confirmed by the extraction of a small amount of hydnocarpic acid from the combined Fractions 1 and 2, and a small amount of chaulmoogric acid from Fraction 5. The greater part, however, of the products of this distillation improved in melting point on recrystallization until the 48–52° range was reached, after which further crystallization had little effect.

This shows that it is unprofitable to redistill the mixture fraction *by itself*. It has been found, however, that the addition of the mixture fraction to the next lot of mixed fatty acids to be distilled increases very materially the yield of hydnocarpic and chaulmoogric acids which can be obtained from such distillations.

Reference to Fig. 4 will show that the portion of the distillate designated as the hydnocarpic acid fraction consisted of the first 300 cc. distilled off from one kg. (1084 cc.) of mixed fatty acids; that the mixture fraction consisted of the next 350 cc. to distill over, while the chaulmoogric acid fraction included all the remainder of the distillate (approximately 250 cc.).

It has been found lately that in the case of low grade chaulmoogra oil better results are obtained by cutting the distillate from one kg. of material

(300 cc. of mixture fraction from previous distillation plus sufficient crude mixed fatty acids to make 1000 g.) as follows.

Hydnocarpic acid fraction....First	350 cc.
Mixture fraction............Next	300 cc.
Chaulmoogric acid fraction...	250 cc.

Having established a satisfactory procedure for carrying out the fractional distillation of the mixed fatty acids, attention was turned to the second phase of the separation, namely, fractional crystallization. An extended investigation of the relative efficiency of a variety of solvents in various proportions to the weights of the material being crystallized brought out the following facts.

For the chaulmoogric acid fraction the most effective solvent is 80% alcohol in the proportion of 20 cc. of solvent to 5 g. of solute.

For the mixture fraction no solvent has been found which will effectively separate the 2 acids.

For the hydnocarpic acid fraction 80% alcohol in the ratio of 20 cc. of solvent to 5 g. is the most efficient for solutes whose melting point is below 35°. After this point has been passed the most satisfactory solvent is petroleum ether, in the ratio of 30 cc. of solvent to 5 g. of solute.

When the 80% alcohol is used the best results are obtained by allowing the solution to stand overnight in an ordinary refrigerator (about 16°). When petroleum ether is used the treatment is the same until nearly pure hydnocarpic acid has been obtained, which crystallizes best at ordinary room temperature, the time required being 1 to 3 hours.

A scheme for the systematic fractional crystallization of chaulmoogric and hydnocarpic acid fractions has been worked out which has given excellent results. For the chaulmoogric acid fraction 10 receptacles of appropriate size were placed in a rack and the receptacles marked consecutively for material melting: (1) below 25°; (2) 25–35°; (3) 35–45°; (4) 45–50°; (5) 50–55°; (6) 55–60°; (7) 60–63°; (8) 63–65°; (9) 65–67°; (10) pure chaulmoogric acid 68°.

A corresponding set of receptacles was devoted to the hydnocarpic fraction, marked for the following melting point, temperature ranges (1) below 25°; (2) 25–30°; (3) 30–35°; (4) 35–40°; (5) 40–45°; (6) 45–50°; (7) 50–53°; (8) 53–56°; (9) 56–59° (10) pure hydnocarpic acid 60°.

In carrying out a fractional crystallization the crude distillate is first allowed to crystallize from the proper solvent in such a way that a first and second crop, amounting in each case to approximately $^1/_3$ of the original weight of the material are obtained. The final mother liquor is washed with hot water to remove alcohol and the resulting oil dried. This gives a first crop, second crop and residue, which, after taking their melting points, are placed in the receptacles whose indicated melting point ranges cover that of the product as nearly as possible.

All three of these are recrystallized simultaneously from the appropriate solvent, producing 3 first crops, 3 second crops and 3 residues, which are classified according to their melting points. Thus it frequently results that a first crop from low melting material and a second crop from material of intermediate melting point and a residue from high melting material will all melt at about the same point, and since they will be put in the same receptacle, they will automatically be combined and recrystallized together in the next operation.

Thus with a minimum amount of time and effort the pure acids move to one end of the series of receptacles, the liquid material moves to the opposite end, while any other solid acids of definite melting point will automatically accumulate in one of the intermediate receptacles.

Up to the present time no such solid acids have been definitely isolated, but there is reason to believe that several such exist, and this subject, together with the composition of the liquid portions, will be dealt with in a later paper.

As the greater part of this paper has been devoted to tracing the development of this work, with frequent references to the present practise, it is thought worth while at this point to give in some detail the complete method in use at the present time, for the practically quantitative extraction of chaulmoogric and hydnocarpic acids from chaulmoogra oil.

Two hundred and forty g. of sodium hydroxide is dissolved in one liter of hot water and thoroughly mixed with 1500 g. of chaulmoogra oil in a 5-liter, round-bottom flask, and heated in an autoclave under 15 pounds of steam pressure for one hour. Loss by frothing is prevented by inserting a loosely fitting wooden plug or stopper in the neck of the flask through which runs a piece of 16 mm. i. d. glass tubing, which extends about 35 cm. above the flask, where 2 right angle bends lead it into an 800 cc. beaker, which is placed on a shelf in the autoclave. A piece of cheesecloth tied over the top of the beaker, through which the bent tube projects, effectively prevents loss from spattering.

After removing the flask containing the sodium soaps from the autoclave, the contents are poured into about 3 or 4 liters of hot water in a large precipitating jar, and stirred until dissolved.

The soap solution is now acidified with commercial hydrochloric acid, and the liberated fatty acids rise to the top of the water in the form of a thick oily layer. By means of a siphon the aqueous layer, which contains sodium chloride and glycerol, is drawn off and discarded. The remaining oil is washed with successive portions of hot water and finally transferred to a hot-water funnel, where, in the course of one to two hours heating all the water separates from the liquefied fatty acids. The latter are strained through linen of fine mesh before being allowed to solidify. The usual yield of crude mixed fatty acids is between 1350 and 1400 g.

One kg. (1084 cc. when liquefied) of these mixed fatty acids was subjected to vacuum distillation in the apparatus shown in Fig. 2.[1]

The vacuum is applied before the temperature of the liquid in the flask rises above 100°, otherwise serious frothing-over may result. It is best to have both of the 3-way stopcocks open for the vacuum, also the one-way stopcock between the receiving chamber and the graduated receiver. There is usually a tendency for a little of the fatty acid vapor to solidify in the stopcocks, interfering with the vacuum. This difficulty may be obviated by playing a jet of steam against the stopcock. As the stopcocks must remain air-tight, even while hot, it is best to use a mixture of vaseline and talcum powder as a lubricant in them.

The first 350 cc. which distill over is worked for hydnocarpic acid. The next 300 cc., composing the mixture fraction, is set aside to be redistilled as part of the next lot of mixed fatty acids. The rest of the distillate is worked for chaulmoogric acid.

The chaulmoogric acid fraction is recrystallized from 80% alcohol, using the proportions of 20 cc. to 5 g. of the acids, and following the systematic scheme for recrystallizing given above.

The hydnocarpic acid fraction is treated in the same way, except that material which melts above 35° is recrystallized from petroleum ether, using 30 cc. of solvent to 5 g. of solute.

The amounts of chaulmoogric and hydnocarpic acids present vary largely according to the quality of the oil, but from even low grade oil, starting with 1000 g. of mixed acids, this method will give at least 50 g. of pure hydnocarpic acid and 100 g. of pure chaulmoogric acid.

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[1] It has been found that a very effective column for the neck of the flask is obtained by locating 4 diaphragms of 3 mm. mesh wire gauze at intervals of about 37 mm., the lowest being at the bottom of the neck and the highest being about 5 cm. below the outlet into the delivery tube. Resting on the lowest of these diaphragms are as many 25-mm. lengths of glass tubing, 5.5 mm. inside diameter, placed vertically, as the neck of the flask will accommodate. On the next diaphragm a similar set of 4 mm. tubes; on the next a set of 2.5 mm. tubes, while on the highest diaphragm are placed 8 mm. glass beads to a thickness of about 25 mm. The large tubes at the bottom take care of the heavy back-flow of liquid at that point. The increasing density of the column near the top gives an increasingly thorough washing to the up-coming gases. The breaks between sectors in the column prevent the gas pressure from below forcing condensed liquid up through the column.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY AND THE BOTANICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN.]

THE IODOMETRIC DETERMINATION OF AMINO NITROGEN IN ORGANIC SUBSTANCES.

BY H. H. WILLARD AND W. E. CAKE.

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It has been shown by Artmann and Skrabal[1] and independently by E. Rupp and E. Rossler,[2] that ammonia can be accurately determined by oxidation to nitrogen in alkaline solution by means of standard hypobromite solution, the excess of the latter being determined by adding potassium iodide and acid and titrating the liberated iodine with thiosulfate. Since this method is more rapid and convenient than the usual distillation with alkali, it seemed probable that it could be advantageously applied in a modification of the Kjeldahl method, thereby shortening the usual procedure and obviating the necessity of a distillation apparatus.

Since the material must first be decomposed by digestion with hot conc. sulfuric acid until the carbon disappears, attention was directed towards shortening this part of the process. Hot conc. perchloric acid (60 to 70%) either alone or in the presence of sulfuric acid, oxidizes organic matter of all sorts very rapidly. An attempt was made, therefore, to substitute this for sulfuric acid, but although it leaves nothing to be desired as regards the destruction of organic matter, it also causes oxidation of the ammonium salt, thereby giving low results. The organic matter is not always completely destroyed when the solution is colorless; in this case it is oxidized by the hypobromite, giving high results. This is well shown in the following table.

It is obvious that it is practically impossible to avoid loss of nitrogen by this method if the organic matter is completely oxidized. Only by adding the perchloric acid drop by drop, cooling before each addition, and heating afterwards, is it possible to avoid an excess, with consequent oxidation of ammonia. This procedure is too tedious to be of any value.

Conc. hydrogen peroxide (20 to 40%) was tried, but this, too, evidently caused oxidation of ammonia, since the results were always low.

Potassium persulfate was suggested by Scott and Myers[3] in the determination of nitrogen in urine. This was found to give excellent results. However, it is absolutely necessary that it be added *dry* to the cool, *concentrated* acid solution in which the organic matter has been charred, since if any water is present, the results are always low, some ammonia apparently being oxidized. Under these conditions a considerable excess of oxidizing agent does no harm, although from 5 to 10 times the weight

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[1] Artmann and Skrabal, *Z. anal. Chem.*, 45, 5 (1907).

[2] Rupp and Rossler, *Arch. Pharm.*, 243, 104 (1905).

[3] Scott and Myers, THIS JOURNAL, 39, 1044 (1917).

of organic matter is usually sufficient, The solution quickly becomes colorless and the excess is decomposed by heating, with the evolution of oxygen and ozone. Most of the persulfate on the market contains ammonium salts which are very difficult to remove.

TABLE I.—OXIDATION WITH PERCHLORIC ACID.

Expt.	Material.	H_2SO_4 Cc.	$HClO_4$ Cc.	Time of boiling. (Minutes.)	N found. G.	N present. G.	Error in % total N.
1......	0.2 g. sugar + 0.0677 g. $(NH_4)_2SO_4$	..	15	till colorless	0.0156	0.0144	+8.5
2......	0.2 g. sugar + 0.0904 g. $(NH_4)_2SO_4$	..	15	till colorless	0.0206	0.0192	+7.3
3......	0.2 g. sugar + 0.0712 g. $(NH_4)_2SO_4$	..	15	5	0.0144	0.0151	—4.6
4......	0.2 g. sugar + 0.0444 g. $(NH_4)_2SO_4$	..	15	5	0.00927	0.00942	—1.6
5......	0.0775 g. $(NH_4)_2SO_4$	15	..	30	0.0164	0.0164	0.0
6......	0.0596 g. $(NH_4)_2SO_4$	10	5	30	0.00564	0.01264	—55.4
7......	0.2 g. sugar + 0.0572 g. NH_4ClO_4	..	15	till colorless	0.00832	0.00682	+22.0
8......	0.0746 g. NH_4ClO_4	..	20	30	0.00666	0.00889	—25.1
9......	0.4366 g. NH_4ClO_4	10	10	45	0.0324	0.0521	—37.8
10......	0.4684 g. NH_4ClO_4	..	25	120	0.0528	0.0558	—5.4
11......	0.1302 g. acetanilid	..	15	till colorless	0.0138	0.0129	+7.6
12......	0.1138 g. acetanilid	..	15	till colorless	0.0119	0.0113	+5.6
13......	0.1568 g. acetanilid	..	25	till colorless	0.0166	0.0155	+7.1
14......	0.1518 g. acetanilid	..	25	till colorless	0.0163	0.0150	+8.7
15......	0.1598 g. acetanilid	..	15	30	0.0157	0.0158	—0.9
16......	0.2098 g. acetanilid	..	15	30	0.0199	0.0208	—4.0
17......	0.1768 g. acetanilid	10	10	20	0.0100	0.0175	—42.7
18[a].....	0.2206 g. acetanilid	15	10 drops	5	0.0214	0.0218	—2.2
19[b].....	0.1754 g. acetanilid	15	$KClO_4$	5	0.0162	0.0174	—6.9
20[b].....	0.1670 g. acetanilid	15	$KClO_4$	5	0.0166	0.0165	+0.6

[a] Charred with H_2SO_4, then $HClO_4$ added and boiled for 5 minutes.

[b] Charred with H_2SO_4, then $KClO_4$ added and boiled for 5 minutes.

Preparation of the Standard Hypobromite Solution.

A convenient concentration is 0.6 *N*, of which one cc. corresponds to 2.8 mg. of nitrogen. To a cold solution of 30 g. of sodium hydroxide in 800 cc. water, add slowly, with constant stirring, 50 g. of bromine and keep the solution well cooled. This solution should be kept in the dark, and the lower the temperature the slower is its rate of change to bromate and bromide, some oxygen being liberated. At 0° to 5° the change in one week was negligible, but at room temperature it was necessary to standardize the solution each day. The following table shows the rate of change of two different solutions.

TABLE II.—STABILITY OF AN ALKALINE SOLUTION OF SODIUM HYPOBROMITE.

Date.	Temp. °C.	Cc. of 0.1 N thiosulfate equivalent to 10 cc. of solution.
Aug. 19	−3	74.39
Aug. 24	−1	73.58[a]
Aug. 25	−1	73.58
Aug. 28	−1	73.59
Aug. 29	+9	73.39
Aug. 30	0	72.99
July 27	22	66.15
July 29	22	64.87
July 30		
7 P. M.	22	63.92
7 A. M.	22	63.82
Aug. 13	22	57.34
Aug. 16	22	56.14[b]

[a] During this interval the temperature rose to 10° for a day.

[b] 22 cc. of this amount corresponded to bromate present.

Details of the Method.

Weigh out into a short-necked 300-cc. Kjeldahl flask an amount of the sample corresponding to about 10 or 15 mg. of nitrogen. Add 15 cc. of conc. sulfuric acid and heat until the organic matter is completely charred and the rapid evolution of sulfur dioxide has ceased. This usually requires from 5 to 15 minutes. Cool, and to the dark solution add through a thistle tube solid potassium persulfate free from ammonium salts, equal to 10 times the weight of the sample. This method of adding the persulfate is used to prevent any of the latter from sticking to the side of the flask. For the reason mentioned above, it could not be washed in with water. Warm very gently with constant swirling until the solution is colorless. This usually requires about one minute. The heating should take place so slowly that there is no evolution of bubbles of oxygen while the solution is still dark colored. Sometimes it is necessary to make more than one addition of potassium persulfate to oxidize all the carbon, and occasionally material is found that does not require as much as was recommended. After the carbon is completely oxidized, heat the acid to gentle boiling for five minutes to destroy the excess of persulfate, which decomposes with the evolution of oxygen and ozone. Cool, add 70 cc. of water and boil to remove any sulfur dioxide formed during the previous heating of the acid. *Cool,* add a drop or two of aqueous methyl orange or methyl red solution and neutralize with a solution of sodium hydroxide (about 10 N), then add 2 drops more. Cool under running water frequently during this process to avoid loss of ammonia.

The ammonia is now ready for titration. Add 10 cc. of 0.6 N hypobromite solution, sufficient so that not over $^2/_3$ of it is reduced by the ammonia, and let stand for 5 minutes. Evolution of nitrogen takes place thus:

$$2NH_3 + 3NaBrO = 3NaBr + N_2 + 3H_2O.$$

Add 5 g. of potassium iodide and 6 cc. of hydrochloric acid (sp. gr. 1.19). Titrate the liberated iodine with 0.2 *N* sodium thiosulfate solution, using starch as indicator.

The hypobromite is conveniently standardized against pure ammonium sulfate, or against standard thiosulfate after the addition of iodide and acid, as above.

If iron is present, the liberation of iodine by the ferric salt may be prevented by the addition of phosphoric acid, one cc. (sp. gr. 1.7) being sufficient for several mg. of iron.

TABLE III.

Expt.	Substance.	Weight Sample. G.	N found. %.	N present. %.
1.	α-Alanine	0.0816	15.83	15.73
2.	"	0.1332	15.72	15.73
3.	Acetanilid A	0.2493	10.21	10.22
4.	"	0.1394	10.22	10.22
5.	0.2 g. sugar + $(NH_4)_2SO_4$	0.0790	21.10	21.20
6.	"	0.0786	21.05	21.20
7.	"	0.0585	21.06	21.20
8.	"	0.0642	21.32	21.20
9.	$(NH_4)_2SO_4$ alone	0.0552	21.09	21.20
10.	Benzidine	0.1040	15.16	15.20
11.	"	0.1510	15.21	15.20
12.	Acetanilid B	0.1423	10.42	10.37
13.	"	0.1723	10.31	10.37
14.	"	0.2206	10.44	10.37
15.	Acetanilid C	0.3086	9.95	9.90
16.	"	0.1268	9.90	9.90
17.	Michler's ketone	0.2154	10.12	10.13[a]
18.	Gelatin A	0.1000	16.95	16.94
19.	"	0.0932	16.88	16.94
20.	"	0.1328	16.93	16.94
21.	Gelatin B	0.1110	16.70	16.71
22.	Peptone	0.2804	13.01	13.00
23.	"	0.2984	13.00	13.00
24.	"	0.1888	13.02	13.00
25.	"	0.1888	13.06	13.00
26.	Wheat Flour	0.3076	2.15	2.11
27.	"	0.3118	2.05	2.11
28.	"	0.3642	2.18	2.11
29.	"	0.4608	2.16	2.11
30.	Sawdust	0.2192	1.53	1.53
31.	"	0.3164	1.56	1.53
32.	"	0.2076	1.47	1.53
33.	"	0.2378	1.47	1.53
34.	Egg Albumen	0.1474	12.82	12.70
35.	"	0.1728	12.72	12.70
36.	"	0.2859	12.61	12.70
37.	"	0.2580	12.64	12.70

[a] Combustion method.

Precautions.

Potassium persulfate often contains ammonium salts and retains traces even after 3 recrystallizations. In such a case it is necessary to run a blank and apply a correction for the amount used. In running this blank sugar free from nitrogen must be added to reduce most of the persulfate; otherwise some of the ammonium will be oxidized.

It is very essential that there be no water present during the oxidation of the organic matter by the persulfate, since in the presence of water some of the ammonia is oxidized.

A very large excess of persulfate gives low results.

A number of organic substances were analyzed by this method, the results being shown in the preceding table. Some of these substances which were not absolutely pure or of uncertain composition, were analyzed by the official Kjeldahl method (Expts. 12 to 37), and the results are compared. Ten cc. of approximately 0.6 *N* hypobromite solution was added in nearly every case. The thiosulfate was standardized against pure potassium dichromate.

Some preliminary experiments indicate that this method can be used for the determination of nitrogen in coal, but this work has not been completed.

Summary.

1. The Kjeldahl method of determining nitrogen can be made more rapid by adding potassium persulfate to the charred solution of organic matter in conc. sulfuric acid, complete oxidation occurring very quickly.

2. The ammonium salt formed may be accurately and quickly determined by adding to the neutralized solution an excess of standard hypobromite, and determining the excess by adding iodide and acid, and titrating the liberated iodine with thiosulfate.

ANN ARBOR, MICHIGAN.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

OXIDATION OF THE GRIGNARD REAGENT.

BY C. W. PORTER AND CAROLYN STEEL.

Received Sept. 22, 1920.

If the general reactions of organic chemistry were named in the order of their importance from the standpoint of synthetic work the Grignard reaction would be one of the first on the list. Although only 20 years have passed since Grignard's discovery was announced there have appeared more than 500 papers devoted to applications of this reaction.

The formation of phenols through the oxidation of aryl magnesium halides mentioned by Bodroux[1] and Wuyts[2] seemed to us worthy of fur-

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[1] Bodroux, *Bull. soc. chim.*, [3] 31, 33 (1904).

[2] Wuyts, *Compt. rend.*, 148, 930 (1909).

ther investigation, and the work reported in this paper was undertaken to determine the influence of temperature upon the yield of phenol and the yields of the principal by-products, and to secure some evidence concerning the mechanism of the reaction. Bodroux obtained yields of phenol varying between 10 and 20%, and Wuyts identified diphenyl, diphenyl ether, and diphenyl-benzene among the oxidation products of phenylmagnesium bromide.

Ether solutions of the Grignard reagent prepared from magnesium turnings, phenyl bromide and ether were divided into several equal portions; and these aliquot parts of the same preparation were oxidized at different temperatures simultaneously. Each portion of the ether solution was placed in a tall glass cylinder in a thermostat and oxygen freed from carbon dioxide, dried, and finally saturated with ether vapor at the temperature of the thermostat, was bubbled through the solution for 5 hours. Preliminary experiments indicated that no increase in yield of phenol was secured by continuing the process longer than 5 hours. A thermometer was placed in the solution and a partial control of the temperature was accomplished by regulating the rate of flow of the oxygen. During the first 30 minutes of each run it was necessary to keep the liquid surrounding the cylinder below the temperature required in the reaction mixture. As the heat of reaction diminished the temperature of the bath was gradually increased. By this means the temperature of the solution was kept fairly constant, never deviating more than one degree from the mean. The solution acquired a greenish-yellow color as soon as the reaction began, and at the lower temperatures it gradually changed to an orange-red.

After hydrolyzing the oxidation product with ice and dil. hydrochloric acid the mixture was analyzed. Diphenyl was isolated by distillation with steam, then dried and weighed. The yield of diphenyl was practically constant and was as high in solutions that were not oxidized at all as in solutions through which oxygen had been passed for several hours. This indicates clearly that the formation of diphenyl is due exclusively to the direct action of magnesium on the phenyl bromide (Fittig's synthesis).

Phenol was estimated in the distillate and in the residue by titration. Measured volumes of standard potassium bromate and bromide were added to the acidified phenol solutions to precipitate tribromphenol. After adding an excess of potassium iodide the mixture was refluxed at 50° for 15 minutes, then titrated with sodium thiosulfate. As indicated in the following tables the optimum temperature for the formation of phenol is 0°. The calculations are based upon the yields that would have been obtained if the Grignard reagent used had been quantitatively converted into phenol or into diphenyl.

TABLE I.—OXIDATION RESULTS.

	Temp. 7° to 9°.		Temp. 0°.	
	C_6H_5OH. %	$C_6H_5C_6H_5$. %	C_6H_5OH. %	$C_6H_5C_6H_5$. %
	19.7	9.5	24.0	....
	18.9	11.4	24.3	11.7
	19.8	7.5	....	11.3
	20.8	10.1	23.0	11.1
	20.2	9.9	21.4	9.5
	19.4	9.3	22.9	10.9
	....	....	21.8	11.3
Average,	19.8	9.6	22.9	10.9

	Temp. 20°.		Temp. 32°.	
	C_6H_5OH. %	$C_6H_5C_6H_5$. %	C_6H_5OH. %	$C_6H_5C_6H_5$. %
	16.6	12.7	16.6	10.5
	19.1	10.7	17.1	12.2
	20.3	8.6	16.8	10.6
	19.0	10.5	18.0	9.4
	20.1	10.6	17.0	10.9
Average,	19.1	10.6	16.8	10.7

As ordinarily prepared the Grignard reagent is protected from atmospheric oxygen only by ether vapor in the reflux condenser. That such protection is inadequate is shown by the presence of phenol in freshly prepared samples of the reagent. Five preparations of phenyl-magnesium bromide through which oxygen had not been passed gave the following yields:

C_6H_5OH. %	$C_6H_5C_6H_5$ %
3.0	8.4
2.4	10.1
3.2	10.9
2.0	9.3
3.4	10.7
2.8	9.9

When evaporated or distilled with steam the yellow ether extract of the hydrolyzed product yields a tar. This was isolated and distilled under reduced pressure. The major part of the distillate that boiled between 230° and 258°, at 3 mm. pressure crystallized in colorless needles consisting of *p*-diphenyl-benzene, $C_6H_5C_6H_4C_6H_5$ (m. p. 205°). The quantity of the tar varied between $^1/_{10}$ and $^4/_{10}$ of the weight of the phenyl groups in the reagent. From this tar was isolated also, quinone and *p*-*p'*-dihydroxy-diphenyl in quantities sufficient to enable us to identify them by melting points and qualitative tests.

It is a generally accepted principle that in the process of oxidation by air or gaseous oxygen at ordinary temperatures a peroxide is the first product. A molecule rather than a single atom of oxygen takes part in the reaction. The peroxide may be stable or it may have only a transitory existence. If it constitutes only an unstable intermediate product half of the oxygen is liberated in the so-called active or nascent state. Now, the formation of quinone in the oxidation of phenyl-magnesium bromide indicated the presence of active oxygen, for neither phenol nor phenyl bromide is oxidized to quinone by the air alone. Furthermore, when triphenyl-methyl-magnesium bromide is oxidized by air the stable, insoluble triphenyl-methyl peroxide is precipitated.[1] We assume therefore, that phenol is produced as indicated in the following equations:

$$C_6H_5MgBr + O_2 \longrightarrow C_6H_5OOMgBr. \tag{1}$$

$$C_6H_5OOMgBr + C_6H_5MgBr \longrightarrow 2C_6H_5OMgBr. \tag{2}$$

$$C_6H_5OMgBr + H_2O \longrightarrow C_6H_5OH + MgBrOH \tag{3}$$

p-Dihydroxy-diphenyl and diphenyl ether are formed by a reaction between the products of Equations 1 and 2 and subsequent rearrangement or decomposition of the unstable peroxide.

$$C_6H_5OOMgBr + C_6H_5OMgBr \longrightarrow C_6H_5OOC_6H_5 + (MgBr)_2O \tag{4}$$

$$C_6H_5OOC_6H_5 \longrightarrow HOC_6H_4C_6H_4OH \tag{5}$$

$$C_6H_5OOC_6H_5 \longrightarrow C_6H_5OC_6H_5 + O \tag{6}$$

Quinone appears as an oxidation product of the peroxide by the atomic oxygen released as indicated in Equation 6.

Assuming that some phenyl peroxide was formed as indicated above and that Equations 5 and 6 represent relatively slow reactions we hydrolyzed 3 samples in the presence of zinc filings and hydrochloric acid to reduce the peroxide to phenol. The average yield of phenol in the 3 experiments was 24.7%. The average for unreduced runs at the same temperature was 22.9%. When sulfur instead of oxygen is used phenyl disulfide appears as one of the principal products. Taboury,[2] however, concluded that the disulfide is formed chiefly through oxidization of thiophenol, for when the reaction was carried out in an atmosphere of hydrogen less of the disulfide and more thiophenol appeared among the products formed.

Summary.

The optimum temperature for the production of phenol by oxidation of the Grignard reagent is about 0°. The production of diphenyl is nearly constant and is due to a side reaction in the formation of the Grignard reagent.

The presence of quinone and *p-p'*-dihydroxy-diphenyl among the oxida-

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[1] Schmidlin, *Ber.*, 39, 631, 4184 (1906).

[2] Taboury, *Bull. soc. chim.*, [3] 29, 761 (1903); *ibid.*, 31, 1183 (1904).

tion products, the increase in yield of phenol when hydrolyzed in the presence of a reducing agent and the precipitation of triphenyl-methyl peroxide when triphenyl-methyl-magnesium bromide is oxidized, suggests the formation of phenyl peroxide as an intermediate product.

BERKELEY, CALIF.

[CONTRIBUTION OF THE MULFORD BIOLOGICAL LABORATORIES.]

ANTIBODY STUDIES—PART 3. A PRELIMINARY REPORT ON THE CHEMICAL NATURE OF BACTERIAL ANTIBODIES.[1]

BY F. M. HUNTOON, P. MASUCCI, AND EDITH HANNUM.

Received September 28, 1920.

I. Introductory.

This paper deals merely with certain chemical facts concerning bacterial antibodies. A complete discussion of the antigen-antibody reaction will be published at a later date.

Immediately following the signing of the Armistice, a large supply of anti-pneumococcic serum became available. Experiments were undertaken to devise methods for extracting or isolating the protective antibodies from such serums as free from other serum constituents as possible.

The application of the principle of bacterial sensitization was utilized. Pneumococcus antigen variously treated was immersed in its specific serum and after allowing the antibodies to combine with the antigen or better, perhaps, after the antibodies were adsorbed by the antigen, the mixture was centrifuged. The sediment consisting of the highly sensitized bacteria was then treated with various reagents in order to split off the protective antibodies from the antigen. The resultant solution was candle filtered and its antibody content determined by protection tests on mice according to the U. S. Hygienic Lab. method for testing anti-pneumococcic serum.[2]

The filtered solution was almost as clear as water, very rarely showing any opal-escense. A typical proximate chemical analysis of such extracts as well as their content of antibodies shown by protection tests is given in Tables I and II, respectively.

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[1] Presented by P. Masucci before the Division of Biological Chemistry at the Chicago Meeting of the American Chemical Society, September 6–10, 1920.

[2] The protection test is carried out as follows. For each serum or extract tested, 3 white mice, approximately 18 g. in weight are injected with 0.2 cc. of serum, followed within less than 5 minutes by 0.1 cc. or less of culture. Both injections are made intraperitoneally. Similar injections are made at the same time with the Hygienic Laboratory Control Serum on 6 mice, 3 of which are injected at the beginning of the test, and 3 at the end.

The mice are observed for 96 hours, and mice living over 96 hours are taken as survivals (S). Those dying before 96 hours are marked with the number of hours they lived. (See Table II.)

TABLE I.—THE CHEMICAL COMPOSITION OF ANTI-PNEUMOCOCCIC ANTIBODY SOLUTION.

Protein Color Reactions.	
Biuret	Negative
Xanthoproteic	Negative
Adamkiewicz	Negative
Ninhydrin	Negative
Ehrlich's	Negative
Millon's	Negative
Other Tests.	
Sulfur	Negative
Phosphorus	Negative
Total nitrogen	0.035 mg. per cc.
Mono-amino acids	None

Nitrogen in phosphotungstic acid precipitate, 0.028 mg. per cc.

TABLE II.—PROTECTION TESTS ON ANTI-PNEUMOCOCCIC ANTIBODY SOLUTION.

Comparative protection tests are given on the original immune serum, the immune antibody solution, normal serum, and normal serum extract.

Protective substance.	Amt. of culture used. Cc.	Mice.	
None	0.000,000,001	48	48
	0.000,000,01	48	48
Immune serum 0.2 cc.	0.01	S	S
	0.1	S	18
	0.3	S	18
Normal serum 0.2 cc.	0.01	48	48
Immune antibody sol. 0.2 cc.	0.0001	S	S
	0.001	S	S
	0.01	S	S
	0.1	S	S
Normal antibody sol. 0.2 cc.	0.0001	48	48

II. Nature of Antibodies.

The chemical nature of antibodies can only be definitely determined by direct tests on the pure product. Unfortunately, these substances occur in such small proportions that it is impossible to isolate them in pure form.

Whether the substances involved in immunity reactions are colloids or not, we know that antibodies are closely associated with proteins, and that both are taken up by antigen in the process of sensitization. Thus other serum constituents may be given off during the final extraction.

Again, the question of the delicacy of the chemical tests at our disposal, and the competence of any chemical reaction to detect the presence of antibodies as a chemical entity must be considered. The fundamental fact to be borne in mind is that these substances are comparatively unstable and are easily altered by strong chemical reagents.

We have reason to believe that the concentration of antibodies in the extracts is, at the least, in a dilution of 1-100,000. This concentration could hardly be detected chemically. It is, therefore, evident that common chemical methods are of very limited value.

Much information, however, may be gained by indirect chemical and biological methods and by analogous reactions to known chemical substances.

The first question to determine in such a complex problem, is whether antibodies are similar chemically to any of the known serum proteins or whether they are of a non-protein nature. It has long been known that antibodies are apparently associated with certain serum fractions obtained by salting-out methods, and the impression prevails that antibodies are probably of a globulin nature. The salting-out methods, however useful from a practical standpoint, are of little value in determining the true nature of antibodies owing to the adsorption of the latter by serum proteins.

The most that can be stated is that antibodies are carried down by certain precipitates, which when dissolved show some of the characteristic properties of such bodies.

Landsteiner and Jagic,[1] working with extracts of hemagglutinins, concentrated such material until the agglutinin content equaled the original serum, and found the albumin content to be $^1/_{33}$ that of serum.

Liebermann and Fenyvessy[2] produced concentrated and purified extracts of immune hemolysin. They obtained no tests for protein by the biuret, sulfosalicylic acid, the potassium ferrocyanide and the acetic acid methods, and only traces with the xanthoproteic or Millon's reagent. They also state that only a trace of sulfur could be obtained with alkaline lead solutions and heat.

Kosaki[3] states that with his solutions of hemolysin the sulfosalicylic acid and the test with salt and acetic acid did not give the same reactions as were obtained with true proteins.

Presumably these investigators did not work with pure solutions of antibodies as there is always present a certain amount of impurities derived from the antigen employed. As we have already indicated, it is extremely doubtful that even a pure solution of antibodies could be analyzed by the usual protein reagents.

Some of our chemical tests on antibody extracts are given for the purpose of comparison, and also to show that these tests are not as delicate as the biological methods for determining serum proteins. The extracts tested have a comparatively small amount of serum proteins.

The results shown above indicate that the serum protein content of the extracts tested approaches the minimum amount which can be detected with the chemical reagents at our disposal.

The immune antibody solution employed in Table II was also used to de-

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[1] Landsteiner and Jagic, *Münch. Klin. Wochenschr*, 18, 764 (1903).

[2] Liebermann and Fenyvessy, *Cent. Bakt. Parasitenk.*, 47, 274 (1908).

[3] Kosaki, *J. Immunol.*, 3, 109 (1918).

termine its ability to produce serum sensitiveness. Five cc. was injected intraperitoneally into each of 2 guinea pigs. After an incubation period of 15 days, one guinea pig received an intravenous injection of one cc. of normal horse serum. This animal showed a severe anaphylactic reaction but did not die. The second guinea pig received an intravenous injection of one cc. of antipneumococcic immune horse serum and showed some symptoms but not as severe as the other animal.

This experiment led to the routine testing of our extracts by this method. A summary and discussion of the results will be introduced at a later point.

Our results showed that a considerable number of our extracts would produce serum sensitiveness to subsequent injections of horse serum, and it became necessary to consider the source of the proteins producing such sensitiveness. Were the antibodies responsible or were other serum proteins adsorbed in the process of sensitization?

Except in rare cases, the calculated possible dilutions of serum in most of our extracts were too high to expect sensitization from this source. Tests made on the fluids employed for wash purposes failed to show any reactions, so that it must be assumed that such results as we obtained were due to proteins present with the antigen until the final dissociation.

An experiment was made to determine whether the antigen would take up such substances from normal serum. The nitrogen content of this extract was practically the same as that treated with immune serum.

An attempt was also made to determine the nature of the antibody content by employing in the sensitizing tests both normal and immune serum for the final dosage. This was a total failure, for no consistent differences appeared between the response to normal and immune serum.

It must be acknowledged that these tests have failed to demonstrate in one way or another the question of the protein nature of antibodies, but have shown that with the technique employed for sensitization, washing and dissociation , that a certain amount of serum protein remains in solution, in sufficient amount to sensitize a certain proportion of guinea pigs to horse serum. By continued purifications and final concentration of such antibody extracts, we hope to determine definitely whether highly potent solutions may be obtained free from serum proteins which will sensitize guinea pigs to subsequent injection of serum.

III. Experimental.

The fact that direct chemical tests are yet not available to determine the chemical nature of antibodies, and that it is doubtful whether solutions can be prepared totally free from all other serum constituents and extractive substances derived from the antigen used, necessitates the application of indirect physical, chemical and biological methods in order to throw some light on the problem.

In order to determine whether a solution of antibodies is colloidal it may be tested by dialysis, diffusion or ultra-filtration. Of the 3, the simplest one, at our disposal is dialysis. Although this method gives purely qualitative results, it gives, however, an indication of the size of the particle involved, in other words, it tells us whether or not the substance is colloidal in nature.

Kosaki[1] had not been able to dialyze solutions of hemolysin. Some previous work by one of the authors indicated that agglutinins were not dialyzable. Using a parchment bag as a dialyzing medium, we were able to dialyze a protective antibody solution over a considerable period of time without much loss.

In another experiment in which larger quantities were employed there was apparently some loss but when the precipitate which formed during the process was removed and dissolved, it was found that a portion of the antibody content had gone with the precipitate in sufficient amount to account for the loss.

The formation of this precipitate during dialysis is a constant factor being more marked when salt solution and sodium bicarbonate are used for dissociation instead of distilled water.

It can be stated, however, that protective antibodies will remain in solution when the sodium chloride content is $^1/_{1000}$ that of physiological salt solution and that little or none is lost through dialysis.

Assuming that these antibodies have not been adsorbed by protein impurities present, an assumption which is probable, these experiments point to the conclusion that antibodies have a large molecule, ranging from 0.1 micron to 1 micron. In other words, we are dealing with colloidal solutions. Evidence that this colloidal behavior is not due to the protein impurities present but to the antibodies themselves is very strong. During dialysis, as already noted, a great deal of the proteins present is precipitated out of solution, leaving behind the bulk of the antibodies. Were the antibodies combined with these proteins, we should expect to find them largely in the precipitate, which is not the case. We are, therefore, forced to admit that antibodies do not dialyze on account of the large size of their molecule.

Dialysis experiments indicate that antibodies are of a complex nature composed of large molecules. Assuming that they are protein in nature and approaching in chemical composition globulins, we should expect, on digesting with trypsin, the breaking down of the complex molecule into its individual amino acids, with consequent destruction of the antibodies as shown by protection tests.

Experiments were carried out to demonstrate this. As shown in Table III, an excess of trypsin failed to show any reduction in antibody con-

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[1] Kosaki, *J. Immunol.*, 3, 109 (1918).

tent. We made sure that the trypsin was active by running suitable controls on casein. When the acid-alcohol precipitating agent was added to tubes, there was hardly any precipitate in any of the tubes containing trypsin as compared with the control. The enzyme had apparently digested the serum proteins present, but had not attacked the antibodies.

TABLE III.—SHOWING EFFECT OF TRYPSIN ON PROTECTIVE ANTIBODY EXTRACT.

A. Protective antibody extract plus 0.2% of 1/1000 solution trypsin.
B. Protective antibody extract (control).
C. 0.2% of 1/1000 solution trypsin (trypsin control).

Substance. Cc.	Length of digestion. Hours.	Culture used. Cc.	Mice.	
A 0.2	24	0.001	S	S
		0.01	S	40
		0.04	S	70
	48	0.001	S	41
		0.01	S	88
		0.04	S	27
	168	0.001	S	..
		0.01	52	..
		0.04	18	..
B 0.2	24	0.001	S	S
		0.01	S	S
		0.04	S	70
	48	0.001	S	S
		0.01	S	S
		0.04	S	88
	168	0.001	S	..
		0.01	S	..
		0.04	90	..
C 0.2	24	0.000, 000, 01	28	..
		0.000, 000, 1	27	..
Virulence	...	0.000, 000, 01	S	42
		0.000, 000, 1	40	28

Besides shedding light on the nature of antibodies, these experiments reveal the rather remarkable resistance that such an extract offers to the deteriorating influence of a temperature of 37.5° and such an active enzyme as trypsin.

The fact that trypsin fails to digest antibodies is very significant. We are either dealing with a non-protein substance which cannot be broken into tri- di- and mono-peptides and ultimately amino acids, or if we are dealing with a protein substance its composition is such that trypsin does not attack it. The ability to be digested by the enzyme trypsin depends of course, on the several properties of the molecule. As is well known, peptides having the carboxyl-amino linkages (NH — CO) are not split by trypsin. Again, Dakin found that casein and other proteins which have been racemized by dil. alkali are no longer digested by trypsin.

We have, therefore, these 2 facts to work upon. As this is merely a preliminary report on the chemical nature of antibodies, further work is being done to determine more definitely whether we are dealing with a complex peptide containing the carboxyl-amino group or whether the antibodies have been racemized by dil. alkali, which in either case resists the action of trypsin.

Experiments were undertaken to determine the effect of weak bases and acids on antibodies. It was found that 0.5% sodium hydrogen carbonate solution did not injure them, but facilitated filtration due, perhaps, to the reversal of the electrical charge.

The addition of acetic acid produced a slight precipitate, but as shown in Table IV, no great injury took place, although a certain amount of the antibodies was adsorbed by the precipitate formed.

TABLE IV.—SHOWING THE EFFECT OF ACETIC ACID ON PROTECTIVE ANTIBODY SOLUTION.

The precipitate obtained by adding 1% glacial acetic to the solution was dissolved in the proper amount of physiological salt solution and designated A.

The supernatant liquid after neutralization with NaOH was designated B.

Protective Tests.

Substance. Cc.	Culture used. Cc.	Mice.	
Original ext. 0.2	0.001	S	..
	0.01	S	..
	0.04	23	..
A. (Ppt. dissolved in solution) 0.2	0.001	S	..
	0.01	S	..
	0.04	16	..
B. (Supernatant) 0.2	0.001	S	..
	0.01	S	..
	0.04	42	..
Virulence	0.000,000,001	S	..
	0.000,000,01	42	..
	0.000,000,1	28	..

By means of protection tests it was likewise found that a 30% solution of sodium chloride did not destroy antibodies, and that ether does not dissolve them.

IV. Summary.

1. The antibody molecules are of large size, not being dialyzable indicating the colloidal nature of the substance.

2. Antibodies are not affected by trypsin over considerable periods, indicating either that they are not protein in nature, or have been racemized by the dil. alkali used, or belong to the peptide group having a carboxyl-amino linkage.

3. Antibodies are not precipitated by solutions containing little or no electrolyte content, indicating that they are not of a globulin nature.

4. Antibodies are not soluble in ether.

5. Antibodies are not precipitated nor affected by a short exposure to 30% sodium chloride solution.

6. Antibodies are not injured by certain dil. alkalies or acids.

7. Antibodies are not affected by temperature up to 60°. Higher temperatures progressively destroy or alter their nature.

We may state, therefore, that antibodies do not belong to that group of proteins usually considered under the head of serum proteins.

It is felt that in the present state of knowledge of protein chemistry the negative information such as we have obtained by indirect methods is of value in narrowing the possible field of investigation.

GLENOLDEN, PA.

[FORTY-SEVENTH CONTRIBUTION FROM THE COLOR LABORATORY OF THE BUREAU OF CHEMISTRY.]

KRYPTOCYANINES. A NEW SERIES OF PHOTOSENSITIZING DYES.

BY ELLIOT Q. ADAMS AND HERBERT L. HALLER.

Received September 23, 1920.

The alkyl halides (or other quaternary addition compounds) of lepidine of sufficient purity give, when treated with alcoholic alkalies in hot, concentrated solution, dyes of the isocyanine type.[1] When the reaction is carried on in very dilute solution, if the radical attached to the nitrogen is *iso*-propyl, or if the reaction is carried on with exclusion of air and the addition of chloroform or formaldehyde, there result dyes of a type not hitherto described, having an absorption maximum near 7000 Å, and a maximum of photosensitizing action near 7400 Å. For these dyes, prepared with the aid of chloroform or formaldehyde[2] we have adopted the name of "kryptocyanines."

The structure of these dyes has not been established, but a comparison of the 6 types of dyes of the cyanine series (see Table I and Fig. 1) suggests that the kryptocyanines and hypocyanines[2] are related to the dicyanines as the pinacyanols and cyanines, respectively, are to the isocyanines. Since the structure of both pinacyanols and dicyanines is still uncertain this does not determine the structure of the kryptocyanines, but the suggestion is made that they result from abimolecular 4,5'-condensation.

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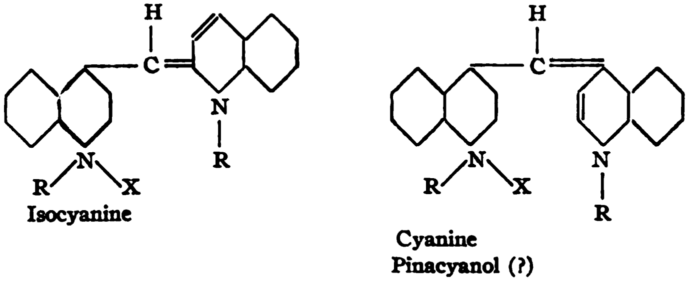
[1] E. Q. Adams and H. L. Haller, THIS JOURNAL, 42 2389–91 (1920).

[2] Since we have not yet established their identity with the dyes of similar properties formed without formaldehyde, etc., we shall provisionally refer to these latter as "hypocyanines."

TABLE I.

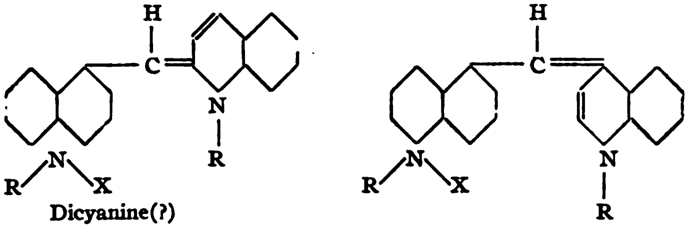
Type of dye.	Condensation of quaternary addition compounds of	Absorption[a] maximum (approx.).	Diff.	Sensitization[a] maximum (approx.).
Isocyanine	quinaldine + quinoline quinaldine lepidine	5600 Å		5800 Å
			400	
Cyanine	lepidine + quinoline lepidine + quinaldine	6000 Å		6400 Å
Pinacyanol	quinaldine (+formaldehyde) quinaldine + quinoline (+formaldehyde)			
Dicyanine	2,4-dimethyl quinoline	6600 Å		7000 Å
			400	
Hypocyanine	lepidine	7000 Å		7400 Å
Kryptocyanine	lepidine (+ formaldehyde)			

[a] W. F. Meggers and F. J. Stimson, *J. Opt. Soc. Am. Pub.*, 4, 91–104 (1920); P. W. Merrill, *Astron. Soc. Pac.*, 32, (185) frontispiece and p. 69.



Isocyanine

Cyanine
Pinacyanol (?)



Dicyanine(?)

Hypocyanine (?)
Kryptocyanine (??)

Fig. 1.

Preparation of Kryptocyanine from Lepidine Ethiodide and Formaldehyde (K III).—A solution of 5.98 g. of lepidine ethiodide (0.02 mol) in 100 cc. of 95% ethyl alcohol is heated to boiling under a reflux condenser in a 300-cc. round-bottom flask. After all the air in the flask has been displaced by alcohol vapor, a freshly prepared mixture of 20 cc. of 0.5 *N* sodium ethylate (0.01 mol) and one cc. of 40% formaldehyde solution is slowly added through the condenser. The addition of the alkali-formaldehyde mixture should require about 20 minutes. Boiling is continued for 10 minutes after all the formaldehyde-alkali mixture has been added, the flask stoppered while hot, and allowed to cool slowly. A slimy mass separates, which is filtered off by suction, washed with ice-cold

80% ethyl alcohol, alcohol-ether, and finally with ether alone. The yield is about 0.43 g. of a purplish-black crystalline powder. The mother liquor on standing yields a further crop of dye.

We have prepared kryptocyanines also from tolulepidine ethiodide (with formaldehyde); from lepidine methiodide (with chloroform); from tolulepidine methiodide (with formaldehyde), and from tolulepidine methnitrate (with formaldehyde). The first 2 formed crystals with a characteristic reflection pleochroism; the latter 2 resembled K III in appearance. In no case was the yield as great as with K III, and none of the other dyes equaled K III in sensitizing power.

Summary.

1. A new type of photosensitizing dye having an absorption maximum near 7000 Å and a sensitization maximum near 7400 Å is described.

2. These dyes are formed by the action of alcoholic alkali and formaldehyde (or chloroform) on the alkyl halides (or other quaternary addition compounds) of (sufficiently pure) lepidine and its homologs.

3. Dyes of the same or similar type are produced under some circumstances in the absence of formaldehyde or chloroform.

4. Tentative suggestions are made as to the structure of these dyes.

5. The name "kryptocyanine" is suggested.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE MISSOURI SCHOOL OF MINES.]

METHYL AMINES FROM METHYL ALCOHOL AND AMMONIUM CHLORIDE.[1]

BY W. D. TURNER AND A. M. HOWALD.

Received September 30, 1920.

It has been shown that ammonia can be methylated with methyl alcohol[2] by heating in an autoclave with zinc chloride as a dehydrator. The object of the present work was to determine the conditions of time, temperature, proportion of reagents, etc., best suited for the preparation of methyl amines by this reaction, and the relative importance of each factor.

Experimental Procedure.

Glass bombs were tried as a container but they failed through lack of tensile strength and through attack by the bases. We eventually found steel bombs of extra heavy 10-mm. pipe welded at one end and closed at the other with copper gasket and steel cap to be quite satisfactory. The bombs were weighed before and after charging, then after heating. In this way the loss on heating was known and this could be

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[1] An abstract of a thesis submitted by A. M. Howald, in partial fulfilment of the requirements for the degree of Master of Science at the Missouri School of Mines and Metallurgy.

[2] V. Mertz and K. Gaskioroski, *Ber.*, 17, 640 (1884).

neglected unless very large, since a complete analysis was made after heating.

Experiments were conducted at 218°, the boiling point of naphthaline, and at 303°, that of acetanilide. The bombs, charged as required, were immersed in the vapor of one of these substances and thus kept at constant temperature for definite periods. After heating the bombs were dropped into a freezing mixture, opened, and the contents washed into very dilute hydrochloric acid.

Methyl alcohol was determined as follows. The solution was distilled, using a Hoffman trap until $^1/_4$ remained. The distillate, made basic with sodium hydroxide, was again distilled and the specific gravity of this distillate determined at 15° and compared with standard tables.

Methyl amines and ammonia were determined as follows. To the original flask containing an acid solution of the bases a solution of sodium hydroxide was added in excess through a dropping funnel and the bases distilled into standard hydrochloric acid. After diluting to definite volume, an aliquot part of this distillate was titrated with standard sodium hydroxide solution, thus giving a basis for calculating the total amount of bases present and incidentally avoiding the contamination of the bulk of the sample with sodium chloride.

The 3 methyl bases and ammonia present in the bulk of the solution as their hydrochlorides were separated and estimated by the method of Berthreume,[1] the principles of which are briefly as follows: The mixed hydrochlorides evaporated and dried in a vacuum are extracted with pure dry chloroform, thus dissolving the di- and tri-amines and leaving monomethylamine and ammonia. The trimethylamine is separated from the di- by precipitating it as the tri-iodide and ammonia is separated from the monomethyl amine by precipitating it with yellow mercuric oxide in basic solution.

Results.

Ten experiments were performed with results as shown in Table I.

TABLE I.

Ratio of Mols. $NH_3 = 1$.

Expt.	Time hrs.	Temp. °C.	NCH_3H_2.	$N(CH_3)_2H$.	$N(CH_3)_3$.	CH_3OH.	$ZnCl_2$.
1....	24	218	0.0154	nil.	nil.	2.97	0.00
2....	60	218	0.0290	nil.	nil.	3.05	0.00
3....	2	218	0.0792	0.0064	nil.	2.30	1.50
4....	5	218	0.055	0.012	nil.	2.17	0.00
5....	5	218	0.325	0.008	nil.	0.49	1.50
6....	5	218	0.432	0.045	0.007	5.11	1.50
7....	5	303	0.689	0.069	0.023	10.15	1.50
8....	5	303	0.098	0.015	nil.	14.04	0.00
9....	5	303	0.227	0.021	0.0034	13.57	0.75
10....	8	303	1.078	0.162	0.026	12.0	1.50

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[1] Berthreume, *Compt. rend.*, 150, 1251 (1910).

In the first 3 experiments where ammonia was used much lower yields were obtained than in the last 7 similar experiments in which ammonium chloride was used.

Summary.

Methyl amines are formed only in traces when ammonia or ammonium chloride and methyl alcohol are heated without a dehydrator to as high as 303°.

Using zinc chloride as a dehydrator good yields of mono- and di-methylamines can be obtained. For example, in 8 hours at 303° (Expt. 10) yields were obtained as follows: monomethyl amine, 55%; dimethylamine, 7.5%; and trimethylamine, 1.86%, of the ammonium chloride used.

The yields increase with the amount of zinc chloride used, with increase in temperature, with increase in time of heating and with increase in ratio of methyl alcohol to ammonia.

In all cases where zinc chloride was used hydrogen was liberated due to the hydrolysis of the zinc chloride and consequent attack of the iron bomb by the hydrochloric acid formed. It was for this reason that no experiments could be carried to equilibrium.

ROLLA, MISSOURI.

[CONTRIBUTION FROM THE HAVEMEYER CHEMICAL LABORATORY, NEW YORK UNIVERSITY.]

THE DECOMPOSITION OF NITRIC ACID IN ORGANIC NITRATIONS.

BY F. O. RICE.

Received October 5, 1920.

The decomposition of nitric acid in organic nitrations is a matter of some industrial importance because there is usually considerable reduction of nitric acid to oxides of nitrogen and if much nitrous oxide or nitrogen is formed there would be a serious loss of nitric acid. Nitric oxide and higher oxides can be reconverted into nitric acid by suitable condensing towers and returned to the system.

Some investigations[1] on the solution of metals in nitric acid have shown that at ordinary temperatures large amounts of nitrous oxide were present in the gases evolved. In many cases the metallic nitrate catalyzed the reduction of the acid to nitric oxide so that near the end of the reaction when there was much of the metal in solution almost pure nitrous oxide was obtained.

It seemed possible, therefore, that a similar reduction of nitric acid to nitrous oxide or nitrogen might take place in organic reactions. The

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[1] Acworth, *J. Chem. Soc.*, **28**, 828 (1875); Acworth and Armstrong, *ibid.*, **32**, 54 (1877); Freer and Higley, *Am. Chem. J.*, **15**, 71 (1893); Higley, *ibid.*, **17**, 18 (1895); Higley and Davis, *ibid.*, **18**, 587 (1896).

process selected for investigation was the nitration of phenol to trinitrophenol. The original experiments were carried out on a technical scale at one of H. M. Factories, England, but the results obtained there have since been checked and extended by laboratory scale experiments. The most difficult part of the work was in devising a fairly rapid method of analysis of the complex gas mixture from the nitrating vessel, since it changed in composition as the reaction proceeded, and the presence of nitrous oxide made it necessary to carry out the analysis in mercury absorption pipets. In one of the early experiments to determine the composition of the gas mixture 200 cc. of the gas was treated with potash to remove higher oxides of nitrogen and carbon dioxide. A considerable amount of nitric oxide was found to be present and this was removed by shaking with strong dichromate solution. There still remained about 60 cc. of gas. When this was passed over a hot platinum spiral a violent explosion occurred, the gas expanded and both oxygen and carbon dioxide appeared, neither of which was present before exploding. This behavior was finally traced to the presence of carbon monoxide and nitrous oxide. These 2 gases exploded on heating and the heat of the reaction decomposed the excess of nitrous oxide which was present, thus accounting for the expansion in volume and the presence of oxygen.

Preliminary experiments showed that the following products were given off during the course of the nitration: nitric acid vapor, nitrogen peroxide and trioxide, nitric oxide, nitrous oxide, nitrogen, carbon monoxide and carbon dioxide.

The following method was finally adopted for analyzing the gases and in ordinary working gave results correct to about 0.5%. The gases were first cooled to condense all of the nitric acid vapor; 100 cc. was then drawn into an ordinary Lunge nitrometer over mercury. This operation was done very rapidly to avoid as far as possible any condensation of higher oxides of nitrogen on the glass walls before the stopcock was closed. Two cc. of water was run into the nitrometer and shaken to remove the higher oxides of nitrogen by solution to give nitrous and nitric acids. The remaining gas was then passed into a water-jacketed measuring tube attached to a compensating tube, and the volume of gas was noted. The nitrogen trioxide and peroxide left in the 2 cc. of water in the nitrometer were estimated as nitric oxide in the usual way by addition of conc. sulfuric acid and shaking.

The gas in the measuring tube was analyzed by passing first into a special mercury pipet and adding 2 cc. of conc. potash solution. After shaking, the gas was returned to the measuring tube and the decrease in volume gave the carbon dioxide present. The gas was then returned to the pipet over the 2 cc. of potash, and pure oxygen was added in excess of that required to oxidize all of the nitric oxide present. Two cc. of strong pyrogallol solution was then run into the pipet to absorb the excess oxygen, and, after shaking, the gas was returned to the measuring tube. The diminution in volume gave the amount of nitric oxide present. The pipet was then washed out and the gas passed into it. Four cc. of ammoniacal cuprous chloride was added, and after gentle shaking the gas was returned to the measuring tube. The diminution in volume gave the amount of carbon monoxide present. The remaining gas consisted of nitrous oxide and nitrogen. The former was determined by shaking with absolute alcohol and finally several times with water. The decrease in volume gave the nitrous oxide and the residual gas was nitrogen. The following is a typical analysis of the gas from an early part of the nitration.

	Volume. Cc.
NO in nitrometer (NO_2 and N_2O_3)	5.4
Remaining gas	96.3
After removal of CO_2	52.3
After removal of NO	40.5
After removal of CO	32.4
After removal of N_2O	13.9

Other methods of analyzing the gases were also used but could not be carried out as quickly and conveniently as this one. They were used only as checks and will not be described.

Nitration Process.

In the usual methods for preparation of trinitrophenol the phenol is first mixed with about 96% sulfuric acid in the proportion of one mol of phenol to 4 or 5 times the weight of acid, and the mixture is heated to about 100° for a few hours with constant stirring. The whole of the phenol is brought to the monosulfonate stage and from 50 to 80% of it goes to disulfonate. The mixture of sulfuric acid and phenol monosulfonate and disulfonate is diluted with about $^3/_4$ of its weight of water and approximately 4 molecules of 65% nitric acid is added, the addition taking 3 to 4 hours. The initial temperature is about 75° but the heat of reaction brings the temperature rapidly to 116° which is about the b. pt. of the mixture.

Nitrations carried out by this method have been investigated very completely both on the industrial scale and in the laboratory. The method of conducting the experiments was as follows. The fumes given off from the nitrating vessel were first cooled to condense any nitric acid, which was collected and estimated. The rate of evolution of the fumes was measured by a gas flowmeter of the resistance-tube type. At intervals of a few minutes samples of the gas were drawn off and analyzed. It was found that the composition of the gases followed, approximately, the stages at which the 3 nitro groups were introduced, and the results did not differ greatly in different experiments. The following results are mean values expressed as nearest whole numbers for a large number of experiments.

	NO_2. %	NO. %	N_2O. %	N. %	CO. %	CO_2. %
First stage...	5.0	10	20	10	10	45
Second stage..	10.0	25	10	10	8	37
Third stage..	21.0	28	4	8	4	35

It is evident from the above figures that the greatest decomposition of nitric acid occurs during the first part of the nitration, for not only is the percentage of nitrous oxide and nitrogen highest but the rate of evolution of gas is also greatest during this period.

When the nitration was completed the contents of the nitration vessel were allowed to stand overnight, after which the picric acid was filtered off, centrifuged and weighed. The sulfuric acid present in the adhering liquid was estimated gravimetrically, and by this means the weight of pure picric acid was obtained. The filtrate, consisting of weak sulfuric acid with a little nitric and nitrous acids was also weighed, and analyzed for sulfuric acid (gravimetrically) total nitric acid (nitrometer) and oxalic acid, by neutralizing, precipitating with calcium chloride, filtering, and titrating the precipitate with standard permanganate. By heating the original filtrate (consisting mainly of weak sulfuric acid) with a little nitric acid and cooling thoroughly, a small additional amount of picric acid could usually be obtained. This was separated and weighed. The weak acid left after nitration gave the following analysis.

Sulfuric acid	45.5%
Nitric and nitrous acids	0.5% (Expressed as HNO_3)
Oxalic acid	1.6%

There were probably also small quantities of other organic nitro products in the acid, but these were not estimated. The following is the mean of 10 experiments, some being on the technical scale using a 12 kg. charge of phenol and others being small laboratory experiments. The results are calculated to a charge of 100 g. of phenol.

It will be seen from these results that less than 80% of the phenol is converted into picric acid, the remainder being broken down into oxalic acid and oxides of carbon. Only 62% of the nitric acid combines with the phenol to give picric acid. 10.2% is broken down to nitrogen peroxide and nitric oxide, and 22.2% is reduced to nitrous oxide and nitrogen, this latter representing a direct loss of fixed nitrogen in the nitration. It was found from experiment that the temperature was the main factor causing the reduction of nitric acid to nitrous oxide and nitrogen. When the temperature was kept well below 100° during the early stages of the nitration and then slowly raised to 100° until the nitration was completed, the evolution of nitrous oxide and nitrogen was very small and amounted to less than 1% of the total nitric acid present. The nitric acid was still decomposed to much the same extent, but nitric oxide was chiefly produced. It was not found possible to prevent decomposition of the phenol and even in the best experiments 20% of the phenol was oxidized away by the nitric acid.

Charge to the Nitrating Vessel.

Phenol	HNO_3	H_2SO_4.
100 g.	260 g.	427 g.

Nitric acid.	HNO_3. G.
Distilled off unchanged	7.2
Evolved as NO_2	9.3
Evolved as NO	17.3
Evolved as N_2O	36.0
Evolved as N	21.7
Contained in 187 g. of picric acid produced	154.0
Contained in second crop of picric acid produced (8 g.)	6.6
Free in 930 g. of weak acid (0.5% HNO_3)	4.6
Combined in weak acid (not estimated)	....
Total	256.7
Phenol.	**Phenol.**
Nitrated to picric acid	76.9
Nitrated to picric acid (second crop)	2.3
Oxidized to oxalic acid (1.6% in weak acid)	5.2
Oxidized to CO	2.4
Oxidized to CO_2	8.1
Remaining in weak sulfuric acid (not estimated)	....
Total	94.9
Sulfuric acid.	**H_2SO_4.**
In 930 grams of weak sulfuric acid (45.5% HSO_4)	422.0

Many experiments were performed in which the various factors, temperature, degree of sulfonation, rate of addition of acid, strength of acids, were altered but without any success. In one experiment in which ferrous sulfate was present the amount of nitrous oxide and nitrogen was much greater than usual and the yield of picric acid poor. This resembles the action of copper nitrate in causing the decomposition of nitric acid and suggests the possibility that a catalyst may be found which will have a positive effect in nitrations.

The best results were obtained when the phenol was thoroughly sulfonated (*i. e.*, converted almost entirely into disulfonate) and the temperature of the experiment was kept well below 100°, especially in the initial stages.

In a few experiments nitration was effected by adding a mixture of nitric acid and sulfuric acid to the phenol sulfonate-sulfuric acid mixture and carrying out the nitration almost at room temperature. Only nitrogen peroxide and nitric oxide were evolved and yields of picric acid slightly over 90% were obtained. Under the best conditions so far obtained almost 10% of the phenol was oxidized with consequent reduction of the nitric acid.

Conclusions.

1. A survey of the literature showed that when metals dissolved in nitric acid, nitrous oxide was produced as well as higher oxides of nitrogen. In some cases the metallic salt acted as a catalyst in the production of nitrous oxide.

2. This reduction of nitric acid to nitrous oxide may also occur in organic nitrations. In the nitration of phenol to trinitrophenol by weak nitric acid as much as 25% of the nitric acid may be reduced to nitrous oxide and nitrogen. The presence of iron salts accelerated this reduction.

3. By keeping the temperature of nitration well below 100° especially in the initial stages the formation of nitrous oxide and nitrogen may be avoided, only higher oxides of nitrogen being produced.

4. It was not found possible to nitrate phenol without causing some reduction of the nitric acid to oxides of nitrogen. The best results were obtained by sulfonating phenol almost to the disulfonate stage with 96% sulfuric acid and then nitrating at low temperatures (30°–40°) with a mixture of sulfuric and nitric acid.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE ORGANIC LABORATORY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.]

DIMETHYL-PROPYL-CARBINOL AND SOME OF ITS DERIVATIVES.

BY ANDRÉ DESCHAMPS.

Received October 8, 1920.

Introduction.

Originally the object of this work was to carry out an idea of M. G. C. Chavanne[1] involving the preparation of trimethyl-propyl-methane. Since Markownikoff's method is both hazardous and expensive, I attempted to prepare the compound by the action of methyl magnesium iodide upon methyl-2-bromo-2-pentane.[2] This reaction also proving impracticable, I resorted to the investigation of dimethyl-propyl-carbinol, which I had obtained as an intermediate product in the preparation of the latter substance.

Preparation of Dimethyl-propyl-carbinol.

This compound was prepared from both *n*-propyl iodide and *n*-propyl bromide by the Grignard reaction. The latter is better than that using ethylbutyrate described by Masson.[3]

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[1] G. C. Chavanne, Professor of Chemistry at University of Brussels (Belgium).

[2] Markownikoff, *Monatsh.*, 34, 1965 (1913).

[3] Masson, *Compt. rend.*, 1901, pp. 132–484.

1. **From *n*-Propyl Iodide.**—19.4 g. of *n*-propyl-magnesium iodide was prepared as usual and after cooling to 0°, a mixture of 5.8 g. of acetone, scrupulously dried, and an equal volume of anhydrous ether was added drop by drop. The reaction was very violent, and since the product was not entirely soluble, the whole was allowed to stand for 24 hours, as advised by Grignard in such cases. The next day the reaction product was poured upon a mixture of 9 g. of powdered ice and 9 g. of glacial acetic acid. After extraction with ether and suitable washings the distillation gave a principal fraction boiling at 110°–132°. The product obtained in this way was always contaminated by iodine compounds.

2. **From *n*-Propyl Bromide.**—14.7 g. of *n*-propyl-magnesium bromide and 5.8 g. of acetone were used in exactly the same manner as in the previous experiment. The course of the reaction was identical, except that in the end no trace of halogen could be discovered in the carbinol so prepared.[1] This was fractionated in a Hempel column, and the fraction boiling at 121°–124° was collected. The boiling point recorded by Beilstein is 122.5°–123.5° at 762 mm. Yield, 50%.

Properties of Dimethyl-propyl-carbinol.

Beilstein records no physical properties of dimethyl-propyl-carbinol except the boiling point. I found it a slightly viscous liquid, almost insoluble in water, soluble in alcohol and ether, and possessing an odor suggesting freshly peeled bark. It boils at 122.5°–123.5° at 762 mm.; $d^{15.5}_{4.4}$ 0.8350, $n^{15.5}$ 1.4125.

Freezing-Point Determination.—Crystallization was not effected at —20°. The carbinol was therefore immersed in liquid air at —193°, whereupon it became more and more viscous, and finally a solid, transparent mass, exhibiting no outward signs of crystalline structure. The freezing point was determined by the use of a potentiometer and suitable thermocouples. As the frozen substance was allowed to stand in the air a break in the curve occurred between —107° and —109°. This can be considered as the true melting point of dimethyl-propyl-carbinol, which therefore probably possesses a minute crystalline structure.

Methyl-2-Bromo-2-Pentane.

The best results were obtained when one mol of dimethyl-propyl-carbinol was boiled with 4 mols of hydrobromic acid (sp. gr. 1.45) for half an hour and then distilled. In the distillate the organic bromide forms a layer above the hydrobromic acid, but the behavior of the meniscus between the liquids is peculiar for it does not remain horizontal when the tube is inclined.

The bromide is so easily decomposed by pure water, that it is best, after separating the layers, to treat it directly with calcium chloride and then remove the hydrobromic acid by a current of air.

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[1] Tested with metallic sodium.

Subs., 0.1000: AgBr, 0.1140.
Calc. for $C_6H_{13}Br$: Br, 48.48. Found: 48.51.

Methyl-2-bromo-2-pentane is not recorded in Beilstein, but N. Nynera[1] obtained it in small quantities by the bromination of dimethyl-cyclopropane. He found the methyl-2-bromo-2-pentane a mobile liquid, having a pleasant odor suggestive of turpentine. It did not freeze at —18°; n^{23} 1.442; d_4^{23} 1.117.

Methyl-2-Chloro-2-Pentane.—One mol of carbinol was treated with 4 mols of conc. hydrochloric acid (sp. gr. 1.20). Butlerow describes this compound[2] as boiling with decomposition at about 100°. It was therefore distilled under reduced pressure, and found to boil at 50° to 53° under 41 mm. pressure.

Phenylurethane of Dimethyl-propyl-carbinol.—When equivalent quantities of phenyl isocyanate and dimethyl-propyl-carbinol were mixed and boiled a few minutes, a reaction ensued producing a heavy precipitation of fine white crystals. These were insoluble in hot ether, water, benzene, cyclohexane, chloroform, and petroleum ether, and somewhat soluble in hot alcohol and acetone. Recrystallization from these 2 solvents gave beautiful, long, white needles melting at 239°.

Subs., 0.1075, 0.093: N, 67.7 cc. (28°, 762 mm.), 57.2 cc. (28°, 762 mm.).
Calc. for $C_{13}H_{19}O_2N$: N, 6.33. Found: 6.89, 6.73.

Benzoate of Dimethyl-propyl-carbinol.—This substance was prepared from benzoyl chloride by the Schotten-Baumann reaction[3] in pyridine solution. After dissolving the pyridine hydrochloride in diluted sulfuric acid, the oil was extracted with ether and we obtained on cooling a white body which was recrystallized from alcohol. It gave beautiful, white needles, melting at 182–183°. It was not analyzed.

Summary.

1. Dimethyl-propyl-carbinol has been prepared with good yields by 2 new methods, and its physical and chemical properties investigated.

2. The following derivatives have also been prepared and studied: (*a*) methyl-2-bromo-2-pentane, (*b*) methyl-2-chloro-2-pentane, (*c*) the phenylurethane, (*d*) the benzoate.

3. Attempts to prepare trimethyl-propyl-methane by several methods proved unsuccessful.

The author wishes to express here his gratitude to Dr. F. J. Moore for many helpful suggestions.

CAMBRIDGE 39, MASS.

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[1] Nynera, *J. Russ. Phys. Chem. Soc.*, 44, p. 178.

[2] *Bull. soc. chim.*, 5, 40 (1866).

[3] Lassar-Cohn, "Arbeitsmethoden für organich-chemische Laboratorien," 1903, p. 224.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HAHNEMANN MEDICAL COLLEGE OF CHICAGO.]
[In affiliation with Valparaiso University.]

THE INDIVIDUALITY OF ERYTHRODEXTRIN.

BY J. C. BLAKE.

Received Oct. 11, 1920.

In 1916[1] the author arrived at the provisional conclusion that fractional precipitation of 1% solutions of dextrins probably yielded pure erythrodextrin as the portion thrown down by 50 to 65% alcohol (by volume). Later[2] it was found that the separation from achro-odextrin became incomplete if the concentration of the dextrin solution was greatly increased, so that the method was more or less impractical. Since that time somewhat extended efforts have been made to prepare and isolate pure erythrodextrin for the purpose of standardizing amylolytic activity and facilitating amylolytic determinations. Without attempting to review all this work in detail, it may be recorded that such dextrins or British gums were found to be preferable as sources of erythrodextrin that give deep red colors with excess of iodine-water, preceded by little or no blue coloration. If much of the blue-producing dextrin (amylodextrin) is present low concentrations of alcohol will remove it completely from part of the erythrodextrin, but probably half of the latter ingredient is lost in the precipitate. In dextrin solutions from which fragments of the cell walls have been removed by filtration this precipitate takes the form of sphero-crystals, in which the erythrodextrin seems to be present in solid solution.[3]

It was thought for some time that after all of the amylodextrin had been removed from approximately 20% solutions in the manner just indicated, all of the higher polysaccharides had also been removed. Nevertheless it was observed in numerous cases that further addition of alcohol, instead of yielding the heavy liquid in which form erythrodextrin subsequently precipitates, continued to yield small crops of sphero-crystals, thus indicating that part of the higher polysaccharides[4] was still present. This conclusion was confirmed by examination of the "erythrodextrin" precipitated by slight further addition of alcohol. The heavy liquids thus precipitated from the same concentration of different dextrins by the same precentage of alcohol had widely varying powers of turning red with iodine and many of them became turbid on standing, and became largely insoluble in cold water.

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[1] THIS JOURNAL, 38, 1251 (1916).

[2] *Ibid.*, 39, 316 (1917).

[3] Blake, *ibid.*, 40, 635 (1918).

[4] The substance mainly responsible for these crystals is thought to be the same as that forming the cell walls of raw starch; hence the name "artificial starch." This substance is probably amylocellulose.

In order to arrive at any definite conclusion with regard to the relative purity of the erythrodextrin in such preparations it was necessary to determine their solid content. Heating to 100° slowly decomposes the erythrodextrin. Further addition of alcohol changes the heavy liquid to a coherent and adherent gum, which seemed even harder to work with than the heavy liquid. Hence 4 such liquids[1] were desiccated over calcium chloride, the resulting solid being powdered as soon as it became

[1] Dextrin (British gum) No. 1 was prepared by heating wheat starch for 65 days at 100°, except that the temperature reached 140° the sixth day. The amylodextrin and higher polysaccharides were precipitated by 30% alcohol from a 7.3% solution (final concentration). The erythrodextrin was precipitated as a heavy liquid by 50% alcohol. This liquid was used in Table I. Further addition of alcohol to the supernatant liquid gave a white solid precipitate by local excess, which quickly redissolved on stirring (achro-odextrin).

Dextrin No. 2 was from a white dextrin kindly furnished for this purpose by the Corn Products Refining Co. Two hundred g. of this material was extracted with 74% alcohol by means of a percolator for 40 days, by the end of which time the extract had reached the constant polarization of 0.54 (glucosimeter degrees), due chiefly to erythrodextrin and amylocellulose (sugars and achro-odextrin having been present in the early extracts). The presence of amylocellulose in the extract from the first was nicely shown by the formation of "artificial starch" on adding ether. As the ether evaporated, the sphero-crystals redissolved. The residue from the 74% alcoholic extract was then leached in a similar manner with 42% alcohol. The first extract with this solvent gave a slight deposit on standing of equal portions of cell fragments and sphero-crystals, together with a few long colorless needles. (Cf. Blake, THIS JOURNAL, 40, 636 (1918).) Extracts No. 2 to 8 of this series contained the most erythrodextrin. From a mixture of these extracts a slight precipitate of amylodextrin and higher polysaccharides was obtained by making the alcoholic content 55%. From the filtrate a gummy precipitate containing most of the erythrodextrin was obtained by increasing the alcoholic content to 75% (used in Table I). The supernatant liquid contained a small amount of achro-odextrin.

Dextrin No. 3 was obtained from a mixture of dextrins made by heating corn starch with acid until about 99% of the material was soluble in cold water. Two hundred g. of this material was extracted with 74% alcohol in the manner just described, a constant polarization of 0.80 being reached after 29 days. Of the subsequent extracts with 42 to 50% alcohol, Nos. 4 to 9 contained the purest erythrodextrin. From a mixture of those extracts a slight precipitate of amylodextrin, higher polysaccharides and some erythrodextrin was obtained by increasing the alcoholic content to 50%. From the filtrate a heavy liquid, containing most of the erythrodextrin, was precipitated by increasing the alcoholic content to 72% (used in Table I). This heavy liquid contained much erythramylum when tested by the method heretofore described (THIS JOURNAL, 40, 623); that is, it gave much red color with little iodine-water before any of the blue color due to amylodextrin appeared. Dextrin No. 4 was from a yellow commercial dextrin rich in erythrodextrin, cell walls insoluble. This dextrin had stood in 10% solution for 2 years, without preservative and without apparent change. Alcohol added to the supernatant liquid up to 44% gave the usual precipitate, containing all but a trace of the amylodextrin. From the filtrate the heavy liquid used in Table I was precipitated by increasing the alcoholic content to 59%.

Dextrin No. 5 (*infra*) was obtained by mixing together several such heavy liquids as those described under dextrins Nos. 2 to 4, obtained from corn starch.

brittle. The weight of Dextrin No. 1 became constant after 6 months; Dextrins Nos. 2 to 4 were still slowly losing weight after one year, at which time the subsequent determinations were made.

Table I contains a summary of the early procedures carried out with these dextrins.

Table I.—Desiccation of Heavy Liquids Containing Erythrodextrin.

Dextrin No.	Source.	Process.	Solubility of cell walls in cold water.	Loss over $CaCl_2$. %.
1............	Wheat starch	Heat (100°)	Mostly soluble	27.4
2...........	Corn starch	Acid and heat	Insoluble	28.9
3...........	"	"	Soluble	34.7
4...........	"	"	Insoluble	46.4
5...........	"	"	Mostly soluble	51.2

In order to determine the nature of these dried dextrins, solutions were made containing 5 g. of the dried material per 100 cc. These solutions were then polarized in a 2-dcm. tube at 25° on a glucosimeter,[1] and their power of coloring red with iodine was determined, as likewise their digestibility to the achromic point with fresh $^1/_{18}$ strength saliva (final concentration), preserved overnight with toluene, and their power of reducing Benedict's quantitative reagent. Table II contains the data thus obtained.

Table II.—Properties of Dried "Erythrodextrins."

Dextrin No.	Polarization on glucosimeter.	Red with iodine for one cc. (corrected), Lovibond scale = d.	Time to achromic point with 1/18 strength saliva in minutes = t.	d/t.	"Glucose" by Benedict's reagent. %
1........	+16.58	53	3.00	18	2.0
2........	+16.00	37	1.97	19	1.9
3........	+15.60	35	1.72	20	1.4
4........	+15.42	33	1.92	17	2.0
5........	+16.20	40	2.25	18	1.6

Accepting these results, momentarily, at their face value one would conclude that these products each contained about 2% sugar. But the original raw dextrins gave only a faint test with Benedict's qualitative reagent and the method of separating the heavy liquids from which these products were obtained precluded the presence of sugar. Hence it seems probable that this uniform copper reduction measures the amount of decomposition of erythrodextrin during the heating necessary to make the test, amounting to 2.0% for the purest erythrodextrin obtained (No. 1).

The other results require further elucidation. Assuming that the depth of the red color given with iodine-water measures the amount of erythrodextrin present, and that the time required for digestion to the achromic

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[1] In all cases tested sodium light gave the same reading as incandescent light. No mutarotation was observed. This instrument reads percentages of glucose when a 200 mm. tube is used.

point measures the same quantity,[1] it is evident that the ratio of these 2 determinations ought to be constant. The values thus obtained are given in Column 5 of Table II, and are probably constant within the experimental error.

In order to establish the last conclusion more firmly and to illustrate the present use of the author's method[2] of determining the depth of the red color given by erythrodextrin with iodine, the details of such determinations, whereby the values given in Table II were arrived at, are here recorded.

TABLE III.—ESTIMATION OF ERYTHRODEXTRIN BY IODINE-WATER.

One cc. of 5% dextrin solution in cylinder of Duboscq colorimeter of 6.55 sq. cm. cross section.

Dextrin No.	1.					2.					3.				
I_2-water, cm.^{3}	2	4	6	8	10	2	4	6	8	10	2	4	6	8	10
Red	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
Blue	0	0	0	0	0	2.0	1.8	1.5	1.5	1.5	2.5	2.0	1.5	1.2	1.0
Yellow	0.2	0.5	0.7	0.8	1.2	0	0.2	0.2	0.2	0.3	0	0	0	0.1	0.1
Total blue	0	0	0	0	0	5	8	9	12?	13?	7	8	8	8	8
Total red	19	32	41	53	60	14	21	30	39	42	14	21	27	35	40
Red less $^1/_2$ yellow, No. 1[a]	18	30	38	49	53	14	20	27	36	37	14	19	24	32	35

	4.					5.				
I_2-water, cm.^{3}	2	4	6	8	10	2	4	6	8	10
Red	5	5	5	5	5	5	5	5	5	5
Blue	1.5	1.2	1.0	0.7	0.7	0	0	0	0	0
Yellow	0	0	0.2	0.2	0.3	1.7	1.9	2.0	2.2	2.4
Total blue	4	5	5	4	5	0	0	0	0	0
Total red	12	19	27	32	37	16	29	38	49	53
Red less $^1/_2$ yellow, No. 1[a]	12	18	25	30	33	13	23	30	30	40

[a] For dextrin No. 5 one-half its own yellow reading was used.

It is well known that the depth and the tone of the color given by iodine with dextrin solutions vary with the proportion of iodine added. In 1918[3] the author indicated that the depth of color produced by iodine with erythrodextrin reaches a maximum when the iodine is added in slight excess, that the presence of amylodextrin is not a disturbing factor, and that the red color due to excess of iodine can be corrected for by subtracting from the total red color observed 40% of the total yellow color observed. It has since been found that no advantage is gained in adding more iodine after its yellow tint becomes distinctly discernible when amylodextrin is present, owing to the fact that the blue iodide neutralizes the yellow color of iodine until considerable excess of the latter is present.

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[1] Blake, THIS JOURNAL, 39, 318 (1917), Table III.

[2] THIS JOURNAL, 40, 623 (1918).

[3] *Ibid.*, 40, 624–26 (1918).

It has likewise been found that the red color of iodine-water equals 50% of its yellow color (expressed on the Lovibond scale), instead of 40% as previously recorded (Table IV).

TABLE IV.—LOVIBOND GLASSES MATCHING DIFFERENT THICKNESSES OF IODINE-WATER.

Red glasses.	Yellow glasses.
0.2	0.5
0.6	1.0
2.5	5.0
3.5	7.2

From the next to the last line of Table III it will be noticed that the total red color steadily increases with increase of iodine-water. The last line of the table contains the same results lessened by $^1/_2$ the yellow color observed with Dextrin No. 1. It will be noticed that the values become nearly constant with the final increases in the proportion of iodine-water. The last value, that obtained with 10 volumes of iodine-water, probably yields for solutions of this strength about the best result obtainable for comparative purposes, since further addition of iodine introduces greater uncertainties in correcting for its red color. This correction for Dextrins Nos. 2 to 4 was made in accordance with the yellow color developed in Dextrin No. 1 because this dextrin was entirely free from amylodextrin, whereas in the case of Dextrins Nos. 2 to 4 the blue color of the iodide of the small amount of amylodextrin present largely neutralized the yellow color due to the excess of iodine, without apparently affecting its red color.

It is plain from the foregoing results that Dextrin No. 1 was far richer than any of the others in erythrodextrin. Its specific rotation at 25°, 174, agrees well with the value (170) heretofore obtained[1] by fractionation of a commercial sample of dextrin "purified by alcohol."

The chief impurity in Dextrins Nos. 2 to 4 was thought to be amylocellulose. It was found that most of the erythrodextrin could be precipitated by ammonium sulfate from the heavy liquids heretofore described, other substances remaining in the supernatant liquid. Accordingly 450 cc. of heavy liquid, resembling those finally used in Nos. 2 to 4, was treated with 197 g. of solid ammonium sulfate. Two liquid layers resulted, the heavier one, consisting of 177 cc., containing nearly all the erythrodextrin. The supernatant liquid contained a considerable amount of other organic material, precipitable, along with ammonium sulfate, by the further addition of alcohol. The heavy liquid just described was freed from ammonium sulfate by heating to 60° with a slight excess of barium carbonate for 2 hours. From the filtrate thus obtained the erythrodextrin was again precipitated as a heavy liquid by 42% alcohol. This liquid (Table I, No. 5) dried to a solid over calcium chloride in 2

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[1] THIS JOURNAL, 39, 320 (1917).

days, and its weight became constant after 48 days, thus showing that the substance which held water so tenaciously in Dextrins Nos. 2 to 4 had been removed by the treatment with ammonium sulfate.

The properties of the material thus obtained are included in Tables II and III, the digestion having been made with the same sample of saliva used with the other dextrins. That saliva preserved with toluene is stable for years was announced by the author at the Cleveland meeting of the American Chemical Society (1918), and independently soon thereafter by Myers and Scott.[1]

It will be noticed from Table III that the last traces of amylodextrin have been removed and that the ratio of the red color with iodine to the time required for digestion to the achromatic point, 18, is the same as that obtained for Dextrin No. 1, which this dextrin most closely resembles. But the red color and the time required for digestion are only 75% of the values given by Dextrin No. 1; that is to say, Dextrin No. 5 contained only 75% as much erythrodextrin as Dextrin No. 1. This loss of erythrodextrin must be attributed to a partial conversion to achro-odextrin during the heating with barium carbonate. The lessened content of erythrodextrin also accounts for the smaller ratio of red to yellow observed on adding the same proportion of iodine-water (Table III).

With this evidence of the individuality of erythrodextrin the author's efforts in this direction will be necessarily terminated, at least temporarily; but erythrodextrin nearly free from amylodextrin will continue in extensive use in this laboratory as an accurate and ready means of determining relative amylolytic activity.

CHICAGO, ILL.

[CONTRIBUTION FROM THE PHARMACOLOGY DEPARTMENT, UNIVERSITY OF MINNESOTA.]

MERCURY COMPOUNDS OF SOME PHENYL CARBINOLS.[2]

BY MERRILL C. HART AND ARTHUR D. HIRSCHFELDER.

Received October 21, 1920.

In spite of the large number of organic mercury compounds which have hitherto been prepared[3] we have been unable to find references to any compounds of mercury and arsenic with phenyl carbinols.

In view of the relatively low toxicity of phenyl carbinols, the presence of carbinol groups in many of the most active natural alkaloids and the interesting local anesthetic and anti-spasmodic properties possessed by

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[1] Myers and Scott, THIS JOURNAL, 40, 1713 (1918).

[2] This work was done with the aid of funds granted by the United States Interdepartmental Social Hygiene Board, for the investigation of the antiseptic and chemotherapeutic action of phenolic alcohols and their derivatives upon the gonococcus and the spirochaete.

[3] F. C. Whitmore, *J. Ind. Eng. Chem.*, 11, 1083 (1919).

phenyl carbinols and their esters[1] it seemed to us that mercury compounds of this group might prove useful as antiseptics and perhaps might also possess valuable chemotherapeutic properties.

Since Hirschfelder, Lundholm, and Norrgard[2] found that out of a number of phenyl carbinols investigated, saligenin (*o*-oxybenzyl alcohol) possessed the lowest toxicity for the tissues and also the best action as a local anesthetic and since this substance is one of the salicyl group which are useful as sedatives, antipyretics and antiseptics, saligenin was selected as the starting point in our research.

The compounds of saligenin and of *p*-hydroxy-*m*-nitrophenyl carbinol and mercury which are reported below have been found to be efficient antiseptics, about as strong as mercuric chloride but much less irritant to the tissues, so that they are being used successfully in the treatment of gonorrheal urethritis. Their antiseptic and therapeutic properties will be reported elsewhere.

Using the same method that was used in the preparation of the mercury compounds of saligenin and *p*-hydroxy-*m*-nitrophenyl carbinol, we have attempted the preparation of mercury compounds of benzyl alcohol, phenylethyl alcohol,[3] cumin alcohol and nitrosaligenin ($(2)CH_2OH(4)NO_2C_6H_3OH$), but found no evidence of combination.

Experimental Part.

Preparation of Saligenin.—Hutchinson's[4] method, modified slightly by Hurd was used for the preparation of saligenin. Salicyl amide was prepared from methyl salicylate by shaking the oil in a mechanical shaker with strong ammonia water for several hours. When the oil was all in solution it was evaporated on a steam-bath to a small volume. On cooling the salicyl amide crystallized out, and was filtered off, washed with water and dried.

Seventy-five g. of the salicyl amide was dissolved in 800 mils of water and 1000 mils of alcohol. To this solution, agitated in a mechanical stirrer, there was added gradually in the course of 2 hours 2700 g. of a 2.75% sodium amalgam[5] and 215 g. of glacial acetic acid. The dilute alcohol solution was separated from the mercury and after being neutralized with a slight excess of sodium hydrogen carbonate, evaporated under

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[1] D. I. Macht, *J. Pharmacol.*, 11, 263 (1918); A. D. Hirschfelder, A. Lundholm, and H. Norrgard, *Science*, N. S., 51, 21 (1920); *J. Pharmacol.*, 15, 263 (1920); D. I. Macht, *ibid.*, 11, 419 (1918).

[2] *Loc. cit.*

[3] The phenylethyl alcohol was kindly furnished by Dr. W. J. Hale of the Dow Chemical Company, Midland, Michigan, and the cumin alcohol by Dr. W. Schwartze and Dr. Max Phillips, of the Bureau of Chemistry, Department of Agriculture, Washington, D. C.

[4] A. Hutchinson, *Ber.*, 24, 173 (1891); Chas. D. Hurd, private communication.

[5] Prepared by Nef's method. J. U. Nef, *Ann. Chem.*, 280, 307 (1893).

reduced pressure to approximately half its volume. This was extracted 5 times with ether. The ether extract on evaporation yielded an oil that solidified on cooling. This was crystallized once from toluene and yielded 43 g. of a yellowish crystalline mass, 63% of the theoretical yield. This product required further purification before it could be used for the preparation of the mercury compound. A 4% aqueous solution of this was made, treated with animal charcoal and after being cooled in ice water, filtered. The filtrate was evaporated under reduced pressure to a small volume, extracted with ether, and the ether removed. The residue from the ether extract was crystallized once from toluene. This method gave a product that consisted of beautiful white, flaky crystals melting sharply at 86° and soluble in water to a clear colorless solution.

Preparation of the Mercury Compound of Saligenin.—Fifteen g. of saligenin was dissolved in 250 mils of 95% alcohol. To this was added a warm filtered solution of 80 g. (2 moles) of mercuric acetate in 150 mils of water to which 5 mils of acetic acid had been added to prevent hydrolysis of the mercuric acetate. This solution was heated on the reflux condenser for 30 minutes and allowed to stand overnight. Hard clumps of needle-like crystals radiating out from a common center had formed. These were filtered off, washed with a little water, alcohol, and ether, and dried. They weighed 67 g. The filtrate on being allowed to stand for several weeks separated 8 g. more of this compound. This reaction also occurred at ordinary temperature by merely mixing solutions of the 2 substances and allowing them to stand for several weeks.

Properties and Salts of the Mercury Compound of Saligenin.—This compound was very insoluble in water and in all the ordinary organic solvents. It dissolved in hot acetic acid with the separation of mercurous acetate on cooling. It was soluble in hot acetic anhydride and in the fixed alkalies. It was not soluble in ammonium hydroxide. In water suspension it was not acted upon by hydrogen sulfide. In alkaline solution it gave gradually with hydrogen sulfide in the course of several hours a precipitate of black mercuric sulfide.

It had no definite melting point. It began to turn brown at 160° and at 169° gas began to form. The material became porous and fluffy with no further change except a gradual darkening up to 250°.

The chloride of this compound is extremely insoluble, the bromide, and iodide less so. The sulfate is insoluble and the nitrate soluble.

The sodium salt of this compound was prepared by pouring gradually a concentrated solution of the mercury saligenin in 10% sodium hydroxide into 95% alcohol. A yellow granular solid separated which was filtered off, washed with alcohol and ether, and dried in a desiccator. This sodium salt when first made is extremely soluble in water giving clear, slightly yellow solution, but on exposure to the air it gradually takes up carbon dioxide and becomes more or less insoluble.

The acetate of the mercury saligenin had in general the same solubilities as its parent substance. It was slowly soluble in sodium hydroxide solutions.

The most interesting fact about this compound is the very great affinity of the saligenin molecule for the mercuric ion. After 15 g. of saligenin had been refluxed with 80 g. of the mercuric acetate for 2 hours and allowed to stand for several hours the mercuric ion was removed quantitatively from solution. No precipitate could be obtained with hydrogen sulfide, showing the practically complete removal of the mercuric ion from solution.

Purification and Analysis of the Mercury Compound of Saligenin.—The crystals of this compound as originally obtained were slightly contaminated with very faint traces of mercurous acetate. This was removed by cooking the finely powdered material with large quantities of water and then drying with alcohol and ether. By this method the material was obtained free from mercurous acetate and completely soluble in 10% alkali solutions. Material for check analyses was also prepared by dissolving the mercury saligenin in 10% sodium hydroxide solution, filtering and reprecipitating by just making the solution acid with acetic acid. The precipitate was filtered off, washed with water, alcohol and ether, and then dried.

The mercury in these compounds was determined by the method of Jamieson[1] by precipitating it as the double thiocyanate with zinc. A 0.2500 g. sample was dissolved in 3 mils of nitric acid to which 2 mils of hydrochloric acid were added. This was heated on the steam-bath until all the chlorine had been boiled off. The residue was then diluted to 50 mils and nearly neutralized with sodium hydrogen carbonate. The mercury was then precipitated by adding 25 mils of a solution containing 39 g. of ammonium thiocyanate and 29 g. of zinc sulfate to the liter. The solution was stirred vigorously for about 10 minutes and then allowed to stand for one hour. The precipitate of the mercury double salt was then filtered off in a weighed Gooch crucible, washed and dried to constant weight at 105°.

This method of analysis was checked by the method used by Whitmore[2] for the analysis of the organic mercury compounds derived from *p*-bromodimethyl aniline. By this method the mercury compound was decomposed by heating with fuming nitric acid in a sealed tube for 36 hours at a temperature of 200°. The mercury was then precipitated as the sulfide using freshly prepared ammonium sulfide. The precipitate was

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[1] G. S. Jamieson, *J. Ind. Eng. Chem.*, 11, 4, 206 (1919).

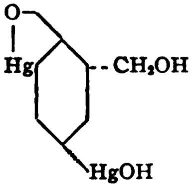
[2] F. C. Whitmore, THIS JOURNAL, 41, 1848 (1919).

filtered off on a weighed Gooch crucible, washed with water and carbon disulfide, dried, and weighed in the usual manner.

Analysis and Probable Formula of the Mercury Compound of Saligenin.—The mercury compound, purified by digesting with large quantities of hot water, alcohol, and ether was used for analysis. The material was completely soluble in sodium hydroxide solution. It was air dried to constant weight and analyzed.

Subs., 0.2500: $HgZn(SCN)_4$, 0.4138.
Calc. for $C_7H_6O_2Hg_2 \cdot 3.5H_2O$: Hg, 66.62. Found: Hg, 66.63.
The material was then dried to constant weight at 100° and analyzed.
Subs., 0.2227: $HgZn(SCN)_4$, 0.4127.
Calc. for $C_7H_6O_2Hg_2$: Hg, 74.41. Found: Hg, 74.60.

These figures agree very closely with those for a compound of mercury with saligenin (Formula I) containing 3.5 molecules of water at ordinary temperature. The mercury in this condition being weakly basic the acetate radicals having been hydrolyzed off during the process of purification and the basic mercury reacting to form an inner anhydride with phenolic hydroxyl *ortho* to it.



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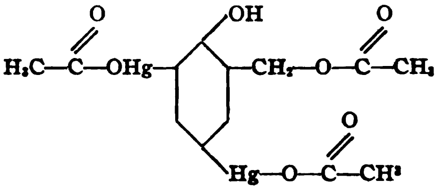

(II).

The Acetate of the Mercury Compound of Saligenin.—Assuming that the Formula I for the mercury compound of saligenin is correct it should form an acetate with 3 acetyl radicals going into the molecule, 2 on the mercury groups and one on the alcohol group. To test this out the acetate was prepared by dissolving the mercury saligenin in hot acetic anhydride and then filtering very rapidly. On continued heating an insoluble amorphous compound is formed probably due to the combination of 2 or more molecules from the dehydrating effect of the acetic anhydride. The acetate is best prepared using small quantities of the materials. On cooling, the acetic anhydride deposits beautiful rod-shaped, flat-sided crystals of the acetate. These were filtered off and washed with a little ether and dried in a vacuum desiccator. From 60 g. of the mercury saligenin, 19 g. of the crystalline acetate was obtained. These crystals were dried to constant weight at 100° and analyzed.

Subs., 0.2500: $HgZn(SCN)_4$, 0.3556.
Calc. for $C_{13}H_{14}O_7Hg_2.H_2O$: Hg, 57.21. Found: Hg, 57.26.

These figures agree very closely with those for a triacetate of the mercury compound, the probable formula of which corresponds to Formula II. This acetate contains one molecule of water of crystallization which it loses on being heated to 110°.

The Mono Mercury Compound of Saligenin.—We attempted to isolate a monomercury compound of saligenin. Equimolecular quantities of the saligenin and of the mercuric acetate were allowed to react at ordinary temperature. The mercury compound of saligenin containing 2 atoms of mercury was formed, and no evidence of a more soluble, monomercury compound of saligenin was discovered in the filtrate.

The Mercury Compound of *p*-Hydroxy-*m*-Nitrophenyl Carbinol.

Preparation of *p*-Hydroxy-*m*-Nitrophenyl Carbinol.[1]—This compound was prepared by the action of bromomethyl alcohol on *o*-nitrophenol.

The bromomethyl alcohol was prepared by the method of L. Henry.[2] 125 mils of 40% formaldehyde was treated in the cold with approximately 270 g. of dry hydrogen bromide in the course of 7 hours. After some time a heavy, dark red liquid separated out which consisted essentially of bromomethyl alcohol. This was then quickly separated from the supernatant aqueous hydrobromic acid by means of a separatory funnel. The bromomethyl alcohol was kept in a tightly stoppered bottle in the cold, as it decomposes at a temperature of 20° or more.

o-Nitrophenol was allowed to stand for several days with a slight excess of bromomethyl alcohol in the presence of a small amount of fused zinc chloride. The *o*-nitrophenol dissolved in the bromomethyl alcohol at first and then gradually the mixture solidified. The solid was then suspended in water and distilled with steam to remove any unchanged *o*-nitrophenol. The water solution remaining in the distilling flask was then filtered and allowed to crystallize. Beautiful long, yellow needles were obtained which after another crystallization from water melted sharply at 97°. The yields by this method were very good.

Preparation of the Mercury Compound of *p*-Hydroxy-*m*-Nitrophenyl Carbinol.—25 g. of the *p*-hydroxy-*m*-nitrophenyl carbinol was dissolved in 500 mils of 95% alcohol. To this was added a warm filtered solution of 94 g. (2 moles) of mercuric acetate in 200 mils of water containing 15 mils of glacial acetic acid. This mixture was refluxed for 6 hours and then allowed to stand at ordinary temperature for some time. Gradually a fine, light, yellow needle-like, crystalline compound separated. This was filtered off at the end of 7 days, and was found to weigh 29 g. Further small crops were obtained by concentrating the filtrate.

Properties and Salts of the Mercury Compound of *p*-Hydroxy-*m*-Nitrophenyl Carbinol.—This substance was contaminated by a slight

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[1] We have also prepared a carbinol, nitrosaligenin ((2) $CH_2OH(4)NO_2C_6H_3OH$) by the action of bromomethyl alcohol on *p*-nitrophenol. This method will probably be found useful for the synthesis of other phenyl carbinols.

[2] L. Henry, *Bull. acad. roy. med. belg.*, [3] 26, 615; *Ber. Gesellsch.*, 27, 336 (1894).

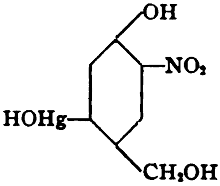
amount of mercurous acetate, otherwise it was completely soluble to a deep reddish-yellow solution in alkaline solutions. It was slightly soluble in water and insoluble in all of the ordinary organic solvents. It was soluble in hot acetic acid and hot acetic anhydride and could be crystallized from these solvents. In aqueous suspension it did not give a precipitate of mercuric sulfide with hydrogen sulfide. In alkaline solution it gave gradually in the course of several hours on treatment with hydrogen sulfide, a black precipitate of mercuric sulfide. It did not melt when heated to 240°.

The chloride of this compound is very insoluble, the bromide, and the iodide less so. The sulfate is insoluble and the nitrate soluble. The acetate of this compound has in general the same solubilities as its parent substance. It was slowly soluble in solutions of alkali, giving a deep reddish colored solution.

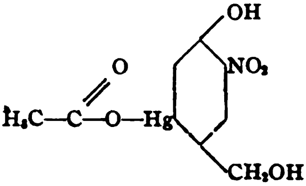
Analysis and Probable Formula of the Mercury Compound of *p*-Hydroxy-*m*-Nitrophenyl Carbinol.—The crude compound was purified for analysis by crystallizing it 3 times from 20% acetic acid. Beautiful long light yellow needle like crystals were obtained. These were completely free from the presence of mercurous acetate as was shown by their complete solubility in dilute sodium hydroxide solution. These were washed with alcohol and ether, dried to constant weight at 100° and analyzed for mercury. The sample in this case was dissolved by heating on the steam-bath for one hour with 3 mils of fuming nitric acid. The solution of the mercury compound was then diluted to 50 mils, nearly neutralized with sodium hydrogen carbonate and the mercury precipitated and weighed in the same manner given above for the analysis of the mercury saligenin.

Subs., 0.2500: $HgZn(SCN)_4$, 0.3250.
Calc. for $C_7H_7O_5NHg$: Hg, 52.02. Found: Hg, 52.33.

These figures correspond very closely to a compound of mercury with *p*-hydroxy-*m*-nitrophenyl carbinol (Formula III). As in the case of the compound of mercury with saligenin, the acetate is hydrolyzed from the mercury, due to the weak basicity of the mercury in this position. The mercury in this compound evidently was not *ortho* to the phenolic hydroxyl because there was no evidence of losing water to form an inner anhydride similar to the mercury compound of saligenin, when this compound was heated to 110° for some time.



(III).



(IV).

The Acetate of the Mercury Compound of *p*-Hydroxy-*m*-Nitrophenyl Carbinol.—If the mercury compound of *p*-hydroxy-*m*-nitrophenyl carbinol has the structure corresponding to Formula III it should form an acetate with one or two radicals of the acetic acid going into the molecule depending on whether the alcohol group was acetylated or not. This compound was prepared by dissolving the mercury compound in hot acetic anhydride and then filtering very rapidly. It was necessary to filter very rapidly in this case, as in the preparation of the acetate of the mercury saligenin, to prevent the formation of an insoluble amorphous compound probably due to the combination of 2 or more molecules from the dehydrating effect of the acetic anhydride. On cooling, beautiful needles, of a little lighter yellow than the parent substance, separated. These were filtered off, washed with a little alcohol and ether, and dried to constant weight at 100°. They were analyzed for mercury, using the same method used for the analysis of the mercury compound of *p*-hydroxy-*m*-nitrophenyl carbinol.

Subs., 0.2500: $HgZn(SCN)_4$, 0.2916.
Calc. for $C_9H_9O_6NHg$: Hg, 46.91. Found: Hg, 46.95.

These figures correspond very closely to those for a mono-acetate of the mercury compound of *p*-hydroxy-*m*-nitrophenyl carbinol, the probable formula of which is shown in Formula IV.

Summary.

1. Saligenin heated on the steam-bath with 2 moles of mercuric acetate reacts with the formation of a dimercury compound of saligenin. The mercury is present as the free base in non-ionic form and probably attached to the ring *ortho* to the phenolic hydroxyl, with which it readily forms an inner anhydride, and *meta* to the alcohol group.

2. Saligenin has a remarkable affinity for the mercuric ion, 15 g. of which on being refluxed for 2 hours with 80 g. of mercuric acetate and allowed to stand for 2 hours removes the mercuric ion so completely from solution that the mixture gives no precipitate of mercuric sulfide with hydrogen sulfide.

3. The mercury compound of saligenin forms salts with the mineral acids. The chloride, sulfate, bromide and iodide are insoluble. The nitrate is soluble. It also forms a soluble sodium and potassium salt. It forms an acetate when crystallized from acetic anhydride, containing 3 acetyl groups, 2 on the mercury group and one on the alcohol group.

4. The aromatic alcohols which did not contain a phenolic hydroxyl group such as benzyl alcohol, phenylethyl alcohol, and cumin alcohol, as well as nitro-saligenin ($(2)CH_2OH(4)NO_2C_6H_3OH$) did not react with mercuric acetate to yield organic mercury compounds.

5. A new method has been developed for synthesizing *p*-hydroxy-*m*-nitrophenyl carbinol and nitro-saligenin by the action of bromomethyl

alcohol on *o*- and *p*-nitrophenol, respectively. This synthesis may prove useful for other carbinols.

6. The zinc thiocyanate method of Jamieson has been found satisfactory for determining the mercury in these aromatic mercury compounds.

7. *p*-Hydroxy-*m*-nitrophenyl carbinol heated on the steam-bath with mercuric acetate reacts with the formation of a monomercury compound. The mercury is present as the free base in non-ionic form and probably attached to the ring *para* to the nitro group.

8. The mercury compound of *p*-hydroxy-*m*-nitrophenyl carbinol forms salts with the mineral acids. The chloride, sulfate, bromide and the iodide were insoluble. The nitrate is soluble. It also forms soluble sodium, potassium and ammonium salts. It forms a mono-acetate when crystallized from acetic anhydride.

9. These organic mercury compounds have been found to be useful antiseptics.

MINNEAPOLIS, MINN.

NEW BOOKS.

Die Leichtflüchtigen Bestandteile im Magma. By PAUL NIGGLI. B. G. Teubner, Leipzig, 1920. viii + 272 pp., 20 x 28 cm., 132 figs. Price, M. 22.

The greater part of the experimental work hitherto carried out on silicate melts has been concerned almost entirely with mixtures of the involatile oxides which go to make up the rocks as they now exist. For this the main reason is that one must first investigate thoroughly the simpler systems before proceeding to the more complex, particularly as the difficulty of carrying out the experiments and of interpreting the results is enormously enhanced when one of the components is volatile within the temperature range in question. A subsidiary reason is that until recently it was not well recognized that the presence of a volatile component in a cooling melt could cause such marked differences as it does in fact; petrologists had, it is true, attributed certain things which they could not explain on the basis of the older chemistry to what they termed "mineralizers,"—somewhat mysterious, presumably volatile substances which had disappeared from the system after doing their work. But with careful investigation of such heterogeneous equilibria, from the theoretical perhaps more than from the experimental standpoint, it became apparent that the presence of a volatile component is competent to account for many phenomena, and that progress along many lines of petrological and volcanological research will be greatly accelerated by extension of accurate knowledge of the sequence of events to be expected when a silicate melt containing a component such as water, cools rapidly or slowly, in a confined space or otherwise.

In this monograph, which was awarded the prize offered by the Fürstlich Jablonowskische Gesellschaft in Leipzig for the best essay on this general topic, Niggli reviews our present knowledge of equilibrium in systems containing a volatile component, and discusses its implications and applications to a large number of geologic instances. Much is still somewhat conjectural and will remain so for some time, as experimental work on this type of system yields results very slowly. But we have attained to a definite point of view which correlates, or promises to correlate, phenomena hitherto apparently diverse; and are enabled to reach certain specific conclusions, such as that the magma, or any system comprising volatile components, may on cooling and crystallizing develop high pressure by reason of the fact that the volatile components are very much less soluble in the solid than in the melt.

The book is written from the standpoint of a petrologist, and is addressed primarily to petrologists; but the author presumes on the part of the reader an acquaintance with the interpretation of equilibrium diagrams which is far from common among chemists and quite exceptional among petrologists. Indeed no one will find this easy reading; but facts are stubborn, and important factors may not be neglected merely because they render the treatment complex and hard to grasp. The first hundred pages bring together material important to any one who may be concerned with a system of this type; many of these are technically important though still inadequately understood, *e. g.*, the solubility of gases in a metal or glass and the influence of temperature upon this equilibrium. This part may be commended to any chemist who wishes to get the available scientific information on this type of system, most of which has been developed within the last few years but has not been readily accessible. In the remainder of the book the general principles derived from the study of systems with volatile components are applied to specific geologic instances, drawn from many sources. JOHN JOHNSTON

La Materialisation de L'Energie, Essai sur La Theorie de La Relativite et sur La Theorie des Quanta. By LOUIS ROUGIER. Paris, 1919.

This is a very attractive description of the results of the newer theories of physical science. It describes in a non-mathematical form the results which are obtained from Einstein's theory of the relativity of motion in free space, from Einstein's theory of the relativity of motion in space containing gravitation fields, and the results of the quantum theory.

The book is written in very clear and delightful French, and can be highly recommended to the reader who wishes to get a qualitative idea of the new things which are brewing. RICHARD C. TOLMAN

Legal Chemistry and Scientific Criminal Investigation. By A. LUCAS. Director Government Analytical Laboratory and Assay Office, Cairo. Edward Arnold, London, 1920. pp. viii + 181. 14.5 × 22 cm. Price, $3.40 net.

The author frankly states in the opening of the preface that the book makes "no pretensions to be a complete treatise on Legal Chemistry, but consists essentially of a collection of notes." Surely no treatise would be complete in the space of this small volume. As a collection of notes based on the author's experience in Egypt the subject matter is interesting, though perhaps not particularly instructive to one engaged in analytical chemical work or in investigations for the law officers in the administration of justice.

The custom in England and her colonies is somewhat different from that in this country where the authorities are more apt, or perhaps more often compelled, to seek help from the scientist connected with some institution. For this reason the director of an English Government Laboratory may be called upon for a wide variety of work such as is represented in this work. Many of the subjects unfortunately are treated very superficially and the knowledge of chemistry necessary is often nil. Though the title specifically states Scientific Criminal Investigation there appears to be no reason why the information is not equally applicable to other actions in law, such as civil cases. Much of the knowledge called for is not so much scientific as it is common knowledge accurately and carefully applied with due attention to detail, which the highly trained layman is so often able to do.

As a narrative of conditions commonly met with in Egyptian jurisprudence there is an evening's pleasant reading awaiting the interested expert.

R. L. EMERSON

Solubilities of Inorganic and Organic Compounds. By ATHERTON SEIDELL. Second edition, enlarged and revised, D. Van Nostrand Company, New York. pp. xxii + 843. Price, $7.50.

The second edition of this book represents a decided advance over the first edition both in the variety of material and completeness of presentation. The earlier edition has been of inestimable value to chemists; the present is even better. In spite of the care of the author, a few errors appear. This is not surprising and as a whole the book is an admirable and accurate compilation of data. A compilation, however, cannot make good deficiencies of the original reports of measurements, as for example, on p. 121 the statement "100 cc. HBr dissolve 0.04 g. $BaSO_4$ at the boiling point" is indefinite, since the strength of acid is not stated. Possibly this is better than no information. On the other hand, on p. 131 appears "The solubility of *o*, *m* and *p*-nitrobenzene." This is a quotation from the original article and doubtless means dinitrobenzene. It is certainly not good use in nomenclature. The descriptive matter accompanying the tables is distinctly valuable and possibly could be enlarged with benefit, particularly in regard to the source and purity of materials. But in this respect also, investigators are notably lax in furnishing adequate information, and the compiler is helpless. The author is to be commended for emphasizing the identity of solubility- and freezing-point data, a fact known to all but not universally appreciated. Many references and tables relative to freezing points of mixtures are included. The author has, so far as possible, recorded the original experimental values. In the hands of anyone but an expert this is probably the best procedure. However, when treated by a competent critic such data are better plotted graphically, preferably the logarithms if temperature is the variable, and the solubilities at round concentrations or temperatures read from the plot. This not only yields results easier to tabulate and use but also furnishes a great deal of information concerning the precision and reliability of the measurements.

It would be a gigantic task to treat the material in this book in such a fashion, but would render it much more serviceable. Dr. Seidell, who, by the way, did all of this work including copying and proof reading practically unassisted, has already paid his full measure of service in this field and deserves assistance. It seems to the reviewer that the National Research Council or other organization for the advancement of science should place a sufficient number of assistants at the disposal of Dr. Seidell so that he might make his material even more useful than he has already done.

The book concludes with a brief resumé of experimental methods for the determination of solubility. E. K. STRACHAN

Everyday Chemistry. By ALFRED VIVIAN, Dean of the College of Agriculture of the Ohio State University. American Book Co., New York, 1920. 560 pages, 245 figures. 13 x 19 cm.

This is one of a series of text-books based on the idea that all school children should know the chemical, physical and biological forces with which they will have to work and the laws which govern them, and acquire some skill in handling them. The book covers "the science and art of chemistry as applied to everyday life, with special emphasis on household economics, soil fertility, and the relation of chemistry to plant and animal production." In preparing it the author has given, first, a brief study of the elements and their important compounds and reactions; this is followed in Part II by organic chemistry, 54 pages, and applied chemistry, 122 pages. Under this last caption are treated chemistry of plant growth, enzymes, digestion, fermentation, principles of nutrition, feeding farm animals, human foods, milk and its products, testing milk, leavening agents, food preservation and disinfectants, textiles, dyeing and bleaching, paints and varnishes, cleaning materials and insecticides and fungicides. Part III, 140 pages, treats of soils and fertilizers.

The book seems to have been carefully compiled; the statements of fact are accurate and the language is simple and clear. No further incursion into the realm of theory has been attempted than was necessary. The desirability of using the experimental method wherever possible is constantly enforced. The mechanical preparation of the book is excellent in every respect.

EDWARD HART

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