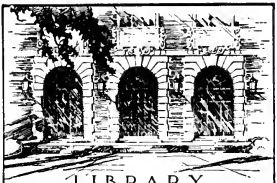

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Contributions from the Chemical Laboratory of Harvard University.

LXXXVIII.—ON THE CONSTITUTION OF PHENOQUINONE.[1]

By C. Loring Jackson and George Oenslager.

Phenoquinone, discovered by Wichelhaus,[2] in 1872, is the simplest respresentative of a class of substances formed by the direct addition of phenols and quinones, of which quinhydrone, prepared from quinone and hydroquinone, is the best known member. As all the members of this class resemble each other in properties and mode of preparation, it is fair to assume that all have the same constitution, and therefore, that the determination of the constitution of phenoquinone will settle that of all these other compounds.

So far as we can find only one attempt had been made before last year to assign graphic formulas to these substances. This proceeded from Kekulè,[3] and is criticised as follows by Nietzki[4] in concluding his investigation of phenoquinone, "Aus vorstehenden Versuchen scheint hervorzugehen dass das Chinhydron das Chinonresorcin blosse Additionsprodukte

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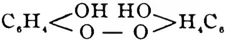
[1] Presented to the American Academy of Arts and Sciences, May 8, 1895.

[2] Ber. d. chem. Ges., **5**, 249 and 849.

[3] Lehrbuch, **3**, 97.

[4] Ann. Chem. (Liebig), **215**, 136.

des Chinons mit phenolartigen Körpern sind, und zwar scheint hierbei die Zahl der im letzteren enthaltenen freien Hydroxyle stets den beiden Chinonsauerstoffen zu entsprechen. Eine Formel im Sinne der Strukturtheorie lässt sich für diese Körper wohl augenblicklich kaum aufstellen, denn die von Kekulè für das Chinhydron vorgeschlagene Strukturformel

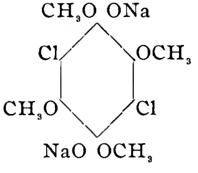


$$C_6H_4 < \begin{array}{c} OH \quad HO \\ O - O \end{array} > H_4C_6$$

lässt sich für die Verbindungen des Chinons mit einwerthigen Phenolen nicht mehr anwenden. Aus den von O. Hesse[1] beobachteten Verhalten des Chinhydrons gegen Essigsäureanhydrid scheint jedoch hervorzugehen dass das Chinhydron keine freie Hydroxyle enthält. Auch das von Wichelhaus beobachtete Verhalten des Monomethylhydrochinons spricht dafür dass Substitutionsprodukte des Chinhydrons in den Hydroxylgruppen nicht existiren.''

This statement by Nietzki, the best authority on the subject, left these substances without graphic formulas, as the assumption that they are only addition-products gives no information in regard to their constitution.

Last year H. S. Grindley and one[2] of us published an account of some compounds we obtained by the action of sodic alcoholates on substituted quinones, and succeeded in proving that these substances were formed by the action of the alcoholate on the carbonyl groups of the quinone; for instance, the methyl compound had the following constitution:



Upon adding an acid to this salt the free substance was obtained, to which the name dichlordimethoxyquinone dimethylhemiacetal was given. We were at once struck by the simi-

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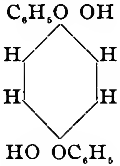
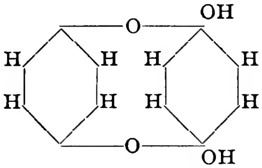
[1] Ann. Chem. (Liebig), **200**, 248.

[2] Proc. Am. Acad., **30**, 409. This JOURNAL, **17**, 577.

larity between phenoquinone, formed by the addition of two molecules of phenol to quinone, and these hemiacetals, formed (theoretically) by the addition of two molecules of alcohol to quinone, and this led us to the hypothesis that these two classes of bodies were similarly constituted. According to this hypothesis the formulas of phenoquinone and quinhydrone would be written as follows:



Phenoquinone.



Quinhydrone.

The object of this paper is to discuss this hypothesis, and we will begin by considering whether it explains the known properties of these compounds. The fact that quinone combines with two molecules of monatomic phenols, such as phenol itself, or monomethylhydroquinone, to which we can add β-napthol, but with only one molecule of diatomic phenols such as hydroquinone or resorcin, are in accord with these formulas. Further no compound with this formula could be formed from a phenol ether which contained no free hydroxyl, and as a matter of fact dimethylhydroquinone does not act on quinone. The new hemiacetals were bodies of slight stability, being decomposed even by dilute acids in the cold; phenoquinone and quinhydrone are even less stable, being decomposed by alkalies as well as acids, the former also by aniline, and the latter even by neutral solvents.[1] This lower stability of these substances is exactly what would be expected, as the study of the hemiacetals showed that those with the largest number of negative radicals on the quinone ring were the most stable, dichlordiethoxyquinone diethylhemiacetal being more stable for example than the corresponding monochlor compound. Therefore in phenoquinone we should expect a very slight stability, as it has no negative radicals attached to the quinone ring. (The phenoxy groups

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[1] Clark: This JOURNAL, 14, 574.

are not considered here, as they correspond to the ethoxy groups of the hemiacetal). The action of acetic anhydride on quinhydrone giving quinone and diacetylhydroquinone is adduced by Nietzki as a proof that this body contains no hydroxyl groups, and therefore at first sight seems to contradict this theory of its constitution. A more careful consideration of the question, however, shows that this is really in accord with our formula, as the dimethylhemiacetal when treated with acetic anhydride gives the substituted quinone from which it is derived and methylacetate, and therefore undergoes a precisely similar decomposition. This too, although it contains two hydroxyl groups, as was abundantly proved by the formation of an ethyl and of a benzoyl derivative under proper conditions.

Turning now to the properties of phenoquinone, which do not agree with our formula, Wichelhaus[1] stated that it did not form salts, although it was turned blue by alkalies. If constituted according to our hypothesis, it should form salts like those of the hemiacetals. Here then was a chance to submit our formula to an experimental test, and accordingly we have studied the formation of salts from phenoquinone. At first we tried the action of sodic phenylate upon quinone, as we feared that phenoquinone would be decomposed if treated directly with an alkaline substance, and we found that, if the substances were mixed in ethereal solution, a dark blue salt was formed having the formula $C_6H_4O_2(C_6H_5ONa)_2$, and therefore corresponding to the sodium salt of phenoquinone. This did not prove, however, that phenoquinone could form salts, for, although it was evident that this was the salt of the diphenylhemiacetal, it was possible that this diphenylhemiacetal might be different from phenoquinone. It would not remove this objection to form phenoquinone from the salt by the addition of an acid, as the hemiacetal, if different from phenoquinone, might break up when it was set free into quinone and phenol, which would then recombine to form phenoquinone. Accordingly we turned our attention to the action of sodic naphthylate on phenoquinone. We selected this substance because a stronger alkaline body might

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[1] Ber. d. chem. Ges., 5, 849.

decompose the phenoquinine, and the use of this reagent would prove whether the salt was formed from the phenoquinone, or by the action of the naphthylate upon quinone which might be formed by the decomposition of the very unstable phenoquinone. In the first case, that is if it were a true salt, we should get the same salt which we had made direct from sodic phenylate and quinone or an isomer of it. In the second case we should obtain a salt of quinone dinaphthylhemiacetal, which would be easily shown by analysis. The experiment proved that we got the same salt obtained by the action of sodic phenylate on quinone. This was proved by the analysis, by its dark blue color, and by the property common to both of taking fire when heated in the steam oven. This result shows that phenoquinone can form a salt containing two atoms of sodium, and therefore that it probably contains two hydroxyl groups as required by the formula under discussion. The first method of formation of this salt by direct addition of sodic phenylate to quinone is exactly parallel to the formation of the hemiacetals from sodic alcoholates and quinones.

On the other hand there are marked differences between the properties of the hemiacetals and the members of the phenoquinone group. The former are all white and insoluble or nearly so in all the common solvents, the latter are strongly colored and soluble in many of the organic solvents. It is possible that these differences may be due to the presence of fatty radicals in the one and of aromatic radicals in the other set of substances, but this explanation does not seem to us wholly satisfactory, and we must therefore leave this objection to our theory for future investigation. Some experiments on the diamyl and dibenzylhemiacetals undertaken with a view to meeting this objection showed that they were colorless and insoluble like the hemiacetals with less complex radicals. These substances and the corresponding quinones and hydroquinones are described in the experimental part of this paper.

The statement of the case just given shows that the formulas we have assigned to phenoquinone and quinhydrone explain satisfactorily the composition of these bodies, and that they resemble the hemiacetals so far as the method of formation, stability, behavior with acetic anhydride, and power of forming salts are concerned, but that they do not resemble these substances in colors or solubilities.

We have also tried some experiments on the formation of substances similar to phenoquinone in order to determine what are the conditions necessary for making substances of this class. These are in part repetitions of experiments mentioned by Wichelhaus in his second paper on phenoquinone,[1] but so far as we are aware never published in detail by him. Quinone reacted with all the unsubstituted monatomic phenols tried (the compound with β-naphthol is described in detail later) but not with tribromphenol or picric acid. Trichlor or tetrachlorquinone did not react even with phenol. It would seem from these observations that making either component more negative prevents the formation of substances like phenoquinone. On the other hand the components should not be too little negative. A salt obtained by the action of sodic ethylate on quinone was so unstable that we did not succeed in analyzing it;[2] it even took fire spontaneously at ordinary temperatures. But by increasing the negative nature of the quinone (using a diethoxydichlorquinone) a hemiacetal can be obtained with sodic ethylate much more stable than phenoquinone. It seems, therefore, that a certain balance of negative properties between the two components is necessary for the formation of substances of this phenoquinone class, thus the negative phenol combines with quinone, but, if we use the alcohols which are nearly destitute of negative properties, the negative nature of the quinone must be increased by substitutions in order to form stable compounds while these substituted quinones form no compounds, or very unstable ones, with the negative phenol.

Thymoquinone acts with phenols as quinone does, but the products show less tendency to crystallize; a new hemiacetal[3] from thymoquinone and hydroquinone is described later.

From β-naphthoquinone, from anthraquinone, and from

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[1] Ber. d. chem. Ges., **5**, 849.

[2] Jackson and Grindley: This JOURNAL, **17**, 654.

[3] We have adopted provisionally the name hemiacetal for the compounds of the phenoquinone group in spite of the objection which still stands against this theory, because we could find no other name which expressed so clearly their composition.

phenanthrenequinone no compounds with monatomic phenols were obtained, and the only ones yet observed with diatomic phenols are the compounds of phenanthrenequinone, nitronaphthoquinone, and fluoranthenequinone with the hydroquinones derived from them. It is hoped that these experiments can be continued in this laboratory during the coming year. The facts already collected show, however, that substances of the quinhydrone class, that is those formed by the union of a quinone with the corresponding hydroquinone, are obtained more easily than those made from the monatomic phenols, and this is still further confirmed by the fact[1] that tetrachlorquinone (chloranil) probably combines with tetrachlorhydroquinone to form an octochlorquinhydrone, whereas chloranil did not unite with phenol to give a body analogous to phenoquinone.

Finally, it may be well to call attention to the fact that the characteristic phenomena attending the melting of quinhydrone are recorded for the first time, so far as we are aware, at the end of this paper. They furnish an admirable means of recognizing this substance.

EXPERIMENTAL PART.

Dichlordiamyloxyquinone Diamylacetal

$C_6Cl_2(OC_5H_{11})_2(OH)_2(OC_5H_{11})_2$.

The sodium salt of this substance was made by stirring together 4 grams of finely powdered dichlordiphenoxyquinone and a solution of sodic amylate made by treating one gram of sodium with 25 cc. of amyl alcohol. Heat was evolved, and the red color of the dichlordiphenoxyquinone disappeared, a dark green solution being formed, since the sodium salt of this hemiacetal is soluble in amyl alcohol; in this respect it differs from the methyl and ethyl hemiacetals which were only slightly soluble in the corresponding alcohols. An attempt to obtain the free hemiacetal by acidification gave no precipitate, and accordingly we precipitated the salt by the addition of ethyl alcohol, which gave it in the form of a white crystalline precipitate. This was freed from the mixture of

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[1] Staedeler: Ann. Chem. (Liebig), 69, 329.

alcohols by filtration, washed with common alcohol, and then dissolved in a large amount of water, filtered again, and the hemiacetal precipitated with dilute acetic acid. To make the sodium salt for analysis the hemiacetal was dissolved in very dilute sodic hydrate, and sufficient alcohol added to make the salt crystallize.

The sample of salt analyzed was prepared in the way described above; a much better yield was obtained by the following modification of the process,—one gram of sodium was dissolved in 25 cc. of amyl alcohol (with a smaller amount it was very hard to convert the sodium into sodic amylate). The solution was then distilled until about 15 cc. of amyl alcohol had passed over, and the residue was poured into a beaker, and stirred while it cooled so as to make the crystals of sodic amylate as small as possible. The 4 grams of dichlordiphenoxyquinone were then added, and afterward 50 cc. of alcohol, when the sodium salt of the diamylhemiacetal crystallized out, and was purified as described above. The yield by this method was one gram of sodium salt from 4 grams of dichlordiphenoxyquinone, that is about 15 per cent. of the theoretical. A solution of sodic amylate in ether gave a greenish crystalline precipitate with dichlordiphenoxyquinone, which was soluble in water, but gave no precipitate with an acid. It was also observed that, if ether or benzol was used instead of alcohol to precipitate the sodium salt, the yield was not so good.

The sodium salt prepared by the method described above was dried over sulphuric acid and caustic potash, and analyzed with the following results,—

I. 0.3900 gram of substance gave 0.0953 gram of sodic sulphate.

II. 0.2377 gram of the substance gave by the method of Carius 0.1167 gram of argentic chloride.

	Calculated for	Found	
	$C_6Cl_2(OC_5H_{11})_2(ONa)_2(OC_5H_{11})_2$.	I.	II.
Sodium	8.09	7.91	....
Chlorine	12.48	....	12.14

Properties of the Sodium Salt of Dichlordiamyloxyquinone Diamylhemiacetal.—It forms white silky needles, which decompose spontaneously on standing, turning brown and giving off an odor of amyl alcohol. Its solution gives precipitates with salts of most of the basic radicals, but these did not seem to be very definite substances. It is soluble in water or amyl alcohol, insoluble to slightly soluble in ethyl alcohol, ether or benzol. Dilute acids precipitate the hemiacetal; even carbonic acid produces this result.

The free hemiacetal was a white solid insoluble in water. It decomposed to a yellow oil in a short time, even before it could be dried in a desiccator. No attempt therefore was made to analyze it. These observations are enough to establish the fact that it is white, which was the point that was of especial interest to us. They show also that it is much less stable than the corresponding ethyl or methyl hemiacetal which could be kept for a moderately long time without decomposition.

Dichlordiamyloxyquinone, $C_6Cl_2(OC_5H_{11})_2O_2$.

The sodium salt of the dichlordiamyloxyquinone diamylhemiacetal was converted into this substance by warming with strong hydrochloric acid, but the quinone was deposited as a yellow oil which could not be brought to crystallization by standing for months, or by treatment with alcohol, ether, or similar solvents. It was finally induced to crystallize by dissolving it in glacial acetic acid, and allowing it to stand for about six weeks. At the end of this time the liquid had evaporated leaving as a residue a reddish yellow crystalline mass, which was purified by dissolving in hot glacial acetic acid, and diluting the acid to such an extent that crystals would not be deposited until the liquid was lukewarm. If too much water was added, the substance was precipitated in an oily state. The purification was finished by crystallization from a mixture of alcohol and benzol. The oil could be made to solidify also by boiling it for several hours with glacial acetic acid in a flask with a return-condenser, then distilling off part of the acid, and bringing about the crystallization with water as described above, but this method is attended with considerable loss from decomposition of the substance by the glacial acetic acid. We are inclined to ascribe the obstinacy with which this substance remained in the liquid state to its forming a loose compound with amyl alcohol, as the odor of amyl acetate was perceptible during the treatment with acetic acid. The substance after crystallization until it showed the constant melting-point 53° was dried in a desiccator, and analyzed with the following results:

0.3131 gram of the substance gave by the method of Carius 0.2558 gram of argentic chloride.

	Calculated for $C_6Cl_2(OC_5H_{11})_2O_2$.	Found.
Chlorine	20.34	20.20

Before the original oily product had solidified we tried to make dichlordiamyloxyquinone by other methods for the sake of comparison, but without success, as potassic chloranilate heated to 140° in a sealed tube with amyl bromide charred, and argentic chloranilate boiled with amyl bromide gave argentic bromide and chloranilic acid. As great pains were taken to exclude moisture, it seems probable that amylene was also formed, but we did not succeed in identifying it.

Properties of Dichlordiamyloxyquinone.—This substance crystallizes from acetic acid in irregular plates or blades of a yellowish-red color with a yellow reflex. It melts at 53°. It is freely soluble in ether, benzol, chloroform, acetone, ligroïne, glacial acetic acid, carbonic disulphide, or amyl alcohol; slightly soluble in ethyl alcohol, or dilute acetic acid. This latter is the best solvent for it. It shows a strong tendency to separate from its solutions in an oily state, and when once crystallized to relapse into an oil. Boiling with glacial acetic acid gradually saponifies it to chloranilic acid. Reducing agents convert it into the hydroquinone described in the next paragraph.

Dichlordiamyloxyhydroquinone $C_6Cl_2(OC_5H_{11})_2(OH)_2$.

This substance was made by reducing the corresponding quinone with zinc dust and glacial acetic acid. It is not necessary to use the pure quinone for this purpose, as the substance was also obtained from the oily product made by the action of sodic amylate on dichlordiphenoxyquinone (see above). After the yellow color of the quinone had disappeared, a few drops of water were added, and the crystalline precipitate formed purified by crystallization from acetic acid and afterward from alcohol until it showed the constant melting-point 128°, when it was dried *in vacuo* and analyzed with the following result:

0.3009 gram of the substance gave by the method of Carius 0.2384 gram of argentic chloride.

	Calculated for $C_6Cl_2(OC_5H_{11})_2(OH)_2$.	Found.
Chlorine	20.19	19.59

In two of our earlier preparations a different substance was obtained, which melted at 90°, and gave on analysis percentages of chlorine (15.79 and 15.88) corresponding fairly well for the diacetate of the hydroquinone (16.32), but as we did not feel any special interest in this substance, we did not try further to settle its nature.

Properties of Dichlordiamyloxyhydroquinone.—It forms long, thin, white plates terminated by one plane at a not very acute angle to the sides. It melts at 128°. It is freely soluble in ether, benzol, chloroform, acetone, glacial acetic acid, or carbonic disulphide; slightly soluble in ligroïne, or dilute acetic acid; insoluble in water. Dilute acetic acid or alcohol is the best solvent for it. It is easily oxidized by the common oxidizing agents, being converted into the quinone just described; this change takes place so readily that even the oxygen of the air converts it partially into the quinone, so that it is hard to get it perfectly white.

Action of Sodic Benzylate on Dichlordiphenoxyquinone.

The sodic benzylate was made by dissolving 0.5 gram of sodium in 15 cc. of benzyl alcohol with the aid of heat. As the liquid cooled it was stirred constantly to prevent the formation of large crystals, and the pasty mixture thus obtained was treated with 2 grams of finely powdered dichlordiphenoxyquinone, which was added in small portions at a time with constant stirring. The proportions are four atoms of sodium to each molecule of the quinone. In a few minutes the red color disappeared, and the liquid turned dark green. At this point about 30 cc. of benzol were added, which in a short time caused the separation of crystals of the sodium salt of dichlordibenzyloxyquinone dibenzylhemiacetal, from which dilute acids precipitated the hemiacetal as a white powder. Both the hemiacetal and its salt were so unstable that no attempt was made to analyze either of them, but analyses were unnecessary, as their behavior showed with sufficient clearness what their composition must be, and the white color of the hemiacetal was the one of its properties which especially interested us. The free hemiacetal almost immediately loses its white color, turning brown from the formation of the corresponding quinone, and the sodium salt, although somewhat more stable in the dry state, was quickly decomposed in aqueous solution with formation of chloranilic acid, so that there seemed little chance of purifying it. The dibenzyl hemiacetal therefore is even less stable than the diamyl hemiacetal.

Dichlordibenzyloxyquinone, $C_6Cl_2(OC_7H_7)_2O_2$.

This substance was first obtained by the action of a dilute acid on the sodium salt of the hemiacetal described in the preceding paragraph, but as the yield was very small, the following method was adopted, which gave a better result. 0.5 gram of sodium were dissolved by the aid of heat in 4 cc. of benzyl alcohol, mixed with 150 cc. of absolute ether and 2 grams of dichlordiphenoxyquinone added to the solution. After a short time a deep green mass was deposited, which was filtered out, washed with ether, and added to water. The green color changed to red and an oily red mass floated on the surface of the liquid, which was colored purple by a salt of chloranilic acid, and also contained a trace of the sodium salt of the hemiacetal, as was shown by the formation of a white precipitate on the addition of an acid. The oily red precipitate was filtered out, and purified by crystallization from a mixture of benzol and alcohol, to remove the excess of benzyl alcohol, to which it owed its semiliquid consistency, until it showed the constant melting-point 142°, when it was dried *in vacuo* and analyzed with the following result:

0.3005 gram of the substance gave by the method of Carius, 0.2197 gram of argentic chloride.

	Calculated for $C_6Cl_2(OC_7H_7)_2O_2$.	Found.
Chlorine	18.26	18.08

The yield of dichlordibenzyloxyquinone by the process given above is 0.5 gram from 2 grams of dichlordiphenoxyquinone that is 23 per cent. of that calculated from the formulas.

Properties of Dichlordibenzyloxyquinone.—It forms long slender plates or flat prisms terminated usually by one plane at an oblique angle, or sometimes by a plane at a right angle. When crystallized from alcohol and benzol quickly it forms irregularly circular groups of little plates radiating from centers. The color of the larger crystals is red with a golden reflex, of the smaller plates orange. It melts at 142°. It is easily soluble in alcohol, acetone, benzol, glacial acetic acid, or ethyl acetate; essentially insoluble in ether, ligroïne, or water. The best solvent for it is a mixture of alcohol and benzol. Reducing agents convert it into the corresponding hydroquinone described in the next paragraph.

Dichlordibenzyloxyhydroquinone, $C_6Cl_2(OC_7H_7)_2(OH)_2$

This substance was obtained by warming a solution of the corresponding quinone in glacial acetic acid with zinc dust. When the orange color of the quinone had disappeared, water was added to precipitate the hydroquinone, and this was recrystallized from acetic acid until it showed the constant melting-point 122°–123°, when it was dried *in vacuo* and analysed with the following result:

0.2302 gram of the substance gave by the method of Carius 0.1680 gram of argentic chloride.

	Calculated for $C_6Cl_2(OC_7H_7)_2(OH)_2$.	Found.
Chlorine	18.16	18.04

The yield is quantitative.

Properties of Dichlordibenzyloxyhydroquinone.—It crystallizes from dilute alcohol in white needles united longitudinally into groups. Larger crystals appear as rather stout needles with a sharp end. It melts at 122°–123°, and is easily soluble in alcohol, ether, benzol, glacial acetic acid, or carbonic disulphide; slightly soluble in ligroïne; insoluble in water. The best solvent for it is glacial acetic acid. The common oxidizing agents convert it into the corresponding quinone; even the oxygen of the air has this effect on its solutions to a limited extent, which increases the difficulty of purifying it.

Some attempts to make the dichlordiphenoxyquinone diphenylhemiacetal led to no result. It seems highly probable that the sodium salt of this body is contained in the black solution formed by adding sodic phenylate to chloranil, but upon acidification we obtained only dichlordiphenoxyquinone and phenol. If then the sodium salt did exist in the solution, the hemiacetal was decomposed as soon as it was set free, and this is not surprising, as all our experience with this class of bodies, tends to show that the stability decreases when the negative nature of the two components rises above a certain point.

Addition of Sodic Phenylate to Quinone.

The sodic phenylate used was made by dissolving 2.5 grams of freshly distilled phenol in about 150 cc. of dry ether and then adding 0.5 gram of sodium in small pieces. The action was slow, but in time all the sodium disappeared, giving an ethereal solution of sodic phenylate with an excess of phenol amounting to 0.5 gram. 1.7 grams of quinone also dissolved in dry ether were then added slowly to the solution of sodic phenylate (which should be freshly prepared). The first drop produced a deep indigo blue precipitate, which increased in amount as the solutions were mixed. After the ethereal solution had been removed as completely as possible by the pump, the precipitate was washed two or three times with dry ether and then spread out in a vacuum desiccator over sulphuric acid and potassic hydrate. As an excess of both phenol and quinone was used, the principal impurity of the precipitated salt was phenoquinone, which was partly removed by the washings with ether, partly by evaporation *in vacuo*. This latter method of purification is to be preferred to thorough washing with ether, as there is danger during this washing that the salt will absorb moisture from the air and become decomposed. That phenoquinone evaporates rapidly *in vacuo* at ordinary temperatures was shown by a special experiment, 0.0485 gram of phenoquinone were allowed to stand in a vacuum desiccator at a pressure of 20 mm. for twenty-four hours, when it was found that it had lost 0.0383 gram, and, as the residue was unaltered phenoquinone, it showed that this method of purification could be used with safety. After the salt had come to a constant weight in the vacuum desiccator (0.4672 gram free from ether lost 0.0084 gram), it was analyzed with the following result:

0.4462 gram of the salt gave 0.1803 gram of sodic sulphate.

	Calculated for $C_6H_4O_2(C_6H_5ONa)_2$.	Found.
Sodium	13.53	13.09

This result is as good as could be expected when it is remembered that the salt could not be recrystallized, and that it is very hygroscopic. It shows that one molecule of the quinone combines with two molecules of sodic phenylate.

Formation of Sodium Salt from Phenoquinone.

When phenoquinone in ethereal solution was added to a solution of sodic phenylate also in ether, a blue salt was obtained exactly similar in properties to that, the preparation of which is described in the preceding section. As it was possible, however, that this salt might not be formed by the replacement of hydrogen in phenoquinone by sodium, but by the addition of sodic phenylate to quinone formed from the very unstable phenoquinone, we modified our process by using sodic β-naphthylate instead of sodic phenylate. In this case, if the second supposition were correct and the salt formed by direct addition of the sodic naphthylate to quinone produced by decomposition of the phenoquinone, a salt would be obtained with an entirely different composition from that mentioned in the previous section, whereas it must have the same composition, if it was formed from the phenoquinone by replacing two atoms of hydrogen by two of sodium, in other words, if it were a true salt of phenoquinone. We accordingly proceeded as follows,—one gram of β-naphthol was dissolved in 150 cc. of dry ether, and treated with 0.13 gram of sodium. After the metal had disappeared, the ethereal solution of sodic naphthylate was added to one gram of phenoquinone also dissolved in ether. A blue precipitate was formed at once, which was filtered out by means of a Gooch crucible, and purified by washing with dry ether and standing *in vacuo* over sulphuric acid and potassic hydrate until it had reached a constant weight, when it was analyzed with the following result :

0.4591 gram of the substance gave 0.1825 gram of sodic sulphate.

	Calculated for $C_6H_4O_2(C_6H_5ONa)_2$.	Calculated for $C_6H_4O_2(C_{10}H_7ONa)_2$.	Found
Sodium	13.53	10.46	12.89

This analysis proves that the substance was a true salt of phenoquinone. The rather low result is not strange, as owing to the instability of the salt we were unable to submit it to a thorough purification. The product from phenoquinone and sodic naphthylate showed the same properties as that obtained from quinone and sodic phenylate.

Properties of the Sodium Salt of Phenoquinone.

It forms an amorphous very dark blue powder when dried *in vacuo*, but, if the salt moistened with ether is allowed to dry on filter-paper in the air, it can be obtained of a bronze color with a strong metallic lustre, recalling in appearance many of the aniline dyes. It is decidedly unstable, as if heated in a steam drying oven, it takes fire spontaneously, and even when kept at ordinary temperatures in a corked tube it decomposes after a few days forming a chocolate brown mass which smells of phenol. When heated carefully in a platinum crucible a white crystalline precipitate with a pleasant odor was deposited on the lid, but we have not studied this action further. It dissolves completely in water giving a clear brown solution, but this solution is evidently accompanied by decomposition, as acids produce no precipitate when added to the liquid. Salts of aluminium, iron, lead, silver and mercury gave brown precipitates with the solution of the salt, but these could not have been salts of phenoquinone, since, as we have just shown, the sodium salt is decomposed by water. As the salt is very hygroscopic, some of this brown decomposition product is formed when it is exposed to the air for some time, and this fact must be borne in mind during its purification. The study of the decomposition products must be postponed till some future time. We can only say at present that, if the solution of the salt is distilled with steam, phenol passes over, and upon evaporating the residue in the flask a brown amorphous mass of uninviting appearance is obtained. The great sensitiveness of the salt toward water probably accounts for the statement made by Wichelhaus[1] that the phenoquinone forms no salts.

We also treated the sodium salt with benzoyl chloride in the hope that a benzoyl compound might be formed sufficiently stable to allow us to establish its constitution by the methods used in the case of the dichlordiethoxyquinone diethyldibenzoylhemiacetal.[2] Our experiments, however, have not led to the desired result, which is not surprising in view of the experience of Grindley and one of us with the diethylhemiacetal. The sodium salt of this compound, if suspended in alcohol and treated with benzoyl chloride, gave the dibenzoyl compound of the hemiacetal, but, if ether or benzol was used as the menstruum, the hemiacetal decomposed with the formation of ethyl benzoate and the substituted quinone. As the sodium salt of phenoquinone is decomposed by alcohol in the same way that it is by water, we could not in this case use the conditions which had succeeded with the hemiacetal, but we were obliged to confine our experiments to the action of benzoyl chloride mixed with benzol or ether. To the sodium salt suspended in benzol a slight excess of benzoyl chloride was added, when a vigorous reaction took place, as was shown by a considerable evolution of heat, the appearance of a brown color in the liquid, and the formation of a black precipitate. This black precipitate was extracted with benzol in a Soxhlet's apparatus as long as any colored substance was removed. Upon evaporating off the benzol from the extract a black residue was obtained, which was treated with alcohol, and thus divided into a yellowish white substance insoluble in the alcohol, and a dark colored solution. The solution on evaporation deposited black fan-shaped crystals with a green reflex, which we recognized as quinhydrone. The yellow substance insoluble in alcohol, after being purified by crystallization from a mixture of alcohol and benzol, melted at 199°.5, and

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[1] Ber. d. Chem. Ges., **5**, 849.

[2] This JOURNAL, **17**, 637.

in its other properties agreed with benzoylhydroquinone, which melts at 199°.

The residue insoluble in benzol from the Soxhlet's apparatus was washed with water, which removed sodic chloride and a little organic matter of a brown color. The residue, which formed the greater part of this portion of the substance, was soluble in alcohol or acetic acid, but all attempts to obtain crystals from either of these solutions have failed. When this residue is heated, it apparently decomposes, and a crystalline substance is volatilized, but we have not yet obtained this product in sufficient quantity for identification, and must therefore leave a careful study of this reaction until a future time.

Preparation of Substances Analogous to Phenoquinone.

Our object in taking up the work described in this section was to determine, if possible, the conditions which were necessary for the formation of substances like phenoquinone, and for this purpose we tried a number of qualitative experiments, making a more careful study of those products which seemed the most manageable.

In the following summary of our results we have inserted also those obtained previously by other observers, so that it gives a fairly complete list of the facts at present known.

Derivatives of Ordinary Quinone $C_6H_4O_2$.—With phenol, phenoquinone is formed. With thymol a yellow oil was produced which after standing for some time turned to a black crystalline mass. With β-naphthol a compound was formed corresponding to phenoquinone, which is described later. With hydroquinonemethylether, quinhydronedimethylether.[1] With hydroquinone quinhydrone is formed. With resorcine resorcinequinone.[2] With thymohydroquinone the product was quinhydrone. This reaction is discussed later. With picric acid there was no action. With tribromphenol also no action.

Derivatives of the other Quinones.— Toluoquinone with toluohydroquinone gives the corresponding quinhydrone,[3]

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[1] Wichelhaus: Ber. d. chem. Ges., **12**, 1501.

[2] Nietzki: Ann. Chem. (Liebig), **215**, 136.

[3] Nietzki: *Ibid.* 158.

and oxyisoxyloquinone with oxyisoxylohydroquinone gives a quinhydrone.[1] Thymoquinone with phenol formed a yellowish red oil which did not solidify on standing. With thymol it gave a similar result, but with hydroquinone the thymoquinone gave a compound similar to quinhydrone described later in this paper. With resorcine it gave a red crystalline solid not further studied. With thymohydroquinone it gives thymoquinhydrone.[2] β-naphthoquinone gave no perceptible reaction with phenol or with hydroquinone, but with β-naphthohydroquinone it has given a quinhydrone.[3] Anthraquinone gave no perceptible reaction with phenol, β-naphthol, or hydroquinone. Phenanthrenequinone gave no perceptible reaction with phenol, β-naphthol or hydroquinone, but with phenanthrenehydroquinone forms the phenanthrenequinhydrone.[4] The quinone from diphenylbutin gave with sulphurous acid a quinhydrone.[5] Finally dichlor,[6]-tetrachlor,[7] hexachlor[8] and perhaps even octochlor[9]-quinhydrones have been obtained from substituted components.

Quinone Dinaphthylhemiacetal, $C_6H_4O_2(C_{10}H_7OH)_2$.

To form this substance 1.5 grams of quinone were dissolved in benzol so as to make a nearly saturated solution, and mixed with a similar solution of 3 grams of β-naphthol. When the two solutions were mixed, a deep brown color appeared, and after evaporating off most of the benzol dark brown crystals were deposited in large quantity ; these were purified by treatment with ligroïne to wash out the excess of quinone, and after drying *in vacuo* were analyzed with the following result :

0.1298 gram of the substance gave on combustion 0.3751 gram of carbonic dioxide and 0.0660 gram of water.

	Calculated for $C_6H_4O_2(C_{10}H_7OH)_2$.	Found.
Carbon	78.79	78.77
Hydrogen	5.05	5.65

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[1] Fittig, Siepermann : Ann. Chem. (Liebig), **180**, 27.

[2] Liebermann : Ber. d. chem. Ges., **18**, 3196.

[3] Stenhouse and Groves : J. Chem. Soc. Lond., 1877, 53.

[4] Anschütz and Schultz : Anu. Chem., (Liebig), **196**, 382.

[5] Zincke and Breuer : Ann. Chem., (Liebig), **226**, 30.

[6] Wöhler : Ann. Chem. (Liebig), **51**, 156.

[7] Staedeler : *Ibid.*, **69**, 314.

[8] Staedeler : *Ibid*, 321 ; Graebe ; **146**, 27.

[9] Sfaedeler ; *ibid*, **69**, 329.

Properties of Quinone Dinaphthylhemiacetal.—It crystallizes in thin brown rectangular plates, showing a bronze reflex. It melts at 82°. It is very unstable, decomposing even at ordinary temperatures in a corked tube, as is shown by the fact that it loses its luster, and finally even its crystalline form giving off at the same time a strong smell of quinone. It dissolves easily in ether, chloroform, benzol, glacial acetic acid, or ethylacetate, but with difficulty in ligroïne.

Sodium Salt of Quinone Dinaphthylhemiacetal. $C_6H_4(OC_{10}H_7)_2(ONa)_2$.

To prepare this substance an ethereal solution of naphthylate was made by dissolving 1.4 grams of β-naphthol in about 200 cc. of dry ether and adding 0.2 gram of sodium in small pieces. The solution was then added to an ethereal solution of 2.3 grams of quinone, and the greenish blue precipitate formed purified by washing with dry ether and standing *in vacuo* in the manner already described under the salt of phenoquinone. This method did not give such good results in the present case, as it had before, but the percentage obtained on analysis is near enough to show that we had obtained the desired compound.

0.5140 gram of the salt gave 0.1537 gram of sodic sulphate.

	Calculated for $C_6H_4O_2(C_{10}H_7ONa)_2$.	Found.
Sodium	10.46	9.69

The salt resembles in properties that derived from phenoquinone, but has a more greenish blue color; like that it decomposes on standing at ordinary temperatures in a corked tube, and gives a brown solution when treated with water.

Thymoquinone Hydroquinonehemiacetal, $C_{10}H_{12}O_2C_6H_4(OH)_2$

This substance was made by mixing 1 gram of hydroquinone with 1.7 gram of thymoquinone, both substances being in ethereal solution; this formed a dark reddish-brown solution, which on spontaneous evaporation deposited fine rectangular plates of the new substance. These were analyzed with the following results:

0.1424 gram of the substance gave on combustion 0.3632 gram of carbonic dioxide and 0.0875 gram of water.

	Calculated for $C_{10}H_{12}O_2C_6H_6O_2$.	Found.
Carbon	70.07	69.55
Hydrogen	6.57	6.83

Properties of Thymoquinone Hydroquinonehemiacetal.—This substance crystallizes from ether in rectangular prisms, sometimes nearly a centimeter long and half a centimeter broad, which have a dark brown color like that of ferric citrate with a very brilliant reflex of a yellowish cantharides green. It melts at 136° to 137°, and gives out a smell of thymoquinone even at ordinary temperatures, although it keeps well in a corked tube. It is easily soluble in alcohol, ether, acetone, or ethylacetate; slightly soluble in cold glacial acetic acid, freely in hot, but most, if not all of these solvents, decompose it. Benzol, chloroform or ligroïne dissolve thymoquinone out of it, leaving hydroquinone behind.

Action of Quinone on Thymohydroquinone.

We tried this experiment in the hope of getting a compound isomeric with that just described. An ethereal solution of one gram of thymohydroquinone was mixed with 0.6 gram of quinone also dissolved in ether. The liquid after standing a short time deposited crystals, which melted between 163° and 170°; these were filtered off, and the filtrate on evaporation gave crystals of the thymoquinone hydroquinonehemiacetal just described melting at 135°. We supposed therefore that we had obtained in the substance melting at 163° to 170° the desired isomer, but its analysis showed that this was not the case.

I. 0.1653 gram of the substance gave 0.4013 gram of carbonic dioxide and 0.0738 gram of water.

II. 0.1461 gram of the substance gave 0.3552 gram of carbonic dioxide and 0.0682 gram of water.

	Calculated for $C_6H_4O_2C_{10}H_{12}(OH)_2$.	Found I.	Found II.
Carbon	70.07	66.18	66.29
Hydrogen	6.57	4.96	5.19

These results, although they do not agree with the percentages calculated for the expected substance, correspond very well with those required for quinhydrone which are as follows:

	Calculated for $C_6H_4O_2C_6H_4(OH)_2$.
Carbon	66.06
Hydrogen	4.58

The appearance of the substance also was like that of quinhydrone, and that it was this body was proved by its behavior when melting. As no definite statements are made, so far as we can find, in regard to the melting point of quinhydrone, we compared its behavior with that of our product, and found them identical in every respect. Quinhydrone has no sharp melting point, as it is a decomposition which takes place rather than a simple fusion, but the attendant phenomena make this decomposition as useful for identification, as if it were a definite melting-point. The decomposition began at about 163°, but was not complete till 170°. After it had taken place a sublimate of yellow crystals (quinone) was found in the cold part of the melting-tube, while just above the substance the tube was coated with white fan-shaped groups of crystals (hydroquinone), or, if the temperature had gone too high, a liquid which on cooling solidified in these white crystals. Above these crystals a dark brown stain coated the tube, which increased with longer heating.

It is evident from the observations described above that the reaction between thymohydroquinone and quinone consists in the first place of the oxidation of the thymohydroquinone to thymoquinone by the quinone, which itself is converted into hydroquinone. The hydroquinone thus formed then combines in part with the unaltered quinone to produce quinhydrone, and partly with the thymoquinone formed to give thymoquinone hydroquinone hemiacetal.

THE CHEMICAL KINETICS OF OXIDATION.

BY HERMAN SCHLUNDT AND ROBERT B. WARDER.

II.—MATHEMATICAL THEORY OF OXIDATION PROCESSES.

BY ROBERT B. WARDER.

My own interest in this subject was first awakened by a copy of Mr. Schlundt's complete paper, as a Bulletin of the University of Wisconsin. So much good work merits further elaboration, and the following commentary is the result.

I.—*Inspection of the Curves.*

Six groups of curves illustrate part I.; the abscissas represent time and the ordinates percentage of iodine liberated in each case. All curves necessarily pass through the origin, and all are concave towards the axis of abscissas, yet nowhere becoming parallel with it,—showing that the rate of change began with a maximum, which gradually diminished through the course of the experiment, without reaching the condition of equilibrium. Curve A, expressing the course of the reaction for equivalent (decinormal)[1] proportions, is repeated on Figs, I., II., III., and V. Each curve may be studied with special reference to the change taking place in equal intervals of time, or to the time required to liberate equal quantities of iodine. For example, to find the mean velocity with regard to equal portions of time, we must note the increasing values of equidistant ordinates: but to find the mean velocity with reference to the change taking place, we must divide equal increments of ordinates by unequal increments of abscissas before summation and division.[2]

Fig. I shows the effect of increasing the potassium chlorate, in two-fold, three-fold and four-fold ratios. That part of the curves which represents the first 100 or 200 minutes shows great difference of slope; increase of the salt increases the speed. It is very clear, however, that the quantity of iodine liberated in a given time is not proportional to the quantity of potassium chlorate. For the interval from 400 to 1320 minutes, all the curves are approximately parallel,

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[1] Under the term "decinormal" Mr. Schlundt includes one- sixtieth gram molecule of potassium chlorate per liter since this is equivalent to decinormal iodide and acid.

[2] The two means will be different in their value and significance, as shown by Fuhrmann; Ztschr phys. Chem., 4, 520 (1889).

indicating nearly equal speed at this time in the four experiments; although the conditions differ greatly, both in the amount of chlorate present and in the percentage of change already accomplished. The curves approach parallelism to the axis of abscissas, and one is tempted to suppose they may be asymptotic to horizontal lines; but it would not be safe to conclude that conditions of equilibrium would be reached short of complete action, unless the experiments had been continued for a much longer period.

The distance between curves A and B, in this latter portion, is about the same as between B and D; that is, the effect of first doubling the potassium chlorate in increasing the total quantity of iodine liberated is about the same as changing from two-fold to four-fold the normal quantity. The horizontal and vertical scales of these curves are so related that it is easier to compare the ordinates for a given abscissa than to compare abscissas for a given ordinate; but the latter enables us to judge of the time required to liberate a certain percentage of the iodine. By noting the points of the several curves which represent the liberation of 10 per cent., 20 per cent., etc., of the iodine, we judge that the time with two-fold quantity of chlorate is about one-half the normal time; for four-fold quantity, about one-fourth the normal time, and so on; yet the mean speed indicated is not uniformly proportional to the mass in this case. It is also worth while to scrutinize the three strips bounded respectively by the curves A and B, B and C, and C and D. These are similar in general form; the width increases rapidly at the origin, more slowly (if at all) later; and probably they diminish in mean width, in the order named. For the portion representing the first 400 minutes, however, (or liberation of 50 per cent. of the iodine), the third space is wider than the second. If experimental errors were excluded, this must imply that during a portion of the change, the fourth equivalent of salt has a greater influence than the third, which seems improbable.

Fig. II, constructed on the same plan as I., shows the effect of increasing the potassium iodide; and in general character, the curves closely resemble those already described. A is identical in the first two figures (as already mentioned) while

B and C agree pretty closely; but the space between C and D is by far the narrowest in the second figure, as would be expected. To assume that the speed is doubled by each doubling of the quantity of potassium iodide would be quite a rough approximation, as will be seen by comparing the abscissas on curves A, B, and D, for 10 per cent., 20 per cent., etc.

Fig. III, exhibiting the acceleration produced by increasing the acid, is in striking contrast to the first two figures; the spaces between curves are broader; the speed is not even approximately proportional to the quantity of acid, but it increases in a much greater ratio; in fact, the time required to reach a given stage with three equivalents of acid is about twice the time required with four equivalents. The curves do not become approximately parallel for an extended portion of their length, as in the former figures, though possibly they would do so if drawn farther.

The area bounded by curves B and C, and that bounded by C and D, become first wider, then narrower (making a "pocket" in each) if we measure the width vertically, but not so if we measure horizontally.

A similar feature may be seen in the first figure, between curves A and B, and in both first and second between C and D. The interpretation is clearly this: with increase of chemicals, the speed is increased in the early stages; and, after a certain interval of time, the solution has become so far exhausted, that the further action proceeds more slowly than after the same interval with less of the active substance at the beginning. Any algebraic formula which may be ultimately adopted must be capable of expressing these facts by introducing the appropriate constants.

Fig. IV, representing increase in both potassium iodide and hydrochloric acid, is such as we might expect from the study of Figs. II and III. The reaction proceeds so rapidly, that detailed features are not so apparent as they might become by increasing the scale for abscissas. However, we find the times are more then twice as great for a given stage on the curve B (three equivalents of two substances) as for the corresponding stage on curve C (four equivalents); here the acid has its great effect, as before, with some aid from the iodide.

Fig. V shows the effect of dilution. Three experiments were made, beginning with decinormal, one-fifth normal, and two-fifths normal concentrations, in the sense already explained. The curves closely resemble those in Figs. I and II, except that the intermediate spaces are much broader in this case. With each doubling of concentraction, the time required to reach a given stage is reduced to a small fraction of the former value. In a "trimolecular" reaction, this fraction should be one-eighth, but it is somewhat larger. Again we are tempted to inquire whether these curves would become parallel to the axis of abscissas if produced; corresponding to a limit in each case, with reversible or incomplete reaction.

Prendlebury and Seward[1] have shown that the reaction between potassium chlorate and hydrochloric acid, (in the absence of iodides) is completely reversed by sun-light, the yellow color disappearing, and the mixture then having no effect upon potassium iodide; but I have found no published data to indicate reversibility in the decomposition of hydriodic acid, except in gaseous condition, as investigated by Lemoine,[2] and by Bodenstein and V. Meyer.[3]

Fig. VI indicates the acceleration produced by decinormal organic acids, added to fifth-normal mixture. Curve A here is the same as curve B in Fig. V. The curves in this group are related to each other very much like those on the first two figures, becoming nearly parallel in the latter part of the course.

II.—*Can We Apply Guldberg and Waage's Law?*

According to the law of mass-action, $\frac{dx}{dt} = f\ (u, v, w\ .\ .)$ where $\frac{dx}{dt}$ expresses the rate of change, and u, v, w, . . . are the quantities of the several active bodies present. If

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[1] Proc. Roy. Soc., **45**, 399 (1889).

[2] Compt. rend., **80**, 792 (1875); **85**, 144 (1877); Ann. chim. phys., [5] **12**, 145 (1877).

[3] Ber. d. chem. Ges., **26**, 1146, 2603 (1893).

there are two or more simultaneous reactions, the principle of coexistence must be applied.

We may now analyze the possibilities involved in the reaction $KClO_3 + 6HCl + 6KI = 7KCl + 3H_2O + 3I_2$.

The work of Pendlebury and Seward indicates that there are at least three stages, thus: (1) Metathesis between the acid and the salts; (2) Reaction between chloric and hydrochloric acids, yielding one or more active oxidizing agents; (3) Liberation of iodine by these oxidizers.

First: We may suppose potassium chloride to be formed instantly by decomposition of a certain portion of the salts, in accordance with the "avidity" of the three acids; unless, indeed, the compounds are completely separated into ions by electrolytic dissociation. This stage is believed to occupy no appreciable time.

Second: The reaction between chloric and hydrochloric acids (or their ions) may follow a variety of possible directions; yielding free chlorine or any of the lower oxides or acids. If chlorous or hypochlorous acid is formed, this may suffer a less complete electrolytic dissociation than chlorates, thus adding to the difficulty of a complete mathematical analysis. This stage seems to consume nearly the whole tlme required.

Third: Whatever may actually result from the second stage, the material seems to exert its full oxidizing power upon an iodide so quickly that the time would not be appreciable in Schlundt's experiments, where a considerable quantity of unused iodide was nearly always present.

The hindering influence of free iodine is also an important factor; perhaps acting by its union with hydriodic acid to limit the influence of the latter; perhaps reacting with the hydrogen to regenerate hydriodic acid. The accelerating effect of all free acid must be taken in account apart from its rôle as "active substances;" and the influence of neutral salts may also be too great to be neglected. A satisfactory application of the law of mass has, therefore, not yet been made to this reaction; but an historical study may lead to a clearer insight into the various aspects of the problem and the best modes for future attacks.

III.—*Earlier Dynamic Investigations of Oxy-Acids.*

The law of mass-action has been very successfully applied to the speed of many reactions, as inversion of sugar, solution of metals and marble in acids, etherification and saponification. The numerical values expressing constants of speed under given conditions are well worth tabulating for use in further generalizations. In many cases secondary influences have hidden the real constants,[1] so that there is a wide field for judicious recalculations, and many quantitative observations have not yet been subjected to mathematical analysis.

In the mathematical discussion of oxidation processes (as likewise in nitrification) many difficulties have been encountered. Valuable data have been obtained, and some of these have been expressed in empirical formulas; but the several attempts to write a differential equation for speed, to integrate, and to apply the resulting rational equation to the course of an oxidation-reaction, have often ended in disappointment.

Harcourt and Esson[2] studied the mutual action of permanganic and oxalic acids, where the reaction begins with remarkable slowness—a phenomenon made familiar in titration. To account for the observed facts, Esson assumed the co-existence of two or more reactions; first, the formation of manganese dioxide (though not manifest to the senses by its usual color and insolubility), and then its further reduction. It would be more logical under modern views, to speak of tetravalent manganese ions. This research, though published far in advance of any general discussion of mass-action, well deserves the study of those who may attempt to learn the mechanism of oxidation by chloric acid.

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[1] In view of the variations observed in so-called constants of speed, Arrhenius prefers tne term "specific speed of reaction," to denote the rate of change divided by the product of the concentrations in active substance: Ztschr. phys. Chem., **1**, 111, (1887).

[2] Phil. Trans., **156**, 193, 216, (1866). For the action of hydrogen peroxide, see Phil. Trans. **157**, 117, (1866). See also Proc. Roy. Soc., **14**, 470, (1865); **15**, 262, (1867); Chem. Soc. Jour. **20**, 54. (1867). Those who have not access to the original, will find the mathematical theory clearly set forth in Urech's "Itinerarium durch die theoretische Entwickelungsgeschichte der Lehre von der chemischen Reactionsgeschwindigkeit," pp. 37-43, (1885). See also the following: Kessler: on induced conveying of oxygen: Ann. der Phys. Pogg., **119**, 218, (1863); Roessler's observation in Dingl. pol. Journ., **242**, 278, (1881), that presence of copper sulphate accelerates the oxidation of sulphurous acid by the air—a similar fact is the basis of Deacon's process for making chlorine—and L. Meyer: on oxygen conveyers: Ber. d. chem. Ges., **20**, 3058, (1887).

Hood[1] investigated the oxidation of ferrous sulphate by potassium chlorate, in equivalent proportions, and the specific speed of reaction proved to be nearly constant. A decrease in its value when 80 per cent. of the iron had been oxidized would, perhaps, be explained by hydrolytic dissociation, a principle recently applied by Kortright[2] to Kahlenberg's[3] work on the oxidizing power of ferric chloride. Thus many of the older data may require systematic examination, in view of recent progress, before they can be regarded as trustworthy.

Landolt,[4] (in conjunction with Antrick), determined the time required for complete oxidation of sulphur dioxide by excess of iodic acid, the end of this reaction being indicated by free iodine with starch. He deduced the formula (for temperature of 20°)

$$t = \frac{524 \cdot 35}{C_s^{0.904} C_j^{1.642}} \text{ seconds };$$

where $t =$ the time for complete change, $C_s =$ the initial concentration in sulphur dioxide, and $C_j =$ the initial concentration in iodic acid; the concentration being expressed in gram-molecules per cubic meter.

The chemical changes here involved may be expressed as follows:

(a) $3SO_2 + HIO_3 = 3SO_3 + HI$;[5] (b) $5HI + HIO_3 = 3H_2O + 3I_2$; (c) $I_2 + SO_2 + H_2O = SO_3 + 2HI$.

Iodic acid would thus be expended in the oxidation of both sulphur dioxide and hydriodic acid; but in the latter case, the free iodine is immediately siezed by the sulphurous acid. The starch turns blue, therefore, only when iodine is liberated according to equation (b) more rapidly than it can be taken up in accordance with equation (c)—that is, when the sulphur dioxide has practically disappeared. Meanwhile an equivalent amount of iodic acid has likewise disappeared, and the concentration for this body is reduced to $C_j - \frac{1}{3}C_s$. A rational

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[1] Phil. Mag., [5] **6**, 371, (1878); **8**, 181, (1879); **13**, 419, (1882).

[2] This Journal, **17**, 116, (1895).

[3] J. Am. Chem. Soc., **16**, 314, (1894).

[4] Berl. Akad. Ber., 1885, 249; 1886, 193, 1007; 1887, 21; Ber. d. chem. Ges., **19**, 1307, (1886); **20**, 745, (1887).

[5] Of course these equations may require further analysis to present the whole truth: *e. g.*, to express bimolecular reactions, Landolt suggests the possible scheme: $SO_2 + HIO_3 = SO_3 + HIO_2$; $SO_2 + HIO_2 = SO_3 + HIO$; $SO_2 + HIO = SO_3 + HI$.

formula for the course of the reaction must distinguish the two reduction-processes (which take place simultaneously), and combine the results; but this has not yet been accomplished. If the speed of a reaction at any moment is proportional to the quantity of each active substance present, the relative speed in two cases may be determined by comparing the periods of time required to reach a given stage. In this case, however, increase in the quantity of sulphur dioxide not only increases the mass of active substance, but also increases the quantity of iodic acid to be reduced in the measured period of time. Moreover, with every change in the ratio $C_s : C_j$, there will be a change in the ratio of initial and mean concentrations in iodic acid. Valuable as Landolt's formula is, affording a concise generalization of many careful experiments, we cannot draw the inference that the speed of the whole reaction is proportional to the exponential factors of the denominator. Landolt continued this study with regard to the influence of temperature (from 5° to 39.5°) and to the acceleration caused by various acids, which proved to be in the same order as the coefficients of affinity previously noted by Ostwald.

Selmons[1] used periodic acid to oxidize sulphur dioxide, adopting Landolt's general formula, and deducing the exponent 1.608 for this oxidizer.

Ostwald[2] greatly extended Landolt's work on acceleration, using the reaction between bromic and hydriodic acids. In attempting to apply the usual equation for bimolecular reactions,

$$\frac{dx}{dt} = C(A-x)^2,$$

it was found that the values calculated for C rapidly diminished in each series; this is due at least in part to the influence of free iodine. Direct experiments showed that iodine retards the reaction, but not in proportion to the quantity present; a small quantity having a certain effect, a larger quantity has somewhat *less* than the proportional effect.[3] The

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[1] Chem. Centrbl., 1887, 502.

[2] Ztschr. phys. Chem., **2**, 127, (1888).

[4] Jakovkin has studied the reversible reaction, $KI_3 \rightleftarrows KI + I_2$, and his work may afford suggestions for relation between the "free" iodine and retardation: *Ibid.*, **13**, 595, (1894); abstract in this JOURNAL, **16**, 554.

most striking result is the correspondence between acceleration-factors and electrical conductivities, in accordance with Ostwald's theory of affinity. Similar values were obtained for acceleration in the oxidation of hydriodic acid by chromic acid; and the general theorem is stated, "*all oxidation and reduction processes are accelerated by the presence of free acids, in proportion to their coefficients of affinity.*"[1] The general doctrine of affinity thus opens up wide possibilities for valuable generalizations regarding the disturbing effect of inactive bodies, upon the course of chemical reactions.

Meyerhoffer[2] continued the work undertaken by Ostwald, and recalculated some of his data, in search for numerical constants of speed. In his experiments, after the withdrawal of each sample of fluid for titration, the flask was filled with glass beads (previously warmed) to avoid error from the escape of iodine vapor into the space which would otherwise have been left vacant. His mathematical treatment also deserves notice, in regard to the influence of the iodine, and the "order" of the reaction. Desiring to express the hypothesis that the retarding action of the iodine is proportional to the mass, he used the equation

$$\frac{dx}{dt} = C\,\frac{(A-x)^2}{x},$$

implying that with any fixed concentration in the reacting bodies, the speed would vary inversely as the mass of the iodine. If it were desired to assume that the change in velocity due to the presence of iodine, acid, etc., is proportional to its mass, this should be expressed by the factor $C+bx$; as for example,

$$\frac{dx}{dt}=(C+bx)\;(A-x)^2,$$

where b would have a negative value for any retarding agent produced by the reaction; but Ostwald had already shown that the influence of iodine does not follow this law. The use of x in the denominator, however, implies that with *very little* iodine the speed would be enormous; and it is not surprising that the values of C, as calculated from Meyerhoffer's formula, are abnormally

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[1] *Loc. cit.*, p. 127.

[2] Ztschr. phys. Chem., **2**, 585, (1888).

small at the beginning of many of the series of observations. The discrepancy would have been more pronounced, if the first portion of the change had not been eliminated from the computation.[1]

If the equation $HBrO_3 + 6HI = HBr + 3H_2O + 6I$, implies that no action takes place except by the simultaneous concurrence of seven molecules, the chances for such opportunity would vary as the seventh power of the concentration. We should then assume $\frac{dx}{dt} = C\ (A - x)^7$. But authorities are not agreed in regard to "molecular" reactions. Thus van't Hoff[2] and Nernst[3] emphasize the *number of reacting molecules*, but Ostwald,[4] *the alteration in the quantities of reacting bodies.* Under the former view, the chemical equation would be of the seventh order; under the latter (since only two substances are diminishing in quantity) it is of the second order. To cover the whole ground, Meyerhoffer applied the formula $\frac{dx}{dt} = C\ (A - x)_n$, giving n successive values from 3 to 7, with no satisfactory result.

From Landolt's formula, it seems probable that equivalent quantities of the two reagents, in a similar case, but in the *absence of free iodine*, would nearly accord with the equation

$$\frac{dx}{dt} = C\ (A - x)^{2.546,}$$

where the fractional exponent does not depend upon the "order" of any one equation, but results from several reactions, not yet distinguished.

Burchard[5] oxidized hydriodic acid with iodic, bromic and chloric acids, and found enormous differences in the speeds; iodic acid oxidizing most quickly and chloric acid most slowly. From his data for the reaction $5HI + HIO_3 = 3H_2O + 3I_2$.

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[1] The hindering influence of free iodine has also been noted in the oxidation of hydriodic acid by the acids of selenium; the iodine is therefore removed from the field of action by distillation, in Gooch and Reynolds' modification of Muthmann and Schäfer's method for estimation of selenious acid.—See Ber. d. chem. Ges., **26**, 1008 (1893); Am. J. Sci. [3] **50**, 254 (1895).

[2] Études de dynamique chimique, p. 8.

[3] Theoretical Chemistry (Palmer's translation) p. 361.

[4] Lehrbuch der alg. Chem., 1st. Ed., II., 626, 633, 805.

[5] Ztschr. phys. Chem., **2**, 796, (1888).

$+ 3I_2$, without excess of either substance, it can be shown that doubling the concentration increases the speed about 20 times; that is, the rate varies in accordance with more than 4th power and less than 5th power of the concentration.

In case of excess of either body, the curves for $(5 + n)HI + HIO_3$ and for $5HI + (1 + n) HIO_3$, lie near together, the latter rising more rapidly at the outset, then becoming flatter and intersecting the former. If the increased speed were due merely to the increased number of collisions, doubling the one reagent should have the same effect as doubling the other; while doubling the hydriodic acid has nearly the same effect as a six-fold increase in iodic acid. In an ordinary reaction of the second order, doubling the concentration will quadruple the speed. The great acceleration noted above from doubling the concentration seems to be largely due to the accelerating power of free acids in general, as shown in Ostwald's theorem, already quoted. In several cases, the data show almost a three-fold increase of speed on adding another acid equivalent to one-third of that taking part in the reaction. For the mixture $5HI + HIO_3 + nHNO_3$, by simple interpolation of published data, the following values appear, for the separation of 11.13 mg. iodine:

n	time in minutes	relative speed	acceleration	$\frac{acceleration}{n}$
0	30.	1.00		
2	10.22	2.94	1.94	.97
5	5.96	5.03	4.03	.81
10	2.93	10.24	9.24	.92

A careful study of all available data may lead to a satisfactory formula for acceleration by acids; and this should naturally precede the development of satisfactory formulas for the oxidation processes.

Following Landolt's hint, Burchard also uses the equation

$$t = \frac{K}{(C_{HIO_3} \cdot C_{HI})^z},$$

where $t =$ the time required to reach any given stage of the reaction. The mean value of z is 2.28, and K varies with the percentage of iodine liberated.

The problem of the oxidation of hydriodic acid by bromic or chloric acid is more complicated than where iodic acid is used, since the number of reaction-products is greater.

Prendlebury and Seward[1] liberated iodine by the action of hydrochloric acid, potassium chlorate, and potassium iodide, in presence of starch; one drop of sodium thiosulphate was added to the clear solution, and the time was noted when the blue color appeared, showing that the reaction had proceeded through a very small measurable range. Formulas were deduced, showing speed as a function of mass, which may be expressed as follows: for the quantity of chloric acid (u), $\frac{dx}{dt}$ varies as $bu + cu^2$; for the quantity of hydrochloric acid (v) (within certain limits), $\frac{dx}{dt}$ varies as $a^1 + b^1v + c^1v$; and for the quantity of neutral salt (s) as accelerator, $\frac{dx}{dt}$ varies as $a'' + b''s$; while potassium iodide behaves as an indifferent salt, provided only it is present in the extremely small quantity needed to show the end reaction promptly. The first two formulas show that increase of speed is more rapid than increase in active substance; and the theory is expressed that both acids have an accelerating function, apart from the influence of their mass in the ordinary sense.[2]

Magnanini has studied the oxidation of hydriodic acid by bromic acid[3] and by peroxide of hydrogen,[4] with special regard to the acceleration resulting from the addition of various quantities of acid. The relation between mass of acid and resulting acceleration is very different in the two reactions; but nowhere did acceleration prove to be proportional to the mass of the accelerator.

Kastle's[5] work on decomposition of monocloracetates must

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[1] Proc. Roy. Soc., **45**, 124, 396, (1888-9).

[2] The authors state (*loc. cit.*, p. 404) that their solution contained 30×51.5 millionth-gram-molecules of potassium chlorate per cc., while the recorded data (30 grams $KClO_3$ made up to 792 cc.) would indicate only one-fifth of this amount for the experiment under consideration. The factor 51.5 occurs repeatedly in the paper, with a somewhat peculiar notation; and I have been unable as yet to learn by correspondence the precise facts which were intended to go on record. While, therefore, there is much of originality to admire in this research, I have been unable to interpret and use the results as I had hoped.

[3] Gazz. chim. ital., **20**, 377, (1890).

[4] *Ibid.*, **21**, 476, (1891).

[5] This JOURNAL, **14**, 586 (1892); **15**, 471: (1893).

also be mentioned. Although water is one of the "active bodies," increasing its quantity greatly diminished the rate of decomposition. The explanation seems to be found in the very incomplete electrolytic dissociation for the ion of feeble affinity. This should be kept in mind in discussing the behavior of concentrated solutions.

Professor A. A. Noyes informs me that experiments have recently been made under his direction upon the mutual action of potassium iodide and potassium bromate in the presence of much acid. Under these conditions, the reaction seems to be of the second order, with speed proportional to the mass of each of the salts used. Details have been forwarded for publication in the *Zeitschrift für physikalische Chemie.*

IV. *Numerical Computations, Based on the use of Potassium Chlorate.*

Mr. Schlundt's experiments were conducted expressly to allow a comparison of curves, with varying mass of one or more active substances. To find the ratio of speed in comparable cases (as Landolt has shown) we have only to determine the times required to reach a given stage of the reaction; but this necessitates interpolation, either by graphic or analytic method. The latter was chosen, as follows: from the coordinates of the first eleven points in curve A, the equation

$$t = 3.116x + 0.228x^2$$

was deduced, by the method of least squares; where t expresses the number of minutes required to liberate x per cent. of iodine; or,

$$t = 7.79f + 1.425f^2,$$

where $f =$ the number of cc. of fluid required in titration; for $x = 2.5f$. Then for each observation represented in the other curves (for liberation of less than 34 per cent. of iodine), the time noted in the experiment is divided into the corresponding value of t on curve A; the quotient shows the mean relative speed in the two cases.

In the following table are given the observed values of t and f (from the first series of determinations with the values calculated for each from the formula. The differences show the aggregate of all error or discrepancy; assuming in the first place that the whole error is in the time-measurement, then in the titration.

t			*f*		
Obs.	Cal.	Dif.	Obs.	Cal.	Dif.
15	14.3	.7	1.45	1.51	−.06
35	37.8	−2.8	3.1	2.93	.17
35	36.2	−1.2	3.0	2.93	.07
60	59.9	.1	4.3	4.31	−.01
70	66.0	4.0	4.6	4.79	−.19
90	98.0	−8.0	6.0	5.67	.33
110	113.5	−3.5	6.6	6.47	.17
150	149.0	1.0	7.85	7.88	−.03
210	199.1	10.9	9.40	9.71	−.31
300	300.8	−0.8	12.05	12.03	.02
300	309.3	−9.3	12.25	12.03	.22
360	367.2	−7.2	13.55	13.40	.15
440	415.0	25.0	14.55	15.05	−.50
520	465.7	54.3	15.55	16.55	−1.00

The equation thus closely represents curve A, from the origin to the liberation of 34 per cent. of iodine, or about 360 minutes. Above this point, the observed values of *t* are greater than expressed by the equation. So far as it holds, it may be utilized to find the speed of the reaction, if desired, by differentiation, thus:

$$\frac{dx}{dt} = \frac{1}{3.116 + 0.456\,x}.$$

More conveniently, we may calculate $\frac{dt}{dx} = 3.116 + 0.456x$, as in the following table, where the differential coefficient expresses time in minutes, divided by change in percentage of iodine liberated. Under *C* is given the concentration of potassium iodide and hydriodic acid, in gram-molecules per liter, the concentration in potassium chlorate being one-sixth as great.

x	C	$\frac{dt}{dx}$
0	0.100	3.116
5	0.095	5.396
10	0.090	7.676
15	0.085	9.956
20	0.080	12.236
25	0.075	14.516
30	0.070	16.796

Remembering that $\frac{dt}{dx}$ is the reciprocal of the speed, it will be seen, for example, that when the concentration is reduced to 80 per cent., (20 per cent. of the iodine being now liberated), the speed is reduced to about one-fourth ; whereas in a simple bimolecular reaction, free from disturbing causes, it would be reduced only to 64 per cent. ; or, in trimolecular reaction, to 51.2 per cent. The differential equation, of course, is empirical, like that from which it is derived ; but this well represents the first part of the reaction as observed. At later stages, the speed is much less than would be implied by the equation.

The several curves of figure V. show the course of the reaction, beginning with decinormal, fifth-normal and two-fifths-normal solutions of the iodide and acid, with the equivalent quantity of chlorate. Treating these by the method already described, we obtain the following results, where subscripts indicate the several curves :

x_B	t_B	t_A	$\frac{t_A}{t_B}$
11.1	10	62.69	6.269
16.8	20	116.15	5.807
29.9	50	296.5	5.930
		Mean . . .	6.002

x_C	t_C	t_A	$\frac{t_A}{t_C}$
30.3	10	303.8	30.38

$\frac{t_B}{t_C}$ is equal to 5.06, as we find by dividing $\frac{t_A}{t_B}$ by the mean value for $\frac{t_A}{t_B}$. Thus doubling the concentration increased the speed six-fold ; doubling the concentration again increased the speed five times more. Applying the exponential formula used by Landolt, time $= \frac{K}{(C_1 \,.\, C_2)^z}$, and remember that when C_1 and C_2 maintain a constant ratio, this is equivalent to

$$\text{time} = \frac{K}{C^{2z}}$$

we find,

for $KClO_3 + 6HCl + 6KI$, $z = 1.29$ and 1.17 ;[1]

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[1] To obtain these numbers, note that $\frac{\log 6.002}{\log 2} = 2.58$, and $\frac{\log 5.06}{\log 2} = 2.34$; the quotients being observed values of $2z$.

for $SO_2 + HIO_3$, $z = 1.273$ (Landolt);
for $4SO_2 + HIO_4$, $z = 1.256$ (Selmons);
for $5HI + HIO_3$, $z = 2.28$ (Burchard);

that is, any change in concentration affects the rate of chemical action enormously in the fourth case, as compared with the first three; while these differ comparatively little.

We next seek to learn more definitely the result of *excess* of either ingredient; but must clearly distinguish between excess as a difference and excess as a quotient. Let A, B, C . . represent two or more bodies which diminish in accordance with a single chemical equation, while a, b, c . . represent the relative quantities implied in the equation. Beginning with $aA + bB + \ldots$, when x per cent. of A has disappeared, the same proportion of each of the others has likwise disappeared, and $(1-.01x)aA + (1-.01x)bB + \ldots$ remains, without excess of either constituent. But if we begin with $aA + nbB + \ldots$ the substances are reduced to $(1-.01x)aA + (n-.01x)bB + \ldots$ The excess, estimated (by subtraction) in actual mass, begins with $(n-1)bB$, and continues thus unchanged; but if we define excess as the ratio of the amount of B actually present to the amount equivalent to A, we begin with n-fold excess, increasing to the ratio $\frac{(n-.01x)}{(1-.01x)}$. For example, if we begin with $2KClO_3 + 6HCl + 6KI$, the actual excess of chlorate at the beginning is $KClO_3$ expressed in any convenient unit. If the reaction proceeds according to a single chemical equation, as generally assumed, this actual excess in constant. But when 32.5 per cent. of the iodide has been decomposed (as expressed on curve B, Fig. I.) we have $(2-.325)$ $KClO_3$ with $(1-.325)$ $(6HCl + 6KI)$ and the relative excess has increased from 2 to $\frac{2-.325}{1-.325} = 2.48$. With constant absolute, but varying relative excess, as thus defined, this stage was reached in 170 minutes; see the 6th line in the following table. By the equation for this part of curve A, 342.1 minutes would have been required to reach the same stage without excess; hence the relative speed is $\frac{342.1}{170} = 2.012$; and we know (unless there are coexistent reactions) that this acceleration is due to an excess of chlorate varying from 2 to 2.48, while the concentration in other active substances (including iodine and other products) was exactly the same at any given stage of the two experiments.

All the determinations appearing in the first part of this paper are thus computed for the following table, so far as the interpolation-formula for curve A is available in estimating the influence of excess. The observed time is here repeated under t, interpolated time under t_A, and the relative speed under $\frac{t_A}{t}$. The extreme values of relative excess are also recorded for each portion of the table.

Excess of Chlorate : Fig. I.

t	t_A	$\frac{t_A}{t}$	Relative excess.
10	13.12	1.312	2 to 2.48
20	33.62	1.681	
30	54.24	1.741	
60	114.79	1.913	
100	216.8	2.168	
170	342.1	2.012	
15	32.98	2.199	3 to 3.93
30	74.57	2.486	
55	153.52	2.791	
85	256.2	3.014	
120	329.2	2.744	
10	33.0	3.30	4 to 5.05
20	74.6	3.73	
40	161.3	4.03	
60	242.7	4.04	
85	364.8	4.54	

Excess of Iodide : Fig. II.

t	t_A	$\frac{t_A}{t}$	Relative excess.
15	26.9	1.79	2 to 2.40
30	68.1	2.27	
50	106.9	2.14	
85	207.9	2.44	
110	276.0	2.51	

t	t_A	$\frac{t_A}{t}$	Relative excess.
10	18.6	1.86	3 to 3.76
20	40.4	2.02	
40	95.6	2.39	
65	161.3	2.48	
100	260.1	2.60	
10	20.0	2.00	4 to 5.21
25	66.0	2.64	
40	116.2	2.90	
60	202.6	3.38	
85	278.0	3.27	

Excess of Hydrochloric Acid: Fig. III.

t	t_A	$\frac{t_A}{t}$	Relative excess.
17	59.9	3.52	2 to 2.47
30	131.4	4.38	
50	237.0	4.74	
70	328.8	4.70	
10	66.0	6.60	3 to 3.54
20	187.2	9.36	

Excess of Hydrochloric Acid and Iodide: Fig. IV.

t	t_A	$\frac{t_A}{t}$	Relative excess.
10	49.3	4.93	2 to 2.40
35	272.0	7.77	
5	79.0	15.8	3 to 3.68
10	244.0	22.4	
5	250.3	50.1	4 to 5.11

This table (which covers the first third of the reaction only) leads to the following conclusions:

I.—The speed is not proportional to the mass; it increases in a less ratio than increase of potassium chlorate or iodide, added in excess; but in far greater ratio than excess of acid.

II.—In the early stages of the reaction, a given excess has less accelerating effect than at later stages.

III.—A two-fold excess of iodide had greater accelerating value than a two-fold excess of chlorate; with three-fold and greater excess of these salts, the reverse is true. A rational equation to express the mass action, must, therefore, take a form which shall distinguish this behavior of the two salts; the difference has already been noted in a qualitative way, in our preliminary inspection of the curves.

Further conclusions could be reached by applying similar methods to other experimental data. If the value of science depends upon accurate generalizations, the results of patient experimental toil are often run through a stamp-mill to get out half the gold, while the rest is lost in the tailings. Chemistry is growing more closely related to mathematical physics; and a division of labor between experimenter and computer is becoming more needful.

To utilize the remainder of curve A, the interpolation-equation must have three constants, as

$$t = A + Bx + Cx^2,$$

since we may not assume that the curve to be thus expressed would pass through the origin. But I need not do more at present, than state a few conclusions reached by graphic interpolation of the several curves.

When a considerable excess of salt is already present, the accelerating effect of further excess is approximately uniform through the course of the reaction; and perhaps (as a rough approximation) is proportional to the mass. Thus in case of potassium chlorate, curve C represents a speed a little less than 1.4 times that of curve B; while further increase (in the ratio of nearly 1.5) is expressed by curve D. Of course the mean concentration here is not in the ratios 2 : 3 : 4; the mean values for curves C and D may stand in a wider ratio than for B and C. With potassium iodide, a very different constant must be assumed; for in curve D the speed is pretty uniformly 1.18 times the speed for corresponding stages on curve C.

In view of the work thus far accomplished, the following steps might be suggested for further inquiry into the course of similar oxidation-processes. Begin with the reaction between iodic and hydriodic acids, where the products are fewest. A method like that of Prendlebury and Seward,—with short intervals of time,—would indicate the speed under various conditions, in absence of free iodine. Make systematic study of the acceleration produced by free non-active acids (with due regard to the affinity-constants) and devise a rational formula, showing how far the speed of each reagent is affected by its mass in the ordinary sense, and how far also by its presence as an accelerator. Find the law for influence of iodine. Having thus secured the factors for a general differential equation, combine them, integrate, and apply the result to the series of observations already published for the course of the reaction. Similar investigations of reactions between the corresponding bromine and chlorine compounds would be of interest. Evidence may be discovered of intermediate products, implying coexisting reactions, each with its own specific coefficient of speed;[1] especially in case of periodic acid, etc. Reactions between compounds of different haloids, as hydriodic and bromic acids, may easily be traced out, if the simpler problems are solved first. The influence of salts in general upon the rate of change should likewise be studied, if salts take part in the reactions chosen. The action of light may reverse the sense of a reaction (as already mentioned, in the case of chloric and hydrochloric acids); care must, therefore, be taken to eliminate any actinic disturbance. Each step should also be studied in the light of recent thermodynamic investigations, the doctrine of affinity, and electrolytic dissociation. Finally, if a practical outcome is desired, we know that theories of speed in oxidation have already been applied to chemical industries, as the manufacture of sulphuric acid; a thousand more applications are possible. But look on that beautiful photograph with its exquisite harmony of light and shade; consider the complex reduction processes required in making the negative, where both the actual and the relative speed must be controlled within the limits required by art. Shall this nice adjustment of conditions be always left to the rule of thumb, or may we hope at some time to find a scientific basis for the development of photographic images, bringing the scale of shades under perfect control? The use of bromide at this point is a most interesting subject, both in practical and

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[1] The several reduction-products of nitric acid have received quantitative study from Higley. See this JOURNAL, **17**, 18, (1895).

in scientific relations. Is it too much to hope that a minute study of the conditions shall ultimately give us the means of avoiding flatness, while yet securing full exposure? May it not even be possible, by proper application of the right means, to heighten the contrasts among dark shades, and thus to obtain a brilliant copy from a flat photograph, from an old and faded painting, or from ancient manuscripts and inscriptions? A further development of the chemical kinetics of oxidation until it shall include the successful quantitative investigation of the speed of reduction of silver salts and the resulting opacity, would be a long step towards the practical solution of this problem.

I should esteem it a favor, if investigators working on time-relations of oxidation and reduction phenomena, would kindly notify me.

HOWARD UNIVERSITY, WASHINGTON, D. C.,
SEPTEMBER, 1895.

Contributions from the Chemical Laboratory of Case School of Applied Science.

XX.—ON THE COMPOSITION OF THE OHIO AND CANADIAN SULPHUR PETROLEUMS.[1]

BY CHARLES F. MABERY.

[*Concluded from page 748, Vol. 17.*]

AROMATIC HYDROCARBONS.

Series C_nH_{2n-6}.

So far as I am aware no attempts have hitherto been made to separate the aromatic hydrocarbons from the Ohio sulphur oil. In American petroleum Pelouze and Cahours found, as already mentioned, no appreciable quantities, but Schorlemmer recognized the presence of benzol and toluol. Beilstein and Kurbatoff were the first to discover the aromatic hydrocarbons in the oil from Baku, and hexahydroisoxylol in Pennsylvania petroleum.

Benzol.

After the sixth distillation of the products from the original quantity of crude oil, 25 grams collected at 77–79°, 35 grams

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[1] Presented to the American Academy of Arts and Sciences, October, 1894. Aid in the work described in this paper was given by the Academy from the C. M. Warren Fund for Chemical Research.

at 79–81°, and 20 grams at 81–83°. In each of these fractions the quantity of benzol was determined by heating carefully for some time a weighed quantity of the fraction with a mixture of nitric and sulphuric acids, distilling off the portion not affected by the acid mixture, and weighing it and the residual nitrobenzol. The fraction 77–79° gave by this method 3 per cent. of benzol; the fraction 79–81°, 15 per cent.; and the fraction 81–83°, 5.8 per cent. The fraction 75–76° and 85–86°, when treated in the same manner, left scarcely any residual product after distillation, and after reduction with tin and hydrochloric acid not a trace of color was visible in applying the exceedingly delicate furfurol reaction for aniline. Calculating from these numbers, the quantity of benzol in the 41.5 kilos of crude oil taken, it amounts to 7.16 grams or 0.017 per cent., which represents approximately the quantity of benzol in the crude oil.

Toluol.

The fractions collected between 107° and 113°, after the sixth distillation under a Hempel column, were examined for toluol by treating a weighed quantity of the oil with nitric and sulphuric acids, keeping the solution cold. After some time crystals of dinitrotoluol separated, and when the hydrocarbons not affected by the acid were removed by distillation, there remained a heavy oil which consisted of the liquid orthonitrotoluol and crystalline dinitrotoluol. The latter soon solidified, and after crystallization from alcohol it was identified by its melting-point, 71°. The loss in weight by the removal of toluol in the fraction 107–109° amounted to 1.14 per cent., in the fraction 109–111° to 13.07 per cent., and in the fraction 111–113° to 2.8 per cent. The total weight of the first fraction was 50 grams, of the second 80 grams, and of the third 65 grams. These fractions, therefore, contained altogether 12.86 grams, which corresponds to 0.03 per cent. of toluol in the 41.5 kilos of crude oil taken. As in the case of benzol, evidently the percentage of toluol is expressed only approximately by these results. After longer distillation the fraction 114–115° was treated in a similar manner, but after treatment with nitric and sulphuric acids, and with tin and hydrochloric acid, the product which remained in considerable quantity after distillation did not dissolve in hydrochloric acid, and it gave no trace of color when heated with ferric chloride or with mercuric chloride. The insolubility in acids excludes in this fraction any appreciable quantity of hexahydroisoxylol which is contained in the higher portions. The oily product of the nitration must therefore be derived from another series, perhaps from an unsaturated hydrocarbon C_nH_{2n} ; it will receive further attention.

Xylols.

In the first allusion to the presence of the aromatic hydrocarbons in petroleum, by De La Rue and Müller,[1] who found in the Rangoon oil benzol, toluol, metaxylol, and cumol, there is no evidence that the isomeric forms of xylol were discovered in that petroleum. Except paraxylol, which Pawlewski found in Galician petroleum and Engler in Pennsylvania petroleum, and metaxylol, which is generally found, it does not appear that the isomeric xylols have elsewhere been recognized in petroleum.

Between 136° and 142° in our distillates, at intervals of 1°, we collected 205 grams, of which the greater portion distilled at 137–138°, 139–140°, and 141–143°. After prolonged distillation these fractions collected in increased quantities at these points ; they were readily acted upon by nitric acid, forming nitro compounds or oxidation products, according to the form of the reaction.

To prove the presence of paraxylol in fraction 137–138°, a portion was treated with a mixture of nitric and sulphuric acids, at first in the cold, then with the aid of gentle heat. Upon distillation of the hydrocarbon not affected, there remained a brown oil that deposited a crystalline product on standing. After crystallization from alcohol, this substance appeared in the form of glistening white needles which melted at 139–140°. It was therefore trinitroparaxylol, melting-point 139–140°.[2] By treating carefully another portion of the same fraction in the cold with fuming nitric acid, long yellow needles sparingly soluble in alcohol were obtained,

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[1] Proc. Roy. Soc,, 1856, p. 221.

[2] Nölting and Geissman, Ber. d. chem. Ges., 19, 145.

melting at 145°, corresponding to dinitroparaxylol, melting-point 147–148°.[1] For further confirmation, another portion of the fraction 137–138° was submitted to oxidation with chromic acid, and the solution extracted with a considerable quantity of ether. Evaporation of the ether left a solid residue in the form of minute prisms insoluble in water, but readily soluble in sodic hydrate. This substance sublimed without melting, and in general its properties corresponded to those of terephthalic acid. After heating for thirty hours a quantity of the same fraction with dilute nitric acid and distilling off the hydrocarbon not affected, there remained an oily product which contained no toluic acid. In repeating this experiment with longer heating, on cooling an oily layer separated above the acid, which was neutralized with sodic hydrate, evaporated to dryness, the salt decomposed with hydrochloric acid, and the solution extracted with ether. Upon evaporation a crystalline solid was left, but not in sufficient quantity for further examination; it was probably paratoluic acid.

In the fraction 139–140° metaxylol was recognized by the formation of the trinitro compound. A portion of the oil was heated with a mixture of nitric and sulphuric acids during forty-eight hours, the oil, together with the crystals which formed, was separated from the acid solution, the oil distilled, and the solid remaining with the first crystals was purified by crystallization from hot alcohol. On cooling, long slender colorless needles separated, melting at 175–176°. This nitro compound was therefore trinitrometaxylol, melting-point 176°. Several different melting-points have been assigned to trinitroxylol. Luhman[2] gave 177°, and Tilden[3] 182°. To explain the latter result Tilden asserted that the lower value of Luhman was due to contamination of the trinitroxylol by the isomeric nitro compounds derived from coal tar, the source of the metaxylol from which the trinitro compound was prepared. But in the preparation of this trinitro derivative from octonaphtene, Markownikoff and Spady[1] gave 179–180° as its melting-point.

An approximate quantitative determination of metaxylol

[1] Lellmann: Ann. Chem. (Liebig), **228**, 250.

[2] Ann. Chem. (Liebig) **144**, 274.

[3] J. Chem. Soc., **45**, 416.

[4] Ber. d. chem. Ges., **20**, 1850.

was made in the fraction 139–140° by heating a portion during one hour with dilute nitric acid, which should oxidize the para- and orthoxylols to the corresponding toluic acids, and the remaining oil was washed with water, dried, and distilled with steam. The decrease in volume was noted, and it corresponded to 6.3 per cent. of the quantity taken. The distillate was next shaken with concentrated sulphuric acid, which dissolves metaxylol, and the decrease in volume corresponded to 16.6 per cent. of metaxylol. In determining the quantity of paraxylol, a weighed amount of the fraction 137–138° was shaken thirty minutes with concentrated sulphuric acid to dissolve the ortho- and metaxylols, with a loss in volume equivalent to 4 per cent. of the quantity taken. The residual oil was then agitated with fuming sulphuric acid, and the diminished volume represented 12.2 per cent. of paraxylol.

In attempting to ascertain the presence of orthoxylol, dependence was placed upon the observation of Jacobsen, that a single drop of orthoxylol may be distinguished in a mixture of the three isomers by treating them in the cold with a mixture of nitric and sulphuric acids. The fraction 142–143° gave immediately an oily layer in considerable quantity between the acid and the lighter oil, which should be the liquid orthonitroxylol. The fraction 139–140° gave no trace of an oily layer even after long standing. By further treatment with the acid mixture with the aid of heat, the oily mononitro product from distillate 142–143° was converted into a crystalline dinitro compound melting at 91°, the melting-point of dinitrometaxylol. By long continued action of the acid mixture, hot, a trinitroxylol was formed, nearly insoluble in alcohol, and melting at 178°, which might be a derivative either of ortho- or metaxylol. Another portion of the distillate 142–143° was heated with dilute nitric acid, which should form orthotoluic acid without affecting metaxylol. Upon extracting the acid solution with ether, an oily residue remained, after evaporation of the ether, with the characteristic odor of toluic acid, but no crystals separated even after long standing. An attempt was made to separate the less soluble sodic orthoxylolsulphonate, but upon evaporation of the solution no crystalline product appeared until the solution was so far concentrated that the sodic metaxylolsulphonate was deposited. Orthoxylol cannot, therefore, be present in any appreciable quantity.

Determinations of the constituents capable of forming nitro products were also made in the fractions containing the xylols by treatment with a mixture of nitric and sulphuric acids according to the method employed for benzol and toluol. The quantity of xylol corresponding to the nitro product represented by the portion not affected by nitric acid in the fraction 137–138° was 54.3 per cent. of the weight of oil taken; in the fraction 139–140°, 72.1 per cent.; and in fraction 141–143°, 31.5 per cent. Calculating the percentage of xylols from the results of the first determination in the 41.5 kilos of crude oil first distilled, the quantity of metaxylol is 0.016 per cent., and of paraxylol, 0.013 per cent. Evidently the xylols were not wholly collected in their respective fractions, although the quantity outside of the limits, 137–143° was doubtless small. Probably at least one-third should be added to these results. But if the percentages were increased to the results obtained by the action of concentrated nitric acid, the quantities of the xylols in the crude oil would still be small. In the fractions 132–136° we observed the presence of aromatic hydrocarbons, although in too small amounts for identification; nitro products were formed by the action of nitric acid. Attempts were made to ascertain the presence of ethylbenzol and hexahydromesitylene, but without success, on account of the limited quantity of the distillates. After treatment of the fraction 135–136° with concentrated nitric acid to convert the hydrocarbons C_nH_{2n-6} into nitro products, and distilling off the hydrocarbons not affected by the acid, the distillate was heated for some time with a mixture of nitric and sulphuric acids. According to Baeyer,[1] fuming nitric acid readily converts hexahydromesitylene into trinitromesitylene; but Konowaloff[2] found that a mixture of nitric and sulphuric acids, or fuming nitric acid, forms the trinitro compound only very slowly. After prolonged heating we obtained a crystalline nitro compound, but in such small quantity that it was impossible further to identify it. A much larger supply of these

[1] Ann. Chem. (Liebig), **155**, 275.

[2] Ber. d. chem. Ges., **20**, 1850.

distillates will be necessary to determine the presence of these bodies.

Series C_nH_{2n}.

Hexahydro compounds (Beilstein and Kurbatoff); naphtenes (Markownikoff and Ogloblin).

The lower members of this series include :

Hexahydrobenzol, C_6H_{12},	boiling-point, 69°
Hexahydrotoluol, C_7H_{14},	boiling-point, 97°.
Hexahydrocumol, C_9H_{18},	boiling-point, 147–150°.
Hexahydrocymol, $C_{10}H_{20}$,	boiling-point, 171–173°.
Hexahydroisoxylol, C_8H_{16},	boiling-point, 118°.
Hexahydromesitylene, C_9H_{18},	boiling-point, 135–138°.

In examining Ohio petroleum for the lower hydrocarbons of this series, the fraction 69–70°, after the fourteenth distillation, was shaken with concentrated nitric acid, then with concentrated sulphuric acid, and finally heated with metallic sodium. Determinations of carbon and hydrogen in the purified oil gave results corresponding to the composition of hexane :

I. 0.1618 gram of the oil gave 0.4934 gram CO_2, and 0.2299 gram H_2O.

II. 0.1891 gram of the oil gave 0.5790 gram CO_2, and 0.2663 gram H_2O.

	Required for		Found.	
	C_6H_{14}	C_6H_{12}	I.	II.
C	83.72	85.71	83.18	83.51
H	16.28	14.28	15.79	15.65

Hexahydrobenzol is therefore not present in appreciable quantities in Ohio petroleum.[1]

The fraction 96–97°, bar. 750 mm., after the fourteenth distillation, was purified as before, and the composition determined by analysis :

I. 0.2083 gram of the oil gave 0.6423 gram CO_2, and 0.2849 gram H_2O.

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[1] Recently Markownikoff (Ber. d. chem. Ges., **28**, 577) has ascertained that hexanaphtene (hexahydrobenzol) which he formerly reported as a constituent of Caucasus naphtha, boiling at 69–71°, is not a single body. Since the discovery by Baeyer of hexamethylene, boiling-point 79°, Markownikoff has discovered that Caucasus naphtha contains rather the same hexamethylene which he has identified by the formation of its nitro products. It will, therefore, be necessary to examine more carefully the corresponding distillates from the oils we have under examination for this body.

II. 0.2010 gram of the oil gave 0.6200 gram CO_2, and 0.2744 gram H_2O.

	Required for.		Found.	
	C_7H_{16}	C_7H_{14}	I.	II.
C	84.00	85.71	84.09	84.72
H	16.00	14.28	15.27	15.17

This oil was evidently heptane contaminated, as shown by the low percentage of the hydrogen, by a hydrocarbon containing less hydrogen. To remove any doubt as to the presence of heptane, the oil was heated during fifteen hours with a mixture of nitric and sulphuric acids, the oil separated from the acid, washed, dried, and boiled for some time with sodium. It was then distilled from the large amount of colored residue, again boiled with sodium, and distilled. The last distillation left very little residue, and the distillate was nearly odorless. The residue from the treatment with sodium crystallized well from alcohol. Upon diluting the acid a heavy nitro product separated in considerable quantities. A combustion of the purified oil gave the following percentages of carbon and hydrogen:

0.1410 gram of the oil gave 0.4224 gram of CO_2, and 0.2065 gram H_2O.

	Required for C_7H_{16}.	Found.
C	84.00	83.75
H	16.00	16.28

In a distillate 95–100° from American ligroïn, Beilstein and Kurbatoff[1] found 84.8 per cent. of carbon and 15.4 per cent. of hydrogen. After prolonged heating with nitric acid, the oil distilled at 98.5–99°.5, and gave on analysis 84.2 per cent. of carbon, and 15.9 per cent. of hydrogen, from which it was inferred that hydrocarbons poorer in hydrogen were contained in the crude ligroïn. A nitro derivative was separated from this fraction with the composition of nitropropane, $C_7H_{15}NO_2$. The fraction from Ohio petroleum gave no nitro compound when treated with nitric acid, and the acid was diluted.

Scarcely any residue remained when the oil was distilled after the treatment with acid. With a mixture of nitric and sulphuric acids, as shown above, much nitro compound sepa-

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[1] Ber. d. chem. Ges., **13**, 2028.

rated upon dilution, which was soluble in potassic hydrate like the nitro derivatives of the series C_nH_{2n+2}, and by boiling with sodium the solid residue was large.

In distillates 85–105° from Bibi-Eibat and from Balakhni, after thirty fractional separations, Milkowsky[1] collected a body that distilled constant at 100–101°, and by the formation of its halogen derivatives proved it to be heptanaphtene. The oil boiling at 101–103°, which Beilstein and Kurbatoff separated from Baku oil, was doubtless the same product, but Beilstein and Kurbatoff considered it to be composed for the most part of hexahydrotoluol, boiling-point 97°.

Hexahydroisoxylol was found by Beilstein and Kurbatoff in Caucasus petroleum,[2] and in American ligroïn;[3] since the American source was not mentioned, it is to be inferred that the ligroïn was prepared from Pennsylvania oil. In testing the fractions 118–119°, fourteenth distillation in a Hempel column, for hexahydroisoxylol, a portion of the oil was heated forty hours with a mixture of nitric and sulphuric acids. The nitro product separated from the oil when cold in long, flat plates, nearly insoluble in cold, more readily in hot, alcohol. When purified by crystallization, this substance melted at 177°, and was, therefore, trinitroisoxylol. A similar crystalline nitro product with the same melting-point was found in the fraction 123–124°. Since the prolonged distillation precluded the possibility that this fraction contained metaxylol, there can be no doubt that the trinitroxylol obtained from fraction 118–119° indicated the presence of hexahydroisoxylol, although it evidently formed only a small proportion of this product. After a portion of the same distillate was agitated thoroughly with a mixture of nitric and sulphuric acids, and distilled over sodium, analysis gave the percentages of carbon and hydrogen required for octane, as has been shown (page 744):

	Required for		Found.		
	C_8H_{18}.	C_8H_{16}.	I.	II.	III.
C	84.20	85.71	84.42	84.28	84.20
H	15.79	14.28	15.19	15.08	16.10

As already explained, Analysis III was made after prolonged treatment with the mixture of acids by which the

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[1] Ber. d. chem. Ges., 18, 187.

[2] *Ibid.*, 13, 1818.

[3] *Ibid.*, 2088.

hexahydro compound is removed very slowly, and the final results show that the fraction is composed chiefly of the more highly hydrogenized hydrocarbon, although it contains a considerable quantity of the other constituent, as shown by the abundant formation of nitro product.

In the intermediary product from the separation of octonaphtene and nononaphtene, by prolonged boiling with sodium and treatment with fuming sulphuric acid, Putochin[1] obtained a hydrocarbon distilling at 122–124°, principally at 122°.5, which corresponds in its composition to the formula C_8H_{16}. It gave a chloride different from the corresponding derivative of octonaphtene, and it was therefore accepted as isooctonaphtene. By treatment of the chloride with alcoholic potassic hydrate, isooctonaphtylene was formed with a higher boiling-point than naphtylene from octonaphtene.

The principal features of the Ohio sulphur petroleum which have appeared in the course of this examination are the following:

1. The crude oil is heavier than the Pennsylvania, and lighter than the Russian oil. In the quantities of the higher distillates, and in its general properties it resembles more nearly the latter.

2. It differs from other petroleums in the large amounts of sulphur compounds which exert an influence on the general properties of the oil.

3. It resembles the Pennsylvania oil in containing below 150° members of the series C_nH_{2n+2}, although in much smaller quantities. The presence in the Ohio oil of the two isomeric series C_nH_{2n+2} confirm the observations of Warren on the Pennsylvania petroleum.

4. The aromatic hydrocarbons are here present in minute quantities, apparently much smaller than in other petroleums. Benzol, toluol, meta- and para-xylol have been identified. The hexahydro series C_nH_{2n} is represented by hexahydroisoxylol, and very probably by higher members, although this has yet to be determined. Hexahydrobenzol and hexahydrotoluol are not contained in this petroleum.

5. By the formation of characteristic nitro products, and the

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[1] Ber. d. chem. Ges., 18, 186.

results of bromine absorption, the presence in the crude oil of unsaturated hydrocarbons C_nH_{2n} seems to be indicated.

Portions of Ohio petroleum have been thoroughly fractioned and are now under examination to establish the identity of the octanes, to ascertain whether isooctonaphtene and hexahydromesitylene are present, and to ascertain whether this petroleum contains a α-nonane, boiling-point 135–137°, and β-nonane, boiling-point 129°.5–131°.5, which Lemoine[1] asserts is contained in Pennsylvania petroleum. Examination of distillates collected above 150° is now in progress.

Canadian Petroleum.

Closely connected with the chemistry of Canadian petroleum are certain features relating to its occurrence, and the associated geological formations, which have not been fully investigated. The deposits of petroleum in Canada have been longer known that those in the Lima and Findlay fields in Ohio. As early as 1857 the existence of oil in considerable quantity in the township of Enniskillen was ascertained, and in 1862 the first flowing well was started. It was estimated by Dr. Winchell[1] that during the summer of 1862 not less than 5,000,000 barrels of oil flowed off on the waters of Black Creek. The flow of these early wells was very large. At a depth of 188 feet as much as 6,000 barrels of oil daily escaped from a single well, and at 237 feet 7,500 barrels daily, nearly equal to the flow of the great wells at Baku.

It is now known that these deposits of oil were mainly in the form of "pockets," and they formed no part of the main fields which are still productive. This oil territory is situated on two parallel anticlinals, about ten miles apart, with the corresponding synclinal between, from which no oil is obtained. In various reports of these oil fields, the larger area of oil-bearing strata at Petrolia is given as twenty-seven square miles, but the really productive field is actually contained within an area of less than eight square miles. The productive fields at Oil Springs are included within an area of less than two square miles. The oil deposits are here found in the Corniferous limestone underlying the Hamilton group

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[1] Bull. Soc. Chim. 41, 164, (1884).

[2] Geological Report of Canada, 1888–89.

of shales and limestones. Unlike the Trenton oil rock in Ohio, the oil-bearing limestone is quite near the surface ; the usual depths of wells at present in the Petrolia field is 465 feet.

I am indebted to the experience and extended observations of Messrs. M. G. Woodward of Petrolia and F. J. Carman for valuable information concerning the geological features and technology of the Canadian oil, of which a more detailed account has elsewhere been given.[1]

Under the general title of American petroleums, with occasional reference to Pennsylvania and to Canada as the particular sources, several partial examinations of crude Canadian oil were early made by French and English chemists. The first examination of Canadian oil was undertaken by Pelouze and Cahours[2] for the purpose of separating and identifying the hydrocarbons therein contained. Their attention was confined to the series C_nH_{2n+2}, and published accounts of their work contain no allusion to any other constituents than this series of hydrocarbons. They failed to observe the presence of aromatic hydrocarbons, although as already mentioned, Schorlemmer discovered the presence of benzol hydrocarbons in "real Canadian rock oil, a thick black liquid of a very unpleasant odor."

My attention was first attracted to Canadian petroleum in 1890, when I procured some of the crude oil and also a quantity of the "sludge" from the refining of burning oil, for the purpose of examining the sulphur compounds. The peculiar features of the distillates in a preliminary examination[3] invited further attention, and I determined to undertake, with the aid of the refiners, as complete an examination as was possible with the appliances at my command. It may seem somewhat surprising that such an examination of the sulphur petroleums in general has not previously been undertaken ; but it should be borne in mind that it requires the facilities of a well equipped organic and technological laboratory for the manipulation of considerable quantities of material, and a corps of efficient chemists with aid from the refinery of crude oils, par-

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[1] A paper presented at the Franklin Institute.

[2] Bull. Soc. Chim., **1**, 228, (1863).

[3] This JOURNAL, **16**, 89.

tially refined products, and residues. Even with all necessary accessories, aside from the tedious routine labor, there are certain features of decomposition and slow separation of constituents that render this work extremely difficult. In view of possible changes in the composition of petroleum, in the course of time, as wells become exhausted or the oil is taken from different depths, or indeed with the possibility of future exhaustion of oil fields which at present appear to be in the zenith of their production, it would seem that a comprehensive study of these oils should not be too long delayed.

From the peculiar nature of petroleum and its numerous constituents, all of which, so far as they have been examined aside from the lighter hydrocarbons of the series C_nH_{2n+2}, or the series C_nH_{2n}, are present in small quantities, any attempt toward a separation of these constituents involves the manipulation of large volumes of the oils in such a manner as to prevent so far as possible decomposition, which cannot be entirely avoided even with the greatest care. On this account satisfactory results can be hoped for only in products that have been obtained, at least in part, in experiments with several hundred barrels of oil, which must be performed with the aid of the appliances in a refinery. On the other hand, an examination of the unstable sulphur oils for certain constituents can be carried on satisfactorily only on a smaller scale, with laboratory appliances.

The products which I obtained through the aid of Messrs. Samuel Rogers & Co., of Toronto, and Mr. J. H. Fairbank, of Petrolia, for the study of Canadian petroleum, included a barrel of crude oil, considerable quantities of the first distillate, naphtha distillate, and burning-oil distillate, none of which had been further refined, besides 200 liters of thoroughly washed sulphur oil from "sludge." The crude oil was thick and nearly black in color; it contained hydric sulphide in small quantity, and some water, which was removed only after long standing in intimate contact with fused calcic chloride, and even then a small quantity appeared in the first distillate. A determination of its specific gravity at 20° gave 0.8621. In a former determination in another quantity of the crude oil we reported 0.8600.[1] Determinations in other specimens gave the following results:

Oil Springs	0.8442
"	0.8427
" (gas oil)	0.8389
Petrolia	0.8553

These numbers are not essentially different from those reported in other examinations of these oils. H. P. Brummel[2] gave as the specific gravity of the Canadian oils 0.804 and 0.808, values which must be accepted as only approximate, rather than as results of accurate determinations. Markownikoff and Ogloblin[3] referred to results of Sainte Claire Deville, which gave 0.844 as the specific gravity of Canadian oil, and 0.887 for Ohio oil. Reference to the original publication of Deville[4] shows that he obtained 0.870 as the specific gravity of Petrolia oil, and 0.844 for oil from "Canada West" (Oil Springs?). The number assigned by Redwood[5] to the oils at Petrolia were 0.859–0.877, and to the oils from Oil Springs 0.844–0.854. As Engler observed in the Alsace oils, it is possible that the specific gravity diminishes with the depth of the well.

Determinations of sulphur in the crude oil gave the following percentages:

	I.	II.	III.	Oil springs.
Sulphur	0.98	0.99	1.06	0.60

Canadian petroleum contains somewhat less carbon and hydrogen than Ohio oils:

I. 0.1908 gram of Petrolia oil gave 0.5874 gram CO_2 and 0.2295 gram H_2O.

II. 0.1914 gram of Oil Springs oil gave 0.5868 gram CO_2 and 0.2305 gram H_2O.

	I.	II.
C	83.94	83.62
H	13.37	13.39

In the Canadian Geological Report above mentioned Brummel gave 85 per cent. for carbon and 15 per cent. for hydrogen.

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[1] This JOURNAL, **16**, 90.

[2] Canadian Geological Report, 1888–89.

[3] Ann. Chim. Phys., [6], **2**, 372.

[4] Compt. Rend., **68**, 485.

[5] J. Soc. Chem. Ind., 1887, 405.

These percentages are evidently only approximate. They do not agree with results earlier obtained by Pelouze and Cahours, who reported a considerable percentage of oxygen.[1]

C.	H.	O.
84.2	13.4	3.0

The variation in composition in the Canadian, Ohio, Pennsylvania, and Russian petroleums is shown in the following table :

	Canadian.	Ohio.	Pennsylvania.	Russian.
C	83.94	84.57	84.19	86.89
H	13.37	13.62	13.70	13.18

After accounting for one per cent. of sulphur in the Canadian oil and 0.70 per cent. in the Ohio oil, the remaining percentage may reasonably be assigned to oxygen, yet in the Russian oils the composition is fully accounted for by the carbon and hydrogen, although the presence of oxygen compounds in considerable quantity has been demonstrated in several independent investigations.

Having an opportunity to collect fragments of the oil rock at Petrolia soon after it had been removed in drilling a well, I have ascertained its composition. Like most wells in this territory, the oil-bearing stratum was reached at a depth of 465 feet. The driller distinguishes two varieties of rock, one stratified and offering less resistance to the drill than the other, which is finer grained and for the most part loose and granular like sand. For convenience these specimens may be designated as I and II consecutively, and their composition is shown by the following results of analysis, to which is appended for comparison the composition of the Trenton limestone at Findlay, Ill., at a depth of 10,096 feet, and of the same oil rock at Lima, IV, at a depth of 1,247 feet.[1]

	I.	II.	III.	IV.
Calcic carbonate	49.80	49.75	53.50	52.66
Magnesic carbonate	44.35	45.44	43.05	37.53
Silicious residue	0.52	0.80	1.70	4.15
Alumina and iron	0.46	1.00	1.25	

It therefore appears that the dolomitic condition is not wanting in the oil-bearing Corniferous limestone ; in fact,

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[1] *Loc. cit.* [2] Orton, Geological Survey, of Ohio, 1890, p. 13.

magnesic carbonate seems to be somewhat in excess of the quantity present in the Ohio Trenton limestone. The specimens were impregnated with oil and were thoroughly washed with gasoline to remove so far as possible the carbonaceous portion.

In a distillation of Petrolia oil under atmospheric pressure, the first distillate appeared at 115°, and the following weights in grams were obtained from 800 grams:

	115-150°.	150-200°.	200-250°.	250-300°.	300-350°.	Residue.	Loss.
Weights	22	62.5	72	43	27	561	12
Per cent.	2.75	7.8	9.5	5.1	3.1	70.1	1.75
Sp. gr.	0.767	0.8026	0.8228	0.8345	0.9037		

In the proportions that distil at different temperatures and in the specific gravity of the distillates, the Oil Springs resembles more nearly the Findlay oil:

	—100°.	100$_4$150°.	150-200°.	200-250°.	250-300°.	306-350°.	Residue.	Loss.
Weights	8	41	90	52	88	47	357	7
Per cent.	1.14	5.86	12.85	8.86	12.6	6.71	51.0	0.98
Sp. gr.		0.7335	0.7675	0.7984	0.8222	0.8386	0.9032	

A comparison of the distillates at increasing temperatures from oils of different localities has been included in considering the properties of the Ohio oils. A clearer idea of the peculiar character of Canadian oil may be gained by comparing the distillates from it with those from oils of other fields. It is evident that the high specific gravity of the Canadian and Ohio crude oils depends upon constituents that do not distil below 350°. In this respect these oils differ essentially from the Russian oil, in which all the distillates show a high specific gravity. The distillates below 150° from Canadian oil are somewhat lighter than the corresponding products from Ohio crude oil. In considering later the properties of the vacuum distillates it will be seen that these proportions are very materially changed by distillation *in vacuo*.

	Apscheron.		Pennsylvania.	
	Per cent.	Specific gravity.	Per cent.	Specific gravity,
120–150°	0.5		19.70	
150–200°	10.9	0.786	8.85	0.757
200–255°	12.8	0.824	15.23	0.788
250–320°	24.7	0.861	20.70	0.809
	48.9		64.48	
Residue,	51.1		35.52	

CANADA.

	Petrolia.		Oil Springs.	
	Per cent.	Specific gravity.	Per cent.	Specific gravity.
—100°			1.14	
100–150°	2.75	0.7670	5.86	0.7335
150–200°	7.80	0.8026	12.85	0.7675
200–250°	9.50	0.8228	8.86	0.7984
250–300°	5.10	0.8345	12.60	0.8222
300–350°	3.10	0.9037	6.71	0.8386
	28.25		48.03	
Residue	70.10		51.00	

OHIO.

	Per cent.	Specific gravity.
110–150°	9.75	0.7282
150–220°	16.63	0.7669
220–257°	10.75	0.7940
257–300°	9.75	0.8138
300–350°	8.63	0.8242
	55.51	
Residue	43.00	

In the percentages of the lower fractions it will be seen that the Canadian oil resembles more nearly that from the Caucasus, but the residue above 350° is much larger than in the oils from other fields. As will appear later, this difference is much less in distillations conducted *in vacuo.*

The percentage of sulphur was determined in each distillate by a combustion in air:

	115–150°.	150–200°.	200–250°.	250–300°.	300–350$_0$.	Residue.
Sulphur	0.28	0.42	0.50	0.51	0.86	0.70

Determinations of the quantity of bromine absorbed indicated a greater capacity for absorption in the higher fractions, but less in the residue than in corresponding fractions from the Ohio oil:

CANADA.		OHIO.	
Fraction.	Per cent. of bromine.	Fraction.	Per cent. of bromine.
115–150°	0.67	110–150°	0.73
150–200°	1.12	150–220°	1.74
200–250°	3.49	220–257°	4.84
250–300°	8.39	257–300°	5.04
300–350°	14.40	300–330°	12.10
+350°	17.80	+330°	19.50

The Oil Springs oil differs essentially in many respects from Petrolia oil, especially in a lower specific gravity, lower percentage of sulphur, and in the proportions in which it distils at different temperatures. In certain peculiarities it approaches Ohio oil. The lower fractions show a higher bromine absorption than either the Petrolia or the Ohio oil:

	Per cent. of bromine absorbed.
—100°	0.0
100–150°	2.31
150–200°	4.09
200–250°	8.98
250–300°	8.41
300–350°	12.00
+350°	33.78

The percentage of bromine absorbed by the crude oils was also determined:

Petrolia.	Oil Springs.	Ohio.
15.11	17.69	10.19

Hydric sulphide escaped in small quantities during the distillation, but below 200° the decomposition was slight, and the distillates were colorless. Above this point the products were somewhat colored, with the disagreeable odor of decomposition. It is probable that cracking begins near this temperature, affecting the unsaturated hydrocarbons if they are present, and perhaps other series as well as the sulphur compounds. Certain constituents of the Canada oil seemed to be more unstable than those of Ohio petroleum. The tendency toward polymerization of unsaturated hydrocarbons separated from distillates corresponding to burning-oil has been observed.[1] An oil that had been distilled many times *in vacuo* and allowed to stand two years, when again heated, suddenly polymerized into a higher product that could not be distilled at any temperature on account of complete decomposition. The conversion of Canadian petroleum into asphalt, upon long standing exposed to the weather, is well known. Large masses of this material may be seen in a pitchy form in the vicinity of Oil Springs.

Determinations of carbon and hydrogen were made in the

[1] This JOURNAL, **16**, 92.

coke from Petrolia oil, in one sample from the crude oil, and in another from a tar distillate with the following results:

	Crude oil.	Tar distillate.
C	94.04	94.34
H	4.19	4.34

A specimen of surface oil was collected at Oil Springs for examination. It was very thick, with the consistency of ordinary molasses. A determination of its specific gravity at 20° gave 0.9059. It contained 0.05 per cent. of nitrogen, and 0.95 per cent. of sulphur. The weight of bromine absorbed was equivalent to 25.46 per cent. This oil is evidently an intermediary product in the formation of the deposits of pitch resembling asphalt, which have long been known at Oil Springs. The pitch is evidently formed by evaporation from the oil of the more volatile constituents, and its formation is doubtless due, in part at least, to polymerization of lower constituents of less stability. A combustion of this pitch gave 64.86 per cent. of carbon and 8.13 per cent. of hydrogen. In a determination of nitrogen 0.40 per cent. was obtained, and the percentage of sulphur was found to be 0.65. The pitch contained 10.13 per cent. of ash, and a qualitative examination showed that it was composed chiefly of calcic oxide, with smaller amounts of aluminic and ferric oxides, besides a trace of magnesic oxide. A determination of its bromine-absorption gave 37.79 per cent.

Nitrogen was determined in each variety of coke, and in several samples of crude oil by the Kjeldahl method:

Coke from crude oil	0.38
Coke from tar distillate	0.31
Petrolia crude	0.16
Oil Springs	0.18
Oil Springs gas oil	0.21

Sulphur was determined in the two varieties of coke, and in a specimen of crude paraffine wax:

Coke from crude oil	0.76
Coke from tar distillate	0.76
Crude paraffine wax	0.97

When it is remembered that this coke in the process of carbonization had been exposed to a temperature closely approaching a red heat, it is not easy to understand how it could retain so large a proportion of nitrogen and sulphur. If the ash were sufficient in quantity, the presence of metallic cyanides and sulphides might be assumed. But 0.07 per cent. of ash is not sufficient to account for such a high percentage of sulphur. Moreover, careful tests failed to show the presence of either sulphides or cyanides. In determinations of sulphur by combustion in air, we have frequently found that the carbon must be completely burned, otherwise the percentage of sulphur is too low.

With the purpose of ascertaining the mineral constituents of Canadian petroleum, I procured a specimen of coke from the distillation of the crude oil, and another from the coking of a tar distillate. Since finely divided mineral matter is frequently held in suspension in the crude oil long after it is taken from the well, it might be inferred that the ash from the crude oil should consist in part of suspended material. The specimen selected was a part of a large fragment, one side of which had evidently been carbonized in contact with the bottom of the still. The portion for analysis was taken from the opposite side, which had evidently been carbonized several inches above the bottom. The residue from combustion in oxygen corresponded in the crude oil coke to 0.17 per cent., and in the coke from the tar distillate to 0.07 per cent. These quantities of ash correspond to 0.012 per cent. in the crude oil. An examination of the ash showed that it was composed of the oxides of magnesium, calcium, iron, and aluminium. It consisted chiefly of the oxides of calcium and magnesium, doubtless derived from the dolomitic reservoir.

A quantity of brine was collected for examination at Petrolia from a well recently drilled. Analysis showed that it contained calcic sulphate, and calcic, magnesic, and sodic chlorides, in the following proportions, in 1,000 parts:

$NaCl$	10.71
$MgCl_2$	2.90
$CaCl_2$	1.20
$CaSO_4$	3.20
Iron and alumina	traces.
	18.00

The specific gravity of this brine at 20° was 1.0165.

The composition of this brine is quite different from that given in the early history of this oil territory by Dr. T. Sterry Hunt. We made no examination for potassic chloride. 1,000 parts of the brine gave in Hunt's analysis :

$NaCl$	4.800
KCl	0.792
$CaCl_2$	12.420
$MgCl_2$	3.650
	21.662

It is practically impossible, at least in glass, to distil the Canadian oil on a small scale unless it is free from water, and the water can be removed only by long standing with large quantities of calcic chloride.

After the first distillation there is less difficulty in removing water except in the least volatile distillates. The necessity of vacuum distillation to avoid decomposition was even more evident in Canadian than in Ohio oil. In quantities of 12 liters each, 64.5 kilos were distilled in a porcelain still under a tension of 50 millimeters, and the following quantities of the distillates were collected at different temperatures:

	—100°.	100–150°.	150–200°.	200–250°.	250–300°.	300–350°.	Residue.
Grams	3870	7288	7159	8578	7869	6698	22059
Per cent.	6.00	11.3	11.1	13.3	12.2	10.4	34.2
					250--350°.		
Per cent. in Ohio oil	18.6	19.8	15.1	18.0	6.2		20.9
Sp. gr.	0.7549	0.7991	0.8245	0.8455	0.9070		0.9189
Sp. gr. of Ohio oil	0.7445	0.7852	0.8161	0.8387	0.8647	0.8759	0.9130

It is peculiar that in distillation under atmospheric pressure as well as *in vacuo* the lowest fraction from the Canadian oil is heavier than that from Ohio oil, while the next following distillates are reversed in the order of their specific gravity. Under the influence of vacuum distillation a large portion of the heavier constituents of the residue above 350°, under atmospheric pressure, are reduced in boiling-points to such an extent that the specific gravity of the lower fractions is very considerably increased. Referring to the specific gravity of the fractions from the Apscheron oil, page 732, Vol. 17, it will be seen that the corresponding fractions *in vacuo* from the Canadian oil are much heavier, and the residue is much smaller. The differences between the weights collected at different temperatures in the Canadian and Ohio petroleums also confirm the marked variation in composition already referred to, and an explanation must evidently be sought in the larger quantities of the series C_nH_{2n+2} in the fractions below 150° from Ohio oil, and the greater quantity of the heavier oils of the series C_nH_{2n}, and a similar series in distillates from Canadian oil above this point.

The percentages of sulphur in these distillates were also determined :

	100°	100°– 50°	150°–200°	200°–250°	250°–300°	300°–350	Residue.
Sulphur	0.25	0.45	0.47	0.75	0.78	0.81	0.83

When distilled without much decomposition the sulphur compounds in Canadian oil collect in smaller quantities in the lower distillates than is the case in the Ohio oil.

Determinations were made of the per cent. of bromine absorbed by the vacuum distillates :

	100	100°–150°	150°–200°	200°–250°	250°–300°	300°–350°	Residue.
Bromine-abs.	0	3.25	4.59	6.2	8.2	15.8	25.82
Bromine-abs. atm. pressure		0.67	1.12	3.49	8.39	14.4	17.8
Br.-abs. Ohio oil, vac. dist.	0	4.57	6.60	250°–350 7.08			24.38

There is a marked difference in bromine-absorption between the distillates collected *in vacuo* and those collected under atmospheric pressure. The capacity for absorbing bromine in the distillates from Canadian oil is greatly increased in the lower fractions by vacuum distillation, and this difference is even more noticeable in Ohio oil. It is probably due to the smaller amounts of Canadian oil distilling at lower temperatures under atmospheric pressure. The larger quantities of bromine absorbed in the fractions collected *in vacuo* is suggestive. It cannot be caused by decomposition, but it seems to be due rather to the reduction in boiling-points by which certain compounds capable of absorbing bromine are carried over at lower temperatures, and doubtless too with less decomposition. The increased absorption above 250° may indicate cracking, or the presence of normal constituents that absorb bromine. Since the difference in the amounts absorbed in the Canadian oil *in vacuo* and under atmospheric pressure is not large except in the residues, and the conditions much less favorable for cracking in the vacuum distillates, it would seem that the absorptive capacity is due to normal constituents of the crude oil.

The fraction 150–200°, containing 0.47 per cent. of sulphur, absorbed 4.59 per cent. of bromine. A portion was treated with alcoholic mercuric chloride, washed, dried, and it was then found to contain 0.063 per cent. of sulphur. A determination of the amount of bromine it absorbed gave 2.8 per cent. This result is evidently independent of the sulphur compounds. It must indicate either normal constituents of the oil with an affinity for bromine, or the presence of decomposition-products due to cracking.

Another portion of the same fraction was agitated with concentrated sulphuric acid, and the quantity of bromine then absorbed was equivalent to 1.15. Since mercuric chloride has been shown to remove nearly all the sulphur compounds from the lower fractions, and sulphuric acid only partially, it is still further evident that there are present in this fraction other bodies capable of absorbing bromine, perhaps unsaturated hydrocarbons, either contained in the crude oil or resulting from decomposition during distillation.

The distillates collected *in vacuo* showed but slight indications of decomposition; they were only slightly discolored, except the residue above 350°. In prolonged distillation the higher fractions gradually become colored by polymerization or other decomposition. Even the residue above 350° showed scarcely any odor, and it had apparently undergone but little decomposition. The distillates above 150° and the residue above 350° are reserved for further study.

As in the study of Ohio petroleum, the lower members of the series C_nH_{2n+2} were sought for in the most volatile refinery distillate. Twenty liters of the very first distillate from Petrolia crude oil was submitted to distillation, and the vapors collected in a Warren condenser filled with a freezing-mixture or with water, according to the boiling-points of the distillates, and with a condensing-worm in front filled with the freezing-mixture. Distillates were collected below 45°, and the distillation of them repeated until they collected for the most part within well defined limits. The following weights were collected as representing the quantities of these products in the twenty liters first distilled:

—10°	10°-20°	20°-25°	28°-30°	30°-35°	36°-38°
100	40	30	175	30	80

The small quantities distilling at temperatures outside of the boiling-points of the well known hydrocarbons were not further examined, since it was assumed that they were merely mixtures. The portion collecting at 29–30° in a vapor-density determination gave 2.54; required for isopentane 2.49.

A vapor-density determination of the fraction 36–37° gave 2.66, which corresponds to the composition of pentane, C_5H_{12}.

Distillation of the portion —10° was continued until 20 grams collected between 7° and 8°. In a vapor-density determination by the method of Hofmann, the value 2.01 was obtained; calculated for butane, C_4H_{10}, 2.01. A considerable portion of this oil collected below 5°; which consisted chiefly doubtless of the butane that boils at 0°. But since this body has been identified no further attempts were made to separate it more completely. Concerning the butane boiling at 8°, what has been said of the same product separated from Ohio petroleum applies also here. It is evident from the weights collected of these volatile hydrocarbons that they are present in much smaller quantities than in Ohio petroleum.

The distillate below 150° *in vacuo* was fractioned twelve times, collecting at first within 5° limits, then within 2°, and finally within 1°, with the aid of Warren condensers containing glass coils and Hempel columns. At the end of the eighth distillation, the last seven under atmospheric pressure, the lower distillates collected as follows, with smaller quantities between these limits:

	—55°	55°-60°	65°-69°	77°-83°
Grams	8	25	40	65

As was mentioned when considering the lower fractions of the Ohio oil, these weights evidently represent only approximately the quantities in the crude oil.

After the eighth distillation, the fractions 55–60° were further purified, until 15 grams distilled constant at 60–61°, bar. 749 mm., and a vapor-density determination of this product gave 2.96; required for isohexane, 2.98.

At 67–68°, after the twelfth distillation, 10 grams of oil collected, which gave as its vapor-density 3.01; required for hexane, 2.98. The distillates 75–85° will be considered with the aromatic series.

At 87–93°, after the eighth distillation, the distillates amounted to 115 grams, and after the fifteenth, 20 grams distilled at 90–91°, bar. 745 mm. A vapor-density determination of this product gave 3.51; isoheptane, C_7H_{16}, requires 3.46.

At the end of the seventeenth distillation, 80 grams collected at 96.5–97°.5, bar. 740 mm., which distilled constant within these limits. A determination of its vapor-density gave 3.63; required for heptane, 3.46. The composition of this oil was further established by analysis:

0.1870 gram of the oil gave 0.5781 gram CO_2, and 0.2514 gram H_2O.

	Required for C_7H_{16}.	Found.
C	84.00	84.31
H	16.00	15.77

Outside of the limits of temperature within which the hydrocarbons C_nH_{2n+2} have been found, the distillates below 105° have been subjected to prolonged distillation, but the quantities collected were so irregular, gradually separating into higher and lower constituents, that it excluded the presence in any considerable quantity of other bodies. The fractions in the vicinity of 111° will be described later, in the examination for toluol.

Concerning the distillates collected at 118–119°, the observations on the corresponding fractions from Ohio oil apply equally here. At 118–119°.5, the distillates amounted to 90 grams after the fifteenth distillation. A vapor-density determination gave 4.02; required for octane, C_8H_{18}, 3.94. As in the case of the Ohio products, this fraction was purified with much care, and the following determinations of carbon and hydrogen were made :

I. 0.2013 gram of the oil gave 0.6226 gram CO_2, and 0.2738 gram H_2O.

II. 0.2036 gram of the oil gave 0.6318 gram CO_2, and 0.2799 gram H_2O.

III. 0.2045 gram of the oil gave 0.6324 gram CO_2, and 0.2762 gram H_2O.

	Required for C_8H_{18}.	Found. I.	II.	III.
C	84.20	84.35	84.61	84.33
H	15.79	15.12	15.28	15.01

From the low percentage of hydrogen and higher percentage of carbon it was evident that this oil still contained a small amount of a hydrocarbon with less hydrogen, probably of the series C_nH_{2n}, although the main constituent was evievidently a member of the series C_nH_{2n+2}. In further attempts to eliminate the hydrocarbon with less hydrogen, the remainder of the oil after analysis was treated several times with hot nitric and sulphuric acids, and boiled repeatedly with sodium until there was no residue left on distillation. Although the boiling-point was not materially changed by this treatment, analysis showed a decrease in the percentage of carbon to 83.91 per cent., and an increase in hydrogen to 16.10 per cent.

As in the Ohio oil, we found that distillates collected with much persistence between 120–126°; after the eleventh distillation the following weights were obtained :

	120–121°	121–122°	122–123°	123–124°	124–125°	125–126°	126–127°	127–128°
Grams	85	70	80	60	30	30	70	60

The quantities between 122–125° were not greatly diminished after the sixteenth distillation ; and, like the distillates from the Ohio oil, these products contained small quantities of the aromatic compounds; they will receive further attention with reference to their chemical reactions. After the twelfth distillation, 110 grams of an oil collected at 126–128°, bar. 752 mm., which was carefully purified in the manner already described. It gave, by the method of V. Meyer, a vapor-density corresponding to octane, C_8H_{18} ; found, 4.24 ;

required, 3.95. What has been said concerning the presence of the octanes in Ohio petroleum applies also to these distillates from Canadian oil, and they evidently require further study. The fractions collected at 130–142° will be considered with the aromatic series. A distillate persisted at 145–146°, as shown by the quantities collected at the twentieth distillation:

	142–143°	143–144°	144–145°	145–146°	146–147°	147–148°
Grams	30	32	50	75	25	22

Since the fractions 144–146° resisted all attempts to separate them into bodies with higher and lower boiling-points, further study is necessary to determine whether they represent an individual product.

Between 149–152°, 160 grams collected at the tenth distillation, a large portion of which distilled constant at 150–151°, bar. 749 mm. After treatment with nitric acid and sodium, with results similar to those observed in the Ohio oil, this product gave, in a vapor-density determination, a value required for nonane; found, 4.56; required for C_9H_{20}, 4.43. Distillation of the fractions from Canadian petroleums above 160° cannot be continued under atmospheric pressure without decomposition, probably caused by the action of air upon the hot oil. Unless, indeed, as some attempts have shown, it will be possible to distil them in an atmosphere of carbonic dioxide. These fractions have been distilled several times *in vacuo*, and further study of them is reserved.

From the results thus far obtained, it seems that the series C_nH_{2n+2} is represented in Canadian oil by the same members as are found in Ohio and Pennsylvania oils, but the lower hydrocarbons are present in much smaller proportions. The peculiar properties of Canadian oil depend, at least partially, on the small quantities it contains of the hydrocarbons C_nH_{2n+2}. The sulphur compounds exert an important influence. The presence of unsaturated hydrocarbons is not yet determined. Whether other series of bodies characterized by their instability form important constituents of the oil can only be ascertained by a critical study of the portions with high boiling-points.

AROMATIC HYDROCARBONS.

Series $C_n H_{2n-6}$.

Benzol

In looking for members of the aromatic series, the same methods were followed as in fractions of the Ohio oil. At the end of the eighth distillation, 20 grams collected at 77–79°, 15 grams at 79–81°, and 30 grams at 81–83°. In treating these fractions, which contain benzol, with nitric acid under the conditions necessary for the formation of nitrobenzol, avoiding loss, so far as possible, and distilling off the unaffected hydrocarbons, the first fraction gave 2.8 per cent. of benzol, the second 4.4 per cent., and the third 4.14 per cent. The benzol calculated from these data, in the total weight of the fractions, gave 3 grams as the total weight in the 64.5 kilos of crude oil taken, equivalent to 0.0047 per cent. Practically all of the benzol was collected within these limits, since scarcely any nitro product was obtained in the higher and lower fractions. The quantity of benzol in the crude oil is probably somewhat larger than is here represented, although it must be considered as somewhat less than the amount contained in Ohio oil. Some loss undoubtedly resulted from distillation *in vacuo*, as well as in the subsequent separations. The nitrobenzol was recognized by conversion into aniline, which gave its characteristic reaction with furfurol.

Toluol.

In the portions containing toluol, between 107–109°, after the eighth distillation, the distillates amounted to 40 grams, at 109–111° to 250 grams, and at 111–113° to 50 grams. These fractions were treated for the formation of nitrotoluol in the same manner as those previously examined, and the fraction 109–111° gave a weight of unaffected hydrocarbon and nitro product equivalent to five per cent. of toluol of the fraction 107–109° one per cent., and in the fraction 111–113° one per cent. The higher and lower fractions gave no nitrotoluol. Referred to the total weights of the fractions, the quantity of toluol was 3.5 grams, equivalent to 0.005 per cent. of the total weight of crude oil taken. As in the case of benzol, it is probable that the quantity of toluol is somewhat larger than is shown by these determinations. This product was shown to be toluol by conversion of the nitro derivative into toluidine, which gave characteristic color reactions.

Xylols.

The single allusion to the presence of xylols in Canadian petroleums is a general statement by Schorlemmer that he obtained reactions for benzol and its homologues, although the only aromatic hydrocarbon he separated was cumol in the form of the trinitro derivative.

After prolonged distillation, having found that fractions collected within limits corresponding to the boiling-points of the xylols, we have spent considerable time in the formation of characteristic compounds as adequate evidence of their presence in the crude oil. In the twentieth distillation, within one degree after the twelfth, the following weights collected between 136° and 143°:

	136–137°	137–138°	138–139°	139–140	140–141°	141-142°	142-143°
Grams	30	40	25	40	25	47	30

On account of the close proximity of the xylols in boiling-points, it would evidently require much longer time in distillation and larger quantities of the distillates to separate them completely. We therefore depended upon the formation of derivatives that are sufficiently well characterized to warrant conclusions concerning the xylols from which they were formed. As a qualitative test for paraxylol, a part of the fraction 137–138° was heated with nitric and sulphuric acids, and the oil which separated was allowed to stand until a crystalline product formed. After crystallization from alcohol, the nitro derivative thus obtained melted at 139–140°, the melting-point of trinitroparaxylol. Another portion of the same fraction was boiled during several hours with chromic acid, and the solution extracted with ether. Upon evaporation, a white powder remained that sublimed without melting, and resembled in its appearance terephthalic acid. To determine the quantity of paraxylol according to the method suggested by Levinstein, a measured portion of the fraction 137–138° was shaken during thirty minutes with concentrated sulphuric acid. The loss in volume corresponded to 10.77 per cent., representing the other aromatic hydrocarbons. The residual oil was then agitated with fuming sulphuric acid to dissolve the paraxylol, with a diminution in volume representing 9.02 per cent. of the xylol.

The quantity of metaxylol in fraction 139–140° was found by treating it first with dilute nitric acid, which, according to Brückner,[1] should not affect metaxylol, and distilling with steam, which carries over the metaxylol. The loss in volume, 7.5 per cent., was noted, and the distillate was agitated first with ammonia, then with concentrated sulphuric acid ; the last diminution represented 8.8 per cent. of metaxylol.

Many attempts were made to prove the presence of orthoxylol by the formation of the nitro compounds, and toluic acid. But no di- or trinitro compounds could be separated after treatment with nitric acid except those whose melting-points corresponded to metaxylol. By the action of dilute nitric acid, which should not affect metaxylol, an acid was formed, but not in sufficient quantity to show that it was toluic acid. In forming the sulphonic acids and the sodium salts, so far as could be observed, no sodium orthoxylolsulphonate was present. It is quite possible that orthoxylol could be detected in a larger quantity of product. The larger amounts of the fractions 140–142° therefore consisted partly of metaxylol. Referring the quantities of meta- and paraxylol to the weights of crude oil, the amount of paraxylol is 0.006 per cent. of metaxylol, 0.003 per cent. in their respective fractions. These numbers cannot be assumed to represent more than an approximate estimation of these xylols, although they are doubtless, for the most part, collected in the fractions 137–143°. In fractions 141–143° the amount of sodic xylolsulphonate formed corresponded to 0.009 per cent. of xylol, and, since orthoxylol could not be detected, this quantity should be added to the total amount of metaxylol in the crude oil. Even then 0.012 per cent. is scarcely more than a trace of this body. As in the similar determinations in Ohio oil, these results serve to show the very small proportion of the xylols contained in the crude oils. In the distillates 130–140° of the Canadian oil there were indications

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[1] Ber. d. chem. Ges., 9, 405.

of bodies capable of forming nitro products, but much larger quantities of these fractions will be needed for their separation.

Series C_nH_{2n}.

The fraction 68–69° of the twelfth distillation was carefully purified with alcoholic mercuric chloride, nitric acid, sulphuric acid, and distillation with sodium. A combustion then gave the following results:

0.1889 gram of the oil gave 0.5784 gram CO_2 and 0.2719 gram H_2O.

	Required for C_6H_{14}.	Required for C_6H_{12}.	Found.
C	83.71	85.71	83.45
H	16.28	14.28	15.99

This fraction therefore consisted essentially of hexane, and it contained no appreciable quantity of hexahydrobenzol.

The fraction 97–98°, by the action of a mixture of nitric and sulphuric acids, gave a nitro compound heavier than water, equivalent to 10 per cent. of the weight taken. The heavy oil turned red with sodic hydrate, and partially dissolved, reprecipitating with acids. By reduction with tin and hydrochloric acid, a substance with the properties of an amido compound was formed. It distilled with steam, was soluble in acids, and was precipitated from the acid solution by sodic hydrate. The prolonged fractional separation excluded benzol, and furthermore the amido derivative gave no reaction with furfurol. In the behavior toward sodic hydrate the nitro compound resembled the unsaturated nitro compounds of the series C_nH_{2n}, but the quantity of the distillate was not sufficient for complete verification. Another portion of the same fraction was heated during several hours with dilute nitric acid, the solution neutralized with sodic hydrate, and evaporated to dryness. A portion dissolved in water gave, with ferric chloride, the characteristic color for acetic acid, and more of the sodium salt, decomposed with hydrochloric acid, and extracted with ether, gave colorless prismatic crystals resembling succinic acid.

In a distillate 95–100°, from the Caucasus petroleum, Beilstein and Kurbatoff[1] observed the formation of acetic acid,

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[1] Ber. d. chem. Ges., **13**, 1820.

considerable succinic acid, and other non-volatile acids. The oil remaining after the treatment with nitric acid, was distilled with sodium, and a combustion gave the following results already stated on page 67 :

	Required for		
	C_7H_{16}.	C_7H_{14}.	Found.
C	84.00	85.71	84.31
H	16.00	14.28	15.77

Since hexahydrotoluol is not affected by nitric acid, but is completely decomposed by a mixture of nitric and sulphuric acids, it cannot be present in any appreciable quantity in this fraction.

In examining the fraction 118–119° for hexahydroisoxylol, after the sixteenth distillation it was heated with a mixture of nitric and sulphuric acids. The acid was much colored from decomposition, and crystals separated which were very sparingly soluble in alcohol. The purified substance melted at 178°, the melting-point of trinitroisoxylol. Hexahydroisoxylol was therefore present, although it formed but a small part of this distillate, as shown by the results of combustions repeated from page 68. It should be borne in mind that the oil analyzed was purified with nitric and sulphuric acids separately :

	Required for		Found.		
	C_8H_{18}.	C_8H_{16}.	I.	II.	III.
C	84.20	85.71	84.35	84.61	84.33
H	15.79	14.28	15.12	15.28	15.01

By furthur treatment with the acid mixture the hexahydro compound was sufficiently removed to prove the presence of a hydrocorbon C_nH_{2n+2}, as shown by the results of analysis already given.

With the limited quantity of distillates 136–138°, which should contain hexahydromesitylene if it is a constituent of Canadian petroleum, remaining from the examination of the xylols, satisfactory conclusions could not be reached concerning the presence of this hydrocarbon. Since Markownikoff has recognized it in the Russian oil, it is very possibly present in the Canada oil. As in the Ohio fractions, after removing the xylols by continued action of the acid mixture, we obtained a small quantity of an oily nitro product that did not crystallize. With a larger supply of this distillate, further attempts will be made.

The lines of study which are now in progress on the Ohio and Canadian oils have been indicated in the preceding pages. Besides the higher vacuum distillates sodium salts of acids have been separated whose composition is now being determined. The facts thus far accumulated are not sufficient to determine whether the acids exist as such in the oils, as is maintained by Aschan, or whether they are oxidation products of other constituents, as Engler and Lachowitz believe. Since sodium salts have been obtained which contain much nitrogen and give the characteristic odor of pyridine compounds when heated, the possibility of pyridine carboxylic acids is suggested. In searching for the oxygen and nitrogen compounds we have separated bodies that give with nitric acid a brilliant red color, similar to what was early observed in our study of the sulphur derivatives.

The characteristic qualities of Canadian petroleum which appear in the results of this examination may be summarized as follows :

1. In its high specific gravity and in the proportions that distil at different temperatures, Canadian petroleum approaches the Russian oil more nearly than the Ohio petroleum. But the specific gravity of the distillates is lower, approaching those of Ohio oil. As indicated by its lower specific gravity, Oil Springs oil is essentially different from Petrolia oil. This is especially evident in the lower percentage of sulphur, the larger quantities of the distillates, the higher specific gravity of these distillates, and the higher bromine-absorption.

2. Petrolia oil is composed principally below 150° of members of the series C_nH_{2n+2}, although in much smaller quantities even than in Ohio oil. Another series is present capable of forming nitro products resembling the nitro compounds of the series C_nH_{2n+2}, or the unsaturated hydrocarbons $C_{2n}H_n$.

3. The aromatic hydrocarbons C_nH_{2n-6}, benzol, toluol, para- and metaxylol are present in minute proportions. The hexahydro series is represented by hexahydroisoxylol, and probably by higher members.

4. By the behavior of the distillates toward bromine, the presence of hydrocarbons capable of forming addition-products is indicated, as well as the formation of unsaturated hydrocarbons due to cracking in the distillates above 200° or 250°.

5. As in Ohio oil, the sulphur compounds have a tendency to collect in the higher fractions.

In the prosecution of this work I have received valuable aid from my assistants, Messrs. Cleveland, Little, and Giessen, and in portions of the work on the Canadian petroleum, from Mr. W. H. King, a student in this Laboratory.

ORIGIN OF PETROLEUM.

In the clear and concise statement of the present condition of the theoretical discussion concerning the formation of petroleum by Professor Edward Orton (Geological Survey of Ohio, 1890), without including the theory of Mendelejeff that highly heated iron or iron carbides within the earth may furnish the world's supply, it is explained that most geologists accept the view that organic matter of vegetable or animal origin constitutes the source, and that it was deposited during the formation of the rock strata. Many insist on substances of vegetable origin as the chief source, and depend upon destructive distillation as an essential agency. A small minority of the geologists, and some chemists, especially the Germans, hold that animal remains may be accepted as the sole source in a process of primary decomposition without distillation.

The chief difficulty in arriving at any satisfactory conclusion concerning the formation of petroleum depends upon the fact that the principal process is completed, and there remains scarcely a trace of the stages through which the original substances have passed; or, indeed, these stages may have been so simple that we have before us in the oil rock all the indications that could ever have been observed concerning the formation of petroleum. Prevailing opinions seem to refer the genesis of the limestone oils to the decomposition of animal remains, and that of other oils to vegetable decomposition.

The most interesting observation on the natural formation of oil that has come to my knowledge is the experience of Mr. R. A. Townsend, of Petrolia, who has recently returned from India, where during fourteen years he has been engaged by the British government in prospecting for minerals and oils. In the oil region of Assam, Beloochistan, and the Punjaub, the surface is bare rock, and the anticlinals are easily located. Approaching an elevation while prospecting, he found at the top a bell-shaped depression, into which he descended to a vertical depth of 2,000 feet, and came upon beds of Tertiary oysters from which petroleum was exuding. The excavation had been formed by a thermal spring that had disappeared, leaving the strata bare. No oil was observed above or below the oyster beds. In oil territory owned by Mr. Townsend in Assam, half decayed tree trunks greasy with oil have been excavated.

One of the serious difficulties for those who believe in destructive distillation is an adequate source of heat. Organic matter, animal or vegetable, decomposes readily enough when exposed to the air at ordinary temperatures, but the products are very different from petroleum.

In the early development of organic chemistry, the nature of the products resulting from the destructive distillation of various forms of organic matter was recognized. Dippel's oil distilled from bones contains the nitrogen compounds pyrrol, pyridine, and their derivatives. Reichenbach[1] identified paraffine as one of the distillation-products of animal and vegetable bodies.

As already mentioned, Warren and Storer established the presence of the hydrocarbons C_nH_{2n+2}, C_nH_{2n}, and C_nH_{2n-6} as distillation-products of a lime soap prepared from menhaden oil. More recently Engler has also prepared the petroleum hydrocarbons by the distillation of menhaden oil under pressure. There can therefore be no question as to the ready formation of petroleum from animal bodies when decomposed with the agency of heat. But that the same products may be formed without the aid of high temperature is not so easily demonstrated. That any considerable elevation in tempera-

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[1] Schweigger's Journal, 61, 273.

ture has accompanied the formation of petroleum, at least in the limestones, is rendered extremely improbable by the condition of the oil rock. Sections of the Corniferous limestones from which wells drilled at Petrolia exhibit very plainly the conditions of stratification, without the slightest indication of metamorphic action. The rock consists of alternate light and dark layers, the light being much more compact than the darker strata, which are more granular, and offer greater resistance to the drill. As our analyses show, the two varieties of rock do not differ essentially in their composition. The darker portions of the strata evidently contain more oil.

Concerning the question whether petroleums can be sharply divided as to their origin, the limestone oils having their source in the decomposition of organic matter of animal origin, and other petroleums in the decomposition of vegetable matter, more experimental evidence is necessary.

The absence of nitrogenous organic bodies from petroleum has been suggested, by the adherents of vegetable matter as the source, as a serious objection to its origin in the decomposition of animal bodies. It is true that in other oils than those found in the limestones the quantities of nitrogen hitherto found are extremely small, as already explained on page 719, Vol. 17. As further evidence of the minute proportion of ntrogen in non-sulphur oils, we have determined this element in Chinese petroleum (1), in a colorless Italian petroleum (2), in Macksburg, Ohio, oil, 1,900 foot level (3), and in a peculiar light yellow Berea Grit oil, 500 foot level (4), from Archer's Fork, Ohio, that is at present refined in large quantities. The last named oil deposits paraffine when cooled to 10°.

Determination by the Kjeldahl method gave the following results :—

	Trenton Limestone Oil.	Corniferous Limestone Oils.
(1) 0.10	(1) 0.26	(1) 0.16
(2) 0.014	(2) 0.23	(2) 0.18
(3) 0.035	(3) 0.21	(3) 0.21
(4) 0.023	(4) 0.13	
	(5) 0.35	
	(6) 0.08	
	(7) 0.07	

Trenton Limestone Oil.

(8) 0.05
(9) 0.05
(10) 0.16
(11) 0.05
(12) 0.06

It is therefore evident that in general a higher percentage of nitrogen is a distinctive quality of the limestone petroleums.

As mentioned above, we now have in hand certain nitrogenous bodies extracted from Ohio petroleum which resemble derivatives of the pyridine bases. In our earlier work on the sulphur compounds in the limestone oils[1] there were indications that these petroleums contain certain ethereal oils of vegetable origin beside other oils resembling the terpenes. A question may therefore arise as to whether the limestone oils have been derived exclusively from organic matter of animal origin.

Recently Zaloziecki[2] has separated from the sulphuric acid extract of Galician oil, bodies which he concludes indicate the presence in the crude oil of the terpenes or allied substances.

On chemical grounds it seems reasonable that changes in organic bodies during long periods of time with exclusion of air, under enormous pressure, are sufficient to explain the formation of petroleum. The modifications that have been observed in various forms of chemical reactions under high pressure would seem to indicate that organic bodies should be affected quite differently than under ordinary conditions. I have in view some experiments on the behavior of organic matter under continued high pressure, fifty to one hundred tons per square inch, for the purpose of ascertaining what changes, if any, may result.

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[1] Proc. Amer. Acad., **25**, 228.

[2] Ber. d. chem. Ges., **27**, 2081.

REVIEWS.

Chemical Analysis of Oils, Fats, Waxes, and of the Commercial Products Derived Therefrom. From the German of Professor Dr. R. Benedikt. Revised and Enlarged by Dr. J. Lewkowitsch, F. I. C., F. C. S., Technical Manager at the Whitehall Soap Works, Leeds, Consulting Chemist and Chemical Engineer. Macmillan and Co.

As indicated in the title-page, this work is much more than a translation of Professor Benedikt's "*Die Analyse der Fette und Wachsarten.*" It is a thorough, and in every way admirable revision of that notable treatise. The character and scope of the translator's task as reviser are clearly expressed in the following quotations from his preface :

" In revising, I had to be guided by such experience as I have gained during many years devoted to the chemistry of fats and oils in the laboratory, as well as in the works, which it has been my lot to manage both in this country and on the continent. If this experience has led me to criticise somewhat freely, I trust I have not transgressed the limits which ought to be observed, but I consider that criticism is decidedly necessary in this branch of applied chemistry, abounding as it does with papers and communications, the contents of which can only have been new to their writers. * * * * No useful purpose would be served by pointing out at length the numerous additions that have been made and the alterations which have been found necessary ; of these every page bears evidence. It may, however, be stated briefly that obsolete processes have been abridged or entirely left out, and that the arrangement of the subject matter has been altered so as to suit practical requirements. A special feature is the tabular form adopted for the constants of the individual oils, fats and waxes. In chapters IX-XII large portions have been entirely rewritten, and differ so widely from the original, that they may be regarded as substantially new. * * * * The *enlarging* has consisted, in the first instance, in devoting more space to the work of English and American chemists than would naturally be the case in a German publication. The new work in fat-analysis published during the last four years has been embodied in the text, and all information up to the last weeks whilst the book has been in press has been included. A large number of my own experiments and observations have been extracted from my note-books and published here for the first time. Thus the bulk of the book has been almost doubled notwithstanding extensive abridgments."

H. N. M.

ANALYTICAL CHEMISTRY. By N. MENSCHUTKIN, Professor in the University of St. Petersburg. Translated from the Third German Edition, under the Supervision of the Authors, by JAMES LOCKE.

The work is divided into two parts, the first treating of qualitative, and the second of quantitative analysis. Under each of these divisions the metals are considered before the metalloids. In Part I the metals are arranged in the usual groups, and the general reactions of the group precede the special ones of the individual members. Following the latter, is presented for each group a systematic course of analysis. The rarer metals are not included in the general schemes, but are given a place in the supplements of the various groups. In the case of the metalloids the treatment is necessarily somewhat less systematic. The last section of Part I is devoted mainly to the preliminary operations in qualitative analysis and to the cautions required by the inexperienced analyst. It also contains supplements on the blowpipe, the flame reactions of Bunsen, and spectrum analysis. Part II is divided into three sections. The first treats of gravimetric analysis; the second of volumetric analysis; and the third of the analysis of organic compounds.

H. N. M.

SOLUTION AND ELECTROLYSIS. BY W. C. DAMPIER WHETHAM, M. A., Fellow of Trinity College, Cambridge. pp. 296, 8vo. Cambridge: The University Press, 1895.

This book deals, for the most part in a simple way, with the more notable properties of solutions. It has the advantage over that part of Ostwald's *Lehrbuch* which has to do with the same subject, that it is compact, that it has been written entirely at one time, and that it has not been made to conform strictly to a chronological sequence in the discussion of the development of the subject. Of course, as the author admits, the greater part of the first half of the book is taken more or less directly from the German writer's treatise; but Mr. Whetham is fortunate in that, in compressing important data into small space, he is able generally to be both concise and lucid. Recent investigations of importance are considered, and the value of the book is certainly increased by reason of the fact that it contains a statement of the results reached by Pickering, and the conclusions drawn therefrom with respect to the nature of solutions. Whatever may be the average reader's opinion of the value of these conclusions, he will be glad to see them candidly discussed.

With regard to the validity of certain of the deductions from the Second Law of Thermodynamics, the present writer does not feel himself at all competent to judge; the fact that the book belongs to a series of which Mr. Glazebrook is editor would seem to insure its general accuracy.

About one-fourth of the book consists of an appendix giving a table of the electrochemical properties of aqueous solutions, compiled by the Rev. T. C. Fitzpatrick, M. A., and reprinted from the Report of the British Association of 1893.

W. W. R.

GRUNDRISS DER ELEKTROCHEMIE. VON DR. HANS JAHN. Vienna, Alfred Hölder, pp. 311, 1895.

The author seems to be in a position with respect to the subject of electrochemistry, which would insure an impartial treatment. He was not one of the founders and has not been one of the advocates of the dissociation theory—"not an ioner,"—and comes to his work with no prejudices. He, however, lays stress on what the theory of Arrhenius has accomplished for chemistry, and calls attention to the fact that, notwithstanding this, comparatively few chemists are yet willing to abandon their distrust in physical chemical results and conclusions.

In the preface, attention is called to the great importance which rigid mathematical analysis is playing, and still more, is destined to play in theoretical chemistry. "Just as there is no physicist to-day, who does not aim to render the theoretical side of his science, more intelligible, by profound mathematical study, so most chemists likewise, gradually recognize that, without the elements of higher analysis, theoretical chemistry will be for them a closed volume. Differential and integral expressions must cease to be for chemists unintelligible hieroglyphics. These symbols must be as familiar as those of stereochemistry, or one will be in danger of losing all comprehension of the development of theoretical chemistry."

The subject is treated under the following headings:—

I. The fundamental laws of electrochemistry. II. The theory of electrolytic dissociation, and some of its important consequences. III. The transformations of energy by electrochemical processes. IV. Galvanic polarization. V. The decomposition of some of the most important chemical compounds by the current, and some applications of electrolysis.

From the above quotation from the preface it can be inferred that this volume was not designed for the beginner in physical chemistry. It is, however, well adapted to the specialist, who wishes a short, systematic account of the large amount of work, which has already been done in the field of electrochemistry. The subject is treated so extensively by Jahn that he has furnished us with a book of references up to very recent date. The name of the author is a guarantee of the excellence of the work.

H. C. J.

GRUNDZÜGE DER WISSENSCHAFTLICHEN ELEKTROCHEMIE AUF EXPERIMENTELLER BASIS. VON DR. ROBERT LÜPKE, Docent in the Imperial Post and Telegraph School in Berlin. With 46 wood cuts. Berlin; Julius Springer, pp. 150. 1895.

The recent advances, which have been made in electrochemistry have thrown light on many problems, and in particular on the origin and conduction of the current in the galvanic and analogous elements. This question, which has been involved in more or less doubt for a century, is now answered in a fairly satisfactory manner. Although there is a standard work discussing these advances; viz., Ostwald's Lehrbuch yet the author has thought it desirable to prepare a smaller treatise, dealing with the principles, underlying these latest developments.

The book consists of three parts:

I. *The New Theory of Electrolysis*, which treats of electrolysis, Faraday's law, migration-velocities of ions, Kohlrausch's law, and the dissociation theory of Arrhenius. II. *Van't Hoff's Theory of Solutions*, containing chapters on osmotic pressure, vapor-pressure of solutions, boiling-point and freezing-point of solutions, and water solutions of electrolytes. III. *The Osmotic Theory of the Current in the Voltaic Element*, discussing the liquid element, the concentration element, the Daniell element, reduction and oxidation elements, the relation between chemical and electrical energy, the solution tension of metals, polarization, the non-reversible element, and accumulators.

The size of the volume prevents it from aiming at completeness, yet omissions of a serious character are not entirely wanting; e. g., the admirable work of Smale on the gas-battery is not considered, nor is reference made to the fact that the theory of Nernst, according to which the solution-tension of metals is a constant, has been shown to be erroneous.

The book as a whole is clearly written, and it is well adapted to the needs of anyone who wishes to obtain a general idea of what has been done in this very important field of physical chemistry. H. C. J.

PRACTICAL PROOFS OF CHEMICAL LAWS. A Course of Experiments upon the Combining Proportions of the Chemical Elements. By VAUGHAN CORNISH, M. Sc., Associate of the Owens College, Manchester, London: Longmans, Green and Co., and New York, 1895. pp. 92, xii.

"These experimental proofs (or more properly *verifications*) of quantitative laws were undertaken by pupils after the qualitative composition of the principal substances employed had been carefully dealt with in the accompanying lecture course." Apparently, the author believes that the proper way to begin chemistry is to lecture on it for a time, and then give the student a few quantitative experiments to do in the laboratory, the main object of these being to verify the laws of chemistry. While, undoubtedly, some quantitative work is desirable for the beginner for the purpose of teaching him the significance of quantitative relations, it is clear that such work alone can not within a reasonable time introduce the student to a sufficient variety of phenomena. However, it is not quite clear what use the author wishes us to make of this course. Somewhere in a general course in chemistry some of these experiments would serve a good purpose. The language of the book is not always as simple as could be desired for pupils "between twelve and eighteen years." What for instance will such a pupil make of this statement of the law of equivalent proportions. "The weights of two elements which are equivalent (*i. e.*, of equal value) in any chemical reaction are equivalent in all?" This is plainly not correct. The equivalent of iron in the ferric state is not the equivalent of iron in the ferrous state. Further on, the author says: "When the student has fully grasped the meaning of the word equivalence in chemistry, which is generally not until he has had some experience of experimental work he will find the following statement useful as a summary of all the laws of chemical combination by weight. Elements combine together in the proportion (or ratio) of their equivalent weights, or in the proportion of whole multiples of their equivalent weights." The term equivalent in chemistry is difficult to define, and its use in the early part of this century gave rise to much confusion. One cannot help feeling that its free use in a book designed for beginners will furnish proof (*or verification*) of the adage "History repeats itself."

While, then, as a guide to put into the hands of beginners this book cannot be highly recommended, it is well calculated to be of service to teachers who want directions for comparatively simple quantitative experiments. I. R.

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Contribution from the Sheffield Laboratory of Yale University.

ON HALOGEN ADDITION-PRODUCTS OF THE ANILIDES.

[SECOND PAPER.]

BY H. L. WHEELER AND P. T. WALDEN.

A preliminary notice was recently given by one of us (Wheeler) on halogen addition-products of the anilides.[1] In the case of metanitroacetanilide[1] products were prepared which contained bromine in various proportions, but, under certain conditions, the total bromine approximated to that calculated for a dibromine addition-product. These products have now been thoroughly reinvestigated and it has been found that, besides free bromine, they contain hydrobromic acid, and that the products described as dibromine addition-products of metanitroacetanilide were mixtures of the perhalides $(C_6H_4.NO_2.NHCOCH_3)_2HBr.Br_2$ and $[C_6H_4.NO_2.NHCOCH_3]_2HBr.Br_4$.

We have attempted to prepare bromine addition-products of metanitroacetanilide and parabromacetanilide, in the absence of hydrobromic acid, but without success. Bromine free from hydrobromic acid can be mixed with these anilides,

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[1] This JOURNAL, 17, 612.

when suspended in pure carbon bisulphide, without any addition taking place. The unaltered anilides are recovered on filtering and drying. When, on the other hand, bromine containing hydrobromic acid or solvents which are attacked by bromine—such as chloroform, glacial acetic acid, or ligroïn—are used, perhalides are formed.

It has been found in general that when bromine is mixed with an anilide under conditions which permit of the formation of hydrobromic acid, the hydrobromic acid unites with the anilide to form an ammonium salt, *i.e.* $[R.NHCOCH_3]_2HBr$[1] and that this salt then adds bromine.

We have prepared the salts $[C_6H_4.NO_2.NHCOCH_3]_2HBr$ from metanitroacetanilide; $[C_6H_4.Br.NHCOCH_3]_2HBr$ from parabromacetanilide; and $[C_6H_5.NHCOCH_3]_2HI$ from acetanilide. These salts gave the following series of halogen addition-products:

$[C_6H_4.NO_2.NHCOCH_3]_2HBr.Br_2.$
$[C_6H_4.NO_2.NHCOCH_3]_2HBr.Br_4.$
$[C_6H_4.NO_2.NHCOCH_3]_2HBr.Br_6.$
$[C_6H_4.Br.NHCOCH_3]_2HBr.Br_2.$
$[C_6H_4.Br.NHCOCH_3]_2HBr.Br_4.$
$[C_6H_5.NHCOCH_3]_2HI.I_2.$
$[C_6H_5.NHCOCH_3]_2HI.I_4.$

These compounds are perfectly analogous to the perhalides $CsBr.Br_2$[2], $CsI.I_4$[3], and $NH_4Br.Br_2$[4]. No perhalides of the salts of the anilides have hitherto been described, but perhalides of other organic halides have frequently been observed, of which the following are examples: $C_6H_6N.N$—$Br.Br_2$;[5] $[C_9H_7N]_2HBr.Br_4$[6]; $C_6H_5(CH_3)_3NI.I_2$; $C_6H_6(CH_3)_3$-$NI.I_4$; and $C_6H_5.C_2H_6(CH_3)_2NI.I_6$.[7]

Method of Analysis.—In order to determine total bromine the weighed sample was treated with dilute ammonia, and in no case were the products analyzed which did not give the un-

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[1] Compare Nölting and Weingärtner: Ber. d. chem. Ges., **18**, 1340; also Roozeboom: Chem. Centrbl, **1886**, 498.

[2] Wells: Am. J. Sci., **43**, 27.

[3] Wells and Wheeler: *Ibid*, **44**, 43.

[4] Roozeboom: Ber. d. chem. Ges., **14**, 2398.

[5] Hantzsch: Ber. d. chem. Ges., **28**, 2754.

[6] Grimaux: Bull. Soc. Chim. (Paris), **38**, 127.

[7] Geuther: Ann. Chem. (Liebig), **240**, 66.

altered anilide with a correct melting-point. The solutions were then acidified with nitric acid and the bromine determined by means of Volhard's[1] volumetric method. In another sample free bromine was determined by weighing the substance into a solution of potassium iodide and then titrating the liberated iodine with a tenth-normal sodium thiosulphate solution. From the difference the hydrobromic acid was calculated. Total iodine was also determined by Volhard's method, the free iodine having been converted into hydriodic acid by means of a solution of sodium arsenate in sodium bicarbonate. Free iodine was determined in a separate sample by means of the sodium thiosulphate solution, and the hydrogen iodide by difference.

Experiments with Metanitroacetanilide.

The 1 : 1 *hydrobromide*, $C_6H_4.NO_2.NHCOCH_3.HBr$, was obtained as a colorless crystalline precipitate when hydrobromic acid gas was led into a chloroform solution of the anilide. It was dried on paper in the air.

	Found.		Calculated for
	I.	II.	$C_8H_8N_2O_3.HBr$.
HBr	30.5	30.8	30.9

The 2 : 1 *hydrobromide*, $[C_6H_4.NO_2.NHCOCH_3]_2.HBr$.—This and the preceding salt were described in the preliminary paper.[2] It seems to be formed when the 1 : 1 salt is treated with glacial acetic acid since perhalides of this salt were invariably obtained when bromine was added to the 1 : 1 salt in the presence of glacial acetic acid.

The *trihalide*, $[C_6H_4.NO_2.NHCOCH_3]_2.HBr.Br_2$. — 2.5 grams of the 1 : 1 hydrobromide were covered with 25 grams of glacial acetic acid (containing some hydrobromic acid) and 3 grams of bromine added. On warming gently, filtering and cooling, beautiful light orange-colored flattened prisms separated. These were washed with chloroform and dried by pressing on filter-paper.

	Found.	Calculated for $C_{16}H_{16}N_4O_6.HBr.Br_2$.
Br (total)	39.2	39.9
Br (free)	26.2	26.6
HBr	13.1	13.4

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[1] Ann. Chem. (Liebig), 190, 1.

[2] *Loc. cit.*

The *pentahalide*, $[C_6H_4.NO_2.NHCOCH_3]_2.HBr.Br_4$, was prepared by suspending the 1 : 1 hydrobromic-acid salt in chloroform and adding bromine in the proportion of 1 molecule of the salt to about 12 atoms of bromine. Solution was effected by warming and adding small quantities of glacial acetic acid. On filtering and cooling, deep orange-colored prisms separated [Analysis I]. This compound was also obtained when 3.5 grams of the 1 : 1 salt were mixed with 11 grams of bromine in 13.8 grams of glacial acetic acid containing a little hydrobromic acid gas [Analysis II].

The crystals that separated from the solution were washed with chloroform containing a little bromine. The material for analysis was dried on paper as rapidly as possible.

	Found.		Calculated for
	I.	II.	$C_{16}H_{16}N_4O_6.HBr.Br_4$.
Br (total)	52.7	51.2	52.5
Br (free)	42.6	40.4	42.0
HBr	10.2	10.8	10.6

The *heptahalide*, $(C_6H_4.NO_2.NHCOCH_3)_2.HBr.Br_6$, was obtained by suspending 3.5 grams of the 1 : 1 hydrobromic-acid salt in 7.8 grams of cold glacial acetic acid (containing hydrobromic acid) ; to this 58.8 grams of bromine were then added and the whole warmed to a blood heat. On cooling to —10° long brick-red needles separated. These were washed free from glacial acetic acid by means of bromine which had been cooled to —10°. The material was drained on the pump, then on a porous plate, and finally pressed on paper [Analysis I]. A portion was exposed somewhat longer than I. to the air [Analysis II].

	Found.		Calculated for
	I.	II	$C_{16}H_{16}N_4O_6.HBr.Br_6$.
Br (total)	61.0	61.3	60.8
Br (free)	53.5	53.0	52.1
HBr	7.5	8.4	8.8

Experiments with Parabromacetanilide.

The 2 : 1 *hydrobromide*, $(C_6H_4.Br.NHCOCH_3)_2.HBr$. — This and not the 1 : 1 salt was obtained when a chloroform solution of the anilide was treated with hydrobromic acid gas. It consisted of colorless needles.

	Found.		Calculated for
	I.	II.	$C_{16}H_{16}N_2O_2Br_2.HBr$.
HBr	15.4	15.9	15.9

The *trihalide*, $(C_6H_4.Br.NHCOCH_3)_2.HBr.Br_2$, was obtained by adding ligroïn to a solution of the above hydrobromic-acid salt in a mixture of ethyl acetate, chloroform, and bromine. The precipitate thus produced was crystallized from chloroform containing some glacial acetic acid. Beautiful, flattened, light-orange colored prisms separated.

	Found.	Calculated for $C_{16}H_{16}N_2O_2Br_2.HBr.Br_2$.
Br (total)	35.8	35.9
Br (free)	24.9	23.9
HBr	10.9	12.1

The *pentahalide*, $(C_6H_4.Br.NHCOCH_3)_2HBr.Br_4$, was obtained by suspending the salt in chloroform, adding a large excess of bromine, and then warming with the addition of small quantities of glacial acetic acid until the whole dissolved. On cooling, small flattened crystals separated. These had a deep orange color.

	Found.		Calculated for
	I.	II.	$C_{16}H_{16}N_2O_2Br_2.HBr\ Br_4$.
Br (total)	46.2	47.5	48.2
Br (free)	36.3	36.3	38.6
HBr	9.8	11.3	9.7

Experiments with Acetanilide.

The 2:1 *hydroiodide*, $(C_6H_5.NHCOCH_3)_2.HI$, separated from a solution of acetanilide in ethyl acetate in the form of shining colorless scales, when hydrogen iodide was led into the solution.

	Found.	Calculated for $C_{16}H_{18}N_2O_2.HI$.
HI	32.2	32.1

The *trihalide*, $(C_6H_5.NHCOCH_3)_2.HI.I_2$.—A solution of 4.1 grams of the above salt, with 2.6 grams iodine in 15 grams of glacial acetic acid deposited ruby-red crystals. These were analyzed with the following result:

	Found.	Calculated for $C_{16}H_{16}N_2O_2.HI.I_2$.
I (total)	58.0	58.4
I (free)	39.0	38.9
HI	19.1	19.6

The *pentahalide*, $(C_6H_5.NHCOCH_3)_2.HI.I_4$, was obtained from a glacial acetic-acid solution of the constituents. It forms glistening prisms of a deep reddish-brown color with the lustre of iodine. They transmit a deep red-brown light.

	Found.	Calculated for $C_{16}H_{16}N_2O_2.HI.I_4$.
I (total)	70.1	70.0
I (free)	57.4	56.0
HI	12.8	14.1

THE ACTION OF THE HALOGENS ON THE METHYLAMINES.

By Ira Remsen and James F. Norris.

In the course of an investigation of the double halides of selenium and the aliphatic amines, the results of which will be published later, a salt of the composition represented by the formula $SeBr_4.SeOBr_2.2(CH_3)_3N.HBr$, was brought to light. This was treated with bromine in order, if possible, to convert it into the salt of the composition $SeBr_4.(CH_3)_3N.HBr$. A crystalline precipitate was obtained, which proved to be something quite different from what was expected. The product dissolved in water with evolution of bromine, and was found not to contain selenium. This led to experiments with trimethylamine and bromine, and afterward, to experiments with the other halogens and other substituted ammonias. At first trimethylamine hydrobromide was treated with bromine, and a compound obtained that contained one more atom of bromine than the hydrobromide. The formula $(CH_3)_3N.HBr.Br$, with which the analytical results are in close agreement, appears highly improbable, and it was suspected that the composition should be represented by the formula $(CH_3)_3N.Br_2$, its formation being due to the substitution of bromine for the hydrogen of the hydrobromide. If this view is correct, the same product should be formed by the direct addition of bromine to trimethylamine. This formation was found to take place, and further experiments showed that this kind of addition can be effected in other similar cases. The following is an account of the work as far as it has been carried. It will be continued in the immediate future.

Historical.—The action of the halogens on the aliphatic amines has frequently been the subject of investigations.

Wurtz,[1] the discoverer of these amines, worked in water solution, and obtained products which he supposed to be formed by substitution of halogen atoms for hydrogen. Thus methylamine gave a dichloro-substitution product, which he believed to have been the constitution CH_3NCl_2. Ethylamine gave a similar product. Raschig[2] obtained a compound of the formula $(CH_3)_2HN.Br_3.2H_2O$, by treating a water solution of dimethylamine with bromine. By working in alkaline solutions other experimenters have obtained products similar to those discovered by Wurtz. Thus Raschig[3] obtained the compounds CH_3NI_2 and $(CH_3)_2NI$. Later Berg[4] and Séliwanow[5] prepared other halogen derivatives of the substituted ammonias, all of them being similar to those prepared by Wurtz and, therefore, quite different from those discovered by us.

A compound of ammonia with iodine perfectly analogous to those obtained by us has been prepared by Seamon[6] by passing dry ammonia over powdered iodine. The product, which was a dark-colored liquid, was shown to have the composition NH_3I_2. This was also prepared by Guthrie[7] by treating ammonium nitrate with potassium hydroxide and iodine.

Action of Bromine on Trimethylamine.

Trimethylamine, liberated from the chloride by potassium hydroxide and dried by sodium hydroxide, was conducted into a Peligot tube containing bromine cooled with ice-water. As the gas was absorbed a yellow precipitate separated. This was dried on a porous plate, and the last traces of free bromine removed by allowing the salt to stand over potassium hydroxide in a desiccator. It proved to be identical with the product formed by the action of bromine on trimethylamine hydrobromide. The latter method is the more convenient. To trimethylamine hydrobromide just enough concentrated hydrobromic acid is added to dissolve it when heated. Bromine, in the proportion 1 molecule to 1 molecule of the salt,

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[1] Ann. chim. phys. [3], **30**, 454.

[2] Ber. d. chem. Ges., **18**, 2249.

[3] Ann. Chem. (Liebig), **230**, 221.

[4] Comptes rendus, **90**, 862; and "Thèses présentées a la Faculté des Sciences de Paris pour obtenir le grade de Docteur ès Sciences physiques." Paris, 1894.

[5] Ber. d. chem. Ges., **25**, 3621.

[6] Chem. News, **44**, 188.

[7] J. chem. Soc. (London), 1863, 239.

is then added and the solution heated. On cooling, the product crystallizes out in light yellow plates. These can be recrystallized from absolute alcohol when they appear in the form of stout prismatic needles. Water alone instantly decomposes the salt with the liberation of half of the bromine. It is insoluble in ether. Analysis of the precipitate first obtained gave the following results:

I. 0.2530 gram salt gave off 0.0921 gram Br when dissolved in water.

II. 0.2443 gram salt gave 0.1781 gram Br after reduction of the free bromine by sulphur dioxide.

	Calculated for $(CH_3)_3NBr_2$.	Found.	
		I.	II.
1 Atom Br	36.53	36.40	....
Total Br	73.06	....	72.90

The salt prepared by treating trimethylamine hydrobromide with bromine was analyzed:

0.2289 gram salt gave 0.1665 gram Br.

Total Br	73.06	Found	72.72

Action of Iodine on Trimethylamine.

Trimethylamine was passed into a solution of iodine in absolute alcohol, and in a short time a yellow precipitate appeared. This was filtered off and washed with absolute alcohol, then dried in a desiccator and analyzed. The properties of the iodide are different from those of the bromide. While the latter is decomposed by simple contact with water, the former is almost insoluble. To effect solution the water must be heated, when decomposition takes place slowly with liberation of iodine. Further, cold alcohol readily dissolves the bromide. Heat is necessary in the case of the iodide, and this causes partial decomposition. In the analysis of the compound the weighed portion was heated in a pressure bottle on a water-bath until the salt was completely decomposed. The total iodine was determined in one sample by reducing the free iodine with sulphur dioxide. The liberated iodine in another was dissolved in potassium iodide and titrated with sodium thiosulphate. The results of the analyses are here given:

I. 0.2820 gram salt gave 0.2293 gram I.
II. 0.3138 " " " 0.1455 " free I.

	Calculated for $(CH_3)_3NI_2$.	Found. I.	II.
Total I	81.09	81.31	....
One Atom I	40.54	....	46.36

From the last analysis it is evident that the decomposition with water is different from that which the bromide undergoes. The amount of iodine set free is considerably more than one atom. This points to the formation of free hydriodic acid, for it was found that dilute acids liberate all of the iodine from the compound. The normal action would be the giving off of one atom of the iodine, but if hydriodic acid is set free at the same time, it would act upon a part of the compound and liberate two atoms of iodine for each molecule of the acid. The iodide when first prepared is of a light yellow color. It gradually darkens and changes to a dark brown viscous liquid. A portion of the salt was treated with dilute hydrochloric acid. There was immediate decomposition with liberation of iodine. This was titrated with sodium thiosulphate with the following result:

0.5319 gram salt gave 0.4287 gram I.

Iodine found 80.60. Theory 81.09.

Action of Chlorine on Trimethylamine.

Dry trimethylamine and dry chlorine were passed into a tall cylinder, the contents being protected from the air. In the first experiment, when there was an excess of trimethylamine, a white solid was formed. When this was removed it was found to be very hygroscopic. It had a strong odor of chlorine. It has not yet been possible to analyze it, but its conduct suggests that it is analogous to the products formed with bromine and with iodine. It is very easily decomposed by the action of moist air. Contact with water destroys the bromide. The iodide is decomposed by boiling water. In a second experiment there was for a time by mistake an excess of chloride. Under these circumstances the trimethylamine on entering the cylinder burned with a brilliant flame, and soot was deposited, showing a complete breaking down of the compound.

Action of Bromine on Dimethylamine.

Dimethylamine was found to take up two atoms of bromine in the same way as trimethylamine. The same product is formed by treating dimethylamine hydrobromide with bromine. Its properties are similar to those of the analogous compound obtained from trimethylamine. The results of the analyses are given below. In analyses I and II the compound formed by the action of bromine on the amine was used. In analyses III and IV that prepared by the action of bromine on dimethylamine hydrobromide was used :

I. 0.2392 gram salt gave 0.1875 gram total Br.
II. 0.2951 " " " 0.1147 " free Br.
III. 0.1989 " " " 0.1557 " total Br.
IV. 0.2351 " " " 0.0918 " free Br.

	Calculated for $(CH_3)_2HNBr_2$.	Found.			
		I.	II.	III.	IV.
1 Atom Br	39.02	....	38.87	....	39.10
Total Br	78.04	78.38	....	78.23	....

Compounds Containing Two Different Halogen Atoms.

When the chloride of either dimethyl- or trimethylamine is treated with bromine a compound is formed containing both bromine and chlorine. It is probable that there is here also a substitution of bromine for halogen which, in the case of dimethylamine, would give the compound $(CH_3)_2HN.BrCl$. The reaction does not appear to be as clean as when bromine acts upon the bromides. An analysis was made of the product formed from dimethylamine hydrochloride, and, though the results were not satisfactory, they pointed to the formula above given.

The chlorides and bromides of both dimethyl- and trimethylamine react with iodine, forming compounds which give up their iodine in contact with water.

Action of Bromine and Iodine on Methylamine.

Methylamine hydrobromide was treated with bromine in the manner described in the case of trimethylamine. There was apparently no action. When the salt was freed from the excess of free bromine, it was found to be the unchanged hydrobromide. When free methylamine was conducted into bromine there was a rise in temperature and a solid substance was formed. When an attempt was made to filter off this compound, there was a slight evolution of gas. The compound proved to be methylamine hydrobromide, which must have been a secondary product.

The amine was passed into an alcoholic solution of iodine. No precipitate was formed. Evidently methylamine forms addition-products with the halogens with much greater difficulty than dimethyl- or trimethylamine.

The results above described show the existence of well characterized halogen addition-products of some of the substituted ammonias. The investigation has been temporarily interrupted, but, as already stated, it will be taken up in the near future.

ON SILICIDES.

(*Preliminary Note.*)

By G. de Chalmot.

Copper Silicide.—If a mixture of sand and charcoal is heated in an electric furnace in the presence of copper, silicides of copper are readily obtained. If an excess of sand and charcoal is used, a crystallized silicide can be obtained, which has probably the formula Cu_2Si_3. I have not thus far obtained entirely pure crystals, and have not found any means of purifying them. The purest specimen gave the following results :

	Calculated for Cu_2Si_3.	Found.
Cu	60.08	60.30
Si	39.92	38.62–38.82
Fe		0.64

The iron originated from the sand which had been used.

The silicide crystals are flat and of a brilliant bluish-white metallic appearance. The specific gravity of the impure crystals was 4.25. This silicide is much softer than iron or silver silicide. It does not scratch glass and can easily be pulverized. The crystals are attacked by *aqua regia*. A part of the copper is then dissolved and silica is formed. The crystals are readily decomposed by a mixture of potassium and sodium carbonate and potassium nitrate.

If a mixture of silica, carbon, and lime (or any other flux) is subjected to a direct electric current of high amperage (240) and low voltage (20–30) and the cathode is made up of copper, a still larger percentage of silicon can be united with the copper. The mixture of sand, lime, and charcoal becomes liquid and is electrolyzed. I obtained in this way an alloy with 51.51 per cent. of silicon and 43.52 per cent. of copper. Larger amounts of calcium were also present.

Silicide of Silver.—By subjecting a mixture of sand, charcoal, lime, and pieces of silver to a current of 240 amperes and 25 volts I obtained a silicide of silver which, however, contains some calcium. This silicide is hard enough to scratch glass and rather tough. The color is grey. It is apparently homogeneous and crystalline. By boiling it with nitric acid ($1HNO_3 + 2H_2O$) for seventy-five minutes only a part of the silver was dissolved, and silica was formed at the same time. I therefore assume that the silicon and the silver are not simply mixed, but have entered into chemical union. This fact is of importance in so far as Moissan states[1] that silicon does not combine with silver, but is dissolved by it, and separates out when the mixture cools. In Moissan's experiments electrolysis was, however, excluded. My results agree with those of Warren.[2]

SPRAY, N. C., Dec. 7, 1895.

Contribution from the Laboratory of the University of California.

SOME OF THE PROPERTIES OF LIQUID HYDRIODIC ACID.

BY R. S. NORRIS AND F. G. COTTRELL.

In the first published account of the preparation of liquid hydriodic acid, it is described[3] as a yellowish liquid resembling liquid chlorine. The author prepared it by the action of sulphuretted hydrogen, iodine and water upon one another under strong pressure. Hydrogen persulphide, iodine and water were placed in separate bends in a stout glass tube

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[1] Compt. rend, **121**, 625.

[2] Dammer's Handbuch für Anorg. Chemie, **2**, 825.

[3] Kemp: Phil. Mag., 3rd Series, (1835), **7**, 444.

which was then sealed. When the hydrogen persulphide decomposed, the hydrogen sulphide which was formed acted upon the iodine, and the water was added to the product. The pressure exerted by the hydriodic acid formed under these conditions was enough to liquify it. None of its chemical properties were determined.

Faraday prepared it ten years later, in 1845, by subjecting gaseous hydriodic acid to the low temperature produced by solid carbonic acid.[1] He found that it attacked "hair, fat, and even the copper and mercury of the apparatus," and solidified at —51° C. to a clear colorless solid. No further determinations of its properties were made.

This is practically all the work that had been done on the liquid acid when we took up the investigation. What we have attempted to do is to determine its action upon some of the more common inorganic substances. We obtained the liquid hydriodic acid by the condensation of gaseous hydriodic acid by means of solid carbonic acid. The method of preparation of the gaseous hydriodic acid which we used was selected in preference to those generally described, on account of its easy manipulation and the small amount of water that came off with the acid. Since it might be used to good advantage for other purposes where an anhydrous acid is wanted, we will describe it in detail. Two grams of *dry* red phosphorus were placed in a quarter liter flask provided with a delivery tube. Twenty-four grams of iodine were then added gradually while the flask was gently warmed and shaken. The phosphorus triiodide thus formed was allowed to solidify, and when ready for use, ten cubic centimeters of water added to it. The reaction sometimes began on the addition of the water, but it was generally necessary to apply heat to start it, and to obtain all of the hydriodic acid from the solution quite a high heat was necessary. By properly regulating the heat it was possible to obtain the hydriodic acid free from iodine.

The hydriodic acid prepared in this manner was passed through a tube containing phosphorus pentoxide, then

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[1] Faraday: Ann. Chim. Phys., 3rd Series, (1845), **15**, 257; and Ann. Chem. (Liebig), **56**, 154.

through a glass stoppered U-tube surrounded with ice to partially cool the gas, and then into the collecting tube, which was surrounded with solid carbon dioxide. The latter was obtained by holding a piece of flannel cloth over a tube connected with the nozzle of an inverted cylinder of liquid carbon dioxide and turning on the stop-cock. The tube in which the liquid hydriodic acid was to be collected was surrounded with the carbon dioxide thus obtained, which in turn was surrounded with several thicknesses of the woolen cloth. Under these conditions the carbon dioxide evaporated quite slowly.

In the first experiments the hydriodic acid was collected in glass tubes, which were sealed after the substance to be tested had been added. But it was found impossible to prevent the formation of a large amount of free iodine in the upper part of the tube in attempting to seal it off, and this altered the conditions of the experiments a great deal in some cases. We therefore discarded this arrangement and substituted tubes closed at one end, and furnished with ground glass stoppers. The hydriodic acid was collected in these in the same manner, the substance added and the tube closed with the stopper previously coated with vaseline. The tube was then removed from the carbon dioxide and placed in a wooden clamp, which held the stopper in place. By this means the liquid hydriodic acid could be kept at the ordinary temperature of the room for 2 to 3 hours before it all escaped.

The hydriodic acid which we obtained in this manner was a colorless limpid liquid, freezing to an ice-like solid of greater density than the liquid. The yellow color of the liquid hydriodic acid which Kemp described was due to some impurity, as out of over twenty samples of the acid which we prepared, using care to prevent the formation of free iodine, none of them had the slightest color. Sunlight decomposes it quite rapidly, setting iodine free, which dissolves in the liquid forming a reddish purple solution resembling the solution of iodine in carbon bisulphide. When such a solution is cooled down the purple color gradually fades until the liquid solidifies, when a light brown color appears, due probably to the solid iodine which has separated out. The action of sunlight becomes less as the amount of free iodine in the solution increases. The prolonged action of sunlight was shown by the following experiment. A thin glass tube about 3 mm. in diameter was two-thirds filled with liquid hydriodic acid and sealed. It was placed in such a position that the sun could shine upon it about eight hours a day. The color of the solution became gradually deeper, and in about two weeks crystals of iodine began to separate out of the solution as it cooled during the night. When warm there were two distinct layers in the solution, the darker one beneath. At the end of two months the iodine that had separated out occupied about one-third of the whole volume. During the third month of exposure the tube disappeared, and we are unable to state what the final action of sunlight is, whether or not a state of equilibrium, due to the pressure of free hydrogen and to the amount of iodine present, would finally be established when no more decomposition would take place.

Action on the Metals.

In experiments with the metals care was taken to obtain the hydriodic acid as free from iodine and water as possible, and to use only the purest metals that we could obtain.

Silver.—The action on silver was quite rapid with the evolution of hydrogen and the formation of silver iodide, which dissolved slightly in the hydriodic acid.

Mercury.—A globule of mercury dissolved quite rapidly with evolution of hydrogen and formation of mercurous and mercuric iodides, as shown by the color. The former showed a slight crystalline structure, indicating that it had dissolved in the acid.

Lead.—The surface of a small piece of lead became dull, but further than this no action was noticed.

Copper.—Metallic copper dissolved slowly with the liberation of hydrogen and the formation of a crust of cuprous iodide on the surface of the metal. This experiment was one of the first made, where sealed tubes were used, and consequently there was free iodine present in the acid to start with. But the iodine was entirely removed by the copper, leaving a colorless solution.

Bismuth.—There was no apparent action on bismuth aside from the formation of a very slight red film on the surface of the metal.

Cadmium.—The only action on metallic cadmium was the formation of a slight tarnish on the surface of the metal, probably due to a small amount of free iodine dissolved in the hydriodic acid.

Tin.—There was no action on tin until the temperature of the solution rose to about 0° C. Above that temperature the action was rapid, but ceased again when the temperature was lowered. The metal dissolved completely with the formation of a yellow solution, from which crystals of stannous iodide deposited on the evaporation of the hydriodic acid. The crystals were difficultly soluble in water.

Arsenic.—There was no evolution of hydrogen from metallic arsenic, but the acid became yellow and left a crystalline deposit on evaporation. The surface of the metal did not tarnish.

Antimony.—In contact with metallic antimony the acid quickly assumed a reddish color and the surface of the metal became coated with a film. There was no evolution of hydrogen, but a slight reddish crystalline precipitate was deposited on the evaporation of the hydriodic acid. This fact can only be explained by the presence of some impurity in either the metal or the acid. It was probably due to a slight amount of the oxide with the metal and a trace of free iodine in the acid.

Iron.—Iron dissolved quite rapidly, forming a dark solution. A greenish black residue was left on the evaporation of the acid.

Aluminium.—Aluminium dissolved rapidly with a copious evolution of hydrogen. As the hydriodic acid evaporated crystals of aluminium iodide were deposited. When a drop of water was added to the crystals they were decomposed with a hissing sound, and evolution of heat, an insoluble grayish residue being left.

Zinc.—A thin gray film, slightly crystalline, was formed on the surface of a small piece of zinc, soon after it came in contact with the acid. But after remaining in the hydriodic acid for several days in a sealed tube, no further action was found to have taken place. In contrast to the action of copper under the same conditions the zinc did not remove the free iodine from the solution.

Magnesium.—The acid had no effect on a piece of magnesium ribbon.

Sodium.—The action of the liquid acid on metallic sodium was rather slow at about the freezing-point of the former, but became very rapid as the temperature rose.

Potassium.—The action on potassium was more violent than on sodium. The metal was attacked very rapidly even at the melting-point of the hydriodic acid.

Boron and Silicon.—There was no apparent action on boron or on crystalline or amorphous silicon.

Thallium.—A yellowish film formed on the surface of a particle of metallic thallium, but otherwise there was no action.

Metallic Oxides.

Cupric Oxide.—Cupric oxide dissolved quickly with the liberation of iodine according to the following equation:

$$2CuO + 4HI = 2CuI_2 + 2H_2O$$
$$2CuI_2 = Cu_2I_2 + I_2.$$

Manganese Dioxide.—The action on manganese dioxide was rapid, iodine being liberated in abundance.

Carbonates.—Neither calcium carbonate nor dry sodium carbonate was acted upon in the slightest degree.

Non-Metallic Substances.

Sulphur.—A small piece of stick sulphur floated on the surface of the acid and gradually dissolved. As the experiment progressed, iodine was liberated, hydrogen sulphide being formed at the same time.

Carbon Disulphide.—The acid formed a homogeneous solution, but there was no further apparent reaction between them.

Water.—Water and liquid hydriodic acid do not mix, even when shaken together. A drop of water, when shaken with the acid, acted the same way as a drop of oil shaken with water, *i. e.*, it broke up into globules, which rose to the surface.

Gases (Liquefied).

In these experiments small, sealed, thin glass tubes containing the various gases in liquid form were dropped into the tubes of liquid hydriodic acid, and the latter then placed in the clamp and shaken until the inner tube was broken. This was the most practicable means that suggested itself for bringing the two substances together in a liquid state at ordinary temperatures, although it had this disadvantage,—the intermediate reactions could not usually be seen on account of the rapidity and violence of the action.

Chlorine.—We were especially fortunate in the experiment with chlorine, a small hole being formed in the tube, which allowed the action to proceed slowly. Iodine was set free as soon as the chlorine came in contact with the acid. Some of the iodine penetrated into the chlorine tube, producing a yellow precipitate of iodine trichloride. As the chlorine issued from the tube it formed a yellow cloud, which, as the action became more energetic, burst into a flame. This increased the violence of the action so much that it caused the outer tube to explode.

Cyanogen.—When the tube containing the liquid cyanogen was broken, the two substances immediately combined with the liberation of iodine, formation of hydrocyanic acid, and of a flocculent precipitate. The latter was deposited as a reddish brown residue upon the evaporation of the hydriodic acid. We did not determine its composition.

Sulphur Dioxide.—Liquid sulphur dioxide reacted with the hydriodic acid setting free sulphur and iodine, and forming sulphuretted hydrogen. The sulphur was deposited in the form of a thin sheet of *yellow* plastic sulphur on the surface of the solution. When removed from the tube it gradually changed into the ordinary brittle form. The presence of hydrogen sulphide was easily detected by its odor upon opening the tube. Three experiments gave similar results. The probable reaction may be represented by the following equation:

$$10HI + 2SO_2 = 4H_2O + H_2S + 5I_2 + S_2.$$

Ammonia.—With liquid ammonia the reaction was violent and accompanied with a considerable rise of temperature. The two substances combined directly to form ammonium iodide.

Two experiments were made, with alcohol and ether respectively, which suggest some very interesting results to be obtained in the field of organic chemistry. Absolute alcohol and ether were each mixed with the liquefied acid. They both combined without any visible reaction to form a syrupy liquid, which separated into two layers, consisting of an aqueous solution of hydriodic acid and ethyl iodide respectively. The reactions may be represented thus:

$$C_2H_5OH + HI = C_2H_5I + H_2O;$$
$$(C_2H_5)_2O + 2HI = 2C_2H_5I + H_2O.$$

Some interesting points are brought out in regard to the difference between the properties of hydriodic and hydrochloric acid, by comparing the results of these experiments with those of similar experiments performed by Gore[1] with hydrochloric acid. There is this difference to be noted, however, in the two sets of experiments,—the above experiments have to do with *liquid* hydriodic acid alone, while in those of Gore on hydrochloric acid the action was generally an intermittent action of the liquid and gaseous acid; and there is no doubt that in some cases this altered the results of the experiments considerably.

None of the metals, except aluminium, were dissolved by liquid hydrochloric acid, and where there was any action it was probably due to the gaseous acid. Even sodium and potassium did not set hydrogen free from the liquid acid, but it is suggested by the author that the two metals may have been entirely converted into the chlorides by the gas before coming in contact with the liquid acid.

In opposition to this we find that liquid hydriodic acid acted upon half of the metals experimented with. Silver, mercury, copper, tin, iron, aluminium, sodium and potassium were attacked. Lead, bismuth, cadmium, arsenic, antimony, zinc, magnesium and thallium were unacted upon. These same metals, excepting mercury, were the ones used by Gore with the results mentioned.

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[1] Phil. Mag. [4], **29**, 541.

Copper oxide and manganese dioxide were not dissolved by liquid hydrochloric acid; whereas they were both attacked by liquid hydriodic acid with the liberation of iodine.

There was no action on calcium carbonate (marble) by either of the acids; and, although sodium carbonate was converted into sodium chloride by the hydrochloric acid, this action was probably due to the hydrochloric acid gas, as no gas was liberated from the carbonate in contact with the liquid hydrochloric acid.

Sulphur was not attacked by liquid hydrochloric acid, but was dissolved by liquid hydriodic acid. Iodine was dissolved by both of them, forming a purple-red solution.

Comparing the action of liquid hydriodic acid with that of the gaseous form and its solution in water, the following points of difference are to be noted. Most of the metals are dissolved by the aqueous solution of hydriodic acid; among them lead, zinc and magnesium, which are not attacked by liquid hydriodic acid. Cyanogen forms with an aqueous solution of hydriodic acid, ethane, ammonia and oxalic acid,[1] and when the same solution is heated glycocol is formed.[2]

$$(CN)_2 + 5HI + 2H_2O = CH_2NH_2COOH + NH_4I + 2I_2.$$

The action is also complicated in the case of the liquid acid, but probably quite different from the above. Sulphur dioxide and hydriodic acid in the gaseous form and dry do not react,[3] but in solution[4] the action is similar to that which takes place between the two substances in liquid form, hydrogen sulphide, water, iodine, and probably sulphur iodide being formed.

The most striking points brought out by the experiments are the action of the acid on sulphur and its inertness toward the carbonates. The explanation which immediately suggests itself for the latter peculiarity is the want of contact between the two substances, or the formation of an impervious layer of carbon dioxide or of the iodide on the surface of the carbonate; but this is certainly untenable in the case of the similar action of liquid hydrochloric acid, or rather lack of action, on a *porous* piece of lime, as determined by Gore, so it

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[1] Berthelot, Jsb., 1867, 347.

[2] Emmerling: Ber. d. chem. Ges., **6**, 1351.

[3] Soubeiran: J. Pharm., **13**, 421.

[4] Dammer: Anorg. Chem.

is at least a doubtful explanation in the case of the carbonates.

The conclusions to be drawn from the experiments and the comparisons which follow are that liquid hydriodic acid is in general more inert than gaseous hydriodic acid or its solution in water, and that it is less stable and more active than hydrochloric acid in the same form.

ON THE PREPARATION OF HYDROBROMIC AND HYDRIODIC ACID.

BY J. H. KASTLE AND J. H. BULLOCK.

It is doubtful if any of the methods proposed for the preparation of these two acids have ever come into general use. That such is the case is shown by the fact that the whole treatment of the chemistry of these two acids is quite brief in even the better text-books and treatises on chemistry. And yet it is just by the aid of these compounds that the greatest knowledge can be gained concerning the chemistry of the halogen family; and it is through the study of these hydrogen compounds that we can make the most satisfactory comparison of chlorine, bromine, and iodine. If, for example, it can actually be shown the student, in the case of hydrochloric and hydriodic acids, that both of these substances are heavy colorless gases, which fume in the air, have powerful acid odors and dissolve in water with great readiness, forming strongly acid solutions, one of which remains unaltered under ordinary conditions—the other changing; and, further, that one of these compounds cannot be decomposed by heat alone, whereas the other can with the greatest ease; that one is readily attacked by oxidizing agents, the other not:—if these phenomena can actually be brought before the student, it is more than likely that he will have some clear conceptions as to the real resemblances and differences existing between chlorine and iodine. On the other hand, if he is shown a great deal about hydrochloric acid and little or nothing about the corresponding iodine compound, as is usually the case, he will probably quit the subject with no clear conceptions as to the nature of the latter compound; and in some instances he may even be troubled with doubts as to its existence. And, further, if attractive and brilliant experiments are possible at all they are possible with just such unstable compounds as these.

Realizing the importance of having these unstable halogen acids at their disposal chemists have made quite a number of attempts to devise satisfactory methods for their preparation. Of the many methods which have been proposed for the preparation of hydrobromic acid, two are certainly worthy of notice as yielding good results. One of these, described by Erdmann,[1] consists in bringing bromine slowly into benzene containing a little ferrous bromide, and purifying the resulting hydrobromic acid gas by passing it through a tube containing ferric bromide and finally through one containing anthracene. The other method, that of Champion and Pellet,[2] consists in leading bromine into paraffin heated to 185° C.

It is believed, however, that the method herein proposed for making hydrobromic acid is simpler and better than either of the above for these reasons: First, the materials used are easy to obtain; secondly, no brominating agent is necessary; and thirdly, the formation of the hydrobromic acid gas proceeds regularly, smoothly, and rapidly without the aid of heat, and with little or no attention after the flow of bromine has been once regulated.

Of the methods proposed for the preparation of hydriodic acid, that involving the use of red phosphorus, iodine, and water seems to have come into most general use. The objection to this method is that, unless great precautions are taken in the beginning, explosions are liable to occur. Hence, it is believed that the method here recommended for the preparation of this acid has advantages over the old method involving the use of red phosphorus, for the reason that no precautions whatever need be taken in preparing the acid rapidly by the process here described.

Preparation of Hydrobromic Acid.

The method here proposed for the preparation of this acid takes advantage of the reaction between bromine and naphthalene. Any one who has ever had occasion to bring these two sub-

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[1] Anleitung zur Darstellung chemischer Präparate: Erdmann.

[2] Compt. rend., 70, 620.

stances together has doubtless remarked the great ease with which they react upon each other. When brought together even at ordinary temperatures, torrents of hydrobromic acid gas are evolved. Therefore it occurred to one of us (Kastle) that this reaction might be employed in the preparation of hydrobromic acid. Such, indeed, has proven to be the case, the mode of procedure being as follows: About 15–20 grams of naphthalene are dissolved in a small quantity of orthoxylene and the solution placed in a Florence flask of one-half to 1 liter capacity. The flask is connected, by means of a bent glass tube, with a double-neck Woulff's bottle, which is partially filled with a solution of concentrated hydrobromic acid[1] holding a small quantity of red phosphorus in suspension; and, in turn, is connected with a U-tube containing red phosphorus and one or more drying tubes partly filled with phosphorus pentoxide. Attached to the farther end of the drying tubes is a tube for the delivery of the dry hydrobromic acid gas. The bromine is introduced into the solution of naphthalene in the flask by means of a tap-funnel, the end of which dips beneath the surface of the liquid. On allowing the bromine to flow slowly into the solution of the naphthalene, action takes place at once, and hydrobromic acid is rapidly evolved. By passing the gas through the concentrated aqueous hydrobromic acid containing red phosphorus in suspension, it is deprived of any free bromine that may pass over along with it, (which, by the way, is never present in any considerable quantity) so that, after passing through the U-tube containing dry red phosphorus and the drying tubes, it is obtained as a perfectly colorless gas. With this simple apparatus, and working with the quantities given in the above, the acid can be prepared quite as rapidly as hydrochloric acid can be prepared from sulphuric acid and salt; and with no more trouble or attention, for the reason that, if the flow of bromine into the solution of the naphthalene be once properly regulated, the formation of the acid proceeds regularly and automatically.

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[1] The object in using a concentrated solution of hydrobromic acid is that this solution allows all of the hydrobromic acid gas to pass through and, at the same time, dissolves and retains any free bromine better than water, thereby giving the red phosphorus a chance to combine with it.

In order to obviate the use of xylene, which is not always easily obtained, some experiments were tried, in which kerosene boiling above 150° C. was used as a solvent for the naphthalene. It was found to work just as satisfactorily as the purest orthoxylene. And, lastly, to put the method entirely within the reach of all lecturers upon chemistry, some experiments were tried with *moth balls*,[1] which were found to consist almost, if not entirely, of naphthalene, in the place of the pure naphthalene. This preparation, viz., the *moth balls*, was found to serve the purpose quite as well as the purest naphthalene, as will be seen from the following results :[2]

I. 50 grams of bromine, with 15 grams of naphthalene, dissolved in 50 cc. of orthoxylene, gave 21 grams of hydrobromic acid. Theory = 26 grams HBr.

II. 90 grams of bromine, with 15 grams of naphthalene dissolved in 50 cc. xylene, gave 33 grams of hydrobromic acid. Theory = 46 grams.

III. 105 grams of bromine, with 12.8 grams of naphthalene dissolved in 20 grams of xylene, gave 40.5 grams of hydrobromic acid. Theory = 53.5 gram HBr.

IV. 95 grams of bromine, with 12 grams of naphthalene (in form of *moth balls*) dissolved in a small quantity of kerosene, gave 47.5 grams of hydrobromic acid. Theory = 48.5 grams HBr.

V.[3] 95 grams of bromine, with 12 grams of naphthalene (in form of *moth balls*) dissolved in a small quantity of kerosene, gave 60.5 grams of hydrobromic acid. Theory = 48.5 grams of HBr.

In all there was obtained 202.5 grams of hydrobromic acid, thetheory being 222.5 grams for the quantity of bromine used ; a loss of only 9.1 per cent.

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[1] As the name indicates, these *moth balls* are used for protecting clothing against moth. The preparation sold under that name in this part of the country has been found to consist almost, if not entirely, of naphthalene, and may be obtained at any drug store for 5 or 10 cents a pound.

[2] In the quantitative experiments the mixture of naphthalene and bromine was gently warmed towards the end of the reaction in order to drive off any small quantities of hydrobromic acid which might remain dissolved in the bromnaphthalene.

[3] That more than the theoretical quantity of hydrobromic acid was obtained in this experiment is accounted for by the fact that, during the operation, the washbottle containing the concentrated hydrobromic acid got quite hot, so that hydrobromic acid distilled over into the vessel in which the acid was finally collected.

In addition to these experiments, which were conducted with the view of finding out the quantity of hydrobromic acid set free, the method has been tried upon the lecture-table with entire success. The gas was collected, handled, and experimented with with the greatest ease. The method is certainly to be recommended for lecture-work and for the preparation of large quantities of the acid.

Preparation of Hydriodic Acid.

The method here proposed for the preparation of this acid depends upon a reaction first observed by Etard and Moissan,[1] viz., that, when iodine and common resin (colophony) are heated together, hydriodic acid is evolved. Not having access to the original papers of Etard and Moissan upon this subject, we are unable to judge from the abstract[2] whether it was ever proposed to utilize the reaction in the preparation of the acid, or whether it was simply their object to call attention to it as being one of the reactions of which iodine is capable. Be this as it may, it is certain that this simple mode of preparation of hydriodic acid has escaped the notice of American chemists ; at least it has never come into general use ; and hence it cannot be amiss to call attention to it with such modifications as have been found advantageous.

When a mixture of iodine and common resin, in about equal parts by bulk, is heated, hydriodic acid, together with small quantities of iodine, are evolved. The mixture foams considerably, however, and a black disagreeable liquid distils over. To obviate this and to render the hydriodic acid as pure as possible, the following method was tried successfully :

10 grams of finely divided iodine are mixed with an equal bulk of finely powdered resin and this mixture is then intimately mixed with a little more than an equal bulk of white sand. The mixture of iodine, resin, and sand is then placed in a small glass retort, the neck of which, accurately fitted with a cork, is connected with one of the necks of a double-neck Woulff's bottle, and extends for some distance into the Woulff's bottle. The other neck of the Woulff's bottle is connected with a U-tube containing red phosphorus. This U-

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[1] Bull. Soc. Chim., **34**, 69.

[2] Ber. d. chem. Ges., **13**, 1862.

tube in turn is connected with a calcium chloride cylinder, which is filled with alternate layers of glass-wool and phosphorus pentoxide, the calcium chloride cylinder being connected with a tube for the delivery of the gas.

On gently heating the retort containing the mixture of iodine, resin, and sand, hydriodic acid gas is freely evolved together with small quantities of iodine and the brownish liquid to which reference has already been made. Both of the latter are condensed in the Woulff's bottle, and, if any iodine escapes condensation at this point it is held back by the red phosphorus in the U-tube through which the gases next pass. On passing through the cylinder containing the phosphorus pentoxide, the hydriodic acid is dried completely, so that it may be collected in cylinders by displacement of air as a perfectly colorless gas. Without special precaution 5.4 grams of hydriodic acid were made from 10 grams of iodine by this method.

It should be said further that the method is a rapid one and in every way adapted to work on the lecture-table. The apparatus once set up and the mixture put in the retort, one can easily collect, in a few minutes, a sufficient quantity of the dry gas to illustrate its remarkable and beautiful properties. For example, the apparatus having been set up, the gas was prepared and collected in quantities sufficient for the following experiments, and the experiments themselves performed all in about a quarter of an hour:

1. Introduction of lighted taper into the gas.
2. Action of dry chlorine on gaseous hydriodic acid to show formation, first of iodine and then of iodine trichloride.
3. Decomposition of the gas into its elements by passing it through a heated tube.
4. Oxidation of the gas by fumes of nitric acid.
5. Absorption of the gas by water, and preparation of aqueous hydriodic acid.

In view of these results there can be no doubt as to the efficiency of this method of preparing hydriodic acid.

In conclusion, it may be said that both of the methods above described for these two acids are highly satisfactory. The materials used in the processes above described are such as are easily accessible to all. There are no explosions attending the formation of these acids, nor is there any troublesome phosphonium bromide or iodide produced to clog up the apparatus, as is the case with the methods involving the use of phosphorus. The methods described in the above are rapid and practically free from the objections which may be urged against the other methods which have previously been proposed for the preparation of these two acids.

STATE COLLEGE OF KENTUCKY,
LEXINGTON, Dec., 1895.

Contributions from the Chemical Laboratory of Harvard College.

LXXXIX.—TURMEROL.[1]

BY C. LORING JACKSON AND W. H. WARREN.

Some years ago one of us, in conjunction with A. E. Menke, described a compound obtained from the oily extract of turmeric, to which the name of turmerol was given.[2] The present paper contains some additional work on this substance, which we are obliged to publish in an unfinished state because the departure of one of us from Cambridge prevents us from continuing the work together.

The turmerol at the time of its discovery was purified by distillation *in vacuo*, but the method used was a very imperfect one, because at that time no description of the best methods now in use had come to our notice, if indeed, they had been described at all. Accordingly, when we returned to the subject we felt it was necessary to revise this part of the work, and for this purpose applied to the tumerol the excellent method of fractional distillation *in vacuo* contrived by Anschütz, and soon found that the preparation studied by one of us and Menke was impure, and therefore that the formula of turmerol needed correction. Our analyses of a sample carefully purified and proved to be homogeneous by the analyses of different fractions led to the formula $C_{13}H_{18}O$ or $C_{14}H_{20}O$. We have been unable to determine which of these is correct, because the difference between them is only 0.25 per cent. for the carbon. This new formula agrees much better with the

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[1] Presented to the American Academy of Arts and Sciences, October 12, 1892.

[2] This JOURNAL, 4, 368.

formulas of the oxidation products already obtained than that assigned to turmerol in the first paper on this subject.

The oxidation of turmerol with dilute nitric acid converted it into paratoluic acid, which was identified by its melting-point, 178°, the analyses of its calcium salt and anilide, and its conversion into terephthalic acid by further oxidation. This observation proves that turmerol contains a benzol ring with a methyl group attached to it, and a long side-chain of six (or seven) atoms of carbon in the para position to the methyl. In regard to the nature of the long side-chain we cannot speak with certainty, but it has been proved that one of the atoms of carbon in it is unsymmetrical, because turmerol shows circular polarization and that the atom of oxygen is attached to this side-chain. The earlier work of Menke and one of us further seems to indicate that turmerol is an alcohol,[1] and that it is oxidized by cold potassic permanganate with formation of acetic acid, carbonic acid, and two acids, $C_{11}H_{14}O_2$ (turmeric acid), and $C_{10}H_{12}O_4$? (apoturmeric acid).[2] We feel, however, that this earlier work needs revision before these points can be considered definitely settled, as the experiments on the alcoholic nature of turmerol are susceptible of an interpretation different from that given to them in the paper in which they were described, and the formula of apoturmeric acid is very doubtful. This revision will be undertaken in this laboratory, it is hoped, during the coming year.

Although it would be easy to assign a provisional formula to turmerol in accordance with the facts already observed, we have thought it wiser to postpone doing this until further investigation has given us a more secure foundation for such a formula.

Purification and Analysis of Turmerol.

The crude turmeric oil extracted from ground Bengal turmeric with ligroïn, as described in an earlier paper,[3] was heated to 150° under ordinary pressure for some time to remove as much as possible of the ligroïn, and then distilled under a pressure of 11–12 mm. according to the method of Anschütz, carrying the temperature to 200°. This separated it into a small lower

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[1] This JOURNAL, **4**, 368.
[2] *Ibid*, **6**, 81.
[3] *Ibid*, **4**, 79.

fraction containing ligroïn, a larger one consisting principally of turmerol, and a viscous retort residue, which formed about one-half of the original oil. The large middle portion was repeatedly fractioned at a pressure of 11–12 mm., which divided it into a small lower fraction containing ligroïn, an insignificant retort residue, and the principal amount boiling from 158° to 163° under 11–12 mm. pressure. To test the purity of this substance it was distilled under the same diminished pressure once more, collecting the product in three fractions, the first and last very small in quantity, the middle one containing most of the substance, and these three fractions were then analyzed with the following results:

I. 0.3701 gram of the lowest fraction gave on combustion 1.1215 gram of carbonic dioxide and 0.3274 gram of water.

II. 0.4331 gram of the middle fraction gave on combustion 1.3071 gram of carbonic dioxide and 0.3802 gram of water.

III. 0.4795 gram of the highest fraction gave on combustion 1.4469 gram of carbonic dioxide and 0.4153 gram of water.

		Found.	
	I.	II.	III.
Carbon	82.64	82.28	82.30
Hydrogen	9.83	9.75	9.62

This experiment showed that the substance was not perfectly pure, since the lowest fraction contained more carbon than either of those which came over at higher temperatures. Accordingly the distillation at a pressure of 11–12 mm. was repeated, removing each time only a very small fraction which came over first, until this small lower fraction gave on analysis the same result as the portion left in the boiling-flask. This occurred after the third distillation, when the following results were obtained:

IV. 0.3408 gram of the small lowest fraction gave on combustion 1.0265 gram of carbonic dioxide and 0.2963 gram of water.

V. 0.3658 gram of the principal fraction gave on combustion 1.1041 gram of carbonic dioxide and 0.3175 gram of water.

	Found.	
	IV.	V.
Carbon	85.13	82.28
Hydrogen	9.66	9.65

To these analyses we add another of an entirely different sample of turmerol.

VI. 0.5045 gram of the substance gave on combustion 1.5246 gram of carbonic dioxide and 0.4375 gram of water.

The percentages of carbon and hydrogen obtained from the analyses of pure turmerol are collected in the following table:

	II.	III.	IV.	V.	VI.
Carbon	82.28	82.30	82.13	82.28	82.39
Hydrogen	9.75	9.62	9.66	9.65	9.64

These results agree nearly with those calculated for the following formulas

	Calculated for	
	$C_{13}H_{18}O$.	$C_{14}H_{20}$.
Carbon	82.10	82.35
Hydrogen	9.47	9.80

Of these we prefer the first, as this brings the calculated percentage of hydrogen below those found. On the other hand the percentages of carbon found are all a little too high for this formula, which may perhaps be due to the presence of a trace of ligroïn. It is evident that it is impossible to decide with certainty from these analyses which of these formulas is the correct one.

Properties of Turmerol.—The turmerol, after the purification described above, forms a yellowish oil, with a peculiar rather agreeable odor. It is decomposed partially by distillation at ordinary pressure, but under a pressure of 11–12 mm. it distils unchanged between 158° and 163°. Its specific gravity at 24°, referred to water at 4°, is 0.9561. Turmerol acts upon polarized light, turning the ray toward the right, with the following specific rotation for sodium light :

$$[a]_D = 24.58°.$$

It mixes easily with the common organic solvents, but is insoluble in water.

Oxidation of Turmerol with Nitric Acid.

In a previous paper[1] one of us with A. E. Menke showed

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[1] This JOURNAL, **6**, 81.

that turmerol, when oxidized in the cold with potassic permanganate, gave in addition to carbonic dioxide and acetic acid two new acids, to which the names turmeric acid and apoturmeric acid, and the formulas $C_{11}H_{14}O_2$ and $C_{10}H_{12}O_4$ (?) were assigned. As in this work the characterization of the apoturmeric acid was far from satisfactory owing to the very small yields and the unmanageable nature of these acids and their salts, and as we hoped by further study of these substances to throw light on the constitution of turmerol, we took up this part of the subject again. Since the preparation and purification according to the methods used in the earlier work were tedious in the highest degree, we tried the action of dilute nitric acid on turmerol in the hope that this might lead us more quickly to the desired result. This did not prove to be the case, but the product obtained was quite as important as the two acids we had hoped to get.

We proceeded as follows. A convenient quantity of turmerol was boiled with nitric acid (one part of acid of 1.38 specific gravity diluted with two parts of water) under a reverse condenser for some time. The yellow solution was filtered hot, and on cooling deposited a white crystalline substance, which sublimed very easily at a little over 170°. It was purified by sublimation, followed by warming with tin and hydrochloric acid to remove any nitro compound which might have been formed; after this it was crystallized from boiling water until it showed a constant melting-point, which stood at 178°. This at once suggested that the substance was the paratoluic acid $CH_3C_6H_4COOH$, which melts according to Beilstein and Yssel[1] at 176° to 177°, according to Fischli[2] at 180°. To confirm this inference we analyzed the calcium salt with the following results:—

I. 0.1106 gram of the air-dried salt lost 0.0165 gram when dried at 140°.

II. 0.1212 gram of the air-dried salt lost 0.0176 gram when dried at 140°.

	Calculated for $(C_8H_7O_2)_2Ca.3H_2O$.	Found. I.	II.
Water	14.83	14.92	14.52

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[1] Ann. Chem.. (Liebig), **137**, 302.

[2] Ber. d. chem. Ges., **12**, 615.

0.2848 gram of the calcium salt dried at 140° gave 0.1246 gram of calcic sulphate.

	Calculated for $(C_8H_7O_2)_2Ca$.	Found.
Calcium	12.90	12.86

The amount of water found (three molecules) corresponds to that obtained by Beilstein and Yssel[1] in the calcium salt of paratoluic acid. We also converted the acid into its anilid by treating it successively with phosphoric pentachloride and aniline. This after repeated crystallization from dilute alcohol melted constant at 143°, and gave the following result on analysis:—

0.1122 gram of the substance gave 7 cc. of nitrogen at a temperature of 29° and a pressure of 753.7 mm.

	Calculated for $C_8H_7ONHC_6H_5$.	Found.
Nitrogen	6.63	6.75

Here again the analysis gave the desired result, but our anilid melted at 143°, whereas according to Fischli[2] the anilid of paratoluic acid melts at 139°, according to Brückner[3] at 140–141°; we felt, therefore, that further proof of the para position of the side-chains in our acid was necessary, and this we obtained by the oxidation of the acid with potassic dichromate, according to the directions given by Beilstein and Yssel. For this purpose 0.5 gram of our acid was boiled in a flask with a return condenser with four parts of potassic dichromate, and an excess of sulphuric acid diluted with twice its volume of water, until there was a copious white precipitate; this was then filtered out, boiled three times with water and the residue converted into its dimethylester, which melted at 140–141°, thus proving that the product was terephthalic acid, and that our acid was paratoluic acid. We may add that a certain amount of the terephthalic acid was always obtained with the paratoluic acid when we oxidized turmerol with dilute nitric acid.

Some unsuccessful attempts to make derivatives of the turmeryl chloride, which was described in a previous paper,[4] may be mentioned here. The chloride was made by heating phos-

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[1] Ann. Chem. (Liebig), **137**, 302.
[2] Ber. d. chem. Ges., **12**, 615.
[3] Ann. Chem. (Liebig), **205**, 132.
[4] This JOURNAL, **4**, 371.

phorus trichloride with turmerol for three hours. The product was purified by washing its ethereal solution with dilute sodic hydrate and water, drying with calcic chloride and distilling off the ether. It formed a dark oil, with a smell very different from that of turmerol, but as it decomposed, even when distilled at a pressure of 12 mm., no attempt was made analyze it again. In the hope of obtaining an aldehyde or ketone from it, 10 grams of the chloride was boiled with an aqueous solution of plumbic nitrate. Some plumbic chloride was formed, but the quantity of the chlorine removed was only 0.2363 gram, whereas the amount calculated for the complete reaction was 1.868 grams; we obtained therefore only 12.65 per cent. of the calculated amount, and, as the reaction was so incomplete, it was not surprising that we were unable to isolate the organic product. We also tried the action of potassic phthalimide on the turmerylchloride in the hope of getting turmerylamine, but found there was no action at 100°, little or none at 150°. From these results it is evident that turmerylchloride is not a very reactive substance.

XC. CERTAIN BROMINE DERIVATIVES OF RESORCINE.[1]

BY C. LORING JACKSON AND F. L. DUNLAP.

THE research described in the following paper was suggested by the observation[2] that tribromnitroresorcine diethylether, when heated with a solution of sodic ethylate, lost two atoms of bromine, which were replaced by two of hydrogen, so that $C_6Br_3NO_2(OC_2H_5)_2$ was converted into $C_6BrH_2NO_2(OC_2H_5)_2$. Considering the easy removal of these two atoms of bromine, it seemed possible that the tribromresorcine diethylether, which differs from it only in the absence of the nitro group, might behave in a similar way. This expectation has not been fulfilled, as our experiments have shown that tribromresorcine diethylether does not give up bromine to sodic ethylate at the boiling-point of alcohol, and that the dibrom ether is not attacked below 200°, and therefore is, if anything, more stable than the symmetrical tribrombenzol, which according to Blau[3] is slowly con-

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[1] Presented to the American Academy of Arts and Science, February 14, 1894.

[2] This Journal, 15, 641.

[3] Monatsh. f. Chem., 7, 630.

verted into dibromanisol at temperatures of 120° to 130°. The behavior of free tribromresorcine was next studied, and it was found that bromine could be removed with great ease, even water at its boiling-point decomposing this substance, while solutions of sodic carbonate, or sodic hydrate, or sodic ethylate dissolved in alcohol acted even more readily. These results show that the ethoxyl groups do not loosen the attachment of the bromine atoms to the benzol ring, whereas the hydroxyl groups have as much of this loosening effect as do the nitro groups in tribromdinitrobenzol.

We have not succeeded in determining the nature of the organic compounds produced by removing bromine from tribromresorcine, as they were brown amorphous bodies, which could not be brought into a state of undoubted purity for analysis. From their properties, however, it can be inferred that they are substituted resorcine ethers formed by a reaction involving the hydroxyl groups of the tribromresorcine. Sodium malonic ester gave a similar unmanageable product with tribromresorcine, but in addition to this acetylenetetracarboxylic ester was isolated. This substance could hardly be formed here otherwise than by the action of brommalonic ester on sodium malonic ester, and the brommalonic ester must have been formed by the replacement by hydrogen of one or more atoms of bromine in the tribromresorcine. It follows, therefore, that in this respect also the two hydroxyl radicals behave like the two nitro groups in tribromdinitrobenzol, in which a similar replacement of bromine by hydrogen has been observed when this substance is treated with sodium malonic ester.

The tribromresorcine diethylether melts at 68°–69°, and is formed by the action of an excess of bromine on the dibromresorcine diethylether, melting-point 99°–100°. This latter substance is prepared by the addition of bromine to a solution of resorcine diethylether in glacial acetic acid. The tribrom product was shown to have the bromine atoms in the symmetrical position to each other by treatment with nitric acid, which converted it into the tribromnitroresorcine diethylether melting at 101°, which is made from symmetrical tribromtrinitrobenzol.[1] The action of nitric acid on dibromre-

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[1] This Journal, **15**, 618.

sorcine diethylether was entirely different, as the product was a new dinitroresorcine diethylether melting at 126°, formed by the replacement of the two atoms of bromine by two nitro groups. A similar replacement of bromine by nitro groups was observed when the tribromresorcine was treated with fuming nitric acid, the product being the bromdinitroresorcine described by Typke[1] and Fèvre.[2] As this substance was obtained by the latter from dibromnitroresorcine, in this case also bromine was replaced by a nitro group, and several other cases are to be found in the chemical literature although they are far from common.

The most important point established by the observations given above is that in these cases hydroxyl or ethoxyl radicals have the same effect upon bromine which they have upon hydrogen attached to the benzol ring; for just as phenols are much more susceptible to the replacement of their hydrogen by halogens or nitro groups than the corresponding hydrocarbons, so the bromine can be replaced by other radicals, including the nitro group, much more easily in tribromresorcine than in tribrombenzol; while on the other hand the phenol ethers hold their hydrogen or bromine as firmly as the corresponding hydrocarbons. The one exception we have met with to this statement is the action of nitric acid upon dibromresorcine diethylether, in which the bromine is replaced by nitro groups, so that in this case the ether behaves like the free tribromresorcine rather than like the corresponding tribrom ether. This exception is the more remarkable, because we have found that toward other reagents, such as sodic ethylate, this dibrom ether shows the same great stability which characterizes the tribromresorcine diethylether.

As we could not remove the bromine from the tribromresorcine diethylether with sufficient ease, and the free tribromresorcine, although it gave up its bromine easily, gave unmanageable products since the hydroxyl groups took part in the reaction, we undertook the study of the tribromresorcine diacetate, which we hoped might give products that could be purified and analyzed; but these experiments did not lead to the desired result, as the acetate was converted into tribrom-

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[1] Ber. d. chem. Ges., **16**, 555.

[2] Bull. soc. chim., **39**, 591.

resorcine by the reagents used, even boiling with water producing this effect to a slight extent, and consequently the products were those already mentioned as obtained from this substance. When treated with fuming nitric acid, the diacetate gives tribromnitroresorcine diacetate which melts at 161°.

The sodium salt of tribromresorcine was also studied. This was obtained in white crystals by precipitating an ethereal solution with alcoholic sodic ethylate, and seemed to contain two molecules of alcohol of crystallization. It was remarkable on account of its slight stability, as even *in vacuo* or in an atmosphere of hydrogen after standing for a short time it suddenly turned black, when there was a considerable evolution of heat, and alcohol vapor was given off. The black residue gave up sodic bromide to water, and also a black soluble salt, while a red product was left behind. The black salt on the addition of acid gave a red precipitate similar to the product insoluble in water, but we were unable to bring either of these red amorphous substances into a condition undoubtedly fit for analysis; and although some analyses led to a very probable formula and reaction for the decomposition we can give no weight to these results, as we have no proof that the samples analyzed were homogenous. There is no question that these substances are very similar to the products obtained from tribromresorcine and sodic ethylate or carbonate.

Dibromresorcine Diethylether, $C_6H_2Br_2(OC_2H_6)_2$.

Resorcine diethylether, prepared by Pukall's method,[1] was dissolved in glacial acetic acid and bromine added to it until no more was taken up and a yellow color appeared in the solution. Crystals were soon seen to separate, and these were recrystallized from alcohol until they showed a constant melting-point, when they were dried in a desiccator and analyzed with the following results:

I. 0.2262 gram substance gave, according to the method of Carius, 0.2644 gram of argentic bromide.

II. 0.2272 gram substance gave 0.2628 gram of argentic bromide.

	Calculated for $C_6H_2Br_2(OC_2H_5)_2$.	Found.	
		I.	II.
Bromine	49.38	49.74	49.22

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[1] Ber. d. chem. Ges., **20**, 1141.

Properties.—The dibromresorcine diethylether crystallizes in white silky long slender prisms terminated by one plane nearly at right angles to the sides; they melt at 99–100°, and are slightly soluble in hot water; readily soluble in ether, benzol, and carbonic disulphide; very soluble in acetone and chloroform; also soluble in ligroïn. Alcohol is the best solvent to use in purification.

In a sealed tube at 100° sodic ethylate does not react with dibromresorcinediethylether, nor was any action observed until the tube was heated to 200°, when, upon distillation of the product with steam, a few oil drops passed over. This experiment shows that the dibromresorcine diethylether is no more reactive than symmetrical tribrombenzol, if in fact as much so, since Blau has converted this latter substance, by heating it at 120–130° with sodic methylate, into dibromphenol and its methyl ether.[1] As the interest in this work lay in the study of the effect of other radicals on the atoms of bromine rather than in the nature of the compounds formed, it was not thought worth while to spend the time necessary to prepare the product in quantity sufficient for its identification.

Dibromresorcine diethylether does not react with aniline in a sealed tube at temperatures ranging from 150–175°, and sodic phenylate at 230° also seems to have no effect upon it. It cannot therefore be called a very reactive substance.

Tribromresorcine Diethylether, $C_6HBr_3(OC_2H_5)_2$.

The crystals of dibromresorcine diethylether were treated with an excess of bromine, and then heated upon a steam-bath until the excess of bromine had evaporated. The reddish oil which resulted soon solidified and was recrystallized from alcohol until it showed the constant melting-point of 68–69°, when it was dried in a desiccator and analyzed.

0.2222 gram substance gave by the method of Carius 0.3177 gram of argentic bromide.

	Calculated for $C_6HBr_3(OC_2H_5)_2$.	Found.
Bromine	59.55	59.70

This body crystallizes beautifully in long pearly fibers, often collected in bunches and sometimes branched, which melt at 68–69° and are practically insoluble in cold water; very soluble in benzol and carbonic disulphide; readily soluble in

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[1] Monatsh f. Chem., 7, 630.

ligroïn and chloroform; rather soluble in acetone, but less soluble in ether. Alcohol is the best solvent for purification.

This tribrom ether reacts but very slightly with sodic ethylate at the boiling temperature of alcohol, and no more strikingly when boiled with sodic amylate. When boiled with aniline, the tribrom ether gave an amorphous black mass from which nothing definite could be obtained. Inasmuch as the sodic ethylate had so little action on this body, it was deemed unnecessary to carry this line of work further, for the reasons given under the dibrom compound.

Constitution of Tribromresorcine Diethylether.

Tribromresorcine diethylether dissolves readily in fuming nitric acid, giving the body $C_6Br_3NO_2(OC_2H_5)_2$, as was proved by its melting-point, 100–101°. As Warren[1] and one of us prepared this substance from symmetrical tribromtrinitrobenzol, this experiment proves the symmetrical position of the three bromine atoms in tribromresorcine diethylether.

Dinitroresorcine Diethylether, $C_6H_2(NO_2)_2(OC_2H_5)_2$.

When dibromresorcine diethylether is treated with fuming nitric acid, the result is different from that obtained with the corresponding tribrom compound. To study this action, some of the dibrom ether was added to an excess of fuming nitric acid, when it immediately dissolved, after which it wast reated with excess of water and the reddish oil which separated allowed to solidify. It was then recrystallized from alcohol until it showed the constant melting-point of 126°, after which it was dried at 100° and analyzed.

0.1313 gram of the substance gave 13.5 cc. of moist nitrogen at a temperature of 26° and a pressure of 746.6 mm.

	Calculated for $C_6(NO_2)_2H_2(OC_2H_5)_2$.	Found.
Nitrogen	10.94	11.19

Properties.—The dinitroresorcine diethylether crystallizes from alcohol in radiated clusters of long white needles, or of smaller curved needles forming woolly masses. It is of a very faint yellow color and melts when pure at 126°. It is readily soluble in chloroform or acetone; slightly soluble in

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[1] This JOURNAL, 15, 618.

ligroïn; soluble in benzol; tolerably soluble in carbonic disulphide; soluble also in ether. Alcohol is the best solvent for purification.

Tribromresorcine, $C_6HBr_3(OH)_2$.

Tribromresorcine was prepared by the method of Benedikt,[1] as this yields better results than the treatment of resorcine dissolved in water with bromine, used by Hlasiwetz and Barth.[2] For this purpose the calculated amount of bromine is run into a solution of resorcine in cold glacial acetic acid. After the addition of the bromine this solution is somewhat warm, and upon cooling a finely crystallized product separates, which is best washed free from acetic acid by decantation. If more than the calculated amount of bromine is added, pentabromresorcine is formed in addition to the tribromresorcine. The yield by this method is slightly over 57 per cent. of the theoretical.

A great many conflicting statements occur in the chemical literature regarding the melting-point of tribromresorcine. Hlasiwetz and Barth, who discovered it, give no melting-point. Typke,[3] in some work on tribromdioxyazobenzol, obtained a body with a constant melting-point of 104°. The amount of this body that he had was too small for analysis, but a careful comparison of its properties, especially its melting-point, its crystalline form, and its solubility, with that of tribromresorcine he had prepared himself, convinced him of the identity of the two substances.

Rudolph Benedikt[4] by the action of tin and hydrochloric acid upon Stenhouse's pentabromresorcine, obtained tribromresorcine which melted at 111°. He also gives analyses which agree very well indeed for the body in question.

Von Pechmann,[5] three years later, obtained a body by the action of an excess of bromine upon benzolresorcinephthaleïn, which he called tribromresorcine on the ground of the melting-point of 103°. He gives no analysis of this body, notwithstanding the fact that Benedikt had previously found its melting-point to be 111°.

[1] Monatsh f. Chem., **4**, 227.

[2] Ann. Chem. (Liebig), **130**, 357.

[3] Ber. d. chem. Ges., **10**, 1578.

[4] *Ibid*, **11**, 2168.

[5] Ber. d. chem. Ges., **14**, 1061.

Beilstein in his "Handbuch" gives only Typke's melting-point of 104°.

All of the tribromresorcine we have made use of in this research melted at 111°, the point given by Benedikt, and repeated recrystallization from water, which seems to be preferable to all other solvents, failed to raise its melting-point higher.

According to Hlasiwetz and Barth,[1] tribromresorcine when recrystallized from water contains water of crystallization, which it loses at 100°. As the presence of water of crystallization might explain the difference in the melting-points given by previous observers, we examined the tribromresorcine in this direction. Some of it was crystallized from hot water and dried in the air to a constant weight. This air-dried salt, which remained constant in a desiccator over calcic chloride, was heated to 100° for ten hours, when 0.2169 gram of the substance lost but 0.4 milligram in weight. Therefore tribromresorcine when recrystallized from water does not contain water of crystallization which it loses at 100°, as Hlasiwetz and Barth state.

In the recrystallization of the tribromresorcine from hot water, especially from boiling water, it was noticed that the crystals had a light pink color, so a study of the action of boiling water upon this body was taken up. One gram of the pure tribromresorcine was boiled in a 500 cc. flask, fitted with an inverted condenser, with 250 cc. of water. The greater part of the solid went into solution, and after the boiling had proceeded but a very short time the liquid became pink in color, which deepened into a dark red after the action had been carried on for twenty-four hours. The portion of the tribromresorcine which did not go into solution melted under the boiling water, its color also changing from a pink to a very dark red after the boiling had been continued for some time. At the end of twenty-four hours' boiling, we found that all of the tribromresorcine had not been changed into the red body, for on cooling crystals of a light pink color separated from the solution, which had the melting-point of 111°. Even further boiling, it seemed, failed to complete the change. Upon the

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[1] Ann. Chem. (Liebig), **130**, 357.

addition of argentic nitrate to this solution, a heavy precipitate of argentic bromide was obtained, showing that bromine had been removed from the tribromresorcine.

The red body which formed the organic product in the reaction was amorphous, and could not be recrystallized from any solvents we could find.

It was thought that possibly in a sealed tube the reaction would run much more smoothly, converting all the tribromresorcine into the amorphous red body. Consequently, quite a number of experiments were tried with varying amounts of the substances, heated from twelve to twenty-five hours at different temperatures, but without success. The tribromresorcine, it seems, is incapable of complete transformation into the red body at temperatures below 200°, while at 200° it is carbonized after heating for a short time. As the solubilities of the red body are practically the same as those of the tribromresorcine, all methods for purification failed, and it could not be brought into a state fit for analysis. It is probable, however, that it contains more hydroxyl groups than the tribromresorcine, forming perhaps in the first place a substituted pyrogallol, (for in alkaline solutions the red body immediately blackens,) which is afterwards converted into more complex substances by reactions in which the hydroxyls bear a part.

Aniline or sodic alcoholates also acted easily with the tribromresorcine, but although much bromine was evidently removed in the form of hydrobromic acid or sodic bromide, in no case could any organic product be isolated in a state fit for analysis.

Sodium Salt of Tribromresorcine, $C_6HBr_3(ONa)_2.2C_2H_5OH$.

This salt cannot be obtained from an aqueous solution, although it seemed to be formed, since upon treating tribromresorcine with a dilute solution of sodic carbonate carbonic dioxide was evolved, but the solution at once turned black and evidently underwent a deep-seated change. The following method for obtaining it was accordingly adopted. One gram of pure tribromresorcine was dissolved in absolute ether, and to this was added less than the calculated amount of sodium dissolved in absolute alcohol (the calculated amount of sodium is 0.13 gram). A precipitate immediately separated, consisting of short flat prisms having a silky luster. These were filtered off and thoroughly washed with absolute ether. In the preparation of this body, the ether must be in large excess; if the reverse was true (that is, if the absolute alcohol were in excess) no precipitate was formed. The crystals were transferred, after washing with absolute ether, to a desiccator and allowed to dry in a stream of hydrogen. Some of the salt thus prepared was submitted to analysis. All the operations with this substance must be carried on as quickly as possible, since it has a strong tendency to decompose, forming a black mixture, and this change takes place even *in vacuo* or in an atmosphere of hydrogen, although not so quickly as when in contact with the air. Even during the weighing in a closed tube, the substance often decomposed, but the following analyses were made with the unchanged substance, although in all the analyses made the samples used were light brown in color, showing that slight decomposition had taken place.

I. 0.1357 gram of the salt gave 0.0396 gram sodic sulphate.
II. 0.1398 gram of the salt gave 0.0416 gram sodic sulphate.

	Calculated for $C_6HBr_3(ONa)_2.2C_2H_5OH$.	Found.	
		I.	II.
Sodium	9.52	9.45	9.64

These results indicate that the salt contained two molecules of alcohol of crystallization, and that alcohol was present in the body was evident, for a great many times, in attempting to weigh it, the contents of the weighing tube would suddenly turn black, giving off heat, while a liquid collected in large drops on the sides of the tube, which was recognized as alcohol.

Properties.—The sodium salt of tribromresorcine crystallizes in short flat prisms of a white color and a silky luster. Its most striking property is its great instability, decomposing rapidly with the elimination of alcohol, the salt becoming black in color; when dissolved in water, the solution immediately turns black. A freshly prepared lot of this sodium salt was divided into two portions, one of which was put into a small tube through which a rapid stream of hydrogen was passing, the other was put into a test-tube which was surrounded by a freezing-mixture of salt and ice, the substance in the test tube being in contact with the air. It was found that the sodium salt in the stream of hydrogen (at ordinary temperature) blackened more rapidly than did the salt which was in the freezing-mixture in contact with the air. This experiment proves that the salt is more stable in the cold than at ordinary temperatures, and also that the blackening is not due to oxidation. Since then we had proved that this behavior was not due to oxidation, it seemed possible that the black mixture obtained by drying at 100° might have the same percentage composition as the dried salt. Accordingly the amount of sodium was determined in a specimen of the salt which had been allowed to blacken and dried to a constant weight of 100°. The black body is slightly hygroscopic, so it must be weighed in a weighing tube.

0.2052 gram of the substance gave 0.0722 gram of sodic sulphate.

	Calculated for $C_6HBr_3(ONa)_2$.	Found.
Sodium	11.76	11.40

An attempt to determine the amount of alcohol present by heating some of the freshly prepared salt to 100° gave the following results :—

	Calculated for $C_6Br_3H(ONa)_2.2C_2H_5OH$.	Found.
Alcohol	19.05	17.97

This determination, although one per cent. too low, is as near as we could expect it to come, inasmuch as it was impossible to obtain a sample for analysis which was perfectly white ; but there is a more serious objection to this result and the determination of the sodium in the salt dried at 100°, as we have no proof that alcohol was the only substance volatilized during the decomposition and subsequent drying. In fact the determinations of the amount of sodic bromide contained in the dried mixture indicated that a certain quantity of hydrobromic acid might have been evolved. The only analyses of the salt, therefore, which are above suspicion, are those first given of the white undecomposed preparation.

The following experiments were tried to prove the nature of this decomposition of the salt. When the black decomposition product was dissolved in water, and dilute sulphuric acid added, a flocculent reddish brown precipitate was formed, which very much resembled ferric hydrate in appearance. The clear filtrate from this gave a very heavy precipitate of argentic bromide upon addition of argentic nitrate. This shows that the decomposition was produced by the elimination of a portion of the bromine from the ring. The amount of sodic bromide formed during the reaction was determined by treating the blackened salt with water of varying temperatures and for different lengths of time, and then the solutions were acidified with dilute sulphuric acid, the precipitate filtered off, and bromine determinations made in the clear filtrates. The results obtained were not constant, varying from 32.01 per cent. to 37.90 per cent. of bromine, and this variation may be explained by the supposition that a certain amount of hydrobromic acid escaped during the decomposition.

The study of the red flocculent precipitate obtained by the the addition of sulphuric acid to an aqueous solution of the sodium salt of tribromresorcine has not led to any trustworthy results. Treatment with water and ether showed that it was not homogeneous, and the different fractions thus obtained could not be brought into a state fit for analysis, as no means of proving that they were pure could be found. Some analyses of these fractions gave numbers agreeing fairly well with the very probable formula $[C_6H_2BrOH]_2O_2$; but for the reason just given it is impossible to accept this formula as established by them.

Tribromresorcine when treated with aqueous sodic carbonate dissolves with the evolution of carbonic dioxide, the solution immediately blackening, as has been stated already; upon acidification with dilute sulphuric acid a reddish brown flocculent precipitate was formed similar to that mentioned above, as the clear filtrate from this body gave a very heavy test for bromides. That in this case the blackening was not due to oxidation was shown by the fact that it took place in an atmosphere of hydrogen, even when the solution had been boiled to insure the absence of dissolved oxygen. Sodic or potassic hydrate has the same effect upon tribromresorcine as the carbonate. The red precipitate obtained upon acidifying has not yet been obtained in crystals, and when heated decomposed without melting, giving off hydrobromic acid. This body is doubtless the same as that obtained by the action of water on tribromresorcine, and also from the blackened sodium salt by acidifying its aqueous solution, as has been described above.

Action of Sodium Malonic Ester on Tribromresorcine.

This reaction was taken up to see if another case of the peculiar substitution of bromine by hydrogen, already noticed by one of us,[1] could be obtained. After a great many trials the best mode for studying the reaction was found to be as follows. Five grams of sodium were dissolved in 250–300 cc. of absolute alcohol, and to this were added thirty-five grams of malonic ester. Twenty-five grams of tribromresorcine were then added, and this turned dark and afterwards dissolved. After boiling the mixture for three hours in a flask fitted with an inverted condenser, the alcohol was distilled off and the contents of the flask were acidified with dilute sulphuric acid. A dark red oil separated, which was dissolved in ether, this solution was then dried over calcic chloride and the ether distilled off. Upon standing several days, the residual oil turned rather viscous, and crystals were seen permeating the mass. These crystals may be obtained by absorbing the oil with bibulous paper or by distilling *in vacuo*. By crystallization from dilute alcohol the constant melting-point 76° was obtained, and as the crystals are white, contain no bromine, and their solubility, mode of crystallization, and shape correspond with those of acetylenetetracarboxylic ester, there can be no doubt that they are this substance. This acetylenetetracarboxylic ester could hardly have been formed otherwise than by the action brommalonic ester on sodium malonic ester, and the brommalonic ester it would seem must have been produced by the interchange of a bromine atom of the tribromresorcine with one of the atoms of hydrogen of the malonic ester. It follows

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[1] This JOURNAL, 11, 93, and 12, 7.

from this reasoning, therefore, that we have here another case of the curious replacement of bromine by hydrogen, so often observed in this laboratory, and that the two hydroxyl groups of the resorcine exert the same action on one or more of the atoms of bromine as the two nitro groups in the tribromdinitrobenzol. The following fruitless attempt was made to isolate the other organic derivative formed. If the red oil absorbed by the bibulous paper, after the acetylenetetracarboxylic ester has been separated as completely as possible, be treated with benzol, it is divided into a soluble and an insoluble portion. The insoluble portion, by precipitating an alcoholic solution of it with benzol, came down in a flocculent form, and when dry was light brick-red in color. It was evidently closely related to the substance obtained by the action of water or sodic carbonate on the tribromresorcine, and like that could not be purified.

Action of Nitric Acid on Tribromresorcine.

Fuming nitric acid reacts easily with tribromresorcine. The product was recrystallized from benzol and upon analysis gave the following results:—

0.2219 gram of the substance gave by the method of Carius 0.1479 gram of argentic bromide.

	Calculated for $C_6HBr(NO_2)_2(OH)_2$.	Found.
Bromine	28.67	28.37

This analysis and the melting-point, 192°–193°, show the body to be one heretofore described by Typke[1] and Fèvre.[2]

We have found, in attempting to prepare the diacetate of dinitrobromresorcine, that dinitrobromresorcine would not react with acetyl chloride when heated with it at 100° for six hours in a sealed tube. Water does not react with dinitrobromresorcine in a sealed tube at temperatures varying from 100° to 120°. At temperatures between 150° and 190° the body is entirely decomposed, leaving a reside in the tube which seemed to be carbon, as it was insoluble in all solvents. It is strange that this substance should be less affected by water than the tribromresorcine, which is slowly acted on by water at its boiling-point. The dinitrobromresorcine reacts with sodic

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[1] Ber. d. chem. Ges., **16**, 555.

[2] Bull. soc. chim., **39**, 591.

ethylate, but, as in the case of the tribromresorcine, the resulting amorphous mass could not be purified or crystallized.

Behavior of Tribromresorcine Diacetate.

While the tribromresorcine itself reacts easily with boiling water and sodic ethylate, but gives unmanageable products, and the di- and tribromresorcine diethyl ethers do not act with these reagents, it was thought that possibly the diacetate of tribromresorcine might be better to work with than either of the ethers or the free phenol, because it holds an intermediate place between the acid tribromresorcine and its neutral ethers. Instead of using Claassen's method[1] of boiling pentabromresorcine with acetic anhydride, then with glacial acetic acid, and finally with water, the tribromresorcine diacetate was directly prepared from tribromresorcine by treating it in a sealed tube for four or five hours at 100° with either acetyl chloride or acetic anhydride, preferably the former. It is best to use a slight excess of acetyl chloride, and after the heating is finished to decompose the excess by means of water. The diacetate is easily recrystallized from alcohol and was identified by its melting-point, 108°.

After boiling tribromresorcine diacetate with water for twenty-four hours, the water was slightly pink in color, and gave a feeble test for bromides with argentic nitrate. This is due, no doubt, to the fact that water at 100° saponifies a small part of the diacetate, yielding tribromresorcine, which in its turn is acted upon by the boiling water, as before noted. In the hope of avoiding this saponification, a sealed tube containing the diacetate was heated over night at 157° with ordinary acetic acid, but the saponification was not prevented, for the result was the same as if the free tribromresorcine had been heated with water alone to that temperature. Sodic ethylate in alcoholic solution when warmed with tribromresorcine diacetate deposited a precipitate which when filtered off soon turned black. This body was undoubtedly the decomposition-product of the sodium salt of tribromresorcine. On account of the readiness, therefore, with which the diacetate was saponified, it was not worth while to carry on this line of investigation further.

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[1] Ber. d. chem. Ges., 11, 1439.

Tribromnitroresorcine Diacetate, $C_6(NO_2)Br_3(OC_2H_3O)_2$.

The diacetate of tribromresorcine when added to an excess of fuming nitric acid immediately dissolved, and after standing several minutes the solution became very warm and began to boil, the body in solution becoming completely oxidized ; but if just before the oxidation took place, when the solution was already hot, it was poured into an excsss of water, the resulting yellowish oil soon solidified. The substance was purified by crystallization from alcohol until it showed the constant melting-point of 161°, when it was dried at 100° and analyzed with the following results :—

0.1752 gram of the substance gave, by the method of Carius, 0.2086 gram of argentic bromide.

	Calculated for $C_6NO_2Br_3(OC_2H_3O)_2$.	Found
Bromine	50.42	50.69

The diacetate therefore behaves toward nitric acid like the tribromether rather than like the tribromphenol itself, for in the latter and in the dibromether atoms of bromine are replaced by nitro groups, as already described earlier in this paper.

Properties.—The tribromnitroresorcine diacetate forms good-sized prisms terminated by two planes at an obtuse angle to each other ; it is very pale yellow, almost white, and melts at 161°. It dissolves slowly in ligroin, is readily soluble in chloroform, benzol, and ether, freely soluble in acetone, and tolerably soluble in carbonic disulphide.

In order to establish if possible the position of the three bromine atoms in tribromresorcine, attempts were made to saponify the tribromresorcinediethylether, which has the three bromine atoms arranged symmetrically. When saponified in a sealed tube with aqueous hydrochloric acid, however, the product was a red body similar to that formed by the action of water on tribromresorcine. Accordingly, in hopes of a better result, dry hydrochloric acid gas was passed for one hour over tribromresorcinediethylether heated in an oil-bath to 200°, but no saponification took place.

XCI.—TRINITROPHENYLMALONIC ESTER.[1]

BY C. LORING JACKSON AND C. A. SOCH.

At the end of his paper on the action of sodium acetacetic ester on picrylchloride, Dittrich[2] states that, in spite of many and varied attempts, he had not succeeded in making a picrylmalonic ester from picrylchloride and sodium malonic ester, but that he obtained in every case sodic picrate and viscous products of the decomposition of the malonic ester. This statement impressed us as a strange one, since in work[3] done in this laboratory it had been found that tribromdinitrobenzol acted much more easily with sodium malonic ester than with sodium acetacetic ester; for whereas a good yield of the substituted malonic ester could be obtained even when the reaction took place in the cold, with the acetacetic ester the yield was small even after the reagents had been boiled together. Accordingly we took up the study of this subject, and found, as we had expected, that the picrylmalonic ester could be obtained without difficulty. It is a white substance melting at 58°, and forms a blood-red sodium salt, which is tolerably stable, dissolving in water without decomposition. The picrylbrommalonic ester, $C_6H_2(NO_2)_3CBr(COOC_2H_5)_2$ was made by treating the substituted malonic ester with an excess of bromine; it melts at 85–86°. One object in undertaking this work was to see whether any trinitrobenzol was formed in the action of sodium malonic ester or sodium acetacetic ester on picrylchloride by the replacement of the atom of chlorine by hydrogen after the analogy of such reductions, which have been noticed frequently in the work done in this laboratory upon tribromdinitrobenzol and tribromtrinitrobenzol. Unfortunately the research was begun so late in the year that we have been unable to arrive at a definite conclusion on this subject, and it is hoped that it will be possible to repeat the experiments on a larger scale and with conclusive results early in the coming term. A bromdinitrophenylbrommalonic ester corresponding to the picryl compound mentioned above was also prepared. It melts at 72–73°.

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[1] Presented to the American Academy of Arts and Sciences, May 9, 1894.

[2] Ber. d. chem. Ges., **23**, 2720.

[3] This JOURNAL, **11**, 93; and **12**, 164.

Trinitrophenylmalonic Ester (*Picrylmalonic Ester*), $C_6H_2(NO_2)_3CH(COOC_2H_5)_2$.

As Dittrich[1] states that the product of the reaction of picrylchloride and sodium malonic ester is viscous, we first turned our attention to the preparation of the sodium salt of the substituted malonic ester in the hope that this might be purified more easily than the free ester.

Sodium Picrymalonic Ester, $C_6H_2(NO_2)_3CNa(COOC_2H_5)_2$.

The picrylchloride used in making this substance was prepared according to the method of Clemm,[2] except that we crystallized the chloride from a mixture of chloroform and alcohol, as we found that the addition of the chloroform made it possible to work with much smaller volumes of the solvent, and also seemed to prevent in great measure the deposition of the picrylchloride in an oily form. A strong cold benzol solution of 10 grams of this picrylchloride was mixed with an alcoholic solution of sodium malonic ester made from 14 grams of malonic ester and the sodic ethylate from 2.1 grams of metallic sodium. The mixture, which took on at once a deep red color, was cooled at first, and then allowed to stand for twelve hours at ordinary temperatures; after which it was diluted with about three-quarters of a liter of water. In this way a red aqueous solution was obtained, and a supernatant layer of benzol which contained a portion of the picrylmalonic ester formed, while the rest was dissolved as a sodium salt in the red aqueous solution, in addition to some sodic picrate and the sodic chloride. Upon acidifying the aqueous liquid with sulphuric acid a yellow precipitate was thrown down, which, as it settled from the liquid, collected in an oily state on the bottom of the beaker. To the oily product a strong solution of sodic hydrate was added, which imparted to it a dark red color, and after thorough mixing converted it into a red crystalline solid. To remove any liquid or viscous impurities from the salt, it was next dissolved in the smallest possible amount of alcohol and treated with an excess of benzol, after which the mixed solutions were evaporated cautiously on the steam-bath until crystals began to form, when upon cooling

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[1] Ber. d. chem. Ges., **23**, 2720.

[2] J. prakt. Chem. [2], **1**, 145.

the sodium salt was obtained in fine red crystals; these were washed with benzol, and after drying in a desiccator gave the following results on analysis:

I. 0.2400 gram of the substance after evaporation with sulphuric acid gave 0.0427 gram of sodic sulphate.

II. 0.8331 gram of the substance gave 0.1429 gram of sodic sulphate.

	Calculated for $C_6H_2(NO_2)_3CNa(COOC_2H_5)_2$.	Found.	
		I.	II.
Sodium	5.85	5.76	5.56

An additional quantity of the salt was obtained by the treatment just described from the residue left after evaporating off the benzol from the solution of picrylmalonic ester in this solvent obtained by adding water to the product of the reaction.

Properties of the Sodium Salt of Picrylmalonic Ester.—It crystallizes from a mixture of alcohol and benzol in dark red crystals often a centimeter long. It is easily soluble in alcohol or ether; somewhat less soluble in water than in alcohol; nearly insoluble in benzol. It does not seem to be decomposed by any of these solvents. Strong sulphuric acid decomposes it, but without any explosion, which surprised us, as it showed a tendency to explode when dry even at comparatively low temperatures.

As the potassium salt of picric acid is so much less soluble than the sodium salt, we prepared the potassium salt of the picrylmalonic ester by treating the free ester with potassic hydrate in strong aqueous solution: but, although this salt was somewhat less soluble in both water and alcohol than the sodium salt, the difference was not very marked, and there would be no advantage in using the potassium salt instead of the sodium salt in the purification of the substance.

The behavior of an aqueous solution of the sodium salt of picrylmalonic ester with various reagents was also studied, and the following more or less characteristic precipitates were obtained:

Salt of magnesium, heavy reddish flocks.

Salts of calcium or barium, granular or crystalline precipitates of an amethyst color.

Salt of manganese, dirty yellow flocks.
Salt of nickel, light red flocks.
Salts of lead or silver, dark red flocks.
Salt of cadmium, reddish yellow flocks.

Picrylmalonic Ester, $C_6H_2(NO_2)_3CH(COOC_2H_5)_2$.

Although in our earlier experiments we prepared this substance through its sodium salt on account of the discouraging statements of Dittrich, we soon found that this was unnecessary, as the substance could be purified directly without difficulty, and in all our later work we have adopted this direct method, which we are about to describe, as it is much more convenient than the method of purification by means of the sodium salt. To prepare the picrylmalonic ester we proceeded according to the method described under sodium picrylmalonic ester, until by the addition of water the product had been divided into an aqueous and a benzol solution. The aqueous solution after acidification with dilute sulphuric acid was allowed to stand until the oily precipitate had separated completely from the mass of the liquid; part of it settled, part floated on the surface, and even during this comparatively short standing the floating part was converted into crystals; which could be used to promote the crystallization of the larger quantity on the bottom of the beaker. The solidification of the main portion of the oily product was effected without difficulty by cooling with running water, one of the crystals from the surface of the water being added if necessary; and the solidified product, after washing with cold water, was crystallized from alcohol. The benzol solution, which had been separated from the aqueous solution, was acidified with dilute sulphuric acid, and allowed to evaporate spontaneously, when it furnished a rather large additional quantity of the oily product, which, however, did not solidify so easily as that obtained from the aqueous portion, since it was necessary to allow it to stand for three or four days with occasional stirring in order to bring it into a crystalline condition. It was then pressed between layers of filter-paper, which removed an oily impurity, after which it was mixed with the crystals obtained from the aqueous liquid, and the whole purified by crystallization from alcohol until it showed the constant melting-point 58°, when it was dried in a desiccator, and analyzed with the following results:

I. 0.2707 gram of the substance gave 28.6 cc. of nitrogen at a temperature of 25° and a pressure of 757.4 mm.

II. 0.2565 gram gave 25.9 cc. of nitrogen at a temperature of 22° and a pressure of 755.8 mm.

	Calculated for $C_6H_2(NO_2)_3CH(COOC_2H_5)_2$.	Found. I.	Found. II.
Nitrogen	11.32	11.75	11.38

It is worthy of remark that, whereas Dittrich from the action of the picrylchloride on sodium acetacetic ester obtained a considerable quantity of dipicrylacetacetic ester, our principal product was the monopicrylmalonic ester, and only on one occasion have we observed a trace of a substance with a much higher melting-point, which we took to be the dipicryl compound. We should add that, in applying the same method to the action of sodium acetacetic ester on picrylchloride, we obtained almost exclusively monopicrylacetacetic ester.

Properties of Picrylmalonic Ester.—It crystallizes from alcohol in white, long, rather slender rectangular plates, which develop into somewhat thick prisms with blunt ends often as much as two centimeters long. It melts at 58°, and is very soluble in chloroform, ether, benzol, or glacial acetic acid; somewhat less soluble in carbonic disulphide; soluble in cold alcohol, freely in hot; rather more soluble in methyl than in ethyl alcohol; insoluble in ligroïn or cold water, slightly soluble in hot water. All the solutions of this substance except that in glacial acetic acid have a pink color, which is the more marked the stronger the solution, and the alcoholic solution imparts to the fingers a crimson color not unlike rosaniline, although less purple. This coloration of the fingers is much deeper than the color of the solution, and is tolerably fast. The formation of these pink or crimson colors from the white crystals is striking, and will be more carefully studied.

Cold strong sulphuric acid dissolves it; if this solution is warmed it turns red, and gives off bubbles of gas; dilution of the red solution after it had cooled precipitated a yellow solid.

Strong nitric acid acted in the same way, except that the picrylmalonic ester dissolves more slowly in cold nitric acid than in sulphuric acid. Strong hydrochloric acid did not dissolve it in the cold, but on warming the substance melted, and then went into solution very slowly. The picrylmalonic ester has well marked acid properties forming the red sodium salt when treated with an aqueous solution of sodic hydrate. As is often the case with substances of this class, the sodium salt is nearly insoluble in a strong solution of sodic hydrate. The sodium salt is also formed by the action of a solution of sodic carbonate on the free ester.

Trinitrophenylbrommalonic Ester (*Picrylbrommalonic Ester*), $C_6H_2(NO_2)_3CBr(COOC_2H_5)_2$.

This substance was made by dissolving some of the trinitrophenylmalonic ester described in the preceding section in a small quantity of glacial acetic acid, and adding liquid bromine until it was present in distinct excess, as shown by the reddish brown color of the liquid. To make certain that the reaction was complete, the liquid was warmed gently on the steam-bath for a few minutes, and then allowed to stand at ordinary temperatures for an hour, after which water was added in excess, giving a pale yellow precipitate partly solid and partly liquid. After this had settled, the supernatant liquid, colored red with the excess of bromine, was poured off, and the liquid part solidified by cooling. It was then washed with water, dried by pressure on filter-paper, and purified by recrystallization from alcohol until it showed the constant melting-point 85°–86°, when it was dried in a desiccator, and analyzed with the following result:

0.1873 gram of the substance gave by the method of Carius 0.0789 gram of argentic bromide.

	Calculated for $C_6H_2(NO_2)_3CBr(COOC_2H_5)_2$.	Found.
Bromine	17.78	17.93

It is obvious that this atom of bromine, the presence of which is shown by the analysis, may have entered the molecule in one of two different places, either replacing the hydrogen of the malonic ester radical, as in the formula given above, or replacing one of the atoms of hydrogen attached to the benzol ring. It is easy to determine which position the bromine occupies, for, if it is attached to the malonic ester radical, the substance will have lost all its acid properties, since the acid hydrogen has been replaced by the atom of bromine. In the second case, where the bromine is attached to the benzol ring, on the other hand, the acid properties will not be interfered with, but on the contrary will be somewhat increased if the bromine atom has any effect whatever. Upon treating our new substance with a solution of sodic carbonate no change was observed, whereas the picrylmalonic ester is converted at once into its red salt by this reagent; as therefore, this substance has no acid properties, it follows that the bromine has entered the malonic ester radical, and the formula given above is the correct one.

Properties of Picrylbrommalonic Ester.—It crystallizes from alcohol in white plates, nearly but not quite square, and much striated; these plates are arranged in irregular rather long rosettes. Less commonly it occurs in bladed or pennate forms. In general appearance it resembles acetanilide. It melts at 85°–86°; and is very soluble in chloroform or benzol; rather less soluble in ether, carbonic disulphide, or glacial acetic acid; soluble in cold alcohol, freely soluble in hot; rather more soluble in methyl than in ethyl alcohol; insoluble in cold ligroin, soluble in it when hot although with some difficulty; essentially insoluble in water, whether hot or cold. The best solvent for it is alcohol. Its alcoholic solution shows a faint pink color, similar to that given by picrylmalonic ester, but less marked. Strong sulphuric acid dissolves it in the cold with a yellow color; upon warming this solution it becomes brownish black, and bubbles of gas are given off. Strong hydrochloric acid seems to have no action on it even when hot. In cold strong nitric acid it is insoluble, but, it dissolves easily if the acid is hot, and boiling this solution for a short time produces no signs of decomposition. A strong solution of sodic hydrate did not act upon it in the cold, but, when heated with it, gave a red solution. The solution here was undoubtedly preceded by removal of the bromine. As has been stated already, sodic carbonate does not act on this substance.

Bromdinitrophenylbrommalonic Ester.

$C_6H_2Br(NO_2)_2CBr(COOC_2H_5)_2$.

This substance was made by dissolving the bromdinitrophenylmalonic ester in glacial acetic acid and adding to the strong solution an excess of liquid bromine. The bromdinitrophenylmalonic ester was made from tribromdinitrobenzol melting at 192° and sodium malonic ester.[1] After an excess of bromine had been added, as shown by the color, the liquid was warmed gently on the water-bath for a short time, and, if the color had disappeared, more bromine added. It was then, after it was cool, precipitated with water, and the substance obtained solidified by cooling, if necessary; after which it was purified by crystallization from alcohol, until it showed the constant melting-point 72°–73°. It is not wise, however, to rely on the melting-point as the only proof of purity, since the bromdinitrophenylmalonic ester from which it is formed melts at 75°–76°; we have therefore always tested our product also with a solution of sodic hydrate, which gives a red salt with the mother-substance, but has no effect in the cold on the desired compound. After purification it was dried in a desiccator, and analyzed with the following results:

I. 0.3196 gram of the substance gave by the method of Carius 0.2451 gram of argentic bromide.

II. 0.1997 gram of the substance gave 0.1550 gram of argentic bromide.

	Calculated for $C_6H_2Br(NO_2)_2CBr(COOC_2H_5)_2$.	Found. I.	II.
Bromine	33.05	32.64	33.02

The fact that this substance is not acted on by cold sodic hydrate proves that it contains the second atom of bromine attached to the malonic ester radical and not to the benzol ring.

Properties of Bromdinitrophenylbrommalonic Ester.—It crystallizes from alcohol in long white prisms terminated by a single plane at an acute angle and arranged in radiated groups;

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[1] This JOURNAL, 11, 93.

these crystals are sometimes a centimeter long. It melts at 72°–73°; and is very soluble in benzol, chloroform, acetone, carbonic disulphide, or glacial acetic acid ; not freely soluble in cold alcohol, but easily in hot ; more soluble in methyl than in ethyl alcohol, insoluble in cold ligroin, slightly soluble in hot ; insoluble in water, but if boiled with water for some time, fresh water being added to take the place of that which evaporates, it is finally brought completely into solution. This action is undoubtedly due to the removal of the side-chain bromine as hydrobromic acid. It will be studied more carefully hereafter. Strong sulphuric acid does not act upon it in the cold, and when hot it acts only very slowly. Strong nitric acid also has no action when cold, but if hot dissolves it. Strong hydrochloric acid does not act upon it in the cold, and when hot has rather less effect than sulphuric acid. Strong solutions of sodic hydrate and ammonic hydrate have little or no action in the cold ; when warmed they convert it into a red substance, probably a salt formed after the removal of the side-chain atom of bromine. The whole subject of the replacement of this second atom of bromine by other radicals must be studied more carefully before any account can be given of it. It is hoped that this work can be carried on in this laboratory during the coming term.

Contributions from the Chemical Laboratory of Case School of Applied Science.

XXI.—THE ARTIFICIAL PRODUCTION OF ASPHALT FROM PETROLEUM.[1]

By Charles F. Mabery and J. H. Byerley.

In the method universally employed for the separation of commercial products from petroleum, as is well known, the final product of the continuous distillation is a porous coke, and the quantity formed ordinarily is approximately equivalent to ten per cent. of the crude oil. This coke still contains a considerable proportion of hydrocarbons, but it is essentially the ultimate product of decompositions that must begin in the early stages of the distillation. The precise temperature at

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[1] The results described in this paper formed the subject of a thesis by Mr. Byerley for the degree of Bachelor of Sciences.

which decomposition begins is quite variable in petroleums from different sources, and it doubtless depends somewhat on the form of the still and the manner of conducting the distillation.

In the early history of the refining of petroleum, it was accidentally discovered that distillation could be carried to a certain point with a gradual increase in the specific gravity of the distillates, when suddenly a lighter oil would appear in considerable quantities evidently formed by the decomposition of higher constituents. Since that discovery "cracking" has been practiced to increase the yield of burning-oil. The precise nature of these decompositions is not well understood.

In studying the action of heat on paraffin, Thorpe and Young[1] found that the products of decomposition included members of the series C_nH_{2n+2} and C_nH_{2n}. Of the first series nearly all the bodies then known up to $C_{10}H_{22}$ were found, and higher members which were not identified. The effect of heat on normal and isohexane and on normal pentane was thoroughly studied by Norton and Andrews.[2] Below 600° no change was observed, but between 600° and 700° decomposition began with the formation of the lower hydrocarbons C_nH_{2n+2} and C_nH_{2n}. Our results indicate that cracking begins in the vicinity of 250°, but further study is necessary concerning the action of heat on the individual higher members. An attempt will be made to determine with greater precision the nature of these decompositions. In ordinary cracking it is evident that the chemical changes may include the reaction upon one another of the various constituents of the crude oil as well as decomposition of the principal hydrocarbons.

It is a general belief that cracking consists in the breaking down of the higher constituents into lower saturated and unsaturated hydrocarbons. Determination of bromine absorption in distillates indicates an unsaturated condition, but a similar condition is likewise shown by the quantity of bromine absorbed in the crude oils, only in a less degree than in the higher distillates. Without doubt the point at which cracking begins is quite variable in oils from different sources.

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[1] Ann. Chem. (Liebig), **165**, 1.

[2] This Journal, **8**, 1.

Indeed it is not difficult to demonstrate the difference in oils from the same source, but from different levels in the same well. In an examination of Berea Grit petroleum by O. C. Dunn and one of us (C. F. M.), which will be described in another paper, distillates were prepared in which bromine absorption was determined for this paper, showing a marked variation in the quantity of bromine absorbed in the oils from different depths.

	1.		2.		3.	
	A.	B.	A.	B.	A.	B.
Crude	7.62	3.00	8.28	2.35	9.49	2.64
35–60°	0.00	0.00	0.00	0.00	0.79	0.51
60–85°	0.00	0.00	0.00	0.00	1.19	0.90
85–110°	0.74	0.20	1.50	0.75	1.82	0.87
110–135°	1.81	0.65	3.03	1.17	2.32	0.77
135–160°	2.32	1.61	3.52	1.39	3.71	0.95
160–185°	2.24	1.36	3.79	1.37	4.94	1.25
185–210°	2.32	0.94	5.20	1.13	5.94	1.83
210–235°	2.08	0.51	5.75	1.93	6.66	2.37
235–260°	3.87	0.52	8.09	2.49	7.76	2.06
260–285°	4.84	1.12	8.66	2.24	9.18	2.58
285–310°	5.69	1.93	9.42	2.76	11.03	3.04
310–335°	4.58	2.01	11.70	3.97	10.98	3.74
335–360°	7.57	2.33	17.01	5.63	24.84	4.53
+360°	9.72	1.12	18.54	6.07	26.38	9.08

	4.		5.		6.	
	A.	B.	A.	B.	A.	B.
Crude	5.93	1.41	9.96	3.47	6.26	2.23
35–60°	0.00	0.00	0.26	0.27	0.00	0.00
60–85°	1.73	1.73	0.54	1.08	0.00	0.00
85–110°	2.92	2.22	1.38	1.66	0.00	0.00
110–135°	3.65	3.36	2.76	1.81	1.56	0.42
135–160°	4.04	1.46	3.75	1.74	1.63	1.54
160–185°	5.03	1.41	5.14	1.48	2.46	1.58
185–210°	5.64	2.08	5.41	2.00	3.54	1.94
210–235°	6.26	2.16	8.00	2.60	4.32	2.41
235–260°	8.54	2.22	8.01	2.27	6.31	2.94
260–285°	10.21	3.15	9.29	2.48	7.58	3.07
285–310°	9.38	2.43	10.47	4.49	9.60	2.83
310–335°	11.24	2.36	10.82	3.09	9.09	3.59
335–360°	18.01	3.23	17.60	6.01	13.59	3.56
+360°	21.84	3.84	20.31	7.08	16.89	5.01

In column A are given the percentages of bromine absorbed, and in column B the percentages of hydrobromic acid set free. Oil No. 1 was taken from the 140 foot sand, Macksburg; oil No.

2 from the 300 foot sand; oil No. 3 from the 500 foot sand; oil No. 4 from the 700 foot sand; oil No. 5 from the 1500 foot sand; and oil No. 6 from the 1500 foot sand, Archer's Fork, Ohio.

It is evident that the hydrobromic acid evolved follows with some regularity the absorption of bromine, increasing with the temperature of distillation. The larger quantity of acid formed in the higher distillates is doubtless due, at least in part, to the presence of normal constituents of the crude oil, since the latter evolves considerable hydrobromic acid.

To ascertain the influence of still higher temperatures, a residue + 360° in an oil taken from a well in the Berea Grit, 1500 foot level at Archer's Fork, Ohio, (I), and a similar residue from Lima oil (II) were further distilled with a 550° thermometer and collected within limits of 25°. The specimen of Lima oil apparently cokes less readily than the other, and its bromine absorption shows less variation.

	300–325°	322–350°	350–375°	375–400°	400–415°	
I.	14.71	24.70	31.22	19.83	Coke	....
II.	....	27.19	19.04	26.98	31.26	Coke

Attention has been called[1] by one of us (C. F. M.) to the necessity of excluding air during distillation at high temperatures to avoid decomposition. In further evidence as to the influence of air, we submitted two portions of Berea Grit oil, 1500 foot level to distillation, one portion (I) under ordinary conditions, and a second portion (II) with a current of air passing through the oil during distillation. The decomposition produced by the action of air on the hot oil is shown by the increase in bromine absorption A, in all distillates. The values in columns B represent the weight of hydrobromic acid evolved from the total weights of the respective fractions. Beyond showing comparative qualities, the latter observations are not of especial importance.

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[1] Proc. Amer. Acad., **31**, 8.

	I.		II.	
	A.	B.	A.	B.
−100°	0.00	0.00	0.00	0.00
100–125°	0.42	0.19	0.49	0.21
125–150°	0.97	0.42	1.74	0.28
150–175°	2.26	1.34	6.11	1.88
175–200°	2.31	0.41	8.15	3.92
200–225°	3.90	1.31	11.66	3.53
225–250°	7.66	2.18	13.48	1.35
250–275°	9.76	1.07	14.28	8.25
275–300°	9.62	3.22	16.36	1.72
300–325°	14.71	2.79	15.54	5.81
325–350°	17.34	18.51	22.51	11.83
350–375°	31.22	20.15	38.64	15.83
375–400°	....	....	49.48	18.86

It has long been felt that products should be obtained from the less volatile portions of petroleum with a greater value than the coke which is the final product in the ordinary process of refining. Many attempts have, therefore, been made to conduct the final distillation in such a manner that the heavier portions may be protected from decomposition and converted into a form suitable for the preparation of asphalt or similar products.

Mr. F. X. Byerley was the first to discover the conditions necessary to prevent ultimate decomposition, and he has perfected a method which renders possible the separation of commercial products that are serviceable in the manufacture of the various grades of asphalt, such as are used in varnishes, roofing and paving. This method has been protected by letters patent, and, under the control of a large corporation, the manufacture of these materials will doubtless assume large proportions.

As shown by our own experiments described above, although the introduction of air during distillation produces greater decomposition, the first series of distillates collected under ordinary conditions, give evidence of considerable change, especially in the higher fractions. In the Byerley method these changes are prevented to a large extent by very slow distillation. The material employed in the preparation of asphaltic products by this method is the heavy residual oil with a specific gravity between 25° and 28° Baumè that remains after distillation of the portion used in the preparaiion of burning oil. A determination of the specific gravity of one specimen of this tar at 20° gave 0.9325. It absorbed 12.18 per cent. of bromine, and gave off 2.23 per cent. of hydrobromic acid.

This tar is subjected to distillation in stills of the "cheese box" type with steel bottoms, enclosed in a brick chamber. These stills are somewhat less in diameter than in height, and the capacity of each is 150 barrels. For the introduction of air every still is supplied with five vertical iron pipes, each one and one-half inches in diameter, extending to within a few inches of the bottom of the still. A six-inch pipe leads from the top of the still to condensers, and these are attached to a closed iron chamber, to which is connected the air-pump for exhaustion. Ordinarily a suction equivalent to five or six inches of water in excess of that required to overcome the column of oil, is sufficient for continuous operation. The stills are filled about one-half with tar, and heat is applied solely to the bottom. The temperature is controlled by means of a pyrometer inserted into the tar. At first it is raised to 450° and later to 650° F., where it is maintained during the distillation. Much depends upon the rate of distillation, since, if it proceeds too rapidly, the yield is small, and the product inferior. The quantity of the distillate affords an easy means of control. The distillate has the properties of the less volatile portions of burning oil; it is dark red in color, but it can be nearly bleached by refining with sulphuric acid. It begins to distil at about 320°, and its specific gravity at 20° varies between 0.8393 in the first distillate and 0.8584 in the later portions. A specimen of the first distillate contained 0.15 per cent. of sulphur, and it absorbed 10.66 per cent. of bromine; the second gave 0.04 per cent. of sulphur, and it absorbed 16.27 per cent. of bromine. After treatment with steam, sulphur was completely removed from the first distillate. In practice one separation is made of the distillates, and both are refined for burning oils. The grade of product depends upon the duration of the distillation which is ordinarily completed in four or five days. The farther it is carried the more solid is the asphalt.

The air doubtless serves several purposes. It causes oxidation to a certain extent, especially if the tar is a residue from a sulphur oil. As shown by analysis, the asphalts contain a small proportion of oxygen, although not much in excess of what should be derived from the crude oil, assuming, which is probable, that the larger portion of the oxygen compounds do not distil with the burning-oil distillates. Then the tar is protected during distillation from the decomposing action of the hot still bottom by the currents of air which keep it constantly in motion. The volatile constituents suffer less decomposition, except from the oxidation of sulphur, than the distillates in the ordinary process of cracking.

Some water is evolved as an oxidation-product, and much sulphur appears in the form of sulphurous and sulphuric acids. A considerable proportion of the sulphur remains still unoxidized in the asphalts and less in the oily distillate. The commercial products include (1) liquid asphalt, (2) roofing asphalt, (3) paving asphalt, (4) Byerlyte or varnish asphalt.

The liquid asphalt (1) is used as a flux for natural asphaltum in the preparation of paving and roofing asphalts. It begins to flow at 25°. Its composition was determined by analysis:

Carbon	86.22
Hydrogen	10.91
Sulphur	0.30
Nitrogen	0.18
Oxygen, by difference	2.39
Specific gravity at 20°	0.9560
Bromine-absorption	14.18
HBr evolved	2.23

The product (2) used in the manufacture of roofing, tar-paper, and in the construction of telephone conduits and insulators was examined as to its chemical and physical properties with the following results:

Carbon	86.48	per cent.
Hydrogen	10.33	"
Sulphur	0.40	"
Nitrogen	0.61	"
Oxygen, by difference	2.18	"
Specific gravity at 20°	1.00	"
Bromine-absorption	14.93	"
HBr evolved	2.91	"

Softening and melting-points :

20°	105°	135°
Easily compressible in fingers.	Shape still retained.	Begins to flow.

The next higher grade (3) that is adapted for paving does not differ essentially in its composition from the preceding ; it flows at a higher temperature :

Carbon	86.90
Hydrogen	10.20
Sulphur	0.39
Nitrogen	0.63
Oxygen	1.88
Specific gravity	....
Bromine-absorption	14.40
HBr evolved	1.64

Softening and melting-points :

20°	135°	150°	165°
Slightly compressible in fingers.	Retains shape ; edges rounded.	Softens.	Begins to flow.

To the grade next higher (4) has been given the name Byerlyte from the inventor of the process. It resembles the natural product Gilsonite, in that it is an excellent material for the manufacture of the best grades of japans and black varnish. Its composition was also determined by analysis :

Carbon	87.44
Hydrogen	9.31
Sulphur	0.41
Nitrogen	0.64
Oxygen	2.20
Specific gravity	1.04
Bromine-absorption	18.93
HBr evolved	4.56

Softening and melting-points :

20°	160°	230°	260°
Not compressible by fingers.	Slightly rounded on edges.	Softens.	Begins to flow.

In testing the solubility of Byerlyte, it was evident that it contains no fixed carbon. It dissolves completely in carbonic disulphide. In light ligroïn, 75–110°, 62.45 per cent. is soluble and 37.55 per cent. insoluble. In petroleum distillate, 200–250°, 59.37 per cent. is soluble, 40.03 per cent. insoluble.

It therefore appears that ultimate decomposition of petroleum tar is entirely prevented by this method of distillation. The influence of air in oxidation evidently affects the removal of hydrogen, as shown by the diminished proportions of this element, and the appearance of water in the process of manufacture, rather than the formation of oxygen compounds in the oil.

As explained above, the product Byerlyte has been found to possess properties desirable in the manufacture of varnishes. It resembles closely in its physical properties and its chemical composition the natural bitumen found in Colorado and Utah, and known in commerce as Gilsonite. This substance is used in large quantities by the manufacturers of varnish. In an analysis of Gilsonite from the Wasatch range in Eastern Utah, we obtained the following results:

		1.	2.	3.
C	86.86			
H	11.89			
N	0.02			
S (by Carius)		0.60		
(by combustion)			0.64	0.68

In an investigation of Utah Gilsonite recently made by Dr. W. C. Day,[1] it was found that this substance like Byerlyte is entirely soluble in carbonic disulphide, but less soluble in petroleum ether than we found Byerlyte to be. As shown by the determinations of sulphur given above, our experience concerning such determinations by combustion and by the Carius method does not coincide with that of Dr. Day. In the adaptation of the Sauer-Mixter-Burton method, perfected by one of us,[2] for the determination of sulphur in volatile organic compounds it was not explained that this method is serviceable in the analysis of non-volatile substances, or, what is doubtless true, that it is applicable to any compounds that can be burned with the formation of volatile products. Gilsonite is somewhat irregular in volatilizing, but not more so than the higher organic sulphides, several of which have

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[1] Journal of the Franklin Institute, June, 1895.

[2] Mabery: Proc. Am. Acad., **30**, 1; This JOURNAL, **16**, 544.

been analyzed in this manner. With adherence to the precautions given in the paper cited above, the combustion can be easily controlled. The same is true in the application of the Carius method to the analysis of Gilsonite. Following the details outlined in the same paper, no difficulty whatever was found in reaching accurate results.[1] Nitrogen was determined by the Kjeldahl method which we have found to be convenient and accurate in the analysis of petroleum and allied products. The marked differences in the percentages of carbon, hydrogen, and sulphur which we obtained, and those given by Day indicate a considerable variation in the composition of Gilsonite.

ON THE ACTION OF PHOSPHORUS PENTACHLORIDE ON PARASULPHAMINEBENZOIC ACID.

BY IRA REMSEN, R. N. HARTMAN, AND A. M. MUCKENFUSS.

Some years ago one of us (I. R.) with Dohme[2] showed that when benzoic sulphinide is treated with phosphorus pentachloride at a somewhat elevated temperature, the principal product of the reaction is orthochlorcyanbenzene, $C_6H_4<^{Cl}_{CN}$. A little later Rich,[3] at the suggestion of one of

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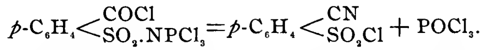
[2] This JOURNAL, 11, 347.

[3] *Ibid.*, p. 348.

[1] There is another feature in the determination of sulphur by combustion that perhaps should be mentioned in this connection. In burning substances with small percentages of sulphur we have found no difficulty in securing accurate results as shown by parallel Carius determinations. Occasionally, compounds with higher percentages of sulphur have given too low results, although usually they have been satisfactory. It has been shown by Lunge and others that methyl orange is not sensitive to neutral sodic sulphite, but the end reaction is determined by the acid sulphite.

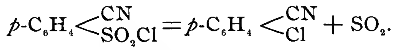
These results have been confirmed in this laboratory by Prof. A. W. Smith in a series of carefully conducted determinations. It is therefore evident that, in substances with low percentages of sulphur, the oxidation is complete with the formation only of sulphuric acid. With high percentages, some of the sulphur may be absorbed as sulphurous acid, although the quantity of this acid is never large. This error may be avoided by the addition of hydrogen dioxide in small amount, which oxidizes any sulphurous acid, and the titration is then only concerned with sulphuric acid.

The objection that has been suggested to the Carius method, that is the small amount of substance, 0.2000–0.3000 gram conveniently oxidized in a closed tube, is not valid, since results by this method agree closely within a few thousandths of one per cent. in low sulphur oils, with values obtained by combustion in air, even when as much as 3.000 grams of oil are completely burned, as we have recently found. In recent experiments, it has been shown that the correct percentage of sulphur can be ascertained only by combustion of the entire quantity of oil weighed. We are us (I. R.), took up the study of the action of phosphorus pentachloride on parasulphaminebenzoic acid. He obtained parachlorcyanbenzene, which he studied to some extent, but the investigation was interrupted, and various circumstances have interfered with its further prosecution until recently. The results of the later investigation are recorded in the following paper. As will be seen, when phosphorus pentachloride acts upon parasulphaminebenzoic acid at a temperature below 70°, a product of the formula $C_6H_4<\genfrac{}{}{0pt}{}{COCl}{SO_2.NPCl_3}$, is formed. When this is heated to between 146° and 200°, phosphorus oxychloride is given off, and paracyanbenzenesulphone chloride, $p\text{-}C_6H_4<\genfrac{}{}{0pt}{}{CN}{SO_2Cl}$, is formed, thus:



$$p\text{-}C_6H_4<\genfrac{}{}{0pt}{}{COCl}{SO_2.NPCl_3}=p\text{-}C_6H_4<\genfrac{}{}{0pt}{}{CN}{SO_2Cl}+POCl_3.$$

When paracyanbenzenesulphone chloride is heated to 205°, it is decomposed, giving sulphur dioxide and parachlorcyanbenzene according to this equation:



$$p\text{-}C_6H_4<\genfrac{}{}{0pt}{}{CN}{SO_2Cl}=p\text{-}C_6H_4<\genfrac{}{}{0pt}{}{CN}{Cl}+SO_2.$$

These facts are of considerable interest, as they give some insight into the nature of the reactions that lead to the shifting of the nitrogen atom from the sulphone group to the carbon atom in the para position. In a later article it will be shown that when parasulphaminebenzoic acid is heated alone to a temperature near its melting-point, it is completely transformed into other substances, the formation of which involves a shifting of the nitrogen atom in the molecule. A similar result is reached when metasulphaminebenzoic acid is heated, and the products of this transformation are now being investigated in this laboratory by Dr. Walter Jones.

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now able to state with confidence, that no method at present known for the determination of sulphur in organic bodies excels in accuracy combustion in air or oxygen. In case of execution no other method approaches it. In the form recently proposed by me, (This JOURNAL, **16**, 544,) I believe it can be applied without difficulty to any organic compound composed of carbon, hydrogen, oxygen, and sulphur. Whether a large percentage of nitrogen would interfere, we have not determined, but probably it would not.

[1] Ann. Chem. (Liebig), **178**, 297.

Action of Phosphorus Pentachloride at 60°. — The parasulphaminebenzoic acid used in these experiments was prepared by oxidizing either paratoluenesulphoneamide according to the method described by Remsen,[1] or from commercial saccharin, of which it forms about fifty per cent., by the method of Remsen and Burton.[2]

10 grams of the dried parasulphaminebenzoic acid and 21 grams of phosphorus pentachloride are thoroughly mixed in a dry mortar and quickly brought into a dry Erlenmeyer flask, which is then kept free from atmospheric moisture by connection with a small U-tube containing a little sulphuric acid. The flask is clamped in position in a sulphuric-acid bath, and the temperature is gradually raised. When, at about 60°, reaction sets in, the flask is raised above the bath until evolution of hydrochloric acid ceases; then it is lowered again, raised again, and so on, until action at 60° is complete. The temperature is then raised slowly to 110°, the flask being shaken from time to time, and this temperature is maintained until no more oxychloride collects in the U-tube, and the liquid in the flask is transparent. The flask is then allowed to cool slowly and about 200 cc. of dry ligroïn is added. The whole is now vigorously shaken for a few minutes. The clear, yellow oil soon solidifies to a mass of beautiful crystals, while the ligroïn, which is poured off, is found to contain phosphorus and chlorine. 500 cc. of fresh ligroïn is now poured into the flask, which is then immersed in water kept at 70°. The mass again becomes oily as the temperature rises, and is constantly stirred up into the ligroïn with a glass rod. When the ligroïn has reached 70°, it is kept there five minutes, and then filtered through a dry fluted filter. The flask is well stoppered, and allowed to stand from twelve to twenty-four hours, when it is found to contain a considerable quantity of very beautiful, transparent, stout prisms, that often attain the length of an inch.

Care must be taken to let the reaction at 60° proceed as slowly as possible, and especially not to heat the ligroïn above 70°. If the heating is carried much above this temperature, dark, oily products are formed, that become hopelessly intermingled with the clear crystals.

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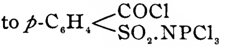
[1] Ann. Chem. (Liebig), 178, 297.

[2] This JOURNAL. 11, 403.

The ligroïn over the crystals is well stirred and poured off. Fresh ligroïn is added several times and the lighter products thus fully poured off. The clinging crystals are then detached from the glass, and all are poured into a beaker under ligroïn, and carefully examined. Every dark piece present is withdrawn. The clear product is then thrown on a filter, washed with fresh ligroïn, quickly and well pressed out on drying paper and placed in a sulphuric-acid desiccator.

Analysis led to the empirical formula $C_7H_4NO_3SPCl_4$, which corresponds to



$p\text{-}C_6H_4<\begin{matrix}COCl \\ SO_2.NPCl_3\end{matrix}$

I. 0.287 gram gave 0.0408 gram H_2O, and 0.2528 gram CO_2.

II. 0.2914 gram gave 0.0385 gram H_2O, and 0.255 gram CO_2.

III. 0.4006 gram gave 15 cc. of nitrogen and 23° and 760.55 mm.

IV. 0.4128 gram gave 16.3 cc. of nitrogen at 26° and 761 mm.

V. 0.2439 gram gave 0.168 gram $BaSO_4$ (Carius).

VI. 0.4472 gram gave 0.1412 gram $Mg_2P_2O_7$.

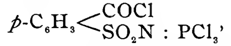
VII. 0.3630 gram gave 0.562 gram AgCl.

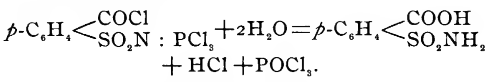
VIII. 0.2887 gram gave 0.4502 gram AgCl.

	Theory.	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
C	23.69	24.02	23.93	...	...	...	...	...	...
H	1.13	1.58	1.47	...	...	...	...	...	...
N	3.95	...	...	4.22	4.37	...	...	...	...
O	13.53	...	...	...	...	...	...	...	...
S	9.03	...	...	...	...	9.46	...	...	...
P	8.74	...	...	...	...	...	8.81	...	...
Cl	39.92	...	...	...	...	...	...	38.35	38.59

Chlorine was determined by placing about 0.2 gram in 400 cc. of water, warming until dissolved, and precipitating as silver chloride. Phosphorus was determined by placing about 0.2 gram in 100 cc. of water, heating to boiling, filtering off the parasulphaminebenzoic acid that separates out on cooling, and precipitating from the filtrate as ammonium magnesium phosphate.

Phosphochlorparasulphaminebenzoic Chloride.—The results above recorded do not agree very closely with the calculated figures, because of the extreme instability of the substance. It absorbs moisture from the atmosphere with great avidity, giving off fumes of hydrochloric acid. The specimens analyzed for chlorine were made at different times, and were in both cases protected from moisture as much as possible; yet the figures are about 1½ per cent. too low, some hydrochloric acid being given off in the process of pressing dry. The loss of chlorine of course increases the percentages of the other elements. The compound has such a tendency to absorb water, give off hydrochloric acid, and become liquid, that it can not be pressed dry with filter-paper except on a dry day. The substance crystallizes beautifully from ligroïn in transparent prisms that are not truncated by any well-defined faces. When exposed to the air the crystals quickly turn white. They break down in water, dissolving quickly if the water is warm, and pure parasulphaminebenzoic acid is deposited from the solution on cooling. The phosphochloride melts at 82°. It is soluble in benzene, but no well defined crystals were obtained from the solution.

Constitution of Phosphochloroparasulphaminebenzoic Chloride.—That the compound has the constitution represented by the formula  $p\text{-}C_6H_3<\begin{array}{l}COCl\\ SO_2N : PCl_3\end{array}$, appears probable in view of the fact that it breaks down so easily with water forming parasulphaminebenzoic acid. The reaction is expressed by the following equation:



$$p\text{-}C_6H_4<\begin{array}{l}COCl\\ SO_2N : PCl_3\end{array} + 2H_2O = p\text{-}C_6H_4<\begin{array}{l}COOH\\ SO_2NH_2\end{array} + HCl + POCl_3.$$

The phosphorus oxychloride would, of course, yield phosphoric acid by the action of the water, and the only products found were parasulphaminebenzoic, hydrochloric and phosphoric acids. Further, an analogous substance has been obtained by the action of phosphorus pentachloride on benzenesulphonamide. Wichelhaus[1] gave the formula $C_6H_5.SO_2NH.PCl_2$ to the product, but Wallach and Huth[2] later showed

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[1] Ber. d. chem. Ges., **2**, 502.

[2] Ibid. **9**, 424.

that it is to be represented by the formula $C_6H_5SO_2.NPCl_3$.

Search for Other Products.—If the mass remaining after the extraction of the phosphochloride is extracted with fresh ligroïn, each successive portion that separates on cooling contains less chlorine than the preceding one, and all pass to parasulphaminebenzoic acid on treatment with water. Thus, 38.35, 37.00, 32.89, and 30.07 per cent. of chlorine were found in the analysis of four successive extracts. The last product, containing 30.07 per cent. of chlorine, was found to be identical with that obtained by treating the phosphochloride with ligroïn at 70°, when phosphorus oxychloride was extracted. About one-fourth of the substance dissolved, and on cooling, a substance separated from the filtrate, that gave 30.14 per cent. of chlorine on analysis and was identical in appearance with that giving 30.07 per cent. It was very difficultly soluble, only about 0.2 gram separating from a liter of ligroïn, and consisted of silky hair-like crystals. It contained no phosphorus.

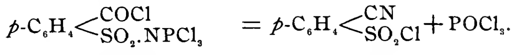
If the same ligroïn, containing phosphorus oxychloride and hydrochloric acid, was used for the successive extracts, a substance was finally obtained that separated in long, slender, arborescent crystals, of very beautiful appearance. These broke up completely on the slightest agitation, and could not be pressed dry for analysis.

If the ligroïn from the phosphochloride was filtered into a wet vessel, fine needles gradually separated. It was not possible to determine the composition of these products. They appeared, however, to be formed by decomposition of the phosphochloride.

Action of Heat on Phosphochlorparasulphaminebenzoic Chloride.—A quantity of the purified phosphochloride was placed at the bottom of a tube, fused at one end, and arranged to rest in a sulphuric-acid bath. Not far from the substance the tube was bent into two successive U-forms, the one nearest the substance being arranged to dip under water and the other being moistened with sodium hydroxide solution. Beyond this latter, the tube was drawn out to a coarse capillary about two inches long. The bath was heated slowly. The phosphochloride melted sharply at 82°, and began to give off vapors at 146°. The temperature was gradually raised to 200°, and kept there until no more gas was evolved. The mass blackened considerably, a yellow substance in the form of clear needles sublimed just above the bath, and a liquid collected in the U-bend nearer the bath. The tube was broken at each end of this bend, and the three parts examined. The substance in the farther bend gave off sulphur dioxide on addition of sulphuric acid. The liquid in the nearer bend was transferred to cold water, when it settled to the bottom as an oil, but gradually dissolved. The solution was found to contain hydrochloric and phosphoric acids.

The tube containing the charred residue and the sublimate was broken into fragments, extracted with benzene, and the filtered extract evaporated to dryness. The residue thus obtained was placed in a distilling-bulb, water added, and half of the liquid distilled over into another vessel. The distillate contained a white substance that had a very decided odor of nitriles, was very volatile with water-vapor, and melted at 93°. These are the properties of parachlorbenzoic nitrile, as will be shown further on. The liquid remaining in the distilling-bulb was filtered, and found to contain hydrochloric acid and a non-volatile acid. It was evaporated to dryness, the solution of the residue neutralized with barium carbonate, and the filtrate from this evaporated to crystallization. Seed-like crystals appeared, which proved to be the barium salt of paracyanbenzenesulphonic acid.

It appears from these observations that among the reactions that take place when the phosphochloride is heated is that represented by this equation :



$$p\text{-}C_6H_4{<}\begin{matrix}COCl\\SO_2.NPCl_3\end{matrix} = p\text{-}C_6H_4{<}\begin{matrix}CN\\SO_2Cl\end{matrix} + POCl_3.$$

Action of Phosphorus Pentachloride between 150° and 200°.

Parasulphaminebenzoic acid and phosphorus pentachloride, in the proportion of two molecules of chloride to one of acid, are thoroughly mixed, and then brought into a retort of suitable size, through whose tubulure a thermometer is introduced in such a way that its bulb is covered by the mass in the retort. The retort, with its contents, is then placed in a bath, of oil or concentrated sulphuric acid, and the temperature gradually raised. Reaction does not take place immediately, but when the mass reaches a temperature of 60° C. it begins to soften, and energetic action soon sets in, with evolution of hydrochloric acid and a considerable rise of temperature. The source of heat is removed at this stage, to moderate the reaction to some extent, as it has been found that too rapid action leads to unsatisfactory results. After the first energetic action is over, and the contents of the retort have become liquid, the temperature is raised again until the reaction continues as before, with evolution of hydrochloric acid and formation of phosphorus oxychloride. When the boiling-point of phosphorus oxychloride (110° C.) is reached, the mass is kept at this temperature until the reaction is apparently completed, and all the oxychloride has distilled off. If the temperature is raised to about 150° C., a second reaction sets in, and another portion of phosphorus oxychloride distils off. The heating is continued gradually until the thermometer dipping into the fused mass indicates a temperature of about 200° C., and the retort is kept at that point until the secondary reaction is over and no more oxychloride distils off. When this stage of the reaction is reached, the contents of the retort, which form a dark-brown semi-transparent liquid, are poured into a suitable vessel, and when cool they crystallize in well-defined prisms, rendered impure by the presence of some phosphorus compounds and a little parachlorbenzonitrile, which is formed in small quantities if the temperature rises too high. It is advisable to proceed quite slowly and not allow the contents of the retort to be heated above 220° C., as at high temperatures the product is gradually decomposed into sulphur dioxide and parachlorbenzonitrile. When the reaction is carried out as here described, a good yield of the new product is obtained. An experiment gave the following result: From 135 grams of parasulphaminebenzoic acid and 280 grams of phosphorus pentachloride, 135 grams of the new product, in approximately pure condition, was obtained. This approaches very closely to the theoretical yield. Experiments carried on with smaller quantities of material gave yields varying between 80 and 95 per cent. The product is separated from phosphorus compounds by treating it with water and by recrystallizing it from chloroform and benzene, from which it separates in large transparent prisms. The product, purified by successive recrystallizations, was then subjected to analysis. The results lead to the empirical formula $C_7H_4O_2SNCl$.

I. 0.2336 gram substance gave 0.3615 gram CO_2, and 0.0497 gram H_2O.

II. 0.2504 gram substance gave 0.3790 gram CO_2, and 0.0530 gram H_2O.

III. 0.3217 gram substance gave 19.90 cc. nitrogen at 18° C. and 760.1 mm.

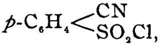
IV. 0.3528 gram substance gave 21.60 cc. nitrogen at 18° C. and 759.3 mm.

V. 0.2569 gram substance gave 0.1775 gram AgCl and 0.2990 gram $BaSO_4$.

VI. 0.1723 gram substance gave 0.2017 gram $BaSO_4$.

VII. 0.2658 gram substance gave 0.1890 gram AgCl.

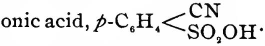
	Calculated for				Found.			
	$C_7H_4SNClO_2$.	I.	II.	III.	IV.	V.	VI.	VII.
C_7	41.67	41.65	41.28	...	...	...	...	...
H_4	2.00	2.33	2.35	...	...	...	...	...
N	6.96	...	...	7.13	7.05	...	...	...
S	15.60	...	...	...	...	16.00	16.90	...
Cl	17.50	...	...	...	...	17.00	...	17.58

These results considered in connection with the conduct of the substance show that it is *p*-cyanbenzenesulphone chloride,  $p\text{-}C_6H_4{<}^{CN}_{SO_2Cl}$, and its formation must be represented by the equation:

$$C_6H_4{<}^{COOH}_{SO_2NH_2} + 2PCl_5 = C_6H_4{<}^{CN}_{SO_2Cl} + 2POCl_3 + 3HCl.$$

Paracyanbenzenesulphone chloride crystallizes beautifully from benzene, crystals several centimeters in length and a centimeter in thickness being easily obtained. They are large rhombic prisms perfectly transparent. Frequently both ends are terminated by well-developed planes. It has a faint odor resembling that of the toluenesulphone chlorides. In the air it is stable, and it is not attacked by cold water. By long boiling with water, however, it is decomposed.

Alcohol dissolves it slowly at ordinary temperatures, the corresponding acid being formed. It dissolves readily in chloroform, benzene, and glacial acetic acid. It is much less soluble in ether, and almost insoluble in ligroïn. It melts at 111–112°, and sublimes in rough, white needles. When heated to about 250°, it is gradually decomposed, giving off sulphur dioxide, and forming parachlorcyanbenzene.

When the chloride is boiled with water it is easily converted into paracyanbenzenesulphonic acid,  $p\text{-}C_6H_4<^{CN}_{SO_2OH}$. When heated with water at 200° in a sealed tube it yields the acid ammonium salt of parasulphobenzoic acid. This was identified by transforming it into the very characteristic acid barium salt described by Remsen.[1] On analysis the salt gave the following results:

	Calculated.	Found.
Ba	23.12	23.03
H_2O	9.10	9.24

When the chloride is treated with aqueous ammonia, a well-characterized amide is formed. This, by treatment with alkalies or by heating with water in a sealed tube, is converted into parasulphaminebenzoic acid. These reactions show clearly that the chloride has the constitution above assigned to it, viz.,  $C_6H_4<^{CN}_{SO_2Cl}$.

Paracyanbenzenesulphonic Acid,  $C_6H_4<^{CN}_{SO_2OH(p)}$.—When paracyanbenzenesulphone chloride is boiled with water it is easily converted into the corresponding acid. This substance is extremely soluble in water even in the cold, but by gradual concentration of the solution it separates in small prismatic crystals. Owing to its great solubility, it was not possible to purify it sufficiently for analysis. Several salts, however, were prepared, the analyses of which leave no doubt as to the composition of the acid.

Barium Paracyanbenzenesulphonate, $(C_7H_5SO_3N)_2Ba$.—This salt is moderately soluble in hot water, difficultly in cold, and crystallizes in spherical aggregates of seed-like crystals without water of crystallization. The analyses gave these results:

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[1] Ann. Chem. (Liebig), 178, 280.

I. 0.2241 gram of salt gave 0.1032 gram $BaSO_4$.
II. 0.3408 gram of salt gave 0.1577 gram $BaSO_4$.

	Calculated for $(C_7H_4SO_3N)_2Ba$.	Found. I.	II.
Ba	27.36	27.09	27.21

Potassium Paracyanbenzenesulphonate, $C_7H_4SO_3NK$.—This is very readily soluble in water, but by slow evaporation of the solution it separates in long transparent prisms, frequently an inch in length. The crystals sometimes have their planes striated longitudinally and are quite characteristic. The analysis of the dry salt gave this result:

0.2132 gram salt gave 0.081 gram K_2SO_4.

	Calculated for $C_7H_4SO_3NK$.	Found.
K	17.68	17.03

Paracyanbenzenesulphoneamide, 
$C_6H_4<^{CN}_{SO_2NH_2(p)}$.—This is quite readily soluble in boiling water, but difficultly in cold water; readily soluble in hot alcohol; very slightly soluble in ether. It crystallizes from water in lustrous prisms, often two inches in length. When heated with a quantity of water insufficient for complete solution, the amide melts to an oil, which solidifies to a crystalline mass on cooling. This property of fusing under water has been noticed in several of the derivatives studied. The amide melts at 168–169° C., and can be sublimed with difficulty. Heated with hydrochloric acid in a sealed tube to 200° C., it gives parasulphaminebenzoic acid. This transformation, as has been shown before, has a direct bearing on the question of the constitution of the amide, and, taken in connection with the method of preparation, shows conclusively that the formula ascribed to the compound is the correct one. The analyses gave these results:

I. 0.1062 gram substance gave 0.2080 gram $BaSO_4$.

II. 0.1849 gram substance gave 0.2369 gram $BaSO_4$.

III. 0.3540 gram substance gave 49.22 cc. nitrogen at 22° C. and 762.8 mm.

IV. 0.2842 gram substance gave 39.15 cc. nitrogen at 21° C. and 758.8 mm.

	Calculated for $C_7H_6O_2N_2S$.	Found. I.	II.	III.	IV.
S	17.60	17.83	17.61	....	....
N	15.42	....	....	15.78	15.62

Paracyanbenzenesulphoneanilide, 
$C_6H_4<\begin{matrix}CN\\SO_2NHC_6H_5(p)\end{matrix}$.—This compound is formed by bringing together, best in benzene or chloroform solution, one molecule of paracyanbenzenesulphone chloride and two molecules of aniline. Reaction takes place at once with evolution of heat. The semi-liquid product is heated for some time to ensure complete reaction of the substances. The product is boiled with water and dilute hydrochloric acid, and is then purified by crystallization from alcohol, from which it separates in long prismatic plates usually with a slight brown color. When crystallized from benzene, the anilide has an entirely different crystal-habit and separates in tufts of fine, flat needles with a satiny lustre. It is readily soluble in alcohol and glacial acetic acid, less soluble in benzene, and almost insoluble in ether. It is very slightly soluble in boiling water, first melting to an oily liquid. When the aqueous solution is concentrated, the anilide separates again, giving the solution a milky appearance. Alkalies dissolve it in the cold, and from this solution it is reprecipitated by acids. The anilide fuses at 112° C. and forms a transparent mass which does not solidify again until entirely cold. The analytical results are as follows :

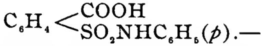
I. 0.3169 gram substance gave 0.2840 gram $BaSO_4$.

II. 0.2398 gram substance gave 0.2210 gram $BaSO_4$.

III. 0.3294 gram substance gave 32.50 cc. nitrogen at 21.2° C. and 753 mm.

IV. 0.3504 gram substance gave 34.20 cc. nitrogen at 10° C. and 759.5 mm.

	Calculated for $C_{13}H_{10}O_2N_2S$.	Found. I.	II.	III.	IV.
S	12.41	12.31	12.66	....	....
N	10.89	....	....	11.09	11.19

Parasulphanilidobenzoic Acid, 
$C_6H_4<\begin{matrix}COOH\\SO_2NHC_6H_5(p)\end{matrix}$.—When paracyanbenzenesulphoneanilide is treated with alkalies at ordinary temperatures no decomposition takes place,

but when it is boiled with a strong solution of sodium hydroxide, ammonia is eliminated and the cyanogen group is converted into the carboxyl group. From the alkaline solution, after the reaction is over, acids precipitate the new substance, parasulphanilidobenzoic acid, as a white flocculent mass insoluble in water.

The acid is difficultly soluble in cold alcohol and ether, readily soluble in boiling alcohol. From the alcoholic solution it separates in feathery plates or needles, white and lustrous, somewhat resembling the crystals of parasulphaminebenzoic acid. It melts at 252–253° C., and at this temperature undergoes partial decomposition. The analytical results are as follows:

I. 0.2202 gram substance gave 0.1917 gram $BaSO_4$.

II. 0.2732 gram substance gave 0.2305 gram $BaSO_4$.

III. 0.3736 gram substance gave 16.95 cc. nitrogen at 23° C. and 762.1 mm.

IV. 0.3523 gram substance gave 16.20 cc. nitrogen at 23° C. and 761.3 mm.

	Calculated for $C_{13}H_{11}O_4SN$.	Found. I.	II.	III.	IV.
S	11.56	11.96	11.59	....	....
N	5.06	....	....	5.11	5.18

Barium Parasulphanilidobenzoate, $(C_{13}H_{10}NSO_4)_2Ba+5H_2O$. —This salt is beautifully crystallized, moderately soluble in boiling water, from which it crystallizes in concentric groups of very fine silky needles, very light and brittle. The salt melts with decomposition at a comparatively low temperature. The analyses are as follows:

I. 0.3897 gram salt lost 0.0446 gram H_2O, and gave 0.1149 gram $BaSO_4$.

II. 0.3026 gram salt lost 0.0350 gram H_2O, and gave 0.0889 gram $BaSO_4$.

	Calculated for $(C_{13}H_{10}NSO_4)_2Ba+5H_2O$.	Found. I.	II.
Ba	17.60	17.34	17.28
H_2O	11.54	11.44	11.56

Potassium Parasulphanilidobenzoate, $C_{13}H_{10}NSO_4K+2H_2O$. —This is very soluble in water, and crystallizes in short prisms. The analyses are as follows:

I. 0.2909 gram salt lost 0.0308 gram H_2O, and gave 0.0665 gram K_2SO_4.

II. 0.3565 gram salt lost 0.0360 gram H_2O, and gave 0.0819 gram K_2SO_4.

	Calculated for $C_{13}H_{10}NSO_4K+2H_2O$.	Found. I.	II.
K	11.11	10.26	10.31
H_2O	10.29	10.58	10.09

Paracyanbenzenesulphone toluide (*p*), 

$C_6H_4<\begin{matrix}CN\\SO_2NHC_7H_7(p)\end{matrix}$.

—The method of preparation of this compound, as well as of the compounds obtained by treating paracyanbenzenesulphone chloride with meta- and paratoluidins, is identical with that employed for the formation of the anilide. Two molecules of orthotoluidine are gradually added to one molecule of the chloride in chloroform or benzene solution.

The crude product is boiled with dilute hydrochloric acid and recrystallized from alcohol. The pure toluide crystallizes in well developed prismatic forms which sometimes occur as plates, and usually have a slight pink color. The melting-point of the orthotoluide is 122–123° C., and, like the anilide, it remains transparent until cooled much below its melting-point. The orthotoluide is slightly soluble in boiling water, under which it first melts, though not as readily as does the anilide. It dissolves in boiling alcohol and glacial acetic acid, but it is almost insoluble in ether. Treated with a solution of an alkali it dissolves unchanged, and it is reprecipitated by the addition of an acid, as a curdy white mass. Boiled with strong alkalies, ammonia is given off and the corresponding acid is formed. The analysis of the orthotoluide gave these results:

I. 0.2961 gram substance gave 0.2543 gram $BaSO_4$.

II. 0.2274 gram substance gave 0.1970 gram $BaSO_4$.

III. 0.3115 gram substance gave 28.30 cc. nitrogen at 17.1° C. and 761.3 mm.

IV. 0.2808 gram substance gave 23.72 cc. nitrogen at 17.4° C. and 758 mm.

	Calculated for $C_{14}H_{12}N_2O_2S$.	Found. I.	II.	III.	IV.
S	11.77	11.80	11.90	....	....
N	10.32	....	....	10.55	10.59

Parasulpho-o-toluidobenzoic acid,  $C_6H_4<{}^{COOH}_{SO_2NHC_7H_7(o)}$.—In general properties this acid closely resembles the anilido acid just described. It crystallizes from alcohol in light, flat needles of a pure white color, which melt at 246–247° C. and are decomposed at this temperature forming a dark-colored liquid. It is practically insoluble in boiling water or ether, but dissolves readily in boiling alcohol. The analytical results are as follows:

I. 0.2232 gram substance gave 0.1848 gram $BaSO_4$

II. 0.2221 gram salt gave 0.1834 gram $BaSO_4$.

III. 0.3769 gram substance gave 16.10 cc. nitrogen at 20° C. and 760 mm.

IV. 0.3600 gram substance gave 17.80 cc. nitrogen at 21° C. and 760 mm.

	Calculated for $C_{14}H_{13}O_4SN$.	Found.			
		I.	II.	III.	IV.
S	11.01	11.37	11.35	....	....
N	4.82	....	....	4.87	4.98

To characterize the acid further, the barium salt was prepared. The crop of crystals separating from the solution on cooling was collected and the mother-liquor was then concentrated in order to obtain a further quantity of the salt. The portion of salt, however, which separated from the mother-liquor had a habit markedly different from the first fraction. Both were carefully recrystallized a number of times, but each retained its individuality. The analyses show that they differ in respect to the number of molecules of water of crystallization contained in them.

Barium Parasulpho-o-toluidobenzoate, $(C_{14}H_{12}O_4SN)_2Ba + 5H_2O$.—This salt crystallized first from the solution. It crystallized in minute white plates, moderately soluble in hot water. The results of the analyses are as follows:

I. 0.1956 gram salt lost 0.0220 gram H_2O, and gave 0.0562 gram $BaSO_4$.

II. 0.2090 gram salt lost 0.0240 gram H_2O, and gave 0.0606 gram $BaSO_4$.

	Calculated for $(C_{14}H_{12}O_4SN)_2Ba + 5H_2O$.	Found. I.	II.
Ba	16.99	16.89	17.05
H_2O	11.24	11.14	11.48

Barium Parasulpho-o-toluidebenzoate, $(C_{14}H_{12}O_4SN)_2Ba + H_2O$.—This salt was obtained from the mother-liquor of the salt above described. It is more soluble in water, and crystallizes in prismatic plates larger than the crystals of the first salt.

I. 0.2716 gram salt lost 0.0073 gram H_2O, and gave 0.0856 gram $BaSO_4$.

II. 0.4095 gram salt lost 0.0103 gram H_2O, and gave 0.1304 gram $BaSO_4$.

	Calculated for $(C_{14}H_{12}O_4SN)_2Ba + H_2O$.	Found. I.	II.
Ba	18.65	18.53	18.73
H_2O	2.45	2.68	2.52

This occurrence of two salts with different amounts of water of crystallization, noticed here, was noticed also in connection with the barium salts of the isomeric parasulpho-*m*-toluidobenzoic acid. The formation of analogous salts had been noticed also in the case of parasulphaminebenzoic acid. Remsen,[1] who was the first to prepare the acid and its salts, obtained a barium salt with 1 molecule of water of crystallization. Later, Noyes[2] prepared a salt with 5 molecules of water, and on further work showed that under different conditions both salts are formed. The principal causes of difference in composition were the degree of concentration and the rapidity with which the solution cooled.

Paracyanbenzenesulphonetoluide(m), $C_6H_4<\begin{matrix}CN\\SO_2NHC_7H_7(m)\end{matrix}$.—From alcohol this compound separates in pure white prisms, melting at 128° C. It is less liable to change than the ortho- and paratoluides, and retains the pure white color, even on long standing. It closely resembles the orthotoluide in properties; is readily soluble in hot alcohol, and in glacial acetic acid; practically insoluble in boiling water and ether. Unlike the orthotoluide, it does not fuse under water. Alkalies dissolve it in the cold, and from the solution it is reprecipi-

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[1] Am. Chem. (Liebig), 178, 302.

[2] This JOURNAL, 7, 147.

tated by acids unchanged. Boiling with strong alkali produces the same kind of change as in the case of the orthotoluide, the corresponding acid being formed. The analyses gave the following figures :

I. 0.2493 gram substance gave 0.2184 gram $BaSO_4$.

II. 0.2166 gram substance gave 0.1890 gram $BaSO_4$.

III. 0.3652 gram substance gave 33.50 cc. nitrogen at 20.7° C. and 758.5 mm.

IV. 0.2853 gram substance gave 25.85 cc. nitrogen at 20° C. and 758.9 mm. pressure.

	Calculated for $C_{14}H_{12}O_2N_2S$.	Found. I.	II.	III.	IV.
S	11.77	12.03	11.98	....	....
N	10.32	....	....	10.42	10.33

Parasulpho-m-toluidobenzoic Acid, 
$C_6H_4\langle{}^{COOH}_{SO_2NHC_7H_7}$ (*m*).
—The metatoluido acid is a beautifully crystallized compound which separates from the solution in alcohol in white, shining plates or leaflets, which have a tendency to assume the prismatic form. It melts with decomposition at 241–242° C. It is almost insoluble in boiling water and ether, but dissolves readily in boiling alcohol. The crystals of this acid are better defined than those of the orthotoluido acid, with a prismatic, rather than acicular habit. This, however, depends somewhat on conditions. The analyses gave the following results:

I. 0.2049 gram substance gave 0.1630 gram $BaSO_4$.

II. 0.2358 gram substance gave 0.1886 gram $BaSO_4$.

III. 0.3779 gram substance gave 16.45 cc. nitrogen at 24° C. and 765.5 mm.

IV. 0.2879 gram substance gave 12.80 cc. nitrogen at 23.6° C. and 770.3 mm.

	Calculated for $C_{14}H_{13}O_4SN$.	Found. I.	II.	III.	IV.
S	11.01	10.93	10.99	....	....
N	4.82	....	....	4.90	5.05

As in the case of the other acids described, the barium salt was prepared by boiling with an emulsion of barium carbonate and separating from the excess of carbonate by filtration. From this solution a salt crystallized out in long prisms, and, upon further concentration of the mother-liquor, another crop of crystals was obtained which differed markedly from the first in form. Suspecting that these salts, as those of parasulpho-*o*-toluidobenzoic acid, differed in the amounts of water of crystallization, a separate analysis of each crop of crystals was made, which showed this to be the case.

Barium Parasulpho-m-toluidobenzoate $(C_{14}H_{12}O_4SN)_2Ba + 5H_2O$.—This salt separates first from the solution obtained by treating parasulpho-*m*-toluidobenzoic acid with barium carbonate. It is a little less soluble than the second modification, and crystallizes with 5 molecules of water in long transparent prisms. The analyses gave these results :

I. 0.2406 gram salt lost 0.0270 gram H_2O, and gave 0.0695 gram $BaSO_4$.

II. 0.2486 gram salt lost 0.0308 gram H_2O, and gave 0.0835 gram $BaSO_4$.

	Calculated for $(C_{14}H_{12}O_4SN)_2Ba + 5H_2O$.	Found. I.	II.
Ba	16.99	17.03	17.26
H_2O	11.14	11.24	10.83

Barium Parasulpho-m-toluidobenzoate, $(C_{14}H_{12}O_4SN)_2Ba + 3H_2O$.—This salt crystallizes from the mother-liquor of the first salt in glittering prismatic plates, resembling somewhat the crystals of potassium chlorate. It is slightly soluble in cold water, readily in hot. The analysis was as follows :

I. 0.4244 gram salt last 0.0307 gram H_2O, and gave 0.1270 gram $BaSO_4$.

	Calculated for $(C_{14}H_{12}O_4SN)_2 + 3H_2O$.	Found.
Ba	17.78	17.59
H_2O	7.00	7.23

Paracyanbenzenesulphonetoluide, 
$(p)C_6H_4<\begin{matrix}CN\\SO_2NHC_7H_7(p)\end{matrix}$.
— Like the isomeric compounds this dissolves in hot alcohol and glacial acetic acid, but is practically insoluble in water, cold alcohol, or ether. From alcohol it crystallizes in rhombic prisms, usually tinged yellow, which melt at 151–152°. Alkalies dissolve it unchanged in the cold, but on heating the solution the corresponding acid, parasulpho-*p*-toluidobenzoic acid, is formed. The results of the analyses are as follows :

I. 0.2617 gram substance gave 0.2298 gram $BaSO_4$.

II. 0.2737 gram substance gave 0.2402 gram $BaSO_4$.

III. 0.2655 gram substance gave 23.90 cc. nitrogen at 22° C. and 756.7 mm.

IV. 0.2864 gram substance gave 26.10 cc. nitrogen at 20.5° C. and 766.1 mm.

	Calculated for $C_{14}H_{12}O_2N_2S$.	Found. I.	II.	III.	IV.
S	11.77	12.06	12.05	....	....
N	10.32	....	....	10.14	10.46

Parasulpho-p-toluidobenzoic acid,  $C_6H_4<\begin{matrix}COOH\\ SO_2NHC_7H_7(p)\end{matrix}$.—Purified by recrystallization from alcohol, this compound is obtained in beautiful white plates or leaflets, sometimes with an acicular habit. It melts at 282–283° C. with decomposition, resembling in this respect the other members of the series. It is readily soluble in boiling alcohol, but almost insoluble in boiling water or ether. The analyses are as follows:

I. 0.2112 gram substance gave 0.1665 gram $BaSO_4$.

II. 0.3477 gram substance gave 0.2876 gram $BaSO_4$.

III. 0.3762 gram substance gave 17.00 cc. nitrogen at 20.8° C. and 761.2 mm.

IV. 0.3278 gram substance gave 14.75 cc. nitrogen at 21.4° C. and 762.5 mm.

	Calculated for $C_{14}H_{13}O_4SN$.	Found. I.	II.	III.	IV.
S	11.01	10.83	11.37	....	....
N	3.82	....	....	5.14	5.11

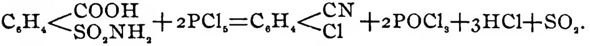
Barium Parasulpho-p-toluidobenzoate, $(C_{14}H_{12}O_4SN)_2Ba + H_2O$.—This salt crystallizes from water in small white prisms which show a tendency to curvature of the planes, and in some cases the crystals are considerably curled up at the ends. The crystals are not so well defined as are those of most of the other salts, and are more difficultly soluble in water. The analytical results are as follows:

I. 0.2827 gram salt lost 0.0041 gram H_2O, and gave 0.0879 gram $BaSO_4$.

II. 0.3345 gram salt lost 0.0089 gram H_2O, and gave 0.1045 gram $BaSO_4$.

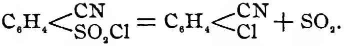
	Calculated for $(C_{14}H_{12}O_4SN)_2Ba+H_2O$.	Found. I.	II.
Ba	18.65	18.30	18.38
H_2O	2.45	2.51	2.66

Formation of Parachlorcyanbenzene.—When a mixture of parasulphaminebenzoic acid and phosphorus pentachloride is heated in a retort as described under the preparation of paracyanbenzenesulphone chloride, reaction first takes place at comparatively low temperatures. By raising the temperature to 250° C. a further reaction takes place; sulphurdioxide is evolved, and parachlorcyanbenzene distils off as an oil which soon solidifies. The reaction is represented by this equation:



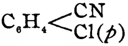
$$C_6H_4{<}\substack{COOH\\ SO_2NH_2}+2PCl_5=C_6H_4{<}\substack{CN\\ Cl}+2POCl_3+3HCl+SO_2.$$

It has been shown, however, that paracyanbenzenesulphone chloride is first formed, and that this then undergoes decomposition as represented by the equation:



$$C_6H_4{<}\substack{CN\\ SO_2Cl}=C_6H_4{<}\substack{CN\\ Cl}+SO_2.$$

The crude product obtained by distillation from the retort is placed in a flask and purified by distillation with steam, with which it is readily volatile.

Parachlorcyanbenzene,  $C_6H_4{<}\substack{CN\\ Cl(p)}$.—The compound closely resembles the isomeric ortho- and metachlorcyanbenzenes already studied by Henry,[1] and by Limpricht and Uslar,[2] respectively, in its general properties, having, however, a higher melting-point. It has a peculiar, rather pleasant aromatic odor, much resembling that of nitrobenzene, but more pungent. A marked property is its ready volatility. Sublimation takes place at low temperatures, and the compound is deposited in the form of long, glittering, prismatic needles, much like those obtained by careful sublimation of phthalic anhydride. Its melting-point is 93° to 94°. It dissolves slightly in boiling water, first melting to a clear oil, and, if the solution is kept at the boiling temperature, it passes off in

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[1] Ber. d. chem. Ges., 2, 492.

[2] Ann. Chem. (Liebig), 106, 35.

the steam. Alcohol and chloroform dissolve it readily. A curious property of the alcoholic solution was noticed. A hot solution was put aside to crystallize, and on cooling, parachlorcyanbenzene separated in long prismatic needles. On longer standing these needles were gradually dissolved, and a new crop of crystals, much shorter and thicker than the first lot, separated out. When boiled with alkalies, parachlorcyanbenzene is converted into parachlorbenzoic acid. The analyses gave these results:

I. 0.2300 gram substance gave 0.2394 gram AgCl.

II. 0.2413 gram substance gave 0.2488 gram AgCl.

III. 0.2338 gram substance gave 22.30 cc. nitrogen at 28° C. and 764.1 mm.

IV. 0.2371 gram substance gave 22.40 cc. nitrogen at 26° C. and 762 mm.

	Calculated for C_7H_4NCl.	Found.			
		I.	II.	III.	IV.
Cl	25.78	25.74	25.50	....	....
N	10.21	....	....	10.50	10.49

For the purpose of comparison parachlorcyanbenzene was made from parachloraniline by diazotizing, and treating the resulting diazo compound with a solution of cuprous cyanide in potassium cyanide, according to the directions of Sandmeyer. The nitrile was separated by distilling the solution with steam, and it was found to be identical with the product obtained from parasulphaminebenzoic acid by treating it with phosphorus pentachloride.

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REVIEWS.

CHEMICAL TECHNOLOGY. BY GROVES AND THORP. VOL. II.—LIGHTING. BY W. Y. DENT, J. MCARTHUR, L. FIELD, F. A. FIELD, BOVERTON REDWOOD, AND D. A. LOUIS. Philadelphia: P. Blakiston, Son & Co. 1895. 8vo. 398 pp.

This book forms the second volume of the series of works on Chemical Technology, edited by Groves and Thorp. It deals with the methods of producing light, excepting gas and electric lighting only, which will form the subjects of a subsequent volume. The book is divided into six sections, each dealing with a class of related topics, which have more or less direct bearing on the materials and means of producing light.

The first section, by W. Y. Dent, is a very good summary of the vegetable and animal fats and oils. The processes of saponifying fats are briefly explained, followed by an excellent synopsis of the usual methods employed in testing fats and oils; descriptions of the most important oils, their mode of extraction and purification with illustrations of the machinery used; characteristic reaction of each oil and the usual adulterants found in commercial samples.

Stearine is the subject of Section II, by John McArthur. In a short history of the industry, due credit is given to the researches of Chevreul on the fats, and to M. M. de Milby and Motard for establishing the industry on a practical basis. The raw materials and their valuation are reviewed briefly. Then follow descriptions of the various methods and apparatus for decomposing neutral fats into fatty acids, and the distillation, crystallization, and pressing of the fatty acids.

Candle manufacture is presented in Section III, by L. Field and F. A. Field. After a short review of the chronological development of the candle from the primitive torch, the authors discuss that important part of the candle,—the wick, and its preparation. Dipped and drawn candles are passed over quickly, and the greater part of the section devoted to moulded candles and the machines for making them. In all some fifteen different candle machines are described, and many of them illustrated by drawings.

Section IV, by Boverton Redwood, is devoted to the petroleum industry, forming the most important division of the book. The early history of petroleum is presented in an interesting manner, the different localities being discussed separately, with maps of many of the regions. The geology, origin, physical properties, and chemistry of petroleum, the methods of obtaining the crude oil in the several countries, and a short account of ozokerite mining in Galicia, follow. The description of oil-well drilling in the United States is largely compiled from the works of Peckham and Crew, and the catalogue of the Oil Well Supply Co., of Pittsburg, Pa., from which the illustrations of tools are taken. Petroleum refining comes next, considerable attention being given to the methods and apparatus used in the United States, but the refining of Russian, Canadian, and Galician oil is less completely described. A brief account of the transport of kerosene is followed by an extended description of the shale-oil industry, the various forms of apparatus being illustrated.

Lamps, other than gas and electric, form the topic of Section V, by Boverton Redwood. Beginning with the primitive lamps of antiquity, the author traces the development of all varieties down to the present time. The subject is considered under two general heads,—lamps for fat oils and lamps for mineral oils. The various types of burners are illustrated and clearly explained. The reader is impressed by the great amount of mechanical ingenuity expended in attempts to secure the most perfect combustion of oil with highest illuminating efficiency. Drawings of nearly ninety varieties of lamps and burners are given. A discussion of accidents arising from the use of mineral oil lamps, and methods of preventing explosions, follows. Since the majority of accidents are caused by dropping or overturning lamps, rather than by explosion as such, the conclusion is reached that lamps should be constructed with metal reservoirs, so arranged that the flame cannot reach the interior and so ignite the mixture of air and oil vapor therein. Air and oil supply, chimneys, wicks, and extinguishing appliances, are fully treated. Mineral spirit, vapor and spray or blast lamps, air gas machines and carburettors and oil gas manufacture are included in this section.

Section VI is devoted to the consideration of miners' safety-lamps, by Boverton Redwood and D. A. Louis. This subject is treated under the following heads :—the development of safety lamps, their requisites, automatic extinction appliances, lamps intended to show the presence of fire-damp, modes of locking lamps, construction of the parts, and oils for use in safety lamps. This description of the numerous locking devices is a curious commentary on the recklessness of the miner in endangering his own and his comrades' lives by opening his lamp while at work.

The book is a valuable addition to the list of English handbooks on Technology. Although issued by an American publishing house, it is the work of Englishmen, and the American reader should bear in mind that the frequent allusions to practices "in this country," refer to England. The illustrations represent in most cases machinery and appliances manufactured by English or Continental firms. The typography is generally excellent and misprints are rare. On p. 45 occurs *cholrestin* for cholesterin, and on p. 207 we read "heavy hydrogen oils," where "hydrocarbons" would seem clearer. An excellent index adds to the worth of the volume.

FRANK H. THORP.

Correction: Vol. XVIII, p. 63, line 9 from bottom : Instead of the sentence beginning "It is peculiar" and ending "their specific gravity" insert the following: "It is worthy of note that the higher specific gravity observed in the crude Petrolia oil appears in all the fractions made *in vacuo*."

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CHEMICAL JOURNAL.

Contributions from the Chemical Laboratory of Cornell University.

THE MOLECULAR WEIGHT OF SULPHUR.

BY W. R. ORNDORFF AND G. L. TERRASSE.

The molecular weight of sulphur was first determined in 1832 by Dumas,[1] who made use of the vapor density method and apparatus now so well known by his name. The following table gives the results of this investigation:

Temperature.	Density.	Calculated for S_6.
506° C	6.512	6.644
493°	6.495	
524°	6.617	
524°	6.581	

This value for the molecular weight of sulphur (192) was so different from that which was naturally expected (64) from the general resemblance between sulphur and oxygen that it led Mitscherlich,[2] who was present when Dumas made his determinations, to repeat the work himself in the following year, with the result that he obtained the value 6.90 for the vapor density of sulphur at a temperature of 509° C., thus fully confirming Dumas' results.

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[1] Ann. chim. phys. [2], **50**, 172. Obtained similar results in 1826 but did not publish them.

[2] Ann. Chem. (Liebig), **12**, 137; Ann. der phys., Pogg., **29**, 193.

It was not until 1860, twenty-seven years after, that the existence of molecules of sulphur containing two atoms (S_2) and corresponding to molecules of oxygen (O_2) was proved by Deville and Troost.[1] Using the Dumas method these chemists found the following values for the vapor density of sulphur:

Temperature.	Density.		Calculated for S_2.
860° C	2.28	2.22	2.22
	2.20	2.21	
	2.23	2.25	

Bineau[2] also claims to have obtained results which pointed to S_2 as the molecular formula of sulphur at about this time.

That the vapor density of sulphur is independent of the pressure was proved in 1878 by Troost,[3] who found the density at a temperature of 440° C. and a pressure of 104 mm. to be 6.7, while at the same temperature but at a pressure of 60 mm. 6.3 was the value obtained.

During the same year Victor and Carl Meyer,[4] using their new method of determining vapor densities, obtained a value 6.58 for the density of sulphur at a temperature which they vaguely describe as below red heat (Glühhitze) and in 1879 the same authors confirmed the results of Deville and Troost when they found the vapor density of sulphur to be 2.17 at yellow heat (Gelbhitze).

Pfaundler,[5] who about this time described a new method of determining vapor densities, states that, using his own apparatus, he had found satisfactory results for the vapor density of sulphur, which, presumably, means that he obtained values agreeing with S_6 as the molecular formula of this substance.

In 1882 Troost[6] again determined the vapor density of sulphur but this time at a temperature of 665° C. 2.92 and 2.94 were the values found at this temperature.

In 1888 Biltz,[7] at the suggestion of V. Meyer, undertook a very thorough investigation of the vapor density of sulphur at different temperatures, using both the apparatus of Dumas

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[1] Ann. chim. phys. [3], **58**, 257.

[2] Compt. rend., **49**, 799. See also Ann. chim. phys. [3], **58**, 257, and **59**, 456.

[3] Compt. rend., **86**, 1396.

[4] Ber. d. chem. Ges., **11**, 2259. and **12**, 1115.

[5] Ber. d. chem. Ges., **12**, 165.

[6] Compt. rend., **95**, 30.

[7] Ztschr. phys. Chem., **2**, 920.

and that of V. Meyer for this purpose. He calls attention to the fact that the only determinations which lead to the acceptance of the molecular formula S_6 are those of Dumas and Mitscherlich and that these estimations were all made within a temperature interval of only 30°, an interval which he thinks is far from being sufficient to warrant the assumption of a second molecular formula. In the following table Biltz's results with the Dumas method[1] are presented :

Temperature.	Density.	Molecular weight.	No. of atoms in molecule.
467.9° C.	7.937	229.2	7.16
480.5	7.448	215.1	6.72
487.4	7.301	210.9	6.59
501.7	7.015	202.6	6.33
518.0	7.036	203.2	6.35
523.6	7.086	204.6	6.40
534.4	6.975	201.4	6.29
580.9	5.509	159.1	4.97
606.0	4.734	136.7	4.27

From these results Biltz concludes that the only molecules of sulphur capable of existing in the gaseous state are those corresponding to the formula S_2, and these only at higher temperatures. At lower temperatures almost any desired greater value may be obtained for the density leading to the arbitrary assumption of molecules S_6, S_7, or in general S_n. Only the value corresponding to the molecule S_2 is constant within a considerable range of temperature and hence it alone should be taken into consideration in deciding the question of the molecular weight of sulphur.

To these conclusions of Biltz, W. Ramsay[2] takes exception and ventures the assertion that they are not entirely justified by the facts. According to him it is by no means proved that molecules corresponding to the formula S_6 do not exist. The results of Biltz simply lead one to suspect that perhaps more complex molecules, possibly S_8 or S_{10} may exist.

Paterno and Nasini[3] in 1888 determined the molecular weight of sulphur in benzene by the freezing-point method,

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[1] The results with the Meyer apparatus are not here given as they are not so reliable as those made by the Dumas method.

[2] Ztschr. phys. Chem., **3**, 67. See in this connection Biltz's answer, Ztschr. phys. Chem., **3**, 228.

[3] Ber. d. chem. Ges., **21**, 2153.

obtaining results which led them to conclude that the molecular weight of sulphur in this solvent was 192 and that molecules having the formula S_6 really do exist.

During the next year (1889) Biltz and Meyer[1] determined the vapor density of sulphur at 1719° C. and found even at this high temperature results agreeing closely with the formula S_2.

Beckmann[2] in 1890 was the first to make use of the boiling-point method for determining the molecular weight of sulphur. He confirms Biltz's statement that but little value can be attached to the results of Paterno and Nasini on account of the slight solubility of sulphur in this liquid. Using carbon disulphide as a solvent he obtained values varying from 247 to 314, according to the concentration, for the molecular weight of sulphur and states that these values are very near that required by the formula S_8 (256). He, however, regards these results as only approximate and suggests the use of other solvents, particularly of sulphur chloride, to decide this question of the true molecular weight of sulphur.[3] He then calls attention to the fact that Biltz's determinations of the vapor density of sulphur at a temperature (468° C.) slightly above its boiling-point do not exclude the possibility of the existence of molecules S_8 at the boiling-point (448° C.) of sulphur.

Acting apparently on a suggestion of Ramsay, C. Schall[4] in 1890 determined the vapor density of sulphur under diminished pressure in the vapor of boiling diphenylamine and phenanthrene. According to this investigator the values obtained in phenanthrene vapor (boiling-point about 340° C.) though they differ considerably from each other (6.34–7.60), seem to indicate the correctness of Biltz's inference, according to which trimolecular sulphur (S_6) does not exist. On the other hand, the remarkably constant results found for the density of sulphur in the vapor of diphenylamine (boiling-point 300° C.), appear to favor the assumption of the existence of tetramolecular sulphur (S_8), near the boiling-point of

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[1] Ztschr. phys. Chem., **4**, 266.

[2] Ztschr. phys. Chem., **5**, 80.

[3] Perhaps it should be noted here that these determinations of the molecular weight of sulphur were among the first made by Beckmann by this method.

[4] Ber. d. chem. Ges., **23**, 1704.

this substance as Beckmann has already shown by the boiling-point method.

E. Riecke[1] regards the decreasing vapor density of sulphur with rise of temperature as a case of dissociation by steps, (stufenweise Dissociation), of molecules S_8 to S_2 and S_6 and that finally S_6 breaks up into three molecules of S_2. According to this author both Beckmann and Schall have shown that sulphur molecules of the formula S_8 exist and the investigations of Biltz make it probable that on vaporizing sulphur at atmospheric pressure molecules S_8 are first evolved and that these split up into S_6 and S_2, and that in the further course of the dissociation the molecules S_6 also break up into three moledules of S_2. By making these and other assumptions he shows a certain coincidence between his calculated results and the values observed by Biltz for the vapor density of sulphur at different temperatures.

The molecular weight of sulphur was determined by J. Hertz[2] in naphthalene by the freezing-point method during the year 1890. His values varied from 262.3 to 279.4 according to the concentration and indicate a molecular weight of 256 for this substance. He also calls attention to the unsatisfactory results of the molecular weight determinations in benzene due to the slight solubility of sulphur in that solvent.

In 1892 Sakurai,[3] making use of an apparatus devised by himself, determined the molecular weight of sulphur in solution in carbon disulphide by the boiling-point method and obtained values varying from 252.3 to 254.9. He concludes from these results that the molecule of sulphur contains eight atoms (S_8).

Helff[4] in 1893 used both the boiling-point and freezing-point methods of determining molecular weights to solve the question as to the molecular weight of sulphur. In carbon disulphide he found values from 258 to 343 according to the concentration, while in melted phosphorus, the material used in the freezing-point method, his results varied from 234.6 to 251.1. Both methods, he states, indicate that the molecular weight of sulphur is 256 (S_8).

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[1] Ztschr. phys. Chem., **6**, 430.

[2] Ztsch. phys. Chem., **6**, 358.

[3] J. Chem. Soc., **61**, 989.

[4] Ztschr. phys. Chem., **12**, 196.

A fourth method of determining molecular weights was used by G. Guglielmo[1] in 1892 to determine the molecular weight of sulphur. From the relative depressions of the vapor pressure which solutions in carbon disulphide show, and which for sufficiently dilute solutions of sulphur are constant, he finds that the molecule of sulphur contains eight or nine atoms according to the concentration.

It will naturally be thought by those reading this review of the very careful work done on the molecular weight of sulphur that the question is settled, that there can be no doubt that the molecular weight of this element at ordinary temperatures is 256 and that there are eight atoms in the sulphur molecule. It will be noted, however, that in none of these investigations has any attempt been made to show whether the two forms of sulphur known as the orthorhombic and monoclinic varieties have the same molecular weight. To be sure, the results in carbon disulphide may be regarded as determinations of the molecular weight of the orthorhombic modification, but no determinations exist of the molecular weight of the other form of sulphur. These two varieties of sulphur differ from each other not only in crystal form and color but also in specific gravity and melting-point so that it seemed *at first* not unlikely that these differences might be due to a difference in molecular weight of the two forms of sulphur.

It was found that sulphur crystallizes from boiling benzene and also from boiling toluene in beautiful transparent monoclinic needles, which, however, soon became opaque on standing from the transformation into the orthorhombic modification. It was naturally thought from this fact that it would be possible to determine the molecular weight of the monoclinic form of this substance by determining the molecular weight of sulphur in benzene and toluene at their boiling-points, since at these temperatures there is no longer any orthorhombic sulphur in solution. The following investigation was begun with this object in view, but the results obtained were so different from what was expected that the investigation was extended so as to include molecular weight determinations by both

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[1] Real. Accad. Linc., 1892, **2**, 210-216.

the boiling- and freezing-point methods in a number of solvents.

Experimental.

Purification of the Sulphur.—Pure roll sulphur was first distilled in an atmosphere of carbon dioxide, rejecting both the first and last distillates and collecting only the middle portion. This middle fraction was again distilled in a stream of carbon dioxide, rejecting the end portions as before, and the middle distillate was then recrystallized several times from toluene in such a way that very small crystals were obtained. Toluene is a much better solvent for the purification of sulphur than carbon disulphide, as it is easily obtained pure and does not cling so tenaciously to the sulphur. The first and last portions of the recrystallized product were always rejected, the middle portion being washed with toluene to take out the mother liquor, drained and then washed with ether to remove the last traces of toluene and dried in the air. The purity of this material was proved by determining the amount of residue left after ignition and by analysis.

2.0241 grams sulphur gave on gentle ignition a residue of 0.0001 gram, corresponding to 0.005 per cent. of impurity.

Analyses by the Carius method, (heating the sulphur in a sealed tube with fuming nitric acid, precipitating and weighing the sulphuric acid formed as barium sulphate), gave the following results :[1]

I. 0.1771 gram sulphur gave 1.2932 grams $BaSO_4$.
II. 0.1833 " " " 1.3373 " "

	Gram sulphur taken.	Gram sulphur found.	Results in percentage.
I.	0.1771	0.17756	100.25
II.	0.1833	0.18362	100.17

$S = 32.06$. $BaSO_4 = 233.49$.

Determinations of the Molecular Weight of Sulphur by the Boiling-Point Method.

Apparatus and Method.—The apparatus used in the determination of the molecular weight by the boiling-point method was that recently described by Orndorff and Cameron.[2] The

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[1] These analyses were made for us by Mr. D. A. Morton, an assistant in the laboratory, to whom we wish here to express our thanks.

[2] This JOURNAL, 17, 517.

thermometer was of the Beckmann differential type, made especially for us by Goetze, of Leipsic. It was graduated in hundredths of a degree, had a shorter, though wider, mercury bulb and larger capillary tube than the thermometers generally used in this work. The scale divisions were larger also, thus insuring greater accuracy in the readings. This thermometer was carefully calibrated on a dividing engine and found to have at no part of the scale an error of more than *one thousandth of a degree in one degree*. The readings were all made with a cathetometer located about two meters from the apparatus, and after every observation, care was taken to read the barometer also. In no case were the results calculated until the whole series of observations had been taken, thus avoiding prejudiced readings. No series has been omitted with the exception of two with benzene as a solvent and one with carbon disulphide. These determinations were made at the beginning of the work and before we thoroughly understood the method. In all other cases the results are given exactly as they were recorded. Whenever possible a series of determinations was made, as this method undoubtedly gives more accurate results. Where the individual values found for the molecular weights in a series do not differ very much from each other, the average of a series of determinations is given as well as the molecular weight at infinite dilution, and where two or more series of determinations are made the average of all the molecular weights at infinite dilution is stated. No corrections have been made for barometric changes or for errors in the thermometer, as these were in all cases *very* small and it was thought best to manipulate the results as little as possible. The solvents were in *all* cases carefully purified before being used. The boiling-points given for these substances were made with great care, using a standardized thermometer, entirely surrounded with the vapor of the boiling substance, to determine the temperature.

In representing the results by the graphic method we have in every case plotted the molecular weights as ordinates and the concentration, (number of grams of the solute in 100 grams of the solvent), as abscissas. This method is not only more accurate than that of plotting the molecular weights against rises or depressions of temperature, as is usually done, but it is more rational, since what we wish to know is the *molecular weight at infinite dilution*. We have drawn a small circle around each point plotted and numbered it so that the reader may see at a glance what determinations belong together and just how much each determination is off its proper curve. The scales have been selected so as to exaggerate variations in molecular weights. Since the difference between the possible molecular weights is small (only 32), it is necessary to work with great care and in some cases to make several series of determinations in order to find the true molecular weight of sulphur.

In order to save time and also to avoid mistakes as far as possible, all the calculations were made on the Brunsviga calculating machine, which we highly recommend for this purpose.

Results with Toluene.—Toluene was the first solvent used by us in the determination of the molecular weight of sulphur by the boiling-point method. It is an ideal solvent for this purpose, as will be seen from the following results:

SULPHUR,

$S_8 = 256$; $S_9 = 288$.

Solvent: *Toluene.*

Boiling-point 109.7° C. at 741.7 mm. barometric pressure.

Molecular elevation for 100 grams, 35°.

I.

	Grams solvent.	Grams substances.	Concentration in 100 grams.	Observed elevation.	Barometer mm.	Molecular weight
1	78.04	0.6222	0.7973	0.097°	738.2	288
2	"	0.9071	1.1624	0.139	738.1	293
3	"	1.1973	1.5342	0.186	738.1	290
4	"	1.5570	1.9951	0.241	738.1	290
5	"	1.8748	2.4024	0.291	738.0	289
6	"	2.2023	2.8220	0.339	738.0	291
7	"	2.6102	3.3447	0.399	738.0	293

Barometer 738.2 — 738.0 mm. Average of series I **290.5**

Molecular weight at infinite dilution **288.5**

Molecular elevation at " " **34.9°**

II.

	Grams solvent.	Grams substance.	Concentration in 100 grams.	Observed elevation.	Barometer mm.	Molecular weight
8	79.68	0.4549	0.5709	0.071°	745.9	281
9	“	0.9950	1.2487	0.153	746.0	286
10	“	1.4584	1.8303	0.230	746.1	279
11	“	2.0134	2.5269	0.318	746.3	278
12	“	2.4814	3.1142	0.397	746.3	275
13	“	2.9432	3.6938	0.468	746.4	276
14	“	3.4002	4.2673	0.536	746.4	279
15	“	4.0384	5.0683	0.631	746.5	281

Barometer 745.8 — 746.5 mm. Average of series II 279.3

Molecular weight at infinite dilution 282.0

Molecular elevation at “ “ 35.7°

III.

	Grams solvent.	Grams substance.	Concentration in 100 grams.	Observed elevation.	Barometer mm.	Molecular weight.
16	84.28	0.4371	0.5186	0.064°	738.0	284
17	“	0.9141	1.0846	0.130	738.1	292
18	“	1.3505	2.6024	0.194	738.2	289
19	“	1.8316	2.1732	0.263	738.2	289
20	“	2.3864	2.8315	0.348	738.3	285
21	“	2.8386	3.3681	0.424	738.4	278
22	“	3.4993	4.1520	0.518	738.6	281
23	“	4.1804	4.9601	0.625	738.7	278

Barometer 738.0 — 738.7 mm. Average of series III 284.5

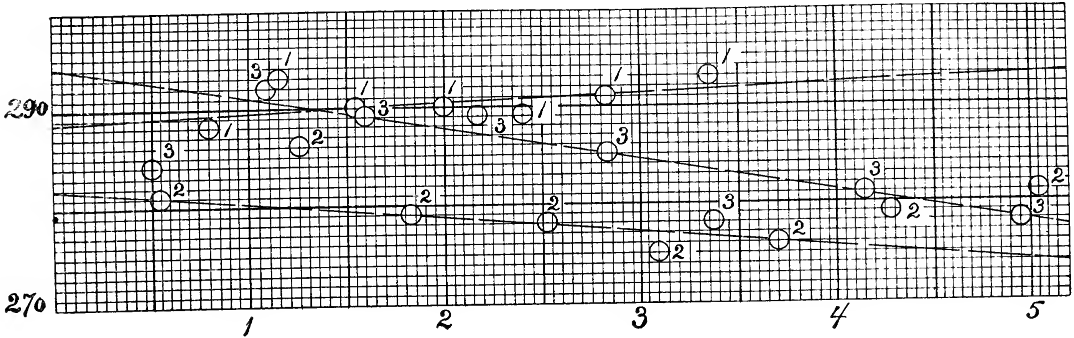
Molecular weight at infinite dilution 294.0

Molecular elevation at “ “ 34.3°

Average of 23 determinations in toluene 284.7

Average of molecular weights at infinite dilution 288.1

Graphic Representation of Determinations of the Molecular Weight of Sulphur in Toluene by the Boiling-Point Method.



These results certainly indicate that the molecular weight of sulphur is 288 and that its molecular formula is S_9.

Results with Carbon Disulphide.—As the molecular weight of sulphur in carbon disulphide has been determined by Beckmann, Sakurai and Helff, and each obtained values approximating 256 (S_8), we were at first inclined to ascribe the difference between our results in toluene and those of these investigators in carbon disulphide to the fact that our results gave the molecular weight of monoclinic sulphur, while those of the others represented the molecular weight of the orthorhombic variety. It seemed hardly possible, however, that the monoclinic sulphur should have a different molecular weight from that of the orthorhombic form and still less probable that it should have a *higher* molecular weight than the other variety, which is the stable modification at ordinary temperatures. We therefore concluded to repeat the work with carbon disulphide. It was soon found that this solvent was by no means so easy to work with as toluene. In order to avoid errors of readings and to get results that agreed with each other, we added at first a large amount of sulphur. After this was done no further difficulty was experienced in getting good readings with this solvent. The introduction of sulphur seemed to make the boiling more uniform and the large amount of sulphur used at first gave a considerable rise of temperature, so that errors in the readings, (which are always greater in the first observations), affected the final results very little. As will be seen from the results the molecular weight increases but slightly with increasing concentration, so that this method gives accurate values for the molecular weight of sulphur.

The following are the results in tabular form:

SULPHUR,

$S_8 = 256$; $S_9 = 288$.

Solvent: *Carbon Disulphide.*
Boiling-point 46.0° C. at 757.4 mm. barometric pressure.
Molecular elevation for 100 grams, 23.75°.

I.

	Grams solvent.	Grams substance.	Concentration in 100 grams.	Observed elevation.	Barometer mm.	Molecular weight.
1	123.70	4.1565	3.3601	0.271°	751.4	294
2	"	6.1128	4.9416	0.419	751.5	280
3	"	7.0244	5.6786	0.481	751.6	280

Barometer 751.1 — 751.6 mm. Average of series I **284.6**

II.

	Grams solvent.	Grams substance.	Concentration in 100 grams.	Observed elevation.	Barometer mm.	Molecular weight.
4	113.68	5.3530	4.7088	0.378°	757.1	296
5	"	7.2579	6.3845	0.518	757.0	293
6	"	9.1103	8.0140	0.650	757.0	293
7	"	11.0012	9.6773	0.781	756.9	294
8	"	13.0693	11.4966	0.928	756.8	294
9	"	15.2140	13.3832	1.070	756.7	297

Barometer 757.4 — 756.7 mm. Average of series II **294.5**

Molecular weight at infinite dilution **289.0**

Molecular elevation at " " **23.7°**

III.

	Grams solvent.	Grams substance.	Concentration in 100 grams.	Observed elevation.	Barometer mm.	Molecular weight.
10	119.03	8.9310	7.5032	0.595°	753.9	299
11	"	10.7175	9.0040	0.716	753.9	299
12	"	12.5151	10.5142	0.840	753.9	297
13	"	14.3147	12.0261	0.950	753.8	301
14	"	15.7343	13.2188	1.041	753.7	302

Barometer 754.1 — 753.7 mm. Average of series III **299.6**

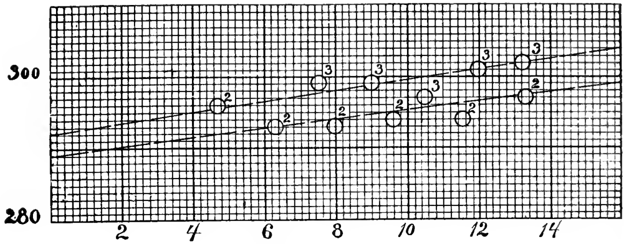
Molecular weight at infinite dilution **292.0**

Molecular elevation at " " **23.5°**

Average of 14 determinations in carbon disulphide **292.9**

Average of molecular weights at infinite dilution **290.5**

Graphic Representation of Determinations of the Molecular Weight of Sulphur in Carbon Disulphide by the Boiling-Point Method.



These results, like those obtained with toluene as a solvent indicate that the molecular weight of sulphur is 288, and that there are nine atoms in the molecule. They also show that both the orthorhombic and monoclinic varieties of sulphur have the same molecular weight.

Results with Benzene.—As the determinations with toluene and carbon disulphide led to conclusions so different from those made by other investigators and referred to above, it was thought advisable to make further molecular weight determinations by this method, using other solvents. Benzene was the the next solvent selected. Sulphur is not very soluble in this liquid, however, even at the boiling-point, and for that reason the results are not quite so satisfactory as those with toluene and carbon disulphide. The change of the molecular weight with increase of concentration is quite rapid, so that here only the molecular weight at infinite dilution is to be considered.

The following table gives the results found :

SULPHUR,

$S_8 = 256$; $S_9 = 288$.

Solvent : *Benzene.*

Boiling-point 79.6° at 744.3 mm. barometric pressure.

Molecular elevation for 100 grams, 26.5°.

I.

	Grams solvent.	Grams substance.	Concentration in 100 grams.	Observed elevation.	Barometer mm.	Molecular weight.
1	83.00	0.2077	0.2502	0.022°	731.7	301
2	“	0.4265	0.5139	0.044	731.6	310
3	“	0.6638	0.7998	0.057	731.4	372
4	“	0.9418	1.1347	0.084	731.2	358

Barometer 731.8 — 731.2 mm.

Molecular weight at infinite dilution 285.0

Molecular elevation at infinite dilution 26.8°

II.

	Grams solvent.	Grams substance.	Concentration in 100 grams.	Observed elevation.	Barometer mm.	Molecular weight.
5	87.96	0.5624	0.6394	0.056°	751.3	303
6	“	1.1489	1.3062	0.116	751.3	298
7	“	1.7543	1.9944	0.175	751.3	302
8	“	2.3488	2.6703	0.230	751.3	308
9	“	3.0083	3.4201	0.296	751.2	306

Barometer 751.2 — 751.2 mm.

Molecular weight at infinite dilution 288.0

Molecular elevation at infinite dilution 26.5°

III.

	Grams solvent.	Grams substance.	Concentration in 100 grams.	Observed elevation.	Barometer mm.	Molecular weight.
10	83.66	0.4760	0.5690	0.054°	738.6	279
11	“	1.0070	1.2037	0.106	738.4	301
12	“	1.6022	1.9151	0.164	738.1	309
13	“	2.2003	2.6301	0.217	737.9	321

Barometer 738.7 — 737.9 mm.

Molecular weight at infinite dilution 289.0

Molecular elevation at infinite dilution 26.4°

IV.

	Grams solvent.	Grams substance.	Concentration in 100 grams.	Observed elevation.	Barometer mm.	Molecular weight.
14	85.52	0.5797	0.6779	0.057°	728.9	315
15	“	1.2161	1.4220	0.120	728.8	314
16	“	1.8741	2.1914	0.179	728.6	324
17	“	2.5856	3.0234	0.239	728.3	335

Barometer 728.9 — 728.3 mm.

Molecular weight at infinite dilution	**295.0**
Molecular elevation at infinite dilution	**25.9°**

V.

	Grams solvent.	Grams substance.	Concentration in 100 grams.	Observed elevation.	Barometer mm.	Molecular weight.
18	86.80	0.4676	0.5387	0.051°	738.9	280
19	"	1.5308	1.7636	0.173	739.1	270
20	"	2.0444	2.3553	0.221	739.1	282
21	"	2.6930	3.1025	0.300	739.2	274

Barometer 739.8 — 739.2 mm.

Molecular weight at infinite dilution	**281.0**
Molecular elevation at infinte dilutiion	**27.2°**
Average of molecular weights at infinite dilution	**287.6**

Graphic Representation of Determinations of the Molecular Weight of Sulphur in Benzene by the Boiling-Point Method.

(See diagram on opposite page.)

These results, it will be seen, point to S_9 as the molecular formula for sulphur and confirm those obtained by us, using toluene and carbon disulphide as solvents.

Results with Naphthalene.—As it is almost certain from the vapor density determinations of sulphur, which have been recorded, that the molecular weight of this substance at temperatures slightly above its boiling-point (448°C) is, at any rate, not greater than 256, it seemed to us probable that in liquids of high boiling-point the molecular weight would be less than 288, and possibly would be 256. We therefore selected naphthalene for the next solvent for this work. Notwithstanding its great tendency to sublime, it is an excellent solvent for molecular weight determinations by the boiling-point method. It is very easily obtained pure, and as sulphur is very soluble in it, the results are quite satisfactory.

The following table gives the results obtained :

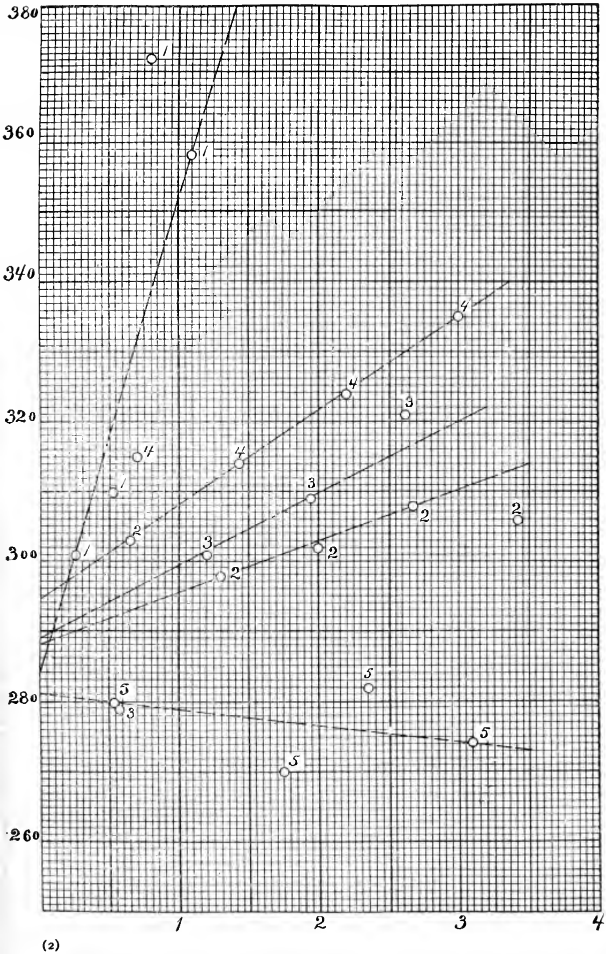
SULPHUR,

$S_8 = 256$; $S_9 = 288$.

Solvent : *Naphthalene.*

Boiling-point 216.7° C. at 741.9 mm. barometric pressure.

Molecular elevation for 100 grams 60.7°.



(2)

I.

	Grams solvent.	Grams substance.	Concentration in 100 grams.	Observed elevation.	Barometer mm.	Molecular weight.
1	89.75	0.4146	0.4619	0.104°	736.1	270
2	"	0.8194	0.9130	0.210	736.2	264
3	"	1.1788	1.3134	0.294	736.3	271
4	"	1.6380	1.8251	0.416	736.3	266
5	"	2.2252	2.4793	0.552	736.3	273
6	"	2.7823	3.1000	0.700	736.3	269
7	"	3.4758	3.8728	0.861	736.4	273
8	"	4.1324	4.6043	1.013	736.4	273

Barometer 736.1 — 736.4 mm.

Molecular weight at infinite dilution 262.0

Molecular elevation at infinite dilution 59.5°

II.

	Grams solvent.	Grams substance.	Concentration in 100 grams.	Observed elevation.	Barometer mm.	Molecular weight.
9	104.92	0.6123	0.5836	0.137°	745.8	259
10	"	1.2037	1.1473	0.270	"	258
11	"	1.7581	1.6757	0.398	"	256
12	"	2.3158	2.2072	0.525	"	255
13	"	2.8983	2.7624	0.662	"	253
14	"	3.4694	3.3067	0.785	"	256
15	"	4.0452	3.8555	0.897	"	261
16	"	4.6793	4.4599	1.022	"	265

Barometer 745.8 mm.

Molecular weight at infinite dilution 252.0

Molecular elevation at infinite dilution 61.7°

III.

	Grams solvent.	Grams substance.	Concentration in 100 grams.	Observed elevation.	Barometer mm.	Molecular weight.
17	101.72	0.4298	0.4225	0.096°	748.4	267
18	"	0.9585	0.9423	0.218	748.3	262
19	"	1.4654	1.4406	0.332	748.3	263
20	"	2.0161	1.9820	0.455	748.3	264
21	"	2.5409	2.4979	0.565	748.3	268
22	"	3.0615	3.0097	0.679	748.2	269
23	"	3.5759	3.5154	0.785	748.2	272
24	"	4.1437	4.0736	0.905	748.2	273

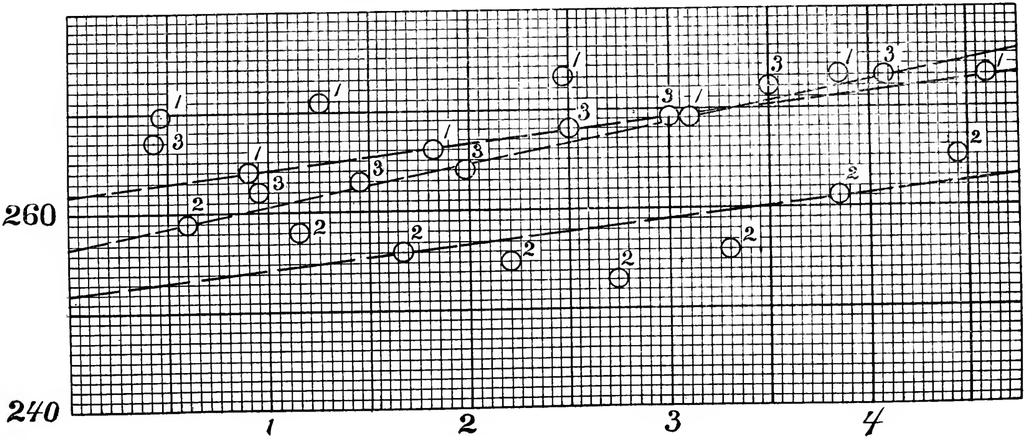
Barometer 748.4 — 748.2 mm.

Molecular weight at infinite dilution 256.5

Molecular elevation at infinite dilution 60.5°

Average of molecular weights at infinite dilution 256.8

Graphic Representation of Determinations of the Molecular Weight of Sulphur in Naphthalene by the Boiling-Point Method.



These results can be interpreted in only one way, namely, that at the boiling-point of naphthalene the molecular weight of sulphur is 256 and that there are eight atoms in the molecule of sulphur at this temperature.

Results with Metaxylene.—Having thus shown that the molecular weight of sulphur is a function of the temperature we wished next to see if this change continued with the increase of temperature, but though we tried a large number of solvents[1] boiling over 200° C. we found none which would dissolve sulphur without decomposition. At this temperature sulphur appears indeed to be very active chemically. Certain solvents were found, however, whose boiling-points lie between those of toluene and naphthalene upon which sulphur did not act. Determinations were therefore made with these substances in order to find out what the molecular weight of sulphur was at temperatures between 100° and 200° C. The following are the results with metaxylene :

SULPHUR,

$S_8 = 256$; $S_9 = 288$.

Solvent : *Metaxylene.*

Boiling-point 138.8° C. at 756.1 mm. barometric pressure.

Molecular elevation for 100 grams, 43.2°.

I.

	Grams solvent.	Grams substance	Concentration in 100 grams.	Observed elevation.	Barometer mm.	Molecular weight.
1	77.13	0.8067	1.0459	0.180°	748.8	251
2	"	1.5990	2.0731	0.333	748.8	269
3	"	2.3771	3.0819	0.475	749.0	280
4	"	3.1933	4.1401	0.626	749.0	286
5	"	3.8914	5.0452	0.750	749.0	291
6	"	4.6038	5.9689	0.868	749.0	297
7	"	5.1124	6.6283	0.950	749.1	301

Barometer 748.8—749.1 mm.

Molecular weight at infinite dilution 250.0

Molecular elevation at infinite dilution 44.2°

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[1] Sulphur is but slightly soluble in or acts upon the following substances at their boiling-points : fluorene, phenanthrene, diphenylmethane, ethylene bromide, ethyl acetate, mesitylene, resorcin, diphenyl, quinoline, monobromnaphthalene, acenaphthene, dihydroanthracene, diphenylketone, acetanilide, phthalic anhydride, anthracene, amyl benzoate, ether, alcohol, acetic acid, heptane and chloroform.

II.

	Grams solvent.	Grams substance.	Concentration in 100 grams.	Observed elevation.	Barometer mm.	Molecular weight.
8	72.37	0.3889	0.5374	0.092°	746.2	252
9	"	0.8102	1.1195	0.175	746.2	276
10	"	1.2724	1.7582	0.263	746.3	289
11	"	1.6885	2.3331	0.342	746.3	295
12	"	2.1421	2.9599	0.432	746.4	296
13	"	2.6924	3.7203	0.544	746.4	295
14	"	3.2286	4.4612	0.651	746.4	296
15	"	3.7982	5.2484	0.763	746.5	297

Barometer 746.2 — 746.5 mm.

Molecular weight at infinite dilution	255.0
Molecular elevation at infinite dilution	43.4°

III.

	Grams solvent.	Grams substance.	Concentration in 100 grams.	Observed elevation.	Barometer mm.	Molecular weight.
16	68.25	0.5163	0.7565	0.119°	747.0	275
17	"	1.0547	1.5453	0.224	746.9	298
18	"	1.5951	2.3371	0.329	746.9	307
19	"	2.1668	3.1748	0.441	746.8	311
20	"	2.6787	3.9248	0.538	746.8	315
21	"	3.1584	4.6277	0.632	746.8	316
22	"	3.6649	5.3698	0.734	746.7	316
23	"	4.1460	6.0747	0.834	746.7	314

Barometer 747 — 746.7 mm.

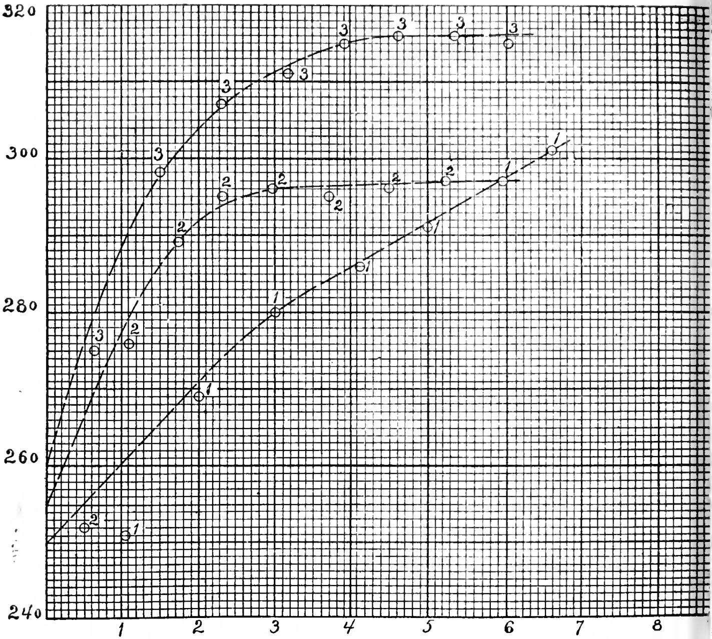
Molecular weight at infinite dilution	261.0
Molecular elevation at infinite dilution	42.4°
Average of molecular weights at infinite dilution	255.3

Graphic Representation of Determinations of the Molecular Weight of Sulphur in Metaxylene by the Boiling-Point Method.

(For diagram see next page.)

Notwithstanding the rapid increase of the molecular weight with increasing concentration these results show that even at the boiling-point of metaxylene the molecular weight of sulphur is 256 and that the change from S_9 to S_8 takes place somewhere between 110° C. and 140° C.

Results with Phenetol.—In all the work previously done,



with the exception of that in which carbon disulphide was used, the solvents have been hydrocarbons. It seemed highly desirable that these results should be confirmed, if possible, with solvents of a different character. For this purpose we selected anisol, phenetol, and phenol, which are excellent solvents for sulphur and for molecular weight determinations. Unfortunately the work with anisol was not completed owing to an accident involving the loss of all the material we had on hand. The following are the results with phenetol :

SULPHUR,

$S_8 = 256$; $S_9 = 288$.

Solvent : *Phenetol.*

Boiling-point 168.3° C. at 756.1 mm. barometric pressure.

Molecular elevation for 100 grams, 49.3°.

I.

	Grams solvent.	Grams substance.	Concentration in 100 grams.	Observed elevation.	Barometer mm.	Molecular weight.
1	117.60	1.0005	0.8508	0.159°	744.4	264
2	"	1.8669	1.5875	0.280	744.4	280
3	"	2.7589	2.3460	0.402	744.3	288
4	"	3.6110	3.0706	0.520	744.3	291
5	"	4.4206	3.7590	0.633	744.2	293
6	"	5.3169	4.5212	0.750	744.2	297
7	"	6.1444	5.2248	0.853	744.2	302
8	"	6.8472	5.8224	0.943	744.1	304

Barometer 744.4 — 744.1 mm.

Molecular weight at infinite dilution 257.0

Molecular elevation at infinite dilution 49.1°

II.

	Grams solvent.	Grams substance.	Concentration in 100 grams.	Observed elevation.	Barometer mm.	Molecular weight.
9	113.88	0.8177	0.7180	0.136°	742.5	260
10	"	1.6025	1.4072	0.259	742.6	268
11	"	2.2771	1.9996	0.363	742.6	272
12	"	3.0257	2.6569	0.470	742.6	279
13	"	3.7132	3.2606	0.570	742.6	282
14	"	4.4323	3.8921	0.675	742.6	284
15	"	5.1957	4.5624	0.782	742.6	288
16	"	5.8743	5.1583	0.875	742.7	291

Barometer 742.5 — 742.7 mm.

Molecular weight at infinite dilution 255.0

Molecular elevation at infinite dilution 49.5°

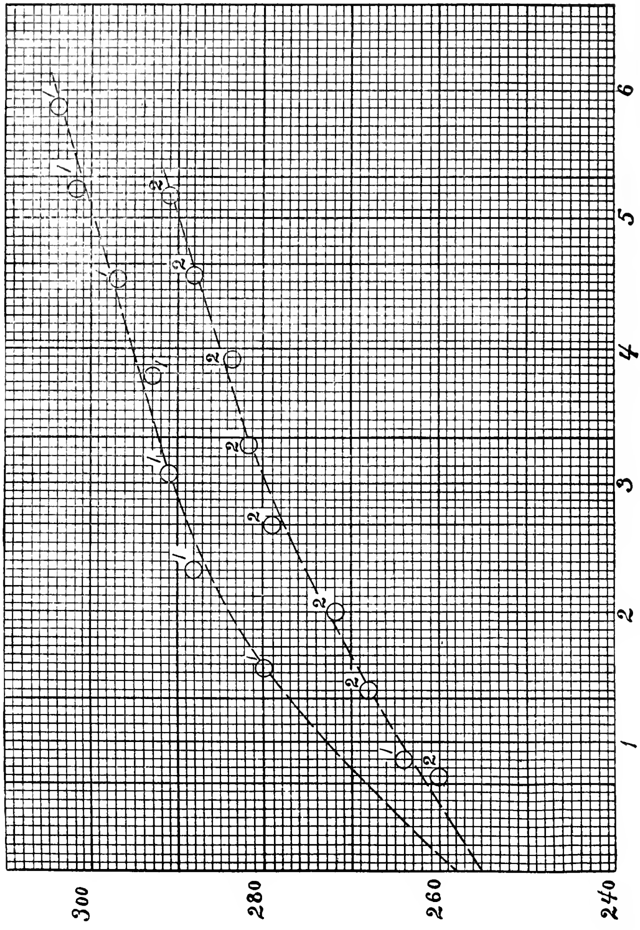
Average of molecular weights at infinite dilution 256.0

Graphic Representation of Determinations of the Molecular Weight of Sulphur in Phenetol by the Boiling-Point Method.

(For diagram see next page.)

It is obvious from these results that the molecular weight of sulphur at the boiling-point of phenetol is 256.

Results with Phenol.—The next solvent employed was phenol and although a slight trace of sulphuretted hydrogen is evolved on long continued boiling this solvent with sulphur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the action is so slight that it does not seem to interfere with molecular weight determinations in this liquid. Sulphur is very soluble in phenol at its boiling-point and this solvent is an excellent one for this work on account of the ease with which it is obtained pure and because the molecular weight of sulphur only increases slightly with increase of concentration. Of course the solvent must be protected from moisture by using a tube filled with calcium chloride. The following table gives the results with this solvent:

SULPHUR,

$S_8 = 256$; $S_9 = 288$.

Solvent: *Phenol.*

Boiling-point 181° C. at 755.9 mm. barometric pressure.

Molecular elevation for 100 grams, 30.4°.

I.

	Grams solvent.	Grams substance.	Concentration in 100 grams.	Observed elevation.	Barometer mm.	Molecular weight.
1	114.05	1.3706	1.2018	0.145°	740.9	252
2	"	2.6329	2.3086	0.278	740.9	252
3	"	4.1131	3.6064	0.429	741.0	256
4	"	5.4603	4.7876	0.569	741.0	256
5	"	6.3172	5.5390	0.660	741.0	255
6	"	7.2016	6.3144	0.744	741.2	258
7	"	7.7975	6.8369	0.806	741.3	258

Barometer 740.9 — 741.3 mm. Average of series I 255.3

Moleculer weight at infinite dilution 251.0

Molecular elevation at infinite dilution 31.0°

II.

	Grams solvent.	Grams substance.	Concentration in 100 grams.	Observed elevation.	Barometer mm.	Molecular weight.
8	116.92	1.7948	1.5351	0.185°	744.2	252
9	"	3.3002	2.8226	0.335	744.2	256
10	"	4.7407	4.0547	0.488	744.2	253
11	"	6.3211	5.4063	0.627	744.2	262
12	"	7.9668	6.8139	0.776	744.2	267
13	"	9.6218	8.2294	0.920	744.1	272
14	"	10.4795	8.9630	0.990	744.1	274
15	"	11.3667	9.7218	1.078	744.1	274

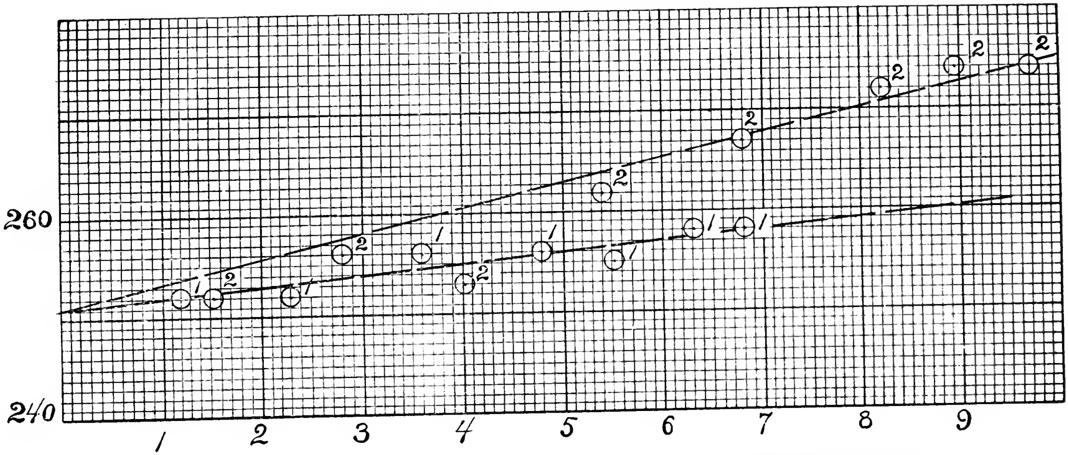
Barometer 744.2 — 744.1 mm. Average of series II. 263.7

Molecular weight at infinite dilution 251.0

Molecular elevation at infinite dilution 31.0°

Average of 15 determinations in phenol 259.5

Graphic Representation of Determinations of Molecular Weight of Sulphur in Phenol by the Boiling-Point Method.



These results confirm in a most striking manner those obtained with metaxylene and phenetol and leave no doubt as to the molecular weight of sulphur at the temperature of boiling phenol.

Results with Sulphur Chloride, (S_2Cl_2).—We have purposely left the recording of the results obtained by the boiling-point method with this solvent till last because of their surprising character and because of the difficulties experienced in working with this liquid. The substance not only has an extremely disagreeable odor and attacks the mucous membrane of the eyes and nose, but it also deposits sulphur wherever it comes into contact with moisture and decomposes rubber and cork with amazing rapidity. Although it is such an unpleasant liquid to work with, it is a most excellent solvent for sulphur. We purified the material by distilling it from sulphur and fractioning until it had a constant boiling-point.

As no reliable data exist as to the heat of vaporization of this substance we calculated the molecular elevation for 100 grams from the boiling-point given by Thorpe (138.12° C. at 760 mm.). This constant[1] was then shown to be very nearly correct by determining the molecular weight of triphenylmethane in sulphur chloride. Owing to the solvent action of sulphur chloride on rubber and cork it was impossible to make a long series with this liquid. The products of the action of the liquid on the stopper go into solution, causing the boiling-point to gradually rise. To overcome this difficulty we made short series working as quickly as possible or made individual determinations, introducing comparatively large quantities of substance to get large rises of temperature. This was easy to do as the material dissolved very readily and readings could be obtained within two minutes after introducing it. We give first the results with triphenylmethane to show that the method is reliable and then those with sulphur.

TRIPHENYLMETHANE,

$CH(C_6H_5)_3 = 244$.

Solvent: *Sulphur Chloride*, (S_2Cl_2).

Boiling-point 136.6° C. at 745.7 mm. barometric pressure.

Molecular elevation for 100 grams, 52.8°.

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[1] $K = \frac{0.0198 \times 411.12 \times 135}{20.81} = 52.8.$

	Grams solvent.	Grams substance.	Concentration in 100 grams.	Observed elevation.	Barometer mm.	Molecular weight.
1	204.49	1.5430	0.7546	0.168°	739.3	237
2	"	2.6777	1.3094	0.298	739.3	232
3	204.49	1.5912	0.7781	0.169	739.6	243
4	"	3.2081	1.5688	0.349	739.6	237
5	"	4.4116	2.1574	0.499	739.6	228
6	204.49	1.1803	0.5772	0.127	739.6	240

Average of determinations 236.0

SULPHUR,

$S_2 = 64$; $S_3 = 96$.

Solvent: *Sulphur Chloride*, (S_2Cl_2).
Boiling-point 136.6° at 745.7 mm. barometric pressure.
Molecular elevation for 100 grams, 52.8°.

I.

	Grams solvent.	Grams substance.	Concentration in 100 grams.	Observed elevation.	Barometer mm.	Molecular weight.
1	210.18	0.4725	0.2248	0.200°	745.3	59
2	"	1.0743	0.5111	0.475	745.2	57

Average of series I 58.0

II.

	Grams solvent.	Grams substance.	Concentration in 100 grams.	Observed elevation.	Barometer mm.	Molecular weight.
3	214.05	0.9490	0.4433	0.455°	748.1	51
4	"	0.8872	0.4145	0.340	748.1	64
5	"	0.9097	0.4250	0.345	748.1	65
6	"	0.8499	0.3971	0.290	748.0	72
7	"	0.7151	0.3341	0.251	748.0	70

Average of results 64.4

III.

	Grams solvent.	Grams substance.	Concentration in 100 grams.	Observed elevation.	Barometer mm.	Molecular weight.
8	219.64	1.0688	0.4866	0.504°	742.4	51
9	"	0.9095	0.4141	0.377	742.4	58
10	"	0.9987	0.4547	0.369	742.3	65
11	"	0.8433	0.3839	0.283	742.3	72
12	"	0.8692	0.3957	0.294	742.2	71

Average of results 63.4

Average of 12 determinations in sulphur chloride 61.9

If these results be plotted in the regular way with the molecular weights as ordinates and the concentrations as abscissas they give for the molecular weight of sulphur at infinite dilution values very near 64.

We then made determinations in this solvent at greater concentrations. As the molecular weight increases quite rapidly with the increase in concentration the molecular weight at infinite dilution must be taken here as the true value. The following are the results obtained in this way.

SULPHUR,

$S_2 = 64$.

13.3588 grams sulphur introduced at first for concentration effect.

Grams solvent.	Grams substance.	Concentration in 100 grams.	Observed elevation.	Barometer mm.	Molecular weight.
210.37	1.1652	0.5539	0.225°	747.8	130
"	1.1032	0.5244	0.202	747.8	137
"	0.9332	0.4436	0.162	747.9	145
"	0.9100	0.4326	0.155	747.9	147

Molecular weight at infinite dilution 55.0

These results indicate that the molecular weight of sulphur in sulphur chloride is 64 and the molecular formula is S_2. In this solvent, therefore, a dissociation of the sulphur molecules S_9 and S_8 takes place entirely analogous to that observed when sulphur is heated to a comparatively high temperature (860°–1700° C.).

Determinations of the Molecular Weight of Sulphur by the Freezing-Point Method.

Results with Naphthalene.—Having obtained the above results with the boiling-point method it was thought important to see if like values for the molecular weight of sulphur could be found by the freezing-point method also. We therefore first repeated the work of Hertz[1] using naphthalene as a solvent. This substance is an excellent solvent for sulphur and there is no difficulty in obtaining good readings with it. We made use of the ordinary Beckmann apparatus and the same thermometer used in the previous work but instead of striking the thermometer occasionally, as usually recom-

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[1] This comprised a series of only *three* determinations.

mended, we arranged an electric hammer so that it struck the metal top of the thermometer continuously, while the determination of the freezing-point of the solvent was being observed. The following are the results obtained:

SULPHUR,

$S_7 = 224$; $S_8 = 256$.

Solvent: *Naphthalene.*
Freezing-point 79.4° C. at 752 mm. barometric pressure.
Boiling-point 217.5° C. at 743.5 mm. barometric pressure.
Molecular depression for 100 grams, 69.4°.

I.

	Grams solvent.	Grams substance.	Concentration in 100 grams.	Observed depression.	Molecular weight.
1	27.624	0.2741	0.9923	0.296°	233
2	“	0.5221	1.8900	0.530	247

Molecular weight at infinite dilution **219.0**

II.

	Grams solvent.	Grams substance.	Concentration in 100 grams.	Observed depression.	Molecular weight.
3	28.349	0.2864	1.0103	0.299°	234
4	“	0.6600	2.3281	0.665	243
5	“	0.8330	2.9384	0.823	248
6	“	1.0572	3.7293	1.015	255
7	“	1.3351	4.7095	1.245	262
8	“	1.7351	6.1205	1.593	267

Molecular weight at infinite dilution **226.0**

III.

	Grams solvent.	Grams substance.	Concentration in 100 grams.	Observed depression.	Molecular weight.
9	31.539	0.3764	1.1934	0.340	244
10	“	0.7566	2.3989	0.664	251

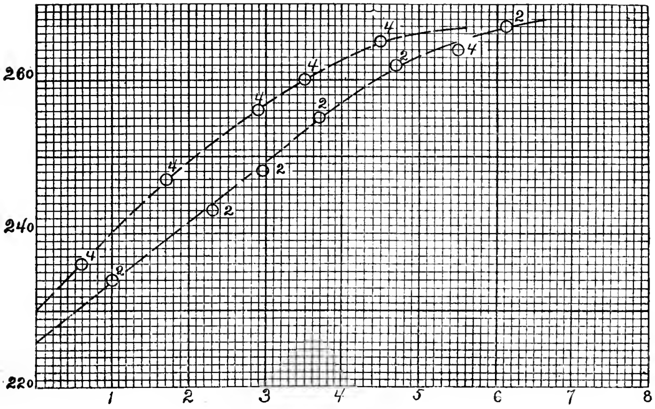
Molecular weight at infinite dilution **237.0**

IV.

	Grams solvent.	Grams substance.	Concentration in 100 grams.	Observed depression.	Molecular weight.
11	29.235	0.1771	0.6058	0.178°	236
12	“	0.4976	1.7021	0.478	247
13	“	0.8459	2.8934	0.783	256
14	“	1.0299	3.5228	0.940	260
15	“	1.3228	4.5247	1.183	265
16	“	1.6075	5.4985	1.446	264

Molecular weight at infinite dilution	230.0
Average of molecular weights at infinite dilution	228.0

Graphic Representation of Determinations of the Molecular Weight of Sulphur in Naphthalene by the Freezing-Point Method.



These results, indicating that the molecular weight of sulphur at the freezing-point of naphthalene is 224, were so surprising and so different from Hertz's results and from those in benzene, at the same temperature, by the boiling-point method, that we at first thought some error had been made. But a repetition of the work only demonstrated its correctness. That the molecular weight of sulphur should be 256 at the boiling-point of naphthalene and 224 at the freezing-point of the same solvent is utterly inconceivable. There must be some error in the freezing-point method of determining molecular weights in the case of this substance. Possibly it may be that the determinations are made too near the cryohydrate temperature of sulphur and naphthalene (74°C), which is only five degrees below the freezing-point of naphthalene. Other examples of abnormal values for the molecular weights by the freezing-point method are well known, though so far as we are aware no good explanation[1] of these anomalies has been given. The explanation offered by Beckmann and Stock[2] for the peculiar results obtained by them for the molecular weight of iodine in benzene solution, *viz.*, that the solid which separates out when the temperature of the solvent is lowered to determine its freezing-point contains iodine will not apply here as the material solidifying was shown to be only naphthalene by examination with the microscope.

Results with Diphenyl.—We endeavored next to find a solvent[3] for sulphur whose freezing-point was not so near the cryohydrate temperature, but without success. Sulphur is either too slightly soluble in solvents that solidify at temperatures that can easily be obtained or else it acts on them at their melting-point or the freezing-point and cryohydrate points lie very close together. We found that diphenyl was an excellent solvent for sulphur, however, and though the cryohydrate temperature of this solvent with sulphur (64.7° C.) is very near its freezing-point, 68.2° C., still we made molecular weight determinations with this substance by the freezing-point method to see if they would confirm the abnormal values obtained with naphthalene. The method and apparatus were the same as those used with naphthalene. The following table gives the results :

SULPHUR,

$S_7 = 224$; $S_8 = 256$.

Solvent : *Diphenyl.*

Freezing-point 68.2° C. at 752 mm. barometric pressure.

Boiling-point 255.3° C. at 743.6 mm. barometric pressure.

Molecular depression for 100 grams, 82.6°.

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[1] Van't Hoff's explanation (Ztschr. phys. Chem., **5**, 334) that a solid solution of the solvent with the dissolved substance separates out instead of the pure solvent when the temperature is lowered to the freezing-point only holds for some of the cases. See in this connection the results of Auwers using benzene and naphthalene as solvents (Ztschr. phys. Chem., **12**, 689, and Ber. d. chem. Ges., **28**, 2878).

[2] Ztschr. phys. Chem., **17**, 120.

[3] The following are some of the solvents we tried : thymol, phenol, benzene, acetic acid, diphenylmethane, anethol, nitrobenzene, aethal and ethylene bromide.

I.

	Grams solvent.	Grams substance.	Concentration in 100 grams.	Observed depression.	Molecular weight.
1	22.939	0.4546	1.9818	0.626°	261
2	“	0.8044	3.5067	1.070	271
3	“	1.1873	5.1759	1.528	280
4	“	1.5471	6.7444	1.932	288

Molecular weight at infinite dilution 252.5

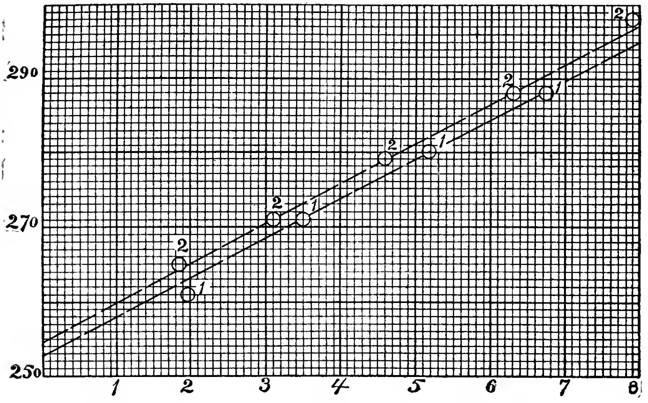
II.

	Grams solvent.	Grams substance.	Concentration in 100 grams.	Observed depression.	Molecular weight.
5	21.073	0.3839	1.8218	0.568	265
6	“	0.6581	3.1230	0.951	271
7	“	0.9693	4.5997	1.360	279
8	“	1.3238	6.2820	1.800	288
9	“	1.6644	7.8983	2.193	298

Molecular weight at infinite dilution 254.5

Average of molecular weights at infinite dilution 253.5

Graphic Representation of Molecular Weight Determinations of Sulphur in Diphenyl by the Freezing-Point Method.



These results indicate that the molecular weight of sulphur in diphenyl at the freezing-point of this solvent is 256 and not 224, the value found using naphthalene as a solvent.

We are not inclined to give much weight, however, to either of the values found for the molecular weight of sulphur by the freezing-point method, first, because they do not agree with each other, and secondly, because neither agrees with the single value (288), found by the boiling-point method in carbon disulphide, benzene, and toluene. Probably the same explanation will be found to hold for these peculiar results in naphthalene and diphenyl. It is certainly significant that in both cases the cryohydrate temperature lies so close to the freezing-point of the solvent. We have given these results here simply to call the attention of chemists to them and in the hope that some explanation may be ultimately offered of their anomalous character.

Summary.

The results of this investigation on the molecular weight of sulphur may be briefly summarized as follows:

1. The molecular weight of sulphur in carbon disulphide, benzene, and toluene is 288 and we must conclude, therefore, that, at the boiling-points of these liquids, the molecular formula of sulphur is S_9. These temperatures, it will be noted, are all below the melting-point of sulphur.

2. In metaxylene, phenetol, phenol, and naphthalene, on the other hand, the molecular weight of sulphur is 256, and hence the molecular formula is S_8 at the temperatures represented by the boiling-points of these solvents, *i. e.*, at temperatures above the melting-point of sulphur.

3. In sulphur chloride the molecular weight of sulphur is 64 and the molecular formula must therefore be S_2. Complete dissociation of the more complex sulphur molecules takes place in this solvent, the results being in close agreement with those obtained by the vapor density method at high temperatures (860–1700° C.).

4. Determinations of the molecular weight of sulphur in naphthalene and diphenyl by the freezing-point method cannot be relied upon in deciding the question of the molecular weight of this element, since the results obtained do not agree with each other nor with those obtained at the same temperatures by the boiling-point method. In naphthalene 224 was

the value found, pointing to a molecule S_7, while in diphenyl 256, indicating a molecule S_8 resulted.

5. The molecular weight of both the orthorhombic and the monoclinic varieties of sulphur is the same (288), since from boiling carbon bisulphide only orthorhombic sulphur crystallizes out while from boiling benzene and toluene monoclinic sulphur alone separates, and since the molecular weight of sulphur in all these solvents is the same, 288.

CORNELL UNIVERSITY, ITHACA, N. Y.,
January, 1896.

Contributions from the Chemical Laboratory of Case School of Applied Science.

XXII.—ON THE DETERMINATION OF SULPHUR IN ILLUMINATING GAS AND IN COAL.

BY CHARLES F. MABERY.

Having recently been called upon to make some determinations of sulphur in illuminating gas, in considering the various methods for this determination I was impressed with the need of an accurate method, which should be at the same time capable of giving desirable results without too close attention. So far as I am aware, all the methods in use depend upon the combustion of a definite volume of gas and passing the products through bromine water or a similar reagent for oxidation and absorption. The sulphuric acid formed is precipitated as baric sulphate. Such methods require an atmosphere free from sulphur in any form, which it is sometimes difficult to obtain in the laboratory. The volume of gas burned must be large to obtain a sufficient weight of baric sulphate, and precipitation in this form is always wasteful of time, whenever it can be replaced by more expeditious means of reaching the desired result. Then it is difficult to adjust lamps to burn regularly without considerable attention.

When Sauer first proposed his method for the determination of sulphur in organic bodies, he suggested that it could be applied to the estimation of sulphur in gases, although he gave no data to demonstrate its efficiency. Valentine[1] had previously devised a method on somewhat the same principle, in which the gas to be burned was mixed with air before it entered the combustion tube. To ensure complete combus-

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[1] Chem. News, 17, 89.

tion the gaseous mixture was carried over platinum sponge, and for absorption the products of combustion were carried through an oxidizing solution, such as potassic chlorate and hydrochloric acid. Valentine found it extremely difficult to completely oxidize and absorb the sulphur. Almost invariably, he states, traces of sulphurous acid were found in his last tower. He further says, "it was evident that no reliance could be placed on the oxidation and absorptive power of the various solutions. Gaseous sulphurous acid is not so readily oxidized nor retained when mixed with an overwhelming amount of other gases, as is generally supposed."

Knublauch[1] burned 15–20 liters in about an hour in an ignition tube containing platinized asbestos, and absorbed the sulphur in potassic carbonate. The amount of sulphur he obtained per cubic meter was between 0.3971 and 0.3135 gram. This wide variation was doubtless due, at least in part, to differences in the composition of the gas.

The first of several methods based on the combustion of gas in a lamp, was described by Letheby.[2] The gas was burned in a funnel-tube and the products carried forward into a wide horizontal tube, washed out, and the acid precipitated with baric chloride. Mixter[3] burned the gas from a platinum-tipped glass tube in a large glass flask (15 liters) in an atmosphere of oxygen, keeping the flask cold, and precipitating with baric chloride. Poleck[4] used a Bunsen lamp to burn the gas, within a wide glass tube, and led the products forward into a solution of sodic hydrate and bromine.

The apparatus of Drehschmidt,[5] constructed on the same principle and now recommended, consists of a special form of lamp for burning the gas within an upright tube closed at the base except for the introduction of air. The necessity of an atmosphere free from sulphur is evident. Fairley[6] suggested the use of hydrogen dioxide as an oxidizing agent.

From the general applicability to the determination of sulphur in oils, asphalts, and other organic bodies, of the method described by me,[7] it seemed possible to apply this method

[1] Ztschr. anal. Chem., **21**, 335.

[2] Chem. News, **7**, 73.

[3] This JOURNAL, **2**, 244.

[4] Ztschr. anal. Chem., **22**, 171.

[5] Ztschr. anal. Chem., **29**, 625.

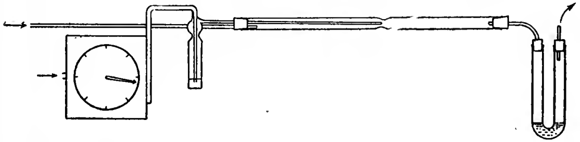
[6] Ztschr. anal. Chem., **29**, 628.

[7] This JOURNAL, **16**, 544.

with suitable modifications to the determination of sulphur in gases.

As in the analysis of oils with minute quantities of sulphur, I found it advantageous to absorb the products of combustion in a centinormal solution of sodic hydrate. Even in such a dilute alkaline solution and with the rapid current of air necessary to maintain the combustion, the sulphuric acid formed is retained with remarkable persistence. As stated in the publication of my results with oils, it was assumed that a considerable excess of the absorbing solution was necessary to avoid loss, on account of the great dilution of the minute quantity of sulphuric acid by the large excess of air. To be sure that no sulphur was lost in the combustion of gas by incomplete absorption, a second absorption tube containing the centinormal alkaline solution was attached in front. Upon titration no change in the standard of the alkaline solution in the second tube could be detected. In this experiment a larger volume of gas was accidentally burned than was intended, and upon titration it was found that the alkaline solution in the first absorption tube had been almost entirely neutralized; there remained only 2 cc. of free alkali. There is, therefore, not the slightest danger of loss from incomplete absorption.

The form of apparatus best adapted for the determination of sulphur in gases by this method is shown in the accompanying figure. The U tube should be of considerable size.



In the analyses described in this paper, the tube used was 34 cm. in height and 25 mm. inside diameter. Above the bend for 8 cm. it is filled with broken glass, which subdivides the bubbles, and brings the gas into intimate contact with the absorption solution. The ignition tube should be 45.50 cm. in total length, and the constriction 30 cm. from the forward end. Air is drawn in from outside the laboratory and admitted through a tube into the rear end of the combustion tube. A rapid current is necessary, and it may be maintained by means of a water pump or any other form of suction pump. For the introduction of the gas to be burned, a tube of hard glass about 2 mm. inside diameter is introduced far enough to deliver the gas just beyond the narrowest point of the constriction. A tube of this size will support a flame 3 cm. in length without depositing soot, which must be avoided. Depending on the size of the delivery tube, the gas may be burned in a continuous flame or in flashes. After setting the meter for measurement, and regulating the size of the flame, the operation needs no further attention until a sufficient quantity of gas has been burned. To regulate the flow of gas, it is convenient for better observation to introduce a wash-bottle with a very little water between the meter and the combustion tube, with a nipper-tap between the meter and wash-bottle.

Titration is made either in the U tube or in a beaker with centinormal sulphuric acid with methyl orange as an indicator. The results of which this method is capable are shown by the following analyses, which were the first obtained in applying this form of combustion :

1. 5.6 liters of gas at 18°, bar. 750 mm., neutralized 6.5 cc. NaOH, equivalent to 0.001073 gram sulphur.

2. 5.6 liters of gas, at 18°.5, bar. 747 mm., neutralized 7.0 cc. NaOH, equivalent to 0.001155 gram sulphur.

3. 5.6 liters of gas, at 18°.5, bar. 747 mm, neutralized 6.8 cc. NaOH, equivalent to 0.001122 gram sulphur.

4. 11.2 liters of gas at 18°.5, bar. 747 mm., neutralized 13.8 cc. NaOH, equivalent to 0.002277 gram sulphur.

5. 28 liters of gas, at 17°, bar 746 mm,, neutralized 33 cc. NaOH, equivalent to 0.005445 gram sulphur.

	Sulphur found.	
	Grams per cubic meter.	Grains per cubic foot.
1	0.2027	0.089
2	0.2118	0.093
3	0.2186	0.096
4	0.2165	0.095
5	0.2095	0.092

While these results are not far outside the limits of error, the determinations were made on different days, and there is doubtless slight variation in the sulphur remaining in the gas after the purification.

The statement of Valentine, given above, conveys the impression that under no circumstances can the sulphur in combustion be completely oxidized to sulphuric acid. If this were true, evidently no reliance could be placed on results of titration without oxidation, since, as is well-known, methyl orange is not sensitive to acid sodic sulphite. In general, our results with combustion have indicated that oxidation with oils and with gas is complete or very nearly so. Since hydrogen dioxide is the only convenient oxidizing agent that can be used in a solution that is to be titrated, it seemed worth while to ascertain beyond question whether, by means of this reagent, the oxidation is complete. A dilute solution of sulphurous acid was neutralized by a centinormal solution of sodic hydrate, and a few drops of an acid-free solution of hydrogen dioxide added. Immediately the solution became a deep pink, showing the formation of the acid sulphate by oxidation, and also that the oxidizing power of hydrogen dioxide could be depended on to convert any trace of sulphurous into sulphuric acid. A determination of sulphur in gas was then made, passing the gases from the combustion tube through two absorption tubes. Titration of the centinormal solution of sodic hydrate in the second tube showed no change. Hydrogen dioxide was then added and the solution again titrated. There was still no change, proving beyond question that all the sulphur was retained in the first absorption tube. After the latter solution was made neutral with decinormal acid, the addition of hydrogen dioxide produced no change. There can, therefore, be no doubt that in this form of combustion the oxidation is complete.

After a great number of sulphur determinations in asphalts, coal tar, and all varieties of petroleum products, and now in gas, we are convinced that this method leaves nothing to be desired in point of accuracy or simplicity for the analysis of any organic compounds which leave no inorganic residue.

For valuable aid in studying this method of analysis, I am indebted to my assistant, Mr. E. Davidson.

Determination of Sulphur and Ash in Coal.

Of the various methods for the determination of sulphur in coal depending on oxidation, none seems to be accurate and entirely satisfactory except the well-known method of Eschka proposed in 1874.[1] In point of accuracy this method seems to be capable of meeting the requirements of technical determinations, but the oxidation must not be carried on too rapidly, and it includes precipitation and manipulation of baric sulphate. In his first statement of the determination of sulphur by combustion, Sauer[2] suggested that his method might be applied to the analysis of coal, and Mixter also includes some analyses of coal in his modifications of the same method. This method, successfully applied, must evidently depend on a moderate rate of combustion, to ensure complete oxidation and absorption in the form of flasks employed, and the same objection to the manipulation of baric sulphate appears. If only a single determination is to be made, and that occasionally, it may be urged that this feature is of minor importance. But, in a long series of analyses, as in other operations when a volumetric method is capable of great accuracy, time may be saved by avoiding the gravimetric manipulations.

In a method depending on the oxidation and volatilization of the sulphur, the amount of sulphur remaining behind in the ash would be the determining feature. For if the ash must always be examined for the amount of sulphur retained, such a method would have no advantage over oxidation in a crucible. But, if no appreciable quantity, or an approximately constant quantity, remained in the ash, evidently the weight of the residue should afford a determination of the ash. It is to be expected that the proportion of sulphur retained should depend to a certain extent at least on the quantity of lime in the ash, with the question as to whether the lime retains its full equivalent of the sulphur. In most coals, lime is nearly or quite wanting, the sulphur being present as pyrite, which is frequently seen in coal heaps in large masses.

In general, the method we have followed is similar to the

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[1] Ztschr. anal. Chem., **13**, 344.

[2] Ztschr. anal Chem., **12**, 32.

estimation of sulphur in oils and asphalts. The coal is weighed in a platinum boat, which has been found to retain all the residue after oxidation. The combustion is carried on in a rapid stream of air entering at the constriction through the inner hard glass tube with a slower current entering through the rear tube to carry forward the volatile portion, and to assist the combustion. White fumes must not appear in the absorption tube. As in asphalts, some care is necessary in distilling the volatile portion, but in this respect coals require less attention than asphalts. Tubes of very hard glass are necessary to maintain a high temperature, although we have not ascertained how low a temperature is really essential. In all our work the temperature has been kept as high as the tube would stand. Under these conditions one combustion tube will serve, with ordinary care, for a great number of analyses. The length of the tube forward of the constriction need not be more than 40 cm., allowing for protection of the cork from burning, and the rear portion need not be more than 25 cm.

As shown in the figure we use a U tube of considerable size to allow the rapid stream of air to pass without danger of bubbles rising to the top of the tube. After some experience with details 0.5 gram of coal may be burned in a half hour, allowing twenty minutes for the distillation of volatile matter, and ten minutes for the combustion of fixed carbon. In burning cokes, the operation is more satisfactorily performed in oxygen. The absorbent solution used in these analyses was a tenth normal sodic hydrate. A little stronger solution, perhaps a fifth normal, would save some addition of the acid solution in titration. The final reaction is clearly defined, and the difference in colors between acid and alkaline is so clearly marked that the contrast is easily observed even in a hundredth normal solution. In the following table are given the results obtained in the analysis of a variety of coals :

	Weight taken.	Cc. $\frac{n}{10}$ NaOH.	Cc. $\frac{n}{10}$ H_2SO_4.	Per cent. sulphur.	Per cent. S_2 by the Eschka method.	Difference.	Weight of ash.	Per cent. of ash.	Per cent. of ash by old method.	Difference.	Per cent. S_2 in ash.	Lime.	Kind of coal.
1	0.5318	35.2	25.1	3.04			0.0585	11.00	11.46	—0.46	0.10	absent	Bit. slack
2	0.4373	29.4	24.0	1.98	2.10	—0.12	0.0128	2.93	2.82	+0.11	0.05	"	"
3	0.4886	29.4	25.5	1.28	1.35	—0.07	0.0112	2.29	2.12	+0.17	0.07	present	Bit.
4	0.4900	35.2	32.7	0.80	0.76	+0.04	0.0094	1.91	1.79	+0.12	0.03	absent	"
5	0.4806	29.4	27.0	0.78	0.78	0.00	0.0076	1.58	1.44	+0.14	0.04	"	"
6	0.5086	35.2	28.2	2.21			0.0530	10.42	10.36	+0.06	0.04	"	"
	0.4956	29.4	22.4	2.23			0 0513	10.35		—0.01	0.04	"	
7	0.5187	29.4	24.4	1.52	1.53	—0.01	0.0111	2.12	1.96	+0.16	0.06	"	"
8	0.5410	29.4	26.9	0.73	0.76	—0.03	0.0096	1.78	1.76	+0.02	0.02	"	"
9	0.5280	29.4	26.7	0.82	0.89	—0.07	0.0092	1.74	1.69	+0.05	0.02	"	Bit. slack
10	0.5161	35.2	20.5	4.55			0.0618	11.95			0.04	"	"
11	0.5003	29.4	22.4	2.21			0.0334	6.67			0.03	"	"
12	0.4949	35.2	31.5	1.21			0.0304	6.16			0.02	"	Anthracite
13	0.4843	29.4	27.6	0.58			0.0388	18.01			0.04		

Average S_2 in ash = 0.043

The solutions used in titrations were not strictly decinormal, but were calculated on that basis that the volumes might be more readily comparable. 30 cc. of sodic hydrate, nearly decinormal, were actually taken for each absorption. It would have been interesting to have procured for analysis a variety of coals from representative districts, and to have established a mean of allowance for the sulphur remaining in the ash, but I was prevented from including this valuable information by great pressure of other affairs. The coals selected, however, present an average which, I think, may be accepted in general analysis for all coals with an ash not highly calcareous. This average, 0.043 per cent., probably represents as an outside limit the sulphur remaining in the ash. The close agreement in the percentages of ash found with other determinations, indicates a high degree of accuracy.

Reference to the column headed lime, shows that only in one instance was lime found in the ash, and here the quantity was not far from 0.05 per cent. With suitable modifications of this method, in an inert gas it would probably be possible to distil the volatile portion of the coal and weigh the residue of fixed carbon before completing the combustion for sulphur. But for want of time, I have not been able to put this suggestion to experimental proof.

For valuable aid in the analyses of these coals, I am indebted to Mr. R. A. Worstall, a student in this laboratory.

XXIII.—INVESTIGATIONS ON AMERICAN PETROLEUM.[1]

By Charles F. Mabery.

CHEMISTRY OF THE BEREA GRIT PETROLEUM.[2]

By Charles F. Mabery and Orton C. Dunn.

The deposits of petroleum in the Berea Grit and allied sandstones in Southern Ohio were among the first in the United States from which commercial products were prepared, yet nothing whatever is known concerning their composition

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[1] For valuable aid in the prosecution of this work I desire to express my obligation to my assistants, Messrs. C. A. Soch and E. Davidson. I am also indebted for pecuniary aid to the C. M. Warren fund of the American Academy of Arts and Sciences.

[2] A portion of this work was presented by Mr. Dunn in a thesis for the Degree of Bachelor of Science.

except the very general knowledge necessary in processes of refining. In the geological column in this section four sandstones furnish oil, some of which have proved to be a prolific source since the early discovery of petroleum. Of these sources, the most important is the Berea Grit, which is below all the other sandstones. This formation, at least from a commercial point of view, is perhaps the most important in the Ohio geological scale; its outcrops supply a valuable building stone, and its submerged strata contain immense quantities of oil and gas, portions of which are collected under the requisite conditions to furnish a profitable supply. It extends over an area of more than 15,000 square miles in Ohio, and it continues into the adjoining states of Pennsylvania, New York, West Virginia and Kentucky. This geological formation was first investigated by Professor Newberry, who named it from the town in which it is best observed, where it furnishes large quantities of stone for construction. Since the discovery of oil, in connection with the drilling of wells, excellent opportunities for studying these strata as a reservoir of oil and gas were offered, and in connection with the labors of the state geological survey, under the direction of Professor Orton, much valuable information has been accumulated. This sandstone varies in thickness from a few feet to one hundred feet or more. For the most part it is a clean white material, quite variable as to coarseness from pebbles of considerable size to very fine sand. Except a few fossils and leaf impressions, the absence of organic remains is noteworthy. There is abundant evidence that it never was a source of petroleum, but it serves rather as a reservoir of oil that was forced up from the black shales beneath, in which the oil was originally formed. The impervious cover of the Berea Grit that holds in confinement the oil and gas is the Berea black shale, ten to fifty feet in thickness. Next above come the Cuyahoga shales, and the lower coal measures that contain at least four sandstones, each roofed with shales, and all these sandstones have yielded oil. With the hard shale overlying, and a soft floor, the Berea Grit is well adapted for the storage of oil. The composition of the Berea Grit sandstone is shown by the following results of our analyses:

	White oil sand.	Blue caprock.
Silica	92.30	91.80
Alumina	4.80	4.60
Ferric oxide	0.92	1.50
Calcium and magnesium oxides	0.28	0.34
Water combined	1.40	1.80
Total	99.70	100.04

In much of its extent the Berea Grit is too fine grained, and the strata too thin to allow of its carrying oil; but in a thickness of ten to fifty feet, and with the coarseness that exists in the oil sections, this sandstone carries one cubic foot of oil in every ten to twelve cubic feet of rock. Altogether during the present year the yield of oil from this source is 3,500 barrels daily or one twentieth of the yield from the Pennsylvania fields. In their best days the Macksburg and Eureka fields furnished one-tenth of the total supply; these fields are again on the increase from the gains in the Corning, Steubenville, and New Castle fields. The first oil obtained in this section in 1860, was well adapted for lubrication; it sold for $28.00 a barrel. The first important well, the "Elm Tree" well, started at 100 barrels in 1861. In 1864 $7,000,000 had been invested in oil companies in Washington and Noble counties alone. Oil in paying quantities was taken from the 140, 300, 500 and 700 foot sands. Since 1881 the Macksburg field has produced nearly 5,000,000 barrels of oil, but only one-third has come from the Berea Grit. All attempts to extend the Macksburg field have been unsuccessful. Oil is now obtained here only from shallow wells, chiefly from the 500 foot sand.

The Eureka field was first opened in 1886, and it is now equal in importance to the Macksburg field and more promising for the future. It lies near the Ohio river, extending four miles into West Virginia and three miles into Ohio. At one time 350 producing wells here yielded 4,500 barrels of oil daily, nearly all from the Berea Grit. At present the yield is about 1,000 barrels daily. The Berea Grit is here about 700 feet below sea level, and 1,350 feet below the level of the Ohio valley. It is between fifteen and thirty feet thick beneath a very black shale, which serves as a cover, approximately thirty feet thick. At first the rock pressure was very great, but now the oil must be pumped. This field is connected with the Macksburg and Pennsylvania fields by a pipe line. The oil has a clear, amber color, with a beautiful fluorescence; it is very clean, and deposits little sediment even on long standing. The specimen of this oil used in our examination was from a well at Archer's Fork, Washington county, not far from the Ohio river. Oil was first obtained in the shallow wells at Mecca in 1861, in a territory which never exceeded in productive area more than a few hundred acres. The flow, never large, is now about 1,500 barrels annually of a good lubricating oil. Other fields, more or less promising, in which the Berea Grit yields oil, and in several sections gas in considerable quantities, include the Corning, New Castle, White Oak, West Virginia, Steubenville, and Cadiz territory. The Belden field, first opened in 1861, is now exhausted.

In undertaking an examination of the petroleum from this section, we procured specimens of the light amber oil from the Berea Grit, and from the principal sandstones of the lower coal measures which overlie this sandstone—the 140, 300, 500 and 700 foot strata—all of which are well developed in the Macksburg field. Petroleum from the 140 foot sand was procured from well No. 9, a small producer, on the Mosely farm, two miles north of Macksburg, where the sandstone is 158 feet deep and 14 feet thick. The composition and properties of the crude oil, which was of a light amber color, as well as the percentages and specific gravity of the distillates are given in the following table:

Crude oil.	C.	H.	N.	Per cent. of dist.	Specific gravity.	Br-Absorp.	HBr set free.
	85.00	13.77	0.027		0.8118	7.62	3.00
110°				0.55		0.74	0.20
110–135°				6.54		1.76	0.65
135–160°				8.38	0.7480	2.41	1.61
160–185°				6.00		2.24	1.36
185–210°				9.60	0.7760	2.32	0.94
210–235°				8.00		2.08	0.51
235–260°				6.60		3.87	0.52
260–285°				9.01		4.62	1.12
285–310°				6.60		5.69	1.93
310–335°				2.62		4.58	2.01
335–360°				11.63	0.8310	7.57	2.33
+360°				29.46	0.8540	9.72	1.12

Another specimen of oil collected from a well in the same sandstone at Olive, Noble County, 8 miles north of Macksburg, where the oil rock is only 40 feet below the bed of the creek, gave as its specific gravity, a value somewhat larger than the other, 0.8241. A determination of nitrogen in this oil gave 0.0293.

For an examination of oil from the 300-foot sand, a specimen was taken from a well on the farm of J. McLauth, one mile south of Macksburg. A small pocket of oil was opened in this sand, but it was soon exhausted, and the well continued to the Berea Grit. This oil had a peculiar reddish tinge that is frequently observed in petroleum from this sand. As will be seen in the following table it differs essentially in its composition and physical characteristics from the 140-foot oil :

Crude oil	C.	H.	N.	Per cent. of dist.	Specific gravity.	Br-Absorp.	HBr set free.
	84.45	13.79	0.018		0.8205	8.45	2.35
60–85°				0.55		0.00	0.00
85–110°				2.70		1.50	0.25
110–135°				3.50		3.03	1.17
135–160°				7.37	0.740	3.52	1.39
160–185°				5.96	0.771	3.88	1.37
185–210°				3.50		5.20	1.13
210–235°				6.66	0.789	5.75	1.93
235–260°				4.89		8.09	2.49
260–285°				7.37	0.811	8.66	2.44
285–310°				4.89		9.42	2.76
310–335°				3.50		11.70	3.97
235–260°				18.59	0.827	17.01	5.63
+360°				28.05	0.891	18.54	6.07

Quantities of oil were taken from Wells Nos. 6 and 9 in the 500-foot sand on the farm of Mr. J. S. Dunn, situated 1½ miles north of Macksburg and 1 mile south of Dexter City.

This oil rock is here 450 feet deep, and these wells are 1600 feet apart. Well No. 9 was drilled between 1861 and 1865, in the early days of oil. It started at 100 barrels and is now running 3 barrels daily. Well No. 6 was drilled in 1889. It started at 125 barrels and is now running 10 barrels daily of a light green oil. The sandstone is here about 22 feet thick, and it varies between medium and coarse sand rock. The specific gravity of the oil from well No. 9 is 0.8067 and that from well No. 6, 0.7971. The latter well is more nearly in the center of the deposit, which doubtless accounts for its lightness. An extended examination was made of the oil from well No. 6, with the following results:

Crude oil.	C.	H.	N.	Per cent. of dist.	Specific gravity.	Br-absorp.	HBr set free.
	84.19	14.75	0.015		0.7971	9.46	2.64
35–60°				1.33		0.79	0.51
60–85°				3.33		1.19	0.90
85–110°				6.33	0.6970	1.82	0.87
110–135°				3.33		2.32	0.77
135–160°				6.00	0.7440	3.71	0.95
160–185°				4.00	0.7640	4.94	1.25
185–210°				7.33	0.7760	5.94	1.83
210–235°				3.33		6.66	2.37
235–260°				8.33	0.7990	7.76	2.06
260–285°				5.00	0.8160	9.18	2.58
285–310°				3.33		11.03	3.04
310–335°				2.67		10.98	3.74
335–360°				20.00	0.8270	24.84	4.53
+360°			0.033	23.34	0.8420	26.38	9.08

Petroleum from the 700-foot sand was obtained from well No. 1, on the Mosely form, 2 miles north of Macksburg and 1 mile east of Dexter City. This well was drilled in 1889, and the sand was reached at 725 feet. It started at 10 barrels and flowed for some time, but now it yields 2–3 barrels daily and is pumped.

The following results were obtained in an examination of this oil:

Crude oil.	C.	H.	N.	Per cent. of dist.	Specific gravity.	Br-absorp.	HBr set free.
	84.56	14.33	0.038		0.3138	5.93	1.91
60–85°				2.41		1.73	1.73
85–110°				3.45		2.92	2.22
110–135°				7.24	0.725	3.65	3.36
135–160°				7.59	7.752	4.04	1.47
160–185°				7.59	0.764	5.03	1.41
185–210°				5.52		5.64	2.08
210–235°				4.83		6.26	2.16
235–260°				5.86		8.54	2.22
260–285°				4.83		10.21	3.15
285–310°				4.45		9.38	2.43
310–335°				4.83		11.24	2.36
335–360°				13.74	0.816	18.00	3.23
+360°				26.21	0.885	21.84	3.48

This examination of the petroleums from the upper sandstones was undertaken with the hope that a better knowledge of their composition would be interesting in comparison with the composition and properties of the Berea Grit oil, and it seemed all the more inviting since one of us (O. C. D.), was able, through his interest in this oil territory, to procure authentic specimens of fresh oil from these several geological formations.

For the examination of the Berea Grit petroleum from the 1500-foot oil sand, three specimens of this oil were procured. One came from well No. 3, on the McLauth farm, one mile south of Macksburg, the second from well No. 1, on the Warren farm, five miles north of Macksburg, and the third from Archer's fork. The latter will be more fully described later. The well from which the first sample was taken was drilled by Mr. J. S. Dunn, in 1884. At a depth of 1400 feet the sandstone was reached, and it was found to have a thickness of 11 feet. The well started with a small volume of oil and 400,000 feet of gas daily, which still continues in smaller quantities.

After the well was torpedoed the yield of oil was one-fourth of a barrel daily, which still continues. This oil has a high specific gravity, 0.8622, doubtless due to the removal of the lighter portions by the gas.

The well from which the second specimen was collected was drilled in 1893. It started at a rate of 85 barrels daily from a depth of 1480 feet, and now yields 3 barrels. Like most wells drilled to the Berea Grit, sufficient gas escaped to cause the well to flow at first, but it soon had to be pumped. This oil was of a beautiful amber color and much lighter than the first. It gave the following results on examination:

Crude oil.	C.	H.	N.	Per cent. of dist.	Specific gravity.	Br-absorp.	HBr set free.
	85.52	14.59	0.064		0.8274	9.96	3.47
35–60°				0.54		0.26	0.27
60–85°				1.08		0.54	1.08
85–110°				1.62		1.38	1.66
110–135°				3.70		2.76	1.81
135–160°				3.70		3.75	1.74
160–185°				5.55		5.14	1.48
185–210°				6.60		5.41	2.00

Crude oil.	C.	H.	N.	Per cent. of dist.	Specific gravity.	Br-absorp.	HBr set free.
210–235°				3.70		8.00	2.60
235–260°				5.55		8.01	2.27
260–285°				5.55		9.29	2.48
285–310°				2.22		10.47	3.09
310–335°				2.22		10.82	3.09
335–360°				11.11	0.8320	17.60	6.01
+360°			0.167	46.29	0.8900	20.31	7.08

As we have observed in other instances, the nitrogen compounds remained almost entirely in the residue above 360°.

The third specimen of this oil was taken from well No. 1, on the J. W. Ward farm at Archer's Fork, Washington County, 20 miles from Macksburg, in the eastern extension of the Eureka field. This well was drilled by Barnsdale & Co., in 1890. The sandstone was reached at 1780 feet, and it was 14 feet thick at this point. At first the well flowed 250 barrels daily. It now yields 11 barrels.[1]

The geological formations and the individual strata encountered in sinking a well to the Berea Grit are very clearly explained by the record of a well drilled in March, 1895, by Mr. J. S. Dunn, 600 feet from the Ward well mentioned above. This well was started on a hill 181 feet above the level of the Ward well. It produced oil in small quantity, but it yielded 500,000 feet of gas daily.

The thickness of the different rock strata and the depths are as follows:

Rock formation.	Thickness in feet.	Depths.
Soil	8	8
Rock sand	10	18
Light slate	43½	61½
Soft red rock	43½	105
Mountain sand	50	155
Light slate Level of Ward well	30	185
Red rock	40	225
Light slate	15	240
Red rock	7	247
Light slate	7	254

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[1] In procuring for examination a quantity of oil from this well as a representative petroleum from the Berea Grit in the Eureka field we are indebted to the zealous interest of Mr. J. S. Dunn, who crossed the country in an indirect course on account of freshets, a distance of 30 miles, in order that we might have some of this oil in unquestionable purity.

Rock formation.	Thickness in feet.	Depths.
Dark slate	5	259
Coal	1	260
Red rock	10	270
Light slate	20	290
Red rock	10	300
Light slate Bottom of 10-inch casing	45	345
Slate	10	355
Red rock	90	445
Slate, water	60	505
Shales with sandstone Bottom of 8-inch casing	345	850
Sandstone, water First Cow Run sand	85	935
Slates	94	1029
Sand rock water Second Cow Run sand	67	1096
Slate	20	1416
Sandstones, light & dark	156	1272
Shale & shells of sandstone	50	1322
Lime and sandstones, bottom of 6-inch casing	23	1345
Sandrock, "Big Indian"	220	1565
Slate	20	1585
Sandrock, "Squaw"	15	1600
Cuyahoga shale	340	1940
Berea black shale	21	1961
Berea Grit, gas	8	1969
Bedford shale	30	2009

A specimen of gas was collected from well No. 8, on the J. S. Dunn farm, near Dexter City. This well was drilled in 1891. It started at 250 pounds of oil daily. The quantity of gas is not large but it contains a considerable proportion of illuminating hydrocarbons. The higher percentage of illuminating constituents in this gas is doubtless due to the fact that it came from an oil well. It was shown by analysis to have the following composition :

Carbonic dioxide	0.30
Carbonic oxide	0.40
Oxygen	4.00
Nitrogen	1.20
Illuminating hydrocarbons	2.60
Marsh gas	91.20
	99.70

A specimen of gas was also collected from well No. 1, on the Mitchell farm, on Buffalo Run. This well was the first to reach the Berea Grit. It has supplied Dexter City with gas for heating, lighting, and manufacturing during eight years. An analysis of this gas gave the following results :

Carbonic dioxide	0.10
Carbonic oxide	0.80
Oxygen	0.30
Nitrogen	1.00
Illuminating hydrocarbons	0.7
Marsh gas	97.0
	99.9

From his observations on the Alsace petroleum, Engler concluded that the specific gravity decreases with the depth of the well. This inference is not fully supported by our study of the sandstone oils of Southern Ohio. It is true that the lightest oil is found in the Berea Grit, but this stratum also contains the heaviest oil. The oil from the 500-foot sand is nearly as light as the Berea Grit 1500-foot sand. These differences will be apparent in comparing the specific gravity of the oils from the different sandstones:

	Specific gravity.
140-foot sand	0.8118
300 " "	0.8205
500 " "	0.7971
700 " "	0.8183
1500 " "	0.8274
" " "	0.7939

The percentages of the more volatile distillates increases with the depth of the well, except the heavier Berea Grit oil. As will be seen later, the largest quantity of volatile constituents are contained in the lighter Berea Grit oil.

From the following comparison of the percentages of nitrogen in the oils taken at different depths, it appears that the proportion of this element increases with the depths, although oil from the 140-foot sand contains more than those from the strata next below :

	Percentage of nitrogen.
140-foot sand	0.027
300 “ “	0.018
500 “ “	0.015
700 “ “	0.038
1500 “ “	0.064
“ “ “	0.036

The 10 gallons of Berea Grit oil which we obtained from the Ward well mentioned above was free from sediment, of a very light amber color, and second in quality only to the famous Pinesborough petroleum. It deposits paraffin in large quantity when cooled to 0°, and crystals appear even at 10°. The composition and properties of this oil are given in the following table:

Crude oil.	C.	H.	N.	Per cent. of dist.	Specific gravity.	Br-absorp.	HBr set free.
	84.35	14.72	0.038		0.7939	6.25	2.23
35–85°				0.66		0.00	0.00
85–110°				7.33	0.6570	0.00	0.00
110–135°				10.00	0.6790	1.56	0.42
135–160°				11.66	0.7393	1.63	1.54
160–185°				7.00	0.7568	2.46	1.58
185–210°				7.00	0.7710	3.54	1.94
210–235°				5.33	0.7904	4.32	3.41
235–260°				5.33		6.31	2.94
260–285°				5.33	0.8127	7.58	3.07
285–310°				5.33		9.60	2.83
310–335°				5.00	0.8288	9.09	3.59
335–360°				4.00		13.59	3.56
+360°				25.00	0.8756	16.89	5.01

As shown in another paper, from conclusions based in part upon results herein described, it is evident that cracking during distillation, begins in these oils at temperatures varying between 185° and 235°. It is still somewhat uncertain, however, to what extent the increase in bromine-absorption is dependent upon normal constituents of the crude oil with an absorptive capacity, and to what extent upon decomposition-products of the distillation.

On account of the very large proportion of the volatile distillates in the Berea Grit oil, it would have been interesting to separate the more volatile hydrocarbons for the purpose of identifying them, and comparing them with the corresponding constituents of Pennsylvania, Ohio, Trenton, and Canadian corniferous, limestone oils, which one of us (C. F. M.) has under investigation. But unfortunately this oil is not refined separately, and to collect the more volatile portions, a larger quantity of the crude oil must be distilled than can be done outside of a refinery. We have assumed, therefore, that these portions have the same composition as those of Pennsylvania petroleum, and we have directed our attention to the less volatile portions of this oil. The 10 gallons of crude Berea Grit oil already mentioned, was separated into 25°, 10°, 5°, and 1° fractions, and distillation of these portions continued under a constant tension of 730 mm., maintained by means of the regulator elsewhere described.[1] The fractions began to collect after the tenth distillation, but much longer distillation was necessary for the separation of the constituents, as well as to show that the intermediate fractions were mixtures of higher and lower products. The quantities collected between 150° and 158° were small. At 159–160° the fractions were sufficiently large to indicate the presence of a single body. On the basis of the statement of Pelouze and Cahours[2] that a decane $C_{10}H_{20}$, boiling-point 161–162°, is contained in Pennsylvania petroleum, all works on organic chemistry mention decane as a constituent of petroleum. The Organic Chemistry by Beilstein, 2d edition, states that the decane found by Pelouze and Cahours, boiling-point 161°, is probably normal decane.

Nevertheless the work of Pelouze and Cahours was not sufficiently thorough to inspire full confidence that they really had in hand a decane. Then other results seemed to disprove the presence in petroleum of a decane with this boiling-point. On this account we have given particular attention to this distillate in the oils now under examination. The fraction 159–160° from Berea Grit petroleum was submitted to prolonged distillation to ascertain beyond question whether the considerable quantities collecting at this point could be subdivided. After the twentieth distillation, however, the quantity at this point remained practically constant, and it

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[1] This JOURNAL, **17**, 723; and Proc. Amer. Acad., **31**, 10.

[2] Ann. Chim. Phys. [4], **1**, 5.

repeatedly distilled at 162–163°, tension 760 mm. Since other oils gave a similar result, even after the fiftieth distillation, it must be assumed that American petroleums contain a hydrocarbon with this boiling-point.

The following analyses were made of the distillate 162–163° from Berea Grit petroleum after drying over sodium :

0.1514 gram of the oil gave 0.4732 gram CO_2, and 0.1979 gram H_2O.

	Calculated for		
	$C_{10}H_{20}$	$C_{10}H_{22}$.	Found.
C	85.71	84.51	85.25
H	14.29	15.49	14.53

The specific gravity of the unpurified distillate at 20° was 0.7629.

A portion of this distillate was heated gently for some time with fuming sulphuric acid. At first it became slightly warm when shaken with the acid, probably on account of the reaction on the aromatic hydrocarbons. The diminution in weight by the action of the acid was equivalent to two per cent. of the weight taken. Evidently the action of the acid consisted merely in removing mesitylene, boiling-point 163°, with which this distillate was contaminated. Indeed, the presence of the latter body was shown by the formation of a barium salt of the sulphonic acid formed by the action of fuming sulphuric acid. Upon neutralizing the acid solution with baric carbonate and evaporating to dryness, a barium salt was obtained, sparingly soluble in water, and crystallizing in clusters of needles.

0.5693 gram of the salt thus obtained lost nothing on standing over sulphuric acid, nor when heated to 100°, but on ignition with sulphuric acid 0.2564 gram of baric sulphate was obtained.

Calculated for $(C_9H_{11}SO_3)_2Ba$.	Found.
25.61	26.45

The purified distillate gave the following results on analysis :

I. 0.1513 gram of the oil gave 0.4691 gram CO_2, and 0.2070 gram H_2O.

II. 0.1545 gram of the oil gave 0.4786 gram CO_2, and 0.2130 gram H_2O.

	Calculated for $C_{10}H_{22}$.	Found. I.	II.
C	84.51	84.57	84.29
H	15.49	15.21	15.24

A determination of the specific gravity of the purified oil gave 0.7475 at 20°.

A determination was also made of the vapor density. 0.1436 gram of the oil gave 69 cc. of vapor at 182°, and under a tension of 395.5 mm.

Calculated for $C_{10}H_{22}$.	Found.
4.90	5.15

The boiling-point of this distillate was scarcely changed by treated with the acid. It nearly all distilled between 162° and 163°. Its odor was very faint, resembling that of the petroleum hydrocarbons in general. Like other hydrocarbons which we have separated from contaminating bodies, sodium remained untarnished in it after standing.

The quantity of the distillates were small above this point to 168°, but between this limit and 173° larger amounts collected, which by further distillation gave 95 grams, which all came over at 174–175°, under a tension of 760 mm. and with the mercury all in the vapor.

One portion (*a*) of this oil was reserved for determinations of carbon and hydrogen, without further treatment. Another portion (*b*) was shaken with concentrated sulphuric acid until a fresh acid produced no coloration. A third portion (*c*) was allowed to stand twenty-four hours with occasional shaking with a mixture of concentrated nitric and sulphuric acids. The latter treatment caused the separation in small quantity of a yellow oil that deposited crystals on standing. After crystallization from alcohol, in which it is rather sparingly soluble, this substance melted at 183–184°, showing it to be trinitropseudocumol, melting-point 185°. It was evidently formed from a small amount of cumol which still remained in this fraction. Another portion of the same product was gently heated during twelve hours with the mixture of acids. A vigorous action set in soon after heat was applied, as should be expected, followed by complete decomposition of more than fifty per cent. of the oil. After a second treatment the oil disappeared entirely and in its place was a black porous solid, insoluble in water, but soluble in alcohol. Evaporation of the alcohol left a thick oily residue, from which no definite product could be separated. During the action of the acid a sublimate formed in the tube of the condenser that gave off the characteristic fumes of nitric dioxide when treated with water. This snbstance gave an acid reaction, and its color resembled that of butyric acid. The black solid formed by the action of the acid mixture had a similar odor. When treated with baric carbonate, a barium salt was formed with effervescence, and upon evaporation a crystalline salt separated, but not in sufficient quantity for analysis. In respect to its behavior toward the action of these acids, this oil resembles the corresponding fractions of other petroleums which are now under examination in this laboratory. Without further purification, carbon and hydrogen were determined in (*a*) with the results given below. For Analysis I the oil was dried over calcic chloride, and for Analyses II and III it was dried over sodium; as in all crude distillates, sodium caused a heavy flocculent, yellow precipitate to separate, which doubtless affected the proportions of carbon and hydrogen.

I. 0.1434 gram of the oil gave 0.4523 gram CO_2, and 0.1878 gram H_2O.

II. 0.1420 gram of the oil gave 0.4425 gram CO_2, and 0.1904 gram H_2O.

III. 0.1538 gram of the oil gave 0.4830 gram CO_2, and 0.2026 gram H_2O.

	Calculated for		Found.		
	$C_{10}H_{22}$.	$C_{10}H_{20}$.	I.	II.	III.
C	84.51	85.71	86.02	84.92	85.65
H	15.49	14.29	14.55	14.90	14.64

A determination of the specific gravity of this fraction at 20° gave 0.7624.

In a determination of its vapor density by the Hofmann method, 0.1628 gram of the oil gave 78 cc. of vapor at 182°, and under a tension of 417.1 mm.

Calculated for $C_{10}H_{22}$.	Found.
4.92	4.93

In a second portion (*b*) of the same fraction that had been treated with sulphuric acid, carbon and hydrogen were also determined.

I. 0.1652 gram of the oil gave 0.5199 gram CO_2, and 0.2136 gram H_2O.

	Calculated for $C_{10}H_{22}$.	 $C_{10}H_{20}$.	Found.
C	84.51	85.71	85.83
H	15.49	14.29	14.37

The specific gravity of this oil at 20° was found to be 0.7607, showing that a heavier body had been removed by the acid.

In determining the vapor density by the method of V. Meyer, 0.0511 gram of the oil gave 8.8 cc. of air at 18.°5, and under a tension of 725 mm.

Calculated for $C_{10}H_{22}$.	Found.
4.92	5.03

The third portion (*c*) of the fraction 173–174°, after long standing with a mixture of nitric and sulphuric acids, was boiled with sodium as long as a flocculent solid continued to separate. Its boiling-point was not changed by this treatment, but analysis showed an appreciable change in the percentages of carbon and hydrogen :

I. 0.1483 gram of the oil gave 0.4596 gram CO_2, and 0.2047 gram H_2O.

II. 0.1540 gram of the oil gave 0.4775 gram CO_2, and 0.2102 gram H_2O.

III. 0.1424 gram of the oil gave 0.4424 gram CO_2, and 0.1989 gram H_2O.

	Calculated for $C_{10}H_{22}$.	 I.	Found. II.	 III.
C	84.51	84.50	84.57	84.72
H	15.49	15.33	15.17	15.52

The specific gravity of this oil at 20° was found to be 0.7509.

In a determination of its vapor density, 0.1186 gram of the oil gave by the Hofmann method, 64 cc. of vapor at 182° and 370 mm.

Calculated for $C_{10}H_{22}$.	Found.
4.92	4.91

In a second determination of the vapor density in a portion of the fraction 173–174°, after warming with fuming sulphuric acid, the following results were obtained :

0.1397 gram of the oil gave 69.4 cc. of vapor at 182°, and under a tension of 386 mm.

Required for $C_{10}H_{22}$.	Found.
4.92	5.11

Carbon and hydrogen were also determined after treatment with fuming sulphuric acid.

I. 0.1529 gram of the oils gave 0.4743 gram CO_2, and 0.2113 gram H_2O.

II. 0.1600 gram of the oil gave 0.5000 gram CO_2, and 0.2230 gram H_2O.

	Calculated for $C_{10}H_{22}$	Found. I.	II.
C	84.51	84.63	84.69
H	15.49	15.36	15.40

The specific gravity of this oil at 20° was found to be 0.7517, practically the same as the product purified with nitric and sulphuric acids.

Since, after the tenth distillation, considerable quantities of distillates collected between 180° and 185°, distillation of the single degree fractions between 174° and 185° (tension 173 mm.) was continued until only small quantities remained within these limits. The bearing of this observation on the results of Pelouze and Cahours, and of Warren in similar fractions from Pennsylvania petroleums, and of Markownikoff in Russian oil, will be more fully considered in connection with the results of work now in progress on the other oils.

After the thirteenth distillation, 110 grams collected at 190–191° (tension 730 mm.), which distilled at 194–196°, nearly all at 195° (tension 760 mm.), with the mercury column wholly in the vapor. An analysis without further treatment gave the following results :

I. 0.6366 gram of the oil gave 0.4250 gram CO_2, and 0.1826 gram H_2O.

II. 0.1504 gram of the oil gave 0.4659 gram CO_2, and 0.2044 gram H_2O.

III. 0.1656 gram of the oil gave 0.5184 gram CO_2, and 0.2166 gram H_2O.

	Calculated for $C_{11}H_{24}$.	Found. I.	II.	III.
C	84.62	85.02	84.55	85.35
H	15.38	14.86	15.11	14.53

The oil used for Analysis I was dried over calcic chloride, while that used in Analyses II and III was dried over sodium.

In drying this distillate over sodium a heavy flocculent precipitate separated, probably formed by the decomposition of unstable constituents.

The specific value of the unpurified fraction at 20° was found to be 0.7802.

A determination of its vapor density by the method of V. Meyer, gave the following values:

I. 0.1383 gram of the oil gave 20.9 cc. at 16°, and a tension of 732.1 mm.

II. 0.1473 gram of the oil gave 22.8 cc. of the vapor at 19.5°, and a tension of 715.6 mm.

Calculated for $C_{11}H_{24}$.	Found. I.	II.
5.31	5.62	5.68

A portion of this distillate was next shaken with concentrated sulphuric acid until agitation with fresh acid produced no coloration. The oil was washed with sodic hydrate and water, and dried for analysis:

I. 0.1478 gram of the oil gave 0.4580 gram CO_2, and 0.2036 gram H_2O.

	Calculated for $C_{11}H_{24}$.	Found.
C	84.62	84.59
H	15.38	15.32

In a determination of its specific gravity the same oil gave at 20°, 0.7696.

Another portion of the same fraction was allowed to stand with occasional shaking twenty-four hours with a mixture of concentrated sulphuric and nitric acids. The washed and dried oil was boiled with sodium as long as it gave a flocculent precipitate. By this treatment neither the percentage composition nor the boiling-point was appreciably changed:

I. 0.1476 gram of the oil gave 0.4575 gram CO_2, and 0.2021 gram H_2O.

II. 0.1507 gram of the oil gave 0.4664 gram CO_2, and 0.2086 gram H_2O.

	Calculated for $C_{11}H_{24}$.	Found. I.	II.
C	84.62	84.53	84.41
H	15.38	15.22	15.38

The specific gravity of this oil at 20° was found to be 0.7622.

In a determination of its vapor density by the method of V. Meyer, 0.1372 gram of the oil gave 20.5 cc. of vapor at 16°, and 734.3 mm.

Calculated for $C_{11}H_{24}$.	Found.
5.31	5.67

After treatment of another portion of this fraction with fuming sulphuric acid, the percentages of carbon and hydrogen were slightly affected.

I. 0.1532 gram of the oil gave 0.4753 gram CO_2, and 0.2131 gram H_2O.

II. 0.1503 gram of the oil gave 0.4648 gram CO_2, and 0.2108 gram H_2O.

	Calculated for $C_{11}H_{24}$.	Found. I.	II.
C	84.62	84.61	84.35
H	15.38	15.45	15.59

The oil treated with fuming sulphuric acid gave 0.7615 at 20°, as its specific gravity, a volume somewhat lower than the portion treated with the mixture of acids.

In continuing the distillation above this point no fractions collected in any considerable quantity below 208°. At 208–210° corresponding to 215°, at 760° a distillate collected, which without further purification, was analyzed.

I. 0.1475 gram of the oil gave 0.4638 gram CO_2, and 0.1895 gram H_2O.

II. 0.1490 gram of the oil gave 0.4660 gram CO_2, and 0.1926 gram H_2O.

	Calculated for $C_{12}H_{26}$.	Found. I.	II.
C	84.71	85.74	85.29
H	15.29	14.28	14.84

After treating this oil with concentrated sulphuric acid, the percentages of carbon and hydrogen were not materially changed.

I. 0.1479 gram of the oil gave 0.4615 gram CO_2, and 0.1975 gram H_2O.

II. 0.1530 gram of the oil gave 0.4794 gram CO_2, and 0.2009 gram H_2O.

	Found.	
	I.	II.
C	85.09	85.45
H	14.84	14.55

To a second portion of the distillate a mixture of nitric and sulphuric acid were added and allowed to stand, with occasional shaking.

In the treatment of all these distillates in this manner, a heavy oil invariably separated, the nitro compound of the aromatic hydrocarbon with a boiling-point near that of the principal constituent. In some instances the oil crystallized, but the quantities were insufficient to identify the product. In other oils these aromatic hydrocarbons are receiving more attention.

The oil treated with the acid mixture was boiled with sodium until it produced no further decomposition. Although the boiling-point was not materially changed, the percentages of carbon and hydrogen were sensibly affected.

0.1524 gram of the oil gave 0.4745 gram CO_2, and 0.2114 gram H_2O.

	Calculated for $C_{12}H_{26}$.	Found.
C	84.71	84.94
H	15.29	15.42

Another portion of this distillate was warmed for some time with fuming sulphuric acid, washed and dried for analysis.

I. 0.1479 gram of the oil gave 0.4595 gram CO_2, and 0.2002 gram H_2O.

II. 0.1511 gram of the oil gave 0.4705 gram CO_2, and 0.2095 gram H_2O.

	Calculated for $C_{12}H_{26}$.	Found.	
		I.	II.
C	84.71	84.72	84.92
H	15.29	15.04	15.40

In a determination of its specific gravity this oil gave 0.7746.

In a former paper allusion was made to the difficulty in removing water from the crude oils. This hygroscopic character seems to be an inherent quality of the individual hydrocarbons, which is perhaps more marked in those with higher boiling-points. It is difficult to remove moisture with fused calcic chloride so that it will not appear in the analysis. However long the oil stands with that drying agent, when brought in contact with metallic sodium, hydrogen is freely evolved. Even when carefully dried with sodium, if the oil is allowed to stand exposed to the air not longer than in redistillation, moisture is rapidly absorbed. Frequently drops of moisture appear after a time on the inside of the bottle, probably on account of changes in temperature. In combustions great care is necessary to maintain the temperature sufficiently high to burn the gases completely, and also to maintain a moderate rate, otherwise some gas escapes combustion. These peculiarities of the hydrocarbons were not fully appreciated until many analyses had been made and repeated.

It cannot be assumed that the oils prepared for analysis in this paper are products of decomposition by the methods of treatment, since no vigorous action was observed unless the solution was strongly heated. Fuming sulphuric acid at first caused a slight rise in temperature, doubtless on account of its action on the aromatic hydrocarbon. By vigorous boiling with nitric and sulphuric acids together, any of these oils may be completely decomposed with the formation of gaseous products, and the same is true of all petroleum distillates so far as we have examined them. In all this work the greatest care has been exercised to avoid, so far as possible, decomposition of the principal constituents.

On comparison of the percentages of carbon and hydrogen in the distillates described above, it is evident that the differences in composition of different homologues are not sufficient to distinguish between members of the series closely related. But the results of analysis are sufficiently well defined to distinguish between the series C_nH_{2n+2}, and the series C_nH_{2n}, or other series more remote.

In other oils now under examination the work is sufficiently advanced to show that the results described in this paper will be confirmed. Further discussion relating to the composition of these portions of American petroleum is reserved until the observations on other distillates are ready for publication.

A METHOD FOR THE STANDARDIZATION OF POTASSIUM PERMANGANATE AND SULPHURIC ACID.

By H. N. Morse and A. D. Chambers.

If potassium permanganate of normal composition can be obtained in a sufficiently pure condition, it should be practicable, by means of a standard solution of it and by use of a neutral reducing agent like hydrogen superoxide, to determine the strength of a dilute sulphuric acid, and, conversely, by means of a standard sulphuric acid to standardize a solution of potassium permanganate.

We have found the method here suggested very expeditious and quite as accurate as the methods usually employed for the standardization of these substances. For the formal comparison, the following reagents were prepared: dilute solutions of sulphuric acid and potassium permanganate, a neutral solution of hydrogen superoxide, pure oxalic acid, and pure potassium tetroxalate.

The concentration of the sulphuric acid was determined gravimetrically by precipitation as barium sulphate. Fifty cubic centimeters of it were found to contain 0.223 gram of the acid.

The solution of permanganate was made from the recrystallized salt, and was filtered through asbestos to remove suspended oxides of manganese. Fifty cubic centimeters of it contained 0.1626 gram of the salt, $KMnO_4$, according to a determination of its concentration by weighed quantities of potassium tetroxalate, and 0.1628 gram according to a similar determination by means of oxalic acid.

The potassium tetroxalate employed in standardizing the permanganate was prepared in the following manner: Nearly pure oxalic acid was dissolved in distilled water free from ammonia. Slightly less than one-fourth part of the solution was exactly neutralized with potassium carbonate made from cream of tartar. The solution of neutral potassium oxalate was then poured into that of oxalic acid. After concentration by evaporation, the crystallized tetroxalate was separated from the mother-liquor, and further purified by recrystallization from water.

The oxalic acid, which was also used to determine the strength of the permangate, was recrystallized, first from a mixture of equal parts of alcohol and ether, and afterwards repeatedly, from water. The oxalic acid and the potassium tetroxalate were compared with each other, and with other acids of known concentration, and were found to have the normal neutralizing power.

The hydrogen superoxide used was the ordinary commercial solution. To render it neutral, it was agitated with zinc oxide, which had been heated in a muffle, and then filtered through asbestos.

Experiment I.

Determination of the Strength of the Permanganate by Means of the Standard Sulphuric Acid.—A considerable excess of the sulphuric acid was measured into a beaker and treated with a small quantity of hydrogen superoxide. Permanganate was then added from a burette, as long as the color disappeared. Afterwards more of the superoxide was introduced and the titration with permanganate resumed. The repitition of this process was continued until about 50 cc. of the permanganate had been reduced, leaving in the solution a minute excess of the hydrogen superoxide. Finally, the acid remaining free was determined by means of a tenth-normal solution of ammonia, using litmus as the indicator. The quantity of permangate found in 50 cc. of the solution (calculated according to the equation $2KMnO_4 + 5H_2O_2 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$) was 0.1626 gram; while, as previously stated, the quantities found by potassium tetroxalate and oxalic acid were 0.1626 and 0.1628 gram respectively.

Experiment II.

Determination of the Strength of the Acid.—A new solution of potassium permanganate was prepared, and its concentration determined, as in the previous case, by means of potassium tetroxalate and oxalic acid. By the former, 50 cc. were found to contain 0.1743 gram of $KMnO_4$, and by the latter 0.1744 gram. The sulphuric acid was the same as that used in the first experiment. Proceding as previously described, and regarding 50 cc. of the permanganate as containing 0.17435 gram of $KMnO_4$, 50 of the acid were found to contain 0.223 gram of sulphuric acid, a result identical with that obtained when its concentration was determined by precipitation as barium sulphate.

The figures here given are in each case the mean of several determinations. The graduated apparatus used in the work was calibrated according to the system recently described,[1] which permits of the accurate measurement of liquids to the hundredths of a cubic centimeter.

Contributions from the Chemical Laboratory of Harvard College.

XCII.—SOME DERIVATIVES OF UNSYMMETRICAL TRIBROMBENZOL.[2]

By C. Loring Jackson and F. B. Gallivan.

The study of the behavior with various reagents of aromatic compounds containing bromine and nitro groups has been carried on for some years in this laboratory, but the greater part of the work has been devoted to derivatives of symmetrical tribrombenzol. It seemed of interest, therefore, to investigate on the same lines nitro compounds derived from unsymmetrical tribrombenzol. Of these compounds the tribromdinitrobenzol, melting at 135°, seemed the most promising, but before taking up the study of its behavior, it was necessary to determine its constitution, for, although the constitution usually assigned to it (Br1, Br2, $NO_2$3, Br4, $NO_2$5) was the most probable, it did not rest on an experimental basis. For this purpose, it was reduced with tin and hydrochloric acid, when a monobromphenylene diamine, melting at 93–94°, was obtained, which was converted by bromine water into a tetrabromphenylene diamine, melting at 213°. As this same

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[1] This Journal, **16**, 479. (Note—Attention is called to an error which escaped the notice of the proof reader. The formula on page 479 should read $V = P\frac{p}{d}$.)

[2] Presented to the American Academy of Arts and Sciences, May 8, 1895.

monobromphenylene diamine has been made in this laboratory from tetrabromdinitrobenzol, in which the two nitro groups are in the meta position to each other, this proves that tribromdinitrobenzol, melting at 135°, has the constitution Br1, Br2, $NO_2$3, Br4, $NO_2$5, usually ascribed to it.

When this tribromdinitrobenzol is treated with aniline, two of the atoms of bromine are removed, and a bromdianilidodinitrobenzol melting at 191–192° is formed. This is what would be expected, as only two of the atoms of bromine which it contains are in positions favorable to renewal, (one ortho para, the other diortho to the nitro groups), while the third, (meta to the nitro groups) would be removed, if at all, only by more violent action. It resembles in this respect, therefore, tribromtrinitrobenzol, which with aniline gives trianilidotrinitrobenzol.

The behavior of the tribromdinitrobenzol 1, 2, 4, 3, 5 with sodic ethylate brings out still more strongly the similarity between this substance and tribromtrinitrobenzol. With this latter body two reactions take place simultaneously, one consisting in the replacement of the three atoms of bromine forming trinitrophloroglucine triethylether, the other in that of two nitro groups forming tribromdinitroresorcine, diethylether.[1] In the same way the action of sodic ethylate upon this tribromdinitrobenzol gives two or more organic products, one a bromdinitrophenol, melting at 67°, formed by replacing the two more loosely attached atoms of bromine by ethoxy radicals, and another, a tribromresorcine diethylether, melting at 158°, and formed by the replacement of the two nitro groups by ethoxy radicals. On one occasion a small amount of a third organic product was obtained, but not enough for identification. In these experiments, therefore, the bromine atom, which was meta to the two nitro groups, behaved like the third nitro group in tribromtrinitrobenzol, in this respect resembling the similarly placed atom of bromine in tetrabromdinitrobenzol.[2] It, is, however, strange that the two ethoxy groups should have replaced the two nitro groups leaving the bromine atom unaffected, especially as in the case of tetrabromdinitrobenzol, one nitro group and the bromine

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[1] Proceedings Amer. Acad., **27**, 283.

[2] *Ibid.*, **24**, 293.

atom are replaced in the parallel reaction. It is possible that the third product, which we could not obtain in a quantity sufficient to identify, was a dibromnitroresorcine diethylether formed in this way, but, if this were the case, the reaction was a very subordinate one.

The action of sodium malonic ester on this tribromdinitrobenzol gave a trace of a red sodium salt, but we have not succeeded in modifying the conditions of the reaction so to as obtain enough of this product even for purification. The failure to obtain this reaction, we regret the more, because the study of this case promised to throw light on the strange replacement of bromine by hydrogen in nitrobrombenzols, which has been a subject of study for many years in this laboratory.

In addition to the work just summarized we have determined the constitution of the tetrabrombenzol melting at 175°, a substance which was usually considered symmetrical, although this conclusion was not based on experimental grounds. We have done this in two ways: First, by replacing the nitro group in the tribromnitrobenzol, melting at 93°, by bromine directly, that is, by heating it with bromine and water; and second, by converting this same tribromnitrobenzol into the corresponding tribromaniline, and replacing the amido group by a bromine atom by means of Griess's reaction. In both cases the product was the tetrabrombenzol, melting at 175°, and as this tribromnitrobenzol has the constitution $Br1, Br2, Br4, NO_25$, it follows that this tetrabrombenzol really has the symmetrical constitution usually attributed to it.

The new tribromaniline ($NH_21 Br2, Br4, Br5,$) made in the course of this work melts at 80°, its acetanilide at 188°. It differs from the ordinary tribromaniline also in that it forms salts with greater ease. Its chloride, bromide and sulphate were prepared and analyzed.

An attempt to prepare nitro compounds from the symmetrical tetrabrombenzol did not lead to the desired result, the product being hexabrombenzol.

Some attempts were also made to prepare the adjacent tetrabrombenzol, but our work in this direction is so far from finished that the publication of it must be postponed for the present.

Preparation of Tribrombenzol (1, 2, 4).

After trying a number of the methods recommended for making unsymmetrical tribrombenzol, we finally adopted that from dibromacetanilide given by Griess,[1] and also used by Körner,[2] which after a few modifications gave satisfactory results. We proceeded as follows: Fifty grams of acetanilide suspended in five liters of water were treated with a stream of air loaded with bromine vapor, until the acetanilide was converted into a reddish-brown oil. A smaller amount of water must not be used, as in that case tribromaniline was formed in considerable quantity. This may have been due to a partial saponification of the acetanilide by the hydrobromic acid formed in the process. The red oil obtained in the way described was treated with dilute sodic hydrate, when it solidified, and, after a thorough washing with water, was boiled under a return condenser with dilute sulphuric acid of specific gravity 1.44, until all the organic matter had dissolved. As the solution cooled, fine crystals of the sulphate of dibromaniline separated, which were filtered from the large excess of sulphuric acid and then suspended in water acidified with sulphuric acid, and converted into the diazo compound by adding a little more than the calculated amount of sodic nitrite; as the diazo compound is formed the crystals go into solution. Bromine and potassic bromide were then added, forming a yellow precipitate of dibromdiazobenzol perbromide, which was filtered out, dried on filter-paper and decomposed by warming it with glacial acetic acid. On cooling the solution deposited the tribrombenzol as an oil, which solidified on standing and melted at the proper temperature, 44°. In this way five grams of tribrombenzol were obtained from five grams of dibromaniline, instead of 5.8 grams, that is, 86 per cent. of the theoretical yield. The dibromaniline could also be converted into tribrombenzol to advantage by carrying on the Griess reaction in a concentrated solution of hydrobromic acid, and disregarding the yellow precipitate of dibromdiazo-

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[1] Jahresb., 1866. 454.

[2] Gaz. Chim., 4, 405.

benzol bromide, distilling with an additional quantity of concentrated hydrobromic acid. Both these processes give better results than the decomposition of the perbromide with sodic carbonate or alcohol, which yielded considerable amounts of tarry impurities, or than the Sandmeyer reaction, from which we did not succeed in getting a good yield.

Constitution of Tribromdinitrobenzol, Melting at 135°.

Before studying the behavior of this substance it was necessary to establish its constitution, which had not yet been done experimentally; although there could be little doubt as to its graphic formula, because the unsymmetrical tribrombenzol gives by the action of nitric acid two mononitro derivatives, which have been proved to have the constitutions Br1, Br2, Br4, NO_25, and Br1, Br2, NO_23, Br4 respectively,[1] and it is probable, therefore, that the dinitro compound obtained by the more energetic action of nitric acid has the constitution Br1, Br2, NO_23, Br4, NO_25. To settle the point definitely we submitted the tribromdinitrobenzol, melting at 135°, to reduction. Ten grams of this substance, moistened with a little alcohol, were allowed to stand with a mixture of tin and hydrochloric acid. The color changed quickly from yellow to grayish white, and at the end of fifteen minutes the gray solid dissolved with a slight rise in temperature. The liquid poured off from the tin was then treated with an excess of sodic hydrate, until the precipitate of hydrate of tin had dissolved completely. The undissolved substance was filtered out and crystallized from a mixture of alcohol and ligroïn until it showed the constant melting-point 93–94°. This melting-point is the same as that of the monobromphenylene diamine obtained by Calvert and one[1] of us by the reduction of the tetrabromdinitrobenzol, melting at 227°. To characterize this substance still more certainly, it was treated with bromine water, as this reagent converts the monobromphenylene diamine (from tetrabromdinitrobenzol) into tetrabromphenylene diamine, melting at 214°. By this treatment with bromine water our substance gave a product which after purification

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[1] Körner. Gaz. Chim., **4**, 413.

by crystallization from a mixture of chloroform and alcohol, melted at 213° and gave the following result on analysis :

0.2310 gram of the substance gave 0.4088 gram of argentic bromide by the method of Carius.

	Calculated for $C_6Br_4(NH_2)_2$.	Found.
Bromine	75.47	75.34

These observations prove that the reduction products of tetrabromdinitrobenzol and of tribromdinitrobenzol, melting at 135°, are identical, and as the two nitro groups in the former substance are in the meta position, it follows that the two nitro groups in the tribromdinitrobenzol, melting at 135°, must also be in the meta position to each other, and that this substance has the constitution usually assigned to it Br1, Br2, $NO_2$3, Br4, $NO_2$5.

Behavior of Tribromdinitrobenzol (1, 2, 4, 3, 5,) with Aniline.

Two grams of tribromdinitrobenzol, when mixed with an excess of aniline, went into solution in a short time. To make certain that the reaction was complete, this solution was warmed for a minute or so on the steam bath. The excess of aniline was then removed by the addition of dilute nitric acid, followed by thorough washing with water, and the undissolved portion recrystallized from a mixture of benzol and alcohol, until it showed the constant melting-point 191–192°, when it was dried at 100° and analyzed with the following results :

I. 0.2216 gram of the substance gave by the method of Carius 0.0991 gram of argentic bromide.

II. 0.2017 gram gave 0.0891 gram of argentic bromide.

	Calculated for	Found.	
	$C_6HBr(C_6H_5NH)_2(NO_2)_2$.	I.	II.
Bromine	18.64	19.03	18.80

The substance was, therefore, formed by replacing two of the atoms of bromine by anilido groups, and is a bromdianilidodinitrobenzol.

Properties of Bromdianilidodinitrobenzol.—It crystallizes from a mixture of benzol and alcohol in yellowish orange needles

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[1] Proc. Am. Acad., **31**, 155.

in radiating groups, forming woolly masses. The crystals, when better developed, are slender prisms with square ends. It melts at 191° to 192°, and is slightly soluble in cold alcohol, more freely in hot ; soluble in ether, chloroform, benzol, acetone; essentially insoluble in water. The best solvent for it is a mixture of alcohol and benzol. Hydrochloric acid has no apparent action on it. Nitric acid dissolves it, but the addition of water seems to precipitate the unaltered substance. Strong sulphuric acid also dissolves it, but on dilution the substance precipitated has a different color from that of the original bromdianilidodinitrobenzol.

Behavior of Tribromdinitrobenzol (1, 2, 4, 3, 5,) with Sodic Ethylate.

Thirteen grams of tribromdinitrobenzol were dissolved in benzol and mixed with an alcoholic solution of sodic ethylate containing four molecules of the ethylate to each molecule of the tribromdinitrobenzol. The solution turned yellow at first, and this color gradually changed to a brownish red. To complete the reaction it was allowed to stand at ordinary tempertures over night, when it was found that a considerable amount of solid matter had been precipitated. This was filtered out and proved to be mostly inorganic salts ; its solution in water gave good tests for sodic nitrite and sodic bromide. The filtrate from these salts was allowed to evaporate spontaneously, the dark-colored residue thoroughly washed with water and then crystallized from alcohol until it showed the constant melting-point 158°, when it was dried at 100° and analyzed with the following result :

0.2430 gram of the substance gave by the method of Carius 0.3407 gram of argentic bromide.

	Calculated for $C_6HBr_3(OC_2H_5)_2$.	
Bromine	59.55	59.67

The substance is, therefore, a tribromresorcine diethylether, formed by the replacement of the two nitro groups by two ethoxy radicals.

Properties of Tribromresorcine Diethylether.—It crystallizes from alcohol in long, white pearly plates terminated by two planes at an acute angle, which is usually truncated by a basal plane. It has a disagreeable, rather characteristic odor and melts at 158°. It is nearly insoluble in cold alcohol, soluble in hot; soluble in chloroform, benzol or acetone; slightly soluble in cold ligroïn, more soluble in hot. The best solvent for it is hot alcohol.

The appearance of sodic bromide as one of the products of the reaction shows that this tribromresorcine diethylether could not be the only organic product of the action, and this second organic product was found in the aqueous wash waters used on the residue from the spontaneous evaporation of the organic solvents. The presence of this substance was indicated by the strong orange color of this aqueous solution. It was accordingly concentrated and acidified with dilute sulphuric acid, which precipitated an oil that usually remained obstinately liquid; even standing for two months did not bring it to crystallization, nor was treatment with sodic ethylate, precipitation of the salt formed with benzol, and setting free the phenol with sulphuric acid more successful. The precipitate was still oily. Finally a new preparation undertaken with great care, furnished us with some phenol which would crystallize. The preparation was carried on as follows: Ten grams of the tribromdinitrobenzol were dissolved in 100 cc. of benzol dried over sodium and mixed with an alcoholic solution of the sodic ethylate from two grams of sodium in a flask provided with a chloride of calcium tube. When the mixture had stood at ordinary temperatures over night it was acidified with dilute sulphuric acid and allowed to evaporate spontaneously, after which the residue was treated as before. The oily phenol obtained in this way soon crystallized in broad, thin scales, which melted at 67° after recrystallization from chloroform, and gave the following results on analysis:

0.1754 gram of the substance gave by the method of Carius 0.1162 gram of argentic bromide:

	Calculated for $C_6HBr(OH)_2(NO_2)_2$.	Found.
Bromine	28.67	28.20

It was formed, therefore, by the replacement of two of the bromine atoms by ethoxy radicals, which were afterward saponified to hydroxyls by a trace of moisture. From the experience obtained by work on related substances in this laboratory, we should infer that the two bromine atoms replaced were those in the ortho-para and diortho positions to the two nitro groups, and that, therefore, the substance is a bromdinitroresorcine, but this conclusion rests only on an analogy. If correct the substance is constituted as follows: $Br1$, $OH2$, NO_23, $OH4$, NO_25.

Properties of Bromdinitroresorcine.—It crystallizes from chloroform in broad, thin scales of slightly brownish color, which melts at 67°. It is very soluble in alcohol, ether, acetone or benzol; soluble in chloroform; insoluble in cold ligroïn, soluble in hot. With sodic hydrate it forms a soluble salt of a rather dark orange color.

On one occasion the reaction with sodic ethylate yielded a small quantity of a substance crystallizing in long needles and melting at about 80°, but, although we varied the conditions of the reaction in a number of ways, we have not succeeded in preparing this substance again, and therefore can give no account of its composition.

Behavior of Tribromdinitrobenzol (1, 2, 4, 3, 5,) with Sodium Malonic Ester.

Our experiments on this part of the subject led to no new compound. Ten grams of the tribromdinitrobenzol dissolved in absolute alcohol with a little benzol were mixed with 12 grams of malonic ester previously converted into sodium malonic ester, by treatment with an alcoholic solution of the sodic ethylate from 1.5 grams of sodium. After the mixture had stood for some time at ordinary temperatures, a dark red color had appeared, resembling that of the salts of other similar substituted malonic esters prepared in this laboratory. This seemed to indicate that the reaction had run in the desired way, but after the mixture had stood over night, and the product had been worked up in the usual manner more than 80 per cent. of unaltered tribromdinitrobenzol was recovered. Other experiments were then tried, allowing the mixture to stand for several days; heating it, and even carrying on the experiment with amyl alcohol as the solvent at its boiling-point, but in every case most of the tribromdinitrobenzol was recovered unaltered. From all these experiments a very minute quantity of a substance was obtained, which behaved like a substituted malonic ester, since it gave a red solution with sodic hydrate, the color of which was discharged on acidification, but it was evident that it was not worth while to attempt to prepare enough of this substance for study.

Reduction of Tribromnitrobenzol (1, 2, 4, 5.)

Five grams of tribromnitrobenzol, melting at 93°, were moistened with a little alcohol and reduced with tin and hydrochloric acid by warming the mixture gently. The tribromnitrobenzol did not dissolve, but its yellow color gradually changed to gray, and when the reduction was complete the product was left as a grayish mass clinging to the tin. The liquid was filtered off, the residue washed thoroughly with water to remove stannous chloride and then purified by recrystallization from alcohol until it showed the constant melting-point 80°, when it was dried *in vacuo* and analyzed with the following results:

I. 0.3020 gram of the substance gave by the method of Carius 0.5165 gram of argentic bromide.

II. 0.2593 gram of the substance gave 0.4427 gram of argentic bromide.

	Calculaled for $C_6H_2Br_3NH_2$.	Found.	
		I.	II.
Bromine	72.73	72.79	72.66

The substance is, therefore, a new tribromaniline, and as it is made from the tribromnitrobenzol, melting at 93°, it must have the following constitution: Br1, Br2, Br4, $NH_2$5. It is worth mentioning that zinc dust and acetic acid did not reduce the tribromnitrobenzol.

Properties of Tribromaniline (1, 2, 4, 5.).—It crystallizes from alcohol in yellowish white, rather short needles, united longitudinally to form narrow plates with parallel sides and serrated or irregular ends. These plates are usually strongly striated. It melts at 80°. It is very soluble in alcohol, ether, chloroform, or benzol; moderately soluble in cold ligroïn, soluble in hot; insoluble in water. It distils with steam, although with some difficulty. With acids it forms salts more easily than the ordinary tribromaniline (1, 3, 5, 2), since the chloride can be obtained by the long continued action of hot strong hydrochloric acid on the free base, and the sulphate by heating the base with strong sulphuric acid. The chloride, although soluble in cold water, is decomposed by hot water into hydrochloric acid and the tribromaniline. The most convenient method, however, for making the chloride or bromide is by passing the gaseous acid through a solution of the tribromaniline in benzol. The chloride, bromide and sulphate were studied more in detail, as described in the following sections.

Chloride of Tribromaniline (1, 2, 4, 5), $C_6H_2Br_3NH_3Cl$.—This salt could be made by heating the tribromaniline for some time with concentrated hydrochloric acid. The solid base slowly dissolved, forming a solution of the chloride. A much more convenient method, however, was that used by Gattermann[1] for making the chloride of the ordinary tribromaniline. Our tribromaniline was dissolved in benzol, and treated with gaseous hydrochloric acid, which gave a precipitate of the pure chloride.

0.5480 gram of the salt was dissolved in water, and after the base had been removed with ammonic hydrate, gave 0.2306 gram of argentic chloride.

	Calculated for $C_6H_2Br_3NH_3Cl$.	Found.
Chlorine	9.69	10.40

The chloride crystallizes from alcohol in white branching needles. It is soluble with some difficulty in cold water, but decomposed by hot water into tribromaniline and hydrochloric acid; soluble in alcohol or ether; insoluble in benzol.

Bromide of Tribromaniline, (1, 2, 4, 5,) $C_6H_2Br_3NH_3Br$.—This salt was formed like the chloride by passing gaseous hydrobromic acid through a benzol solution of the tribromaniline. It gave the following results on analysis:

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[1] Ber. d. chem. Ges., **16**, 636.

0.4047 gram of salt gave after precipitation of the tribromaniline with ammonic hydrate, 0.1845 gram of argentic bromide.

	Calculated for $C_6H_2Br_3NH_3SO$.	Found.
Bromine	19.47	19.41

The bromide resembles the chloride most closely in its properties.

Sulphate of Tribromaniline (1, 2, 4, 5,) $C_6H_2Br_3NH_3SO_4H$.—This salt was made by heating tribromaniline with strong sulphuric acid. It separated out from the acid as it cooled and was purified by crystallization from alcohol. It gave the following result on analysis :

0.2796 gram of the salt gave 0.1560 gram of baric sulphate.

	Calculated for $C_6H_2Br_3NH_3SO_4H$.	Found.
SO_4	22.43	22.94

The salt crystallizes from strong sulphuric acid in white plates; from alcohol in needles. It is rather soluble in water, very soluble in alcohol.

Tribromacetanilide, (1, 2, 4, 5), $C_6H_2Br_3NHC_2H_3O$.—Four grams of the tribromaniline were mixed with an excess of acetic anhydride and the mixture warmed on the water-bath until all the solid had dissolved, when it was treated with water, which threw down a voluminous precipitate. This, after recrystallization from alcohol until it showed the constant melting-point 188°, was dried at 100°, and analyzed with the following result :

0.2885 gram of the substance gave by the method of Carius 0.4390 gram of argentic bromide.

	Calculated for $C_6H_2Br_3NH_3C_2H_3O$.	Found.
Bromine	64.52	64.77

The substance is, therefore, a monacetyl compound, which is surprising, as Remmers[1] states he obtained a diacetyl derivative from the ordinary tribromaniline by the action of acetic anhydride.

Properties of Tribromacetanilide.—It crystallizes from alco-

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[1] Ber. d. chem. Ges., **7**, 350.

hol in white, woolly masses, which are seen under the microscope to be composed of radiating groups of branching needles, or, if very well developed, slender prisms with blunt ends. It melts at 188°; soluble in alcohol, ether, acetone, chloroform, benzol, or glacial acetic acid; insoluble in cold ligroïn, soluble in hot; insoluble in water. Alcohol or ligroïn is the best solvent for it. Fuming nitric acid converts it into a nitro compound, which was not further studied.

Constitution of Tetrabrombenzol Melting at 175°.

The constitution of this substance has never been determined experimentally, although it has been usually considered the symmetrical compound 1, 2, 4, 5. We have established its constitution by two different methods, both of which proceed from the tribromnitrobenzol, melting at 93°, which has the known constitution 1, 2, 4, 5.

First Method.—Five grams of tribromnitrobenzol, melting-point 93°, were mixed with bromine in slight excess over the amount necessary to give equal molecules of the two substances and with 2 cc. of water, and heated to 175–200° in a sealed tube for four hours. The product was washed with dilute sodic hydrate, and afterwards with water and then purified by crystallization from glacial acetic acid, when it showed the melting-point 173°, and gave the following result on analysis:

0.2143 gram of the substance gave by the method of Carius 0.4085 gram of argentic bromide.

	Calculated for $C_6H_2Br_4$	Found.
Bromine	81.21	81.13

These results leave no doubt that the substance is the tetrabrombenzol, although the melting-point is two degrees low, and as it is hardly possible that the reaction could be other than the replacement of the nitro group by an atom of bromine, proves that this tetrabrombenzol has the symmetrical constitution. It can be objected, however, that the reaction took place at a high temperature, 175–200°, which may have been enough to cause intramolecular transformation. Accordingly we attacked the problem by another method, which was not open to this objection.

Second Method.—The tribromaniline already described in this paper, made by the reduction of the tribromnitrobenzol, melting at 93°, was converted into the sulphate of tribromdiazobenzol by treating it, suspended in dilute sulphuric acid, with the required amount of sodic nitrite. Bromine dissolved in potassic bromide was then added, and the heavy yellow precipitate of the diazoperbromide thus obtained was filtered out, dried as quickly as possible and decomposed by heating it with glacial acetic acid. On cooling the solution deposited beautiful white needles, which melted at 174–175°, and gave the following results on analysis :

0.2045 gram of the substance gave by the method of Carius 0.3890 gram of argentic bromide.

	Calculated for $C_6H_2Br_4$.	Found.
Bromine	81.21	80.95

This second method leads to the same conclusion as the first, and there can be no doubt that the tetrabrombenzol, melting at 175°, has the symmetrical constitution 1, 2, 4, 5.

We also attempted to make nitro compounds from the symmetrical tetrabrombenzol, in order to study their behavior with reagents, but without success. The symmetrical tetrabrombenzol, when boiled with fuming nitric acid alone, remains unchanged. When a mixture of fuming nitric acid and strong sulphuric acid was used, a white precipitate was obtained upon pouring the acid solution into water, which crystallized from benzol in long, silky needles, did not melt even when heated to 310°, but sublimed with tolerable ease. These properties indicated that the substance was hexabrombenzol, and this conclusion was confirmed by its analysis.

0.2152 gram of the substance gave 0.4413 gram of argentic bromide.

	Calculated for C_6Br_6.	Found.
Bromine	86.95	87.28

Riche and Berard[1] state that they obtained by the action of nitric acid on the tetrabrombenzol, melting at about 160°, a

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[1] Ann. Chem. (Liebig), 133, 52.

mononitrotetrabrombenzol. We are inclined to think, in view of our experimental results, that this nitro compound may have been formed from some impurity in the tetrabrombenzol, since the melting-point ascribed to it is rather indefinite, but a more careful study of the subject will be necessary in order to explain satisfactorily these discordant results.

REVIEWS.

HELIUM.

A short review of the progress made in the investigation of the sources and properties of helium was recently published in this JOURNAL[1]; it is proposed in this second note to call attention to some of the work the records of which have been received since the earlier review was written.

Prof. Lockyer[2] seems to have been the first to show that "helium" from different sources exhibited spectroscopic differences, and that the so-called permanent lines of the solar chromosphere, at least in most cases, coincide with certain of the characteristic lines of helium. Deslandres also has shown[3] that but one of these permanent lines is absent from the spectrum of cleveite gas. Reports from various observers[4] have established the fact that the D_3 line of the chromosphere and the yellow line of cleveite gas are both double, the less refrangible being much the weaker of the pair in each case. Measurements of the distance between the lines would finally seem to have put beyond question the identity of solar and terrestrial helium.

At the meeting of the British Association, Lord Rayleigh reported upon the refractive indices and viscosities of argon and helium.[5] Compared with that of air taken as unity, the refractive index of the latter substance is but 0.146—by far the lowest yet reported. Dr. Gladstone announced that the specific refractive energy of argon, as deduced from Lord Rayleigh's results, indicates an element with an atomic weight of about 20 and not of about 40. This evidence would tend to offset that furnished by the ratio of the specific heats of argon and of helium.[6]

A very notable paper read at the same meeting was that of Profs. Runge and Paschen, of Hanover, on the spectra of

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[1] Vol. **17**, 630.

[2] Proc. Roy. Soc. **48**, 67, 113, 116, 192, 193; **49**, 1, 4.

[3] Compt. Rend. **120**, 1112, 1331.

[4] See, for example, Chem. News, **72**, 27; "Nature," **52**, 327, 458. For an adverse criticism on this view, see Wilde: Phil. Mag. **40**, 466.

[5] See "Nature," **52**, 533; Chem. News, **72**, 152.

[6] For an account of this discussion, see Chem. News, **72**, 223.

cleveite gas.[1] Earlier papers on the same subject had shown[2] that the spectrum of pure helium is absolutely free from any of the lines characteristic of argon, and that the spectra of two constituents are to be distinguished. In the present communication, after calling attention to the fact that by substituting in succession the numbers from 3 to 30, for m in the formula $\frac{m^2}{m^2-4}$, figures are obtained proportional to the wave-lengths of the visible lines of hydrogen, and that the formula $\frac{1}{\lambda}=A-\frac{B}{m^2}-\frac{C}{m^4}$ will enable one to calculate the wave-lengths of the members of a series of lines where two are known; they showed that whereas practically every element exhibits, a spectrum consisting of three series of lines, cleveite gas gives a spectrum containing six such series, and that these fall into two groups of three series each. Further, one of these groups has been seen without the other: one contains the "permanent" lines of the chromosphere, the other consists of lines only occasionally observed. One consists of double lines only—one of which, of course, is D_3,—the other of single lines. The average position—if such a phrase is permissible—of the lines of one group is farther towards the violet end of the spectrum and approaches that of the group of the lines of lithium; whereas that of the other group is nearer the average position of the lines of hydrogen. The conclusion to be drawn is therefore that cleveite gas contains two and only two constituents, one heavier than the other. By allowing the gas to flow through a porous plug into a vacuous sparking-tube, it was noticed that the spectrum first observed was almost exclusively that of the lighter, less refrangible constituent, and that D_3 and the other "permanent" lines made their appearance only gradually. The rule is thus borne out that the series of lines shift towards the violet as the atomic weight rises, provided the elements compared follow one another in a series of Mendeléeff's System. Since, from the determinations of the density of cleveite gas, the constituents may be assumed to have atomic weights between those of hydrogen and lithium, they would thus belong to the same series of the System and hence the denser—helium proper—would possess the more refrangible series of lines. A more recent communication[3] by the same authors points out that there are several lines noted by Crookes[4] in the spectra of specimens of "helium" exam-

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[1] "Nature," **52**, 520; Chem. News, **72**, 181.

[2] Sitzb. Acad. Berlin, June 20 and July 11, 1895. For a translation of the second paper, see Phil. Mag. **40**, 297; Astrophys. J., January, 1896.

[3] "Nature," **53**, 245.

[4] Chem. News, **72**, 87; "Nature," **52**, 428.

ined by him, which do not coincide with any of the lines thus far mapped by themselves as produced by cleveite gas.

Prof. Lockyer has discussed[1] the papers of Runge and Paschen and has pointed out where his own researches[2] had led him to similar conclusions as to the dual composition of cleveite gas.

Langlet has published[3] an account of experiments made upon the density of helium and upon the ratio of its specific heats. The former he finds to be 2.0 as compared with hydrogen as unity; the latter, 1.67—in close accord with the results obtained by Ramsay.

Olszewski has been unable[4] to produce the liquifaction of helium furnished him by Ramsay, even under the conditions which were successful in the case of hydrogen—*i. e.*, allowing the gas, under a pressure of 140 atmospheres, and cooled to —210° C., to expand suddenly.

Troost and Ouvrard maintain[5] that both argon and helium are completely absorbed when sparked in a tube furnished with magnesium terminals.

Helium appears to be a constituent of the gases contained in certain spring-waters,[5] and even, at times, of air.[6]

An examination of the coefficients of expansion of argon and helium as compared with those of air and hydrogen has been made by J. P. Kuenen and W. W. Randall.[7] The object in view was to determine what change occurred in the rate of expansion of the newly discovered gases as temperature rose, and thus to obtain evidence of any dissociation which might take place. A gas-thermometer filled with each of the four substances in turn was kept successively at some six or seven temperatures ranging between 0° and 281°, while the pressure required to keep the volume constant was carefully determined. The only change in the volume of the gas was that due to the expansion of the glass bulb. After making all the necessary corrections, the coefficient of expansion of argon between 0° and 100° was found to be 0.003668, and that of helium, 0.003665. No evidence of molecular change could be obtained, when the expansion of these gases was compared with that of air and hydrogen, at the boiling-points of chlorbenzene (132.1°), aniline (184.4°), quinoline (237.4°), and bromnaphthalene (280.4°).

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[1] "Nature," **52**, 547. See also Chem. News, **72**, 271; "Nature," **53**, 167.

[2] *Loc. cit.*

[3] Ztschr. anorg. Chem., **10**, 287; Chem. News, **72**, 259.

[4] "Nature," **52**, 544.

[5] Compt. Rend., **121**, 394; Chem. News, **72**, 153.

[5] *Cf.* Compt. Rend. **121**, 392, 798, 819; Chem. News, **72**, 152, 223, 309, 310.

[6] H. Kayser: Chem. News, **72**, 89.

[7] Proc. Roy. Soc., **59**, 60; Chem. News, **72**, 295.

In a recent paper[1] it is stated that a zirconiferous sand, containing uranium, and yielding an "abundant" supply of helium, is found in large deposits on the coast of Brazil.

Finally, attention may be drawn to a paper on "Argon and Helium" in the number of the *Edinburgh Review* for October, 1895. Written—of course anonymously—in what is called a "popular" style, this article does not altogether fail to be amusing even if at times not instructive. The effort to overbalance the conclusion of the scientific world upon certain personal questions by the use of an extravagant metaphor or a sneering phrase, would be exasperating if it had to be taken seriously.

W. W. R.

TWO RECENT PUBLICATIONS UPON CARBOHYDRATES.

The amount of pure research and noteworthy attainment in the field of the carbohydrates during the past ten years has probably equalled that in any other branch of organic chemistry. Some of this research may justly be regarded as classic, notably the series of difficult syntheses of the monosaccharides by E. Fischer, and the confirmation thereby, in the most conclusive manner yet recorded, of the theoretical principles underlying stereochemistry. Less prominent but hardly less important are the numerous fundamental reactions which have been discovered and developed, and which have served as the most indispensable agents contributing to the success of investigators. Such are the methods for oxidation and reduction used by Fischer, his development of the phenylhydrazine reactions, and his methods of transforming the stereoisomeric acids into each other; Kiliani's method for increasing the number of carbon atoms in a sugar by the addition of hydrocyanic acid, and Wohl's successful "Abbau" of hexoses to pentoses through the glycosoxime; the application of Raoult's method to the determination of the molecular weights of the carbohydrates, etc. Explorative research has added new carbohydrates to those already known to occur in nature, chief among which are those of pentatomic character. These and many other minor discoveries have served wholly to revolutionize the former views regarding carbohydrates. At one time hardly considered worthy of attention by pure scientists, these bodies now serve to demonstrate some of the most important chemical theories. At the present time the interest in carbohydrates, while not less from the practical standpoint, has largely grown on the side of theoretical and pure chemistry. One immediate effect of this is the necessity

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[1] H. Wilde: Phil. Mag., 40, 468.

for revision of text-books and a demand for new and modern treatises. Two works of this kind have opportunely appeared during the year and those interested in this subject have reason to rejoice that they are from the hands of two men of such experience and knowledge in this special field as Professor Tollens and Dr. von Lippmann, both of whom have formerly published leading works on this subject.

These recent books leave little or nothing to be desired, the one offering a comprehensive review of the entire class of carbohydrates, and the other a highly specialized monograph upon the sugars. No fact or discussion of any importance bearing upon the subjects has been omitted from these works, and they bring within the reach of the student and investigator the substance of the diffused and scattered literature on the carbohydrates, revised and classified by the two persons best fitted for the task. The two works are in no sense duplicates of each other, and both are indispensable to one who would acquire command of the subject or have at hand accurate references.

KURZES HANDBUCH DER KOHLENHYDRATE. VON DR. B. TOLLENS, Professor der Chemie an der Universität, Göttingen. Zweiter Band enthaltend die Forschungsergebnisse der Jahre 1888–1895. Breslau. Verlag von Eduard Trewendt. 1895. pp. 407.

When the first edition of the Handbuch appeared, in 1888, it was rightly regarded as the most valuable work upon the subject existing. The great extension of knowledge in this field since then necessitates a quite new and modified view of the carbohydrates which this second edition admirably supplies. The former heterogeneous group of substances included under the name carbohydrates has now undergone such revision and investigation that a more or less complete systematic classification is possible. Many of these bodies are found to be members of an extended homologous series of chemical bodies of similar constitution, while others of less evident theoretical relationship are nevertheless undoubtedly connected with the better identified members of the family. The study of these bodies from the standpoint of pure chemistry has become attractive and productive of important results. This work, therefore, properly devotes much of its space to a discussion of the purely chemical characteristics of the carbohydrates, and to recording the results of the latest investigation in this line. Some of the more technical features of the first edition have been omitted, but not in a way to lessen the value of the work in any sense.

A concise definition of a carbohydrate is not ventured by the author, although one of less experience might have so committed himself. He no longer limits the term to those compounds containing six atoms of carbon, as in the earlier edition, but extends the term over the series containing from four to nine carbon atoms and possessing the other well known properties of sugars. For these simple monosaccharides, which all reduce alkaline copper solution, the general name "glycose" is suggested, the distinction being made between this class and "glucose" or grape sugar. Other sugars are included in the divisions of di- and tri-saccharides, while the amorphous carbohydrates of evident close relationship are included under the general term polysaccharides. Other related bodies such as the higher alcohols and the acids derived from the sugars by oxidation, are all considered in due place, so that every substance showing any relation to, or derivation from, the true carbohydrates receives attention. The greater portion of the work is devoted to the descriptions of the individual bodies, including their reactions, occurrence, recognition, etc. Even those bodies of doubtful place and character are not excluded. This comprehensive feature is especially valuable to the investigator, supplying as it does all available information in each case. References to original publications are given in great number. This arrangement of these references in a body at the end of the work is not the most convenient, but is compensated for by the absence from the text of the confusing parenthetical references.

The discussion of the constitution of the carbohydrates is very full and satisfactory. The author himself is an advocate of the ethylene-oxide structure for dextrose, but gives with equal detail all of the arguments for the aldehyde structure, and suggests at the close the probability that different substances exist having the same composition, of which the one may have the aldehyde and the other the ethylene-oxide formula. The configuration of the different sugars according to the theory of stereoisomerism is fully illustrated by graphic formulas. The synthetic processes employed by Fischer are also fully described.

The work is the only one of its kind in existence and is an indispensable guide and reference book to both student and investigator.

DIE CHEMIE DER ZUCKERARTEN. VON DR. EDMUND O. VON LIPPMANN. Director der Zucker-Raffinerie zu Halle. Zweite völlig umgearbeitete Auflage der vom Vereine für die Rübenzucker-Industrie des Deutschen Reiches mit dem ersten Preise gekrönten Schrift. Die Zuckerarten und Ihre Derivate. Braunschweig. Friedrich Vieweg und Sohn. 1895. pp. 1174.

As the outcome of a prize monograph upon sugars, presented in 1878 by Dr. von Lippmann, the author published in 1882 a modest work entitled "Die Zuckerarten und ihre Derivate" of which the present treatise is hardly a second edition but rather a new work with a new title. It treats, as the name indicates, of sugars only, other related carbohydrates being ignored. The author abides strictly by a rational classification on a structural basis, which is more easily done than if the entire group of carbohydrates were under consideration. All sugars are classified as mono-, di- or trisaccharides, typified respectively by glucose, sucrose, and raffinose. Properly enough, no distinction is made in treatment between the natural and artificial sugars. Beginning with glycolic aldehyde, $C_2H_4O_2$, each member of the homologous series is discussed with great detail up to and including the a-manno-nonose, $C_9H_{18}O_9$. The cyclic compounds, such as quercite, chinite, inosite, etc., are also described, although not strictly sugars. The plan of the work is to give a complete resumé of all that is known about each sugar, including references to original papers with the names of investigators. For each sugar the systematic order of treatment is as follows: Occurrence, preparation, and formula; 2. Physical properties; 3. Behavior toward heat; 4. Behavior towards reagents; 5. Fermentation; 6. Compounds and derivatives; 7. Recognition and estimation.

A close examination of the work reveals a painstaking thoroughness and completeness of treatment deserving of unqualified admiration. The great number of references shows a complete familiarity with the literature of the subject, of which the author has already given evidence in his "Geschichte des Zuckers." No fact is considered of too little importance to be given a place, although the mass of material has been so carefully edited that one feels that each reference has been given its proper emphasis. This method of treatment, when applied to some of the more important sugars, yields an exhaustive monograph in itself. For instance, the discussion of dextrose occupies 240 pages, while some forty pages more are given to invert sugar. The subject of sucrose covers over 250 pages, and so on. There are special chapters on the constitution, configuration and synthesis of sugars, the origin of sugar in plants, their physiological importance, etc., in which the results of all the most important recent investigations find place. Even many publications appearing after the work went to press, have been carefully abstracted and the abstracts added in a supplementary part, and the whole is indexed for authors and subjects separately with great minuteness. The work of preparing such a treatise is great, and the result is wholly satisfactory, easily surpassing all other works in its particular field. W. E. STONE.

OSTWALD'S KLASSIKER DER EXAKTEN WISSENSCHAFTEN. No. 63. ZUR ENTDECKUNG DES ELEKTROMAGNETISMUS. 33 pp., price 1.40 marks; No. 66. DIE ANFAENGE DES NATÜRLICHEN SYSTEMES DER CHEMISCHEN ELEMENTE, 34 pp., 0.60 mark. Leipsic. W. Engelmann, 1895.

Two of the most recent numbers of Ostwald's collection of scientific classics[1] are reprints of chemical papers. One of them contains the researches of Oersted (1820) and of Seebeck (1821) on electromagnetism (its discovery) and the "Magnetism of the Galvanic Cell," with editorial comments by von Oettingen; and the other is made up of the papers by Doebereiner (1829) and Pettenkofer (1850) on the arrangement of the chemical elements in triads, the scheme which ripened in the discovery of the periodic law. The latter collection is edited with great care by Lothar Meyer, and is concluded by a new paper by him on "The further development of the systemization attempted by Doebereiner and Pettenkofer." The importance of these convenient and inexpensive little books needs no comment. J. E. T.

DIE LEHRE VON DER ELEKTRIZITAET. By G. WIEDEMANN. Second (rewritten) edition, volume iii. Large 8vo. 1139 pp. Braunschweig: Vieweg, 1895. Price, 28 marks.

Comment has already been made in this Journal[2] upon the appearance of the first and second volumes of Wiedemann's great book on electricity. The third volume of this remarkable and authoritative work is now before us; it treats electrodynamics and electromagnetism, and its most prominent characteristics are those of the foregoing volumes—a comprehensive mass of material and the always attractive historical-critical method. The subjects treated would seem to have little to do with any forms of chemical action, and the volume will certainly interest the chemist less upon the whole than the preceding second volume which is devoted to electrochemistry, yet the present number is not devoid of chemical inter-

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[1] See this Journal, p. **17**, 629.

[2] This Journal, **15**, 606; **16**, 563.

est. We find, for example, studies on the influence of magnetization upon reactions which involve salts of iron, or upon the readiness with which metallic iron dissolves in solutions of salts and acids; there appears a full account of work done upon the electromotive forces of the electrolytic currents which arise between magnetized and unmagnetized electrodes, and upon the similar currents observable when diamagnetic bismuth electrodes are employed; and we note an interesting application of thermodynamic theory made by Pellat in the endeavor to account for the experiments of Remsen.

The mechanical execution of the work is excellent and the material presented is brought thoroughly down to date. Its scope may be inferred from the fact that the volumes now issued include nearly thirty-four hundred closely printed large octavo pages.

J. E. T.

PHYSIKALISCH-CHEMISCHE PROPAEDEUTIK. By H. GRIESBACH. Large 8vo First half, 272 pp. Leipsic, W. Engelman, 1895. Price six marks.

The *Propaedeutik* of Griesbach is a rather impressive mixture of many things. It is intended to serve as an introductory text book on physical chemistry, for the use of students of chemistry and of medicine. The office of its first half is apparently to supply an introductory store of philosophical, astronomical, historical, biographical, etymological, and biological information, leaving the reader to hope that the second half—soon to appear—may contain some details more immediately concerning physical chemistry.

The book begins with a disquisition upon philosophy in general, and Greek philosophy in particular. Measurement and measuring instruments are then taken up in great detail, ordinary dividers and the coördinate paper used for drawing curves being, for example, minutely described, and these things are followed by a lecture on matter. The discussion of matter leads our author easily and naturally, by way of the nebular hypothesis and the experiments of Plateau upon capillarity, to the doctrine of energy; and here we meet the assertion that energy, being a constituent of substance, must itself be an independent entity. Now this is simply ridiculous, and in fact this failure to regard energies as work-equivalents whose analytical forms depend upon the definition of work leads at once (p. 105) to the absurd conclusion that the conception of work is *derived* from the idea of energy.

We are next conducted through a number of chapters on such things as velocity, circular motion, friction, the constitution of matter and of ether, and thirty-seven pages of the history of ideas concerning atoms; all this leading up to a not unpretentious treatise on biology. Deep water appears here, for we are instructed in cell biology, ferments, and infectious diseases, phases of physical chemistry into which the attainments of the present writer unfortunately do not extend.

There appears throughout the text a multitude of biographical sketches of philosophers, mathematicians, physicists, chemists, etc., to whose work or ideas reference is made; and also a great mass of material concerning the etymology of the terms employed. And the whole is enlivened by occasional quotations from Latin poets—especially Ovid. Some of the biography and anecdote is interesting, some amusing, and all presumably authentic, but still one does not seek information of this kind in an introductory text-book on physical chemistry. And all the etymological Greek, Latin and Arabic is interesting enough in its place, but its place would seem to be a dictionary or other philological work rather than a treatise on physical science. The author has, in brief, collected a lot of things which it is desirable to know, but which do not necessarily belong together, and which owe their connection with physical chemistry solely to the fact that everything seems to be in some wise related to everything else. The book is certainly an industrious compilation, but it is a compilation of essentially heterogeneous materials, and where the physical chemistry comes in is not as yet easily seen.

J. E. T.

A LABORATORY MANUAL OF ORGANIC CHEMISTRY. A Compendium of Laboratory Methods for the Use of Chemists, Physicians and Pharmacists. By DR. LASSAR-COHN, Professor of Chemistry in the University of Königsberg. Translated, with the Author's Sanction, from the Second German Edition, by ALEXANDER SMITH, B.Sc. PH.D., Assistant Professor of General Chemistry, in the University Chicago. London and New York: Macmillan & Co. 1895. 8 vo. pp. 403. Price, $2.25.

This book has already gone through two editions in the original German, and a French translation has appeared, all in the short space of three years. These facts speak well for the value placed on the book by chemists, and make it probable that the present English translation will meet with a warm welcome from all workers in the field of organic chemistry, both in this country and in England.

It covers a field not previously occupied by any of the numerous text-books and laboratory manuals on organic chemistry, and is exactly what its title claims it to be; a compendium of the methods actually employed in the laboratory of organic chemistry. The attempt has been made to bring together here the methods which may be used in carrying out all the common operations of organic chemistry without reference to the particular substance employed, though many examples are given to show how various investigators have overcome difficulties in particular cases.

The book is one that should be in every laboratory in which work in organic chemistry is carried on. It cannot fail to be of value to both teachers and students of this very important branch of the science of chemistry. On every page will be found valuable suggestions culled from long experience in the practice of organic chemistry, and hidden away in the great mass of literature on this subject, and therefore practically inaccessible to the average student.

The author very modestly states in his preface to the first German edition of the book, that "Its object will have been attained if the book encourages work in the field of organic chemistry and lightens the labor of the workers." That this object has been accomplished will be gratefully acknowledged by those who have had occasion to use the book.

The translation is well done, and the author is to be congratulated that the translator is an experienced worker in the field which the book covers. The print is excellent, and the same may be said of the illustrations and the flexible binding. Altogether the book is one which does credit to both the translator and the publishers. W. R. O.

JAHRBUCH DER ELEKTROCHEMIE. Berichte über die Forschritte des Jahres, 1894. Im wissenschaftlichen Theile bearbeitet von Dr. W. Nernst, Professor an der Universität Göttingen, Direktor des Instituts für physikalische Chemie und Elektrochemie. Im technischen Theile bearbeitet von Dr. W. Borschers, Lehrer an der Kgl. Maschinenbau und Hüttenschule zu Duisburg. I Jahrgang. Wilhelm Knapp. Halle a. S., 1895. pp. 274.

As the Jahrbuch der Chemie furnishes brief abstracts of the work done in the entire field of chemistry during the year for which it purports to be a record, so the Jahrbuch der Elektrochemie gives an account of the advances made in electrochemistry for any given year. The first volume, which appeared about the middle of this year, reviews the work published in 1894.

The chapters on physical chemistry, in the Jahrbuch der Chemie, are written by Nernst and Küster. The scientific electrochemistry in the Jahrbuch der Elektrochemie is written by Nernst. That part of the former, which has to do with electrochemistry is reprinted in the latter, but this is greatly enlarged and supplemented. We find, in the scientific part of the Jahrbuch der Elektrochemie an account of the recent work on Solution of Solids; Electrolytic Dissociation; Electrolytic Conduction of the Current; The Dilution Law; Dissociation of Water; Potential Differences between Solutions; Potential Differences between Metal and Solution; Anomalous Potential Differences; and on Electrodes of the second kind.

The applied electrochemistry is discussed extensively by Borchers, with the aid of a large number of illustrations of apparatus. Among the subjects treated are; Accumulators; Electro-thermal Apparatus and Methods; Deposition of the Metals and Non-Metals; The Alkali and Chlorine industry, etc.

About one-fourth of the volume is devoted to the scientific side, the remainder to the applied. The electro-chemist will thus be provided, yearly, with an account of the most recent work done in his field. H. C. J.

ANLEITUNG ZUR MOLEKULARGEWICHTSBESTIMMUNG, NACH DER "BECKMANNSCHEN" GEFRIER-UND SIEDEPUNKTS-METHODE. Von DR. GOTTHOLD FUCHS, Assistent am Laboratorium für angewandte Chemie, Erlangen. With 18 wood-cuts. Wilhelm Engelmann. Leipzig, 1895. pp. 41.

This little book gives an account of the Beckmann freezing-point and boiling-point methods, for determining the molecular weight of substances in solution, together with a sufficient number of illustrations to make clear the discussion of the forms of apparatus, which Beckmann has devised for carrying out these methods.

The instruction is not purely mechanical, the theoretical significance of the results being treated fully enough to give the reader an intelligible view of the fundamental ideas on which these methods are based.

The value of the book would, however, have been enhanced by treating, not only of the "Beckmann methods," but of the freezing- and boiling-point methods in general, as applied to the determination of molecular weights. Thus the boiling-point method of Beckmann has been very greatly improved as a method for determining molecular weights by Hite,[1] whose apparatus is preferable to any form ever suggested by Beckmann, enabling one to determine *more accurately* the boiling-point of a low-boiling solvent, or of a solution.

On page 8, there is an error, which is of special interest to the writer of this notice. We are told that "recently a

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[1] This JOURNAL, 17, 507.

thermometer, divided into $\frac{1}{1000}°$ has been constructed, and applied by *Meyer Wildermann* and his scholars, in scientific investigations." The writer wishes to state that *he employed, first*, a thermometer answering the above description in the laboratory of Ostwald, in which Wildermann was working. The thermometer, which Götze constructed, at the suggestion of Ostwald, the apparatus and method of work were observed by Wildermann, who, about *a year later*, obtained a similar instrument and began his work in England. The facts speak for themselves.[1] H. C. J.

EINFÜHRUNG IN DIE MATHEMATISCHE BEHANDLUNG DER NATURWISSENSCHAFTEN. Kurzgefasstes Lehrbuch der Differential und Integralrechnung mit besonderer Berücksichtigung der Chemie. Von W. Nernst, Professor of Physical Chemistry in the University of Göttingen, and A. Schönflies, Professor of Mathematics in the University of Göttingen. With 61 figures in the text. München and Leipzig: Dr. E. Wolff. 1895. pp. 309.

The object of this book is in the words of the authors, "to aid students, who are in the earlier stages of scientific work, in the study of the higher mathematics." The average textbook on the calculus naturally deals with the subject from the standpoint of the mathematician, and from it one may learn to differentiate and integrate with facility, without seeing in many cases, the full significance of these processes, in their applications to the experimental sciences. The authors having this in mind, have pointed out the physical significance of the mathematical expressions in some cases. After the paragraph on the differential coefficient, we find the next on its physical significance. Another paragraph deals with the geometrical and physical significance of integration constants, etc.

The book has twelve chapters, treating of: The Elements of Analytical Geometry; the Fundamental Conceptions of the Differential Calculus; the Differentiation of Simple Functions; the Integral Calculus; Applications of the Integral Calculus; Definite Integrals; the Higher Differential Coefficients and the Functions of Several Variables; the Infinite Series and Taylor's Theorem; the Theory of Maxima and Minima; the Evolution of Numerical Equations; the Differentiation and Integration of Functions, Empirically Determined; and Examples from Mechanics and Thermodymamics.

To the mathematician or the mathematical physicist this work contains much, that will appear to be very elementary, and that is easily accessible in the many texts on the

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[1] See *Zeitschrift für Physikalische Chemie*, **11**, 110, and 529: and **12**, 623.

calculus already existing. It must, however, be remembered that this treatise was not prepared for such, but for those who are not thoroughly versed in mathematics. To these the elementary character of this book will not be objectionable.

H. C. J.

ELEMENTS OF MODERN CHEMISTRY. BY CHARLES ADOLPHE WURTZ. Fifth American Edition. Revised and Enlarged by WM. H. GREENE, M.D., and HARRY F. KELLER, PH.D. (Strasburg). With a portrait of the author and numerous illustrations. Philadelphia: J. B. Lippincott Company. London: 10 Henrietta Street, Covent Garden. 1895. Pp. 808 + 16.

When the first French edition of this book appeared in 1868, the expression "Modern Chemistry" had an important meaning. It meant a change in the system of atomic weights employed, and a complete cutting loose from the dualistic conception of compounds that even up to that time prevailed among all except the younger chemists. To-day the term needs to be explained, and it is unfortunate to see it in the title of a book just published. As regards the book itself, every one who knows anything about chemistry knows that Wurtz was a master, that he was one of those who contributed largely to the development of "Modern Chemistry." His book was always highly esteemed.

This is the fifth American edition. In its preparation "the aim has been to preserve as nearly as possible the original plan and character of the work, but at the same time to make such changes as will entitle it to continue to rank as a truly modern text-book." In spite of the efforts of the revisers, there is abundant evidence that the book is old. The classification of the compounds of carbon is to be mentioned first in this connection. No one now-a-days would begin a work on organic chemistry with the cyanogen compounds, and then lead the student through the intricacies of the cyanides, the ferrocyanides and ferricyanides, cyanic acid, cyanuric acid, urea, biuret, etc., before presenting some of the simpler compounds, the relations between which can easily be traced. It is to be hoped that, when another edition is called for, the revisers will adopt the "modern" classification.

Stereoisomerism is not clearly explained, because too briefly. Would it not be better to make the relation between the three varieties of lactic acid the basis for the explanation, and then show how an extension of the same ideas enables us to explain the relations between the four varieties of tartaric acid, instead of using these latter relations as the basis of the explanation?

A result of the older method of classification is to bring together aconitic acid, a tribasic acid, and itaconic, citraconic and mesaconic acids, which are dibasic. Why? Because they are all formed from citric acid, either directly or indirectly, by heat. Hence the sub-heading "Pyrogenous Acids derived from Citric Acid," (p. 623), which certainly has an antique flavor. Again, the treatment of glucosides under sugars, and before the aromatic compounds have been studied, is not logical, as it requires premature reference to such compounds as benzoic aldehyde, benzoic acid, saligenol, salicin, phloretin, gallic acid, etc.

In discussing the constitution of benzene, the revisers give the preference to the centric formula proposed by Armstrong, and afterwards again brought forward by Baeyer, and the impression is left upon the mind of the reader that Baeyer himself prefers this formula. This, however, is not correct, as, according to the last communication of Baeyer on this subject, he has concluded that the Claus formula is more in accordance with the facts. It is, however, true that Bamberger still uses the centric formula in dealing with the facts presented by naphthalene.

While this book, like other books, is not perfect, it is on the whole a trustworthy guide to chemistry. It appears, however, to contain too much for beginners and not enough for the advanced student. I. R.

NOTES.

The Water of Crystallization of Barium Picrate.

In the year 1841 Dumas[1] mentions this substance and says that the analyses made by Liebig show it to consist of "1 atom of baryta, 1 atom of picric acid and 6 atoms of water." He makes, however, no reference to any other publication by Liebig.

In the same year Marchand[2] gives an accurate description of the same substance: its physical properties and methods of preparation.

He assigns to the compound the (modernized) formula

$$Ba[C_6H_2(NO_2)_3O]_2 + 5H_2O.$$

In 1875, Post and Mehrtens[3] determined the solubility and

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[1] Ann. Chem. (Liebig), **39**, 354.

[2] J. C. Prakt. Chem., **25**, 363. Ann. Chemie (Liebig), **52**, 345.

[3] Ber. d. chem Ges., **8**, 1552.

specific gravity of these crystals and to them assigned (without giving reasons or analytical data) the formula

$$Ba[C_6H_2(NO_2)_3O]_2 + 4H_2O.$$

Finally, in 1885, Tscheltzow,[4] who was engaged in thermochemical study of this compound makes use (without giving reasons or analytical data) of the formula

$$Ba[C_6H_2(NO_2)_3O]_2 + 6H_2O.$$

In connection with some work done in this laboratory it has been necessary to determine definitely the number of molecules of water contained in the crystals. Barium picrate was prepared by treating picric acid with an excess of barium carbonate, filtering the hot solution, from which the crystals separate on cooling. To free from adhering moisture, the crystals were at times simply pressed between filter-paper. (This is the case with Nos. 3 and 5). Again the substance was also dried by exposure to the air for a day. (The substances thus prepared were 1, 2 and 4.)

1. 2.0530 gram barium picrate yielded 0.6803 gram $BaSO_4$.
2. One-fourth of 1.1556 gram of substance yielded 0.0963 gram $BaSO_4$.
3. 0.9977 gram substance yielded 0.3334 gram $BaSO_4$.
4. 1.1160 gram substance yielded 0.4720 gram $BaSO_4$.
5. 0.5002 gram substance yielded 0.1672 gram $BaSO_4$.

Percentage of Barium found.

1	19.57
2	19.58
3	19.65
4	16.59
5	19.64
	19.61

Theoretical for $BaP_2 + 5H_2O$ 20.07 per cent.
" " $BaP_2 + 6H_3O$ 19.55 "

It would seem certain that the specimens which I have analyzed must have contained six molecules of water. In this connection however, the results of Marchand (loc. cit.) are of importance and interest. His results (recalculated by me) show 19.96 and 20.01 per cent. of barium. These figures evidently indicate a salt containing only five molecules of water.

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[4] Comptes rendus, **101**, 381.

Further investigation will be made to determine under what conditions these hydrates can be formed, or to determine whether one exists—that with six molecules of water.

HUBERT GROVE SHAW.

CHEMICAL LABORATORY OF WORCESTER ACADEMY,
WORCESTER, MASS., NOV. 27, 1895.

The Berichte, "Beilstein," and the Centralblatt.

According to a recent circular, issued by the German Chemical Society, the society proposes to undertake the preparation and publication of the future editions of Beilstein's "*Handbuch der Organischen Chemie,*" and of the "*Chemisches Centralblatt,*" and to give up the publication of the *Referate* as a part of the *Berichte*. There can hardly be two opinions in regard to the wisdom of this plan, provided always that the preparation of the abstracts for the new Centralblatt is to be well done, and of this there can be little doubt. The *Referate* have never been satisfactory to any one, owing largely to a lack of money. The Centralblatt has in general well served the purpose for which it is prepared and, as it is understood that the present editor will remain in charge, it is probable that it will be even better in the future. All must feel thankful that the apparent growth of the *Berichte* is to be checked, and that the separate volumes may hereafter be less like cubes, and more of the order of irregular parallelopipeds.

As regards the Handbuch, there is but one who can do its work, and that is Beilstein the Great. No one can worthily succeed him. Others may try their hand at the work, but we cannot expect them to reach the high standard that Beilstein has set. While, therefore, we must recognize the wisdom of the plan proposed by the society, we cannot avoid a strong feeling of regret that the "Beilstein," so familiar, so dear, and so useful to all of us, is not to be "Beilstein" in the future, whatever else it may be. I. R.

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THE ACTION OF LIGHT ON SOME ORGANIC ACIDS IN THE PRESENCE OF URANIUM SALTS.[1]

BY HENRY FAY.

HISTORICAL.

The early history of photo-chemical reactions is involved with the history of photography. Schulze in 1727 proved experimentally that the darkening of silver salts is due to the action of light, and in 1799 Scheele[2] showed the effects of different parts of the spectrum. It had been noticed several centuries before that silver salts are subject to change, but the work of Schulze was the first conclusive evidence that this change is due to the action of light. In the early part of this century the action of light on plant growth was studied by many investigators who received the incentive from a suggestion made by Priestley.

Certain physical phenomena were early noticed, as the effect on crystallization by Petit,[3] who showed, in 1722, that solutions of potassium nitrate and ammonium chloride crystallize more readily in the sunlight than in the dark. These effects were studied more carefully by Chaptal[4] and Dize.[5] In 1848

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[1] From the Author's Thesis, submitted to the Board of University Studies of the Johns Hopkins University for the Degree of Doctor of Philosophy, June, 1895. The work was undertaken at the suggestion of Professor Remsen and carried on under his supervision.

[2] Traité de l' Air et de Feu.

[3] Mèm. de Paris, 1722.

[4] Jour. de. Phys., vol. 34.

[5] Sur la crystallisation, etc., 1789.

Becquerel[1] published his excellent researches on the phosphorescence of the sulphides of barium, calcium, and strontium, but none of these researches threw any light on the chemistry of the reactions caused by sunlight. Photography was being developed in the early part of the century and various effects were noticed, but the chemistry involved was not worked out. During this period many inorganic salts were found to undergo some change when exposed to the sunlight, and in general this change was a reduction, especially if there was an oxidizable organic substance present.

Among the salts most extensively studied were those of uranium. Before taking up the study of the reactions involved when uranium salts are decomposed in the sunlight, it will be well to review the work which has been done on the organic substances which are subject to change when exposed to the light. Many observations have been recorded in which the fact is simply stated that certain substances are sensitive to light, but only in a few cases has the reaction been a clear one. In the cases studied the reactions can be classified under one of these three heads—substitution, direct combination, and polymerization.

Dumas[2] has shown that the hydrogen atoms of the methyl group in acetic acid can be replaced by chlorine when the two substances are brought together in the direct sunlight, forming a substituted acetic acid. Phenomena of a similar nature were brought out by Schramm,[3] who has shown that when aromatic hydrocarbons having a side chain are treated with chlorine in the direct sunlight the substitution always takes place in the side chain.

Under the second head come the researches of Cahours,[4] who prepared perchlormethyl oxalate and formate by bringing together the acids and alcohol in presence of chlorine. When exposed to the sunlight the reaction takes place forming the ethereal salts.

Chastaing[5] exposed acetic and butyric acids with alcohol and by means of titration was able to measure the rate of etherification.

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[1] Ann. Chim. Phys. [3], **9**, 257.

[2] Ann. Chim. Phys. [2], **73**, 77.

[3] Ber. d. chem. Ges., **18**, 350, 606, 1272; **19**, 212.

[4] Compt. Rend., **23**, 1070.

[5] Ann. Chim. Phys. [5], **11**, 145.

Somewhat similar are the facts discovered by Klinger,[1] who showed that aldehydes have the power of combining with phenanthrenequinone. He also noticed that if a reducible substance is exposed to light in presence of an oxidizable one, the solvent is oxidized while the substance in solution is reduced. By this means Klinger was able to convert phenanthrenequinone into phenanthrenehydroquinone, and at the same time the solvent, ether, was oxidized to acetic aldehyde. He found that benzil in ether solution passed over into a substance which he called benzil-benzöin on account of the ease with which it can be broken down into these two substances. He represents the decomposition by the equation,

$$C_{42}H_{32}O_6 = 2C_6H_5.CO.CO.C_6H_5 + C_6H_5.CHOH.CO.C_6H_5.$$

Under the head of polymerization come the facts discovered by Lemoin.[2] He found that chloral and styrolene are polymerized when exposed to the sunlight. Similar facts have been noticed in the field of inorganic chemistry as in the case of phosphorus and sulphur. Yellow phosphorus is converted into the red modification, and a solution of sulphur in carbon bisulphide deposits the insoluble modification.

The work of Tyndall[3] on light reactions cannot be placed under any of these heads as the nature of the reaction is not known. He exposed the vapor of amyl nitrite to a beam of light and found that there was decomposition; oxides of nitrogen were formed but the other products were not examined. Tyndall also found that allyl iodide and isopropyl iodide are effected by light, but he did not study the subject from its chemical side.

Oxalic acid has been extensively used in photo-chemical reactions, especially in form of its salts, and it has been recommended as a means of determining the amount of sunlight. Döbereiner[4] proposed to use ferric oxalate as a photometer in which the ferrous oxalate or the carbon dioxide given off could be measured. He also found that oxalic acid will reduce platinum chloride to metal, and that silver oxalate is partially reduced to metal.

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[1] Ann. Chem. (Liebig), **249**, 137.

[2] Compt. Rend., **93**, 514.

[3] Proc. Roy. Soc., **17**, 92, 104.

[4] Schweigger's Jour., **62**, 90.

Eder[1] used as a photometer a solution of ammonium oxalate and mercuric chloride, which, on exposure to sunlight, gives off carbon dioxide and deposits mercurous chloride according to the equation,

$$2HgCl_2 + (NH_4)_2C_2O_4 = 2HgCl + 2NH_4Cl + 2CO_2.$$

Having reviewed briefly the effects of light on certain organic substances, the history of the reactions which involve the use of uranium salts will be given in detail. The first person to find that uranium salts are sensitive to light was Bucholz,[2] who described (1805,) certain effects produced by the sulphate and alcohol. He says: "Uranium sulphate dissolves in 25 parts of alcohol, and the solution undergoes remarkable changes on exposure to the sunlight; the yellow liquid becomes turbid and deposits a grayish green substance. After several days exposure the solution acquires an odor of nitric ether; the filtrate is colorless and contains no uranium; the precipitate of a green color and retains sulphuric acid." Bucholz further observes that an ether solution of uranyl nitrate becomes green on exposure to sunlight, and a black substance is deposited.

Chemists added little to these results until Ebelman,[3] in 1831, took up the subject. He confirmed the results of Bucholz with the uranium sulphate and alcohol, but noticed in addition that green crystals were formed, which he said were uranium protoxide. The precipitate he called the bi-basic sulphate of the protoxide, and gave it the formula $2UO.SO_3 + 2H_2O$.

Uranium oxalate was also investigated by Ebelman. He observed that a solution of uranyl oxalate decomposed into a brown substance, which he believed to be the hydrated oxide, and into carbon dioxide and carbon monoxide in changing proportions.

St. Victor and Corvissart,[4] working on the action of light on organic substances, noticed that if a solution of oxalic acid is exposed to the light it will quickly reduce a gold solution. They heated to boiling a four per cent. solution of oxalic acid

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[1] Wein. Academy Ber., **2**, 1879.

[2] Ann. Chim. Phys. [1], **56**, 142.

[3] Ann. Chem. (Liebig), **43**, 294.

[4] Compt. Rend., **21**, 00; Ann. Chem. (Liebig), **43**, 114.

with a one per cent. solution of uranyl nitrate, finding that in the dark no decomposition would take place, but after exposing to the sunlight action soon began. They say that carbon monoxide was given off, but do not mention having obtained any carbon dioxide. Another fact of interest discovered by them was that a small quantity of uranyl nitrate increased tenfold the action of light on any amylaceous matter, converting it into dextrin and glucose.

Seekamp[1] repeated the work of St. Victor and Corvissart and found that, after a solution of uranyl nitrate and oxalic acid had been exposed to the light for some time, there was a deposit of a green crystalline powder, the solution became colorless and showed an acid reaction. The acid was identified as formic acid by means of its lead and barium salts. From succinic acid he obtained carbon dioxide and propionic acid and the precipitate which was formed, he believed, to be uranous succinate. Butyric acid and carbon dioxide were obtained from pyrotartaric acid.

H. C. Bolton,[2] in a review of the work done on uranium salts in photochemical reactions, adds some interesting facts discovered while working with certain uranium salts in photographic processes. He obtained a salt which is the double oxyfluoride of uranium and potassium, having the composition represented by the formula $2UO_2F + 3KF$. A solution of this salt acidified with formic acid decomposes in the sunlight, forming a precipitate which gives the formula $4UF+KF$. Oxalic acid causes a similar reduction but with the formation of Ebelman's violet hydrate. Solutions of the nitrate, sulphate, oxychloride, and oxyfluoride are reduced when mixed with glycerin and placed in the sunlight. Even in the dry state the uranium ammonium citrate was found to be sensitive to light.

Wisbar[3] next took up the study of light on uranium salts. He verified Seekamp's work on pyrotartaric acid and showed in addition that butyric acid in presence of uranium salts breaks done into propane and carbon dioxide.

Somewhat similar to the work of Wisbar is that of Louis

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[1] Ann. Chem. (Liebig), **122**, 113.

[2] Amer. J. Sci. [2], **48**, 206.

[3] Ann. Chem. (Liebig), **232**, 262.

Lucien Bonaparte,[1] who obtained a decomposition of valeric acid by exposing it with a solution of uranyl valerate. The products formed he believed to be uranous valerate, and gases which he believed to be carbon dioxide, carbon monoxide, and a hydrocarbon.

Chastaing[2] studied the effect of the red and violet rays of the spectrum on solutions of uranyl nitrate and alcohol and noticed the odor of aldehyde, which is probably the odor Bucholz took for *nitric ether.* Some uranyl acetate was formed in the solution.

At the suggestion of Prof. Remsen, H. C. Jones, working in this laboratory, undertook some time ago the study of the action of light on oxalic acid in the presence of uranium salts. As the results of his work have not been published, a short account of the results which he obtained will be given.

He verified the statement of Seekamp that, in the presence of uranium oxalate, oxalic acid is broken down into carbon dioxide, carbon monoxide, and formic acid. The equation given by Seekamp to express the reaction, is

$$UO_2(C_2O_4) + 2H_2C_2O_4 = U(C_2O_4)_2 + 2CO_2 + 2H_2O.$$

Seekamp[3] thought that the green compound precipitated was uranous oxalate, of the composition $U(C_2O_4)_2.6H_2O$.

A series of experiments was made by Jones in which varying amounts of uranyl oxalate and oxalic acid were used. The amount of carbon dioxide found in every case agreed to within a few cc. with the amount of carbon dioxide which would have been liberated from the oxalic acid used, had it decomposed directly into carbon dioxide, carbon monoxide, and water. The amount of carbon monoxide set free, plus the amount combined as formic acid, was always somewhat less than the carbon dioxide.

The composition of the precipitate formed was found to depend on the amount of uranyl oxalate, relatively to the free oxalic acid originally used. In all cases where a very large excess of oxalic acid was not used, it could be clearly seen that the precipitate was a mixture of crystals and an amorphous mass.

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[1] J. prakt. Chem., **30**, 308.

[2] Ann. Chim. Phys. [5], **11**, 145.

[3] Ann. Chem. (Liebig), **122**, 115.

Analyses of the precipitate formed from various mixtures confirmed the belief that the precipitate was a mixture. When a solution containing three grams of uranyl oxalate and thirty grams of oxalic acid had been exposed to the light for a time it was noticed that green crystals were forming on the bottom and sides of the flask. The solution was then removed from the direct sunlight, and allowed to stand in diffused light for some time, when a considerable quantity of the crystals was obtained free from impurities. An analysis of the crystals dried between filter-paper gave 45.05 per cent. uranium, which agreed fairly well with the composition $U(C_2O_4)_2.6H_2O$, which requires 45.8 per cent. of uranium, on the basis $U = 240$, $C = 12$, $O = 16$.

Finally, a solution was prepared containing 3 grams uranyl oxalate and 45 grams oxalic acid. Pure crystals were obtained, as described above, which contained 46.05 per cent. of uranium. It thus appears that the crystalline compound is formed pure only when a very large excess of oxalic acid is used.

It was then hoped that, by using a large amount of uranyl oxalate relatively to oxalic acid, the amorphous compound might be obtained in pure condition. For this purpose a solution containing 2 grams of uranyl oxalate and 2 grams of oxalic acid was exposed to the light. A greenish mass was at first precipitated, which, on longer exposure, became purplish-brown. A solution of uranyl oxalate exposed alone to the direct sunlight apparently underwent the same transformation.

It was found further, that a very small amount of uranyl oxalate will decompose a very large, if not an unlimited amount of free oxalic acid, if exposed *continuously* to the direct sunlight. If not continuously, the crystalline compound will separate out of the solution and the action will cease. Thus the reaction suggested by Seekamp, and given above, cannot express the whole truth, since, according to it, 1 molecule of uranyl oxalate can decompose only 2 molecules of free oxalic acid.

The uranyl salt seems to act in some way as an oxidizing agent, as is indicated by the fact that the product precipitated is some reduction-product of the uranyl compound originally used.

Decomposition of Oxalic Acid in the Presence of Uranyl Oxalate.

As the nature of the precipitate formed when oxalic acid is exposed to the sunlight in presence of uranyl oxalate was not cleared up by Jones on account of lack of time, it was decided, at Prof. Remsen's suggestion, to continue the work and study the products of decomposition. For this purpose, solutions containing oxalic acid and uranyl oxalate in varying proportions were exposed to the direct sunlight, and in all cases it was found that after considerable gas had been given off the solution became cloudy, and then deposited a light green crystalline powder. When all of the oxalic acid was decomposed, and the evolution of gas had ceased, the remainder of the uranium in solution was deposited as a flocky, purplish-brown substance. Evidently, concordant results could not be obtained by working with the precipitate as a whole, and it was decided to remove the light green-colored precipitate when first formed.

To obtain it 3 grams uranyl oxalate and 2 grams oxalic acid were dissolved in a liter of water, and exposed to the direct sunlight. When some of the green precipitate first formed had settled to the bottom of the flask it was filtered off, washed with water, and then dried between filter-papers. The dry substance has a very pale green color, and showed no tendency to oxidation or change of any kind.

The uranium was determined by heating the substance in a porcelain crucible and weighing as the oxide U_3O_8. In all of the analyses made this method was used; frequently, however, the oxide formed was converted into the nitrate and the nitrate again decomposed. This was done simply to control the results, as the oxide U_3O_8 is more readily formed from the nitrate than from the uranium salt of organic acids.

The green-colored substance gave these results:

I. 0.2637 gram substance gave 0.1776 gram $U_3O_8 = 57.17$ per cent. U.

II. 0.2015 gram substance gave 0.1369 gram $U_3O_8 = 57.68$ per cent. U.

III. 0.2560 gram substance gave 0.1725 gram $U_3O_8 = 57.20$ per cent. U.

Calculated for $U(C_2O_4)_2$, 57.69 per cent U.

This shows the substance to be uranous oxalate. It can be obtained at any time, provided the solutions be continuously exposed to the sunlight, and not too large an excess of oxalic acid be present. It was shown by Jones that, when a large excess of oxalic acid is present, and the solution removed after a short exposure to the light, there is a strong tendency to the formation of the crystalline product $U(C_2O_4)_2.6H_2O$. If the solutions are exposed until all of the oxalic acid is decomposed, some of the purplish-brown substance is then formed.

Desiring to obtain the purplish-brown precipitate in pure condition, several attempts were made to get it from solutions containing oxalic acid and uranyl oxalate by removing the uranous oxalate formed and subsequent exposure, but in all cases the precipitate contained a mixture of the two precipitates. When uranyl oxalate in solution is exposed to the sunlight, the same purplish-brown precipitate is formed, and it was decided to use the uranyl oxalate alone for the purpose of obtaining it.

Decomposition of Uranyl Oxalate.

Four grams of uranyl oxalate were dissolved in a liter of water, and the solution filtered to get rid of a small amount of undissolved substance. The solution was exposed to direct sunlight, and within five minutes after exposure the clear yellow solution had become cloudy. The cloudiness increased rapidly. In half an hour there was a deposit of the purplish-brown substance on the bottom and side of the flask nearest the source of light. There was no evolution of gas.

Thinking that possibly the solution held the gas, several attempts were made to collect any gas formed by attaching large tubes filled with uranyl oxalate solutions to nitrometers containing mercury. Under much reduced pressure, and even by gentle heating, it was impossible to collect any gas. The precipitate formed in the above solutions was filtered off, washed with water, and left to dry in the air. The brown substance on drying changed to yellow, so that it was impossible to prepare it in this way for analysis. Even on drying rapidly between filter-papers there was some change noticed. If the brown substance is allowed to stand in the flask in which it is precipitated the same change takes place, although not so rapidly. The filtrate was always neutral to litmus, and contained nothing but traces of uranium salts which were thrown out on evaporation to small volume. It was impossible in any case to get the uranium precipitated entirely, although the portion remaining in solution was extremely small in comparison with the whole amount of uranium present.

Determination of Uranium in the Brown Precipitate.

Some of the freshly prepared substance was partially dried between filter-papers, transferred to a porcelain boat, and then dried at 100° in a stream of dry hydrogen. The substance, prepared in this way, has a pale, grayish-green color, resembling somewhat uranous oxalate, and in this condition shows very little tendency to pass over into the yellow substance. It was weighed rapidly, placed in a combustion-tube and heated in a current of oxygen. When heated under these conditions, the substance begins to glow, and the combustion spreads rapidly throughout the mass. After a very few minutes the substance is changed into the oxide U_3O_8. The boat is then withdrawn and weighed. The oxide obtained in this way is of a pale olive-green color, and appears to be perfectly pure. The uranium was determined in 6 separate specimens in this way.

I. 0.4768 gram gave 0.4407 gram U_3O_8 = 78.47 per cent. U.
II. 0.2373 " " 0.2180 " " = 77.99 " "
III. 0.1372 " " 0.1249 " " = 78.00 " "
IV. 0.1556 " " 0.1414 " " = 77.15 " "
V. 0.1856 " " 0.1699 " " = 77.58 " "
VI. 0.1454 " " 0.1314 ‘, ‘, = 77.41 " "

Average for the 6 determinations, 77.76 per cent. U.

These results, it will be seen, are fairly concordant, but good results could not be obtained for carbon.

Several attempts were made to determine the percentage of carbon, but, on account of the relatively small amount present, the results were not satisfactory. The substance, when heated alone, gives off small amounts of carbon monoxide, but even by passing the gases over ignited copper oxide, good results were not obtained. The yellow substance, into which the brown one passes on standing, gave better results. These will be spoken of later. Various attempts were made to isolate the acid contained in this salt, but without success. The substance dissolves readily in hydrochloric, sulphuric, and nitric acids, forming green solutions, from which ammonia precipitates the black uranous hydroxide. All that can be said at present in regard to this salt is that it is a reduction-product of uranyl oxalate. There can be no doubt that it contains a small percentage of carbon, as will be made more evident when the yellow transformation-product is considered. Ebelman believed it to be a hydrated oxide, but the presence of carbon proves this assumption to be wrong. Bolton obtained the same precipitate by exposing a solution of the double oxyfluoride of uranium and potassium acidified with oxalic acid. He however did not analyze the product. If this were the simple hydrated oxide, it seems that it should also be formed with other acids than oxalic acid, especially when the same salt of Bolton is acidified with formic acid. In this case only the salt $4UF + KF$ is formed.

Analysis of the Yellow Substance Obtained from the Purplish-brown Precipitate.

The best way to prepare the yellow salt is to allow the brown substance to stand in a desiccator for four or five days. It is also formed when allowed to stand in the air, but it is more convenient to use the desiccator, as in this way the yellow salt can be obtained in dry condition having constant weight. For the analysis of this salt, it was dried to constant weight over sulphuric acid or by heating in an air-bath to 100°. The substance is also formed when the brown precipitate is allowed to stand under water for several weeks. A preliminary test for carbon was made by heating the substance in a tube through which pure air was drawn. The gases were passed into barium hydroxide solution. There was considerable barium carbonate formed, showing carbon to be present.

This substance was heated in a combustion-tube as in the previous case, and the uranium oxide afterward weighed, the uranium, carbon, and hydrogen being thus estimated in the same operation. The substance was first converted into a brick-red substance, probably U_2O_5, and on higher heating gave the oxide U_3O_8.

Different preparations gave the following results on analysis:

	U.	C.	H_2O.
I.	75.46 per cent.	1.36 per cent.	8.58 per cent.
II.	75.40 " "	1.02 " "	8.04 " "
III.	75.10 " "	1.2 " "	8.50 " "
IV.	74.9 " "	1.15 " "	8.7 " "
V.	75.44 " "	....	....

These results are selected from a much larger number of analyses, all of which agree very closely with the ones given.

It is difficult to account for the small amount of carbon present, but as none of the carbon was given off in the original decomposition, and the brown substance does not lose any carbon dioxide in drying, it is safe to say that all of the carbon is in combination with the uranium. In what form it exists it is impossible to say, as the substance dissolves in acid without separation of any organic acid. If all the uranium is precipitated and the filtrate separated, there is no evidence of any organic substance remaining behind.

Formation of Formic Acid in the Decomposition of Oxalic Acid.

Jones showed that the equation of Seekamp, representing the decomposition of oxalic acid by uranyl oxalate, does not express the reaction, as it does not account for the formic acid nor for the carbon monoxide. It was thought advisable to make a few experiments to see whether formic acid can be built up from carbon monoxide and water in presence of uranium salts. For this purpose the following experiments were made:

I. A 250 cc. Erlenmeyer flask was filled with a solution of uranyl oxalate, and about 100 cc. carbon monoxide introduced into it. The inverted flask was connected with a long tube bent twice at right angles to show the pressure. The flask was exposed to the direct sunlight. Within two hours the decomposition of the uranyl oxalate was complete The precipitate was the same as the one spoken of above when uranyl oxalate decomposes. No free acid was detected in the solution.

II. Carbon monoxide and water were exposed for fifteen days in the direct sunlight. On examination, at the end of this time, the water was perfectly neutral.

III. Mixtures of equal values of carbon moxoxide and carbon dioxide, in the presence of water, were exposed to the direct sunlight, but no formic acid was obtained.

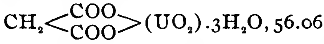
From these experiments it is shown that the formic acid obtained in the decomposition of oxalic acid is from the oxalic acid itself, and not from the combination of carbon monoxide and water.

Decomposition of Malonic Acid.

The study of malonic acid was next taken up, and it was my purpose to proceed as in the case of oxalic acid, but unexpected difficulties arose.

Uranyl malonate was prepared by bringing together hot concentrated solutions of malonic acid and uranyl nitrate. It separates in a few moments as a bright yellow crystalline powder, adhering firmly to the sides of the beaker. It is nearly insoluble in water and alcohol, more readily soluble in nitric acid, and easily soluble in a solution of malonic acid.

On analysis it gave the following results for uranium :



Calculated for $CH_2{<}^{COO}_{COO}{>}(UO_2).3H_2O$, 56.06 per cent.

0.2526 gram gave 0.1656 gram $U_3O_8 = 55.65$ per cent. U.
0.3682 " " 0.2416 " " = 55.70 " " U.
Heated to 110° for 4 hours it lost 9.15 per cent. H_2O.
Calculated for $2H_2O$, 8.78.

At 180°, 0.2670 gram lost in weight 0.0325 gram = 12.16 per cent. H_2O.

Calculated for $3H_2O$, 12.6 per cent. H_2O.

This, like many uranium salts, loses some water readily, but loses the last molecule only at high temperatures.

As this salt is almost insoluble in water, it could not be used in this work. Accordingly, dilute solutions of uranyl nitrate and malonic acid were exposed to the light, but within a few minutes the uranyl malonate was completely precipitated. The uranyl malonate dissolves in potassium malonate, and it was hoped to use such a solution for the decomposition. The double salt of potassium and uranium was made by dissolving the uranium malonate in the required amount of potassium malonate. On evaporation, well-formed but small, very bright yellow crystals were obtained. Solutions of this salt, with and without free malonic acid, were exposed to the sunlight for several days, but there was no indication of decomposition in either case. They seemed to be perfectly stable in the brightest sunlight.

The same results were obtained when the uranyl malonate was dissolved in malonic acid and the solution exposed. The malonic acid decomposes when a dilute solution of uranyl oxalate and malonic acid is exposed to the sunlight, but the rate of decomposition is so extremely slow that it was not considered advisable at the time to carry the work further.

Decomposition of Succinic Acid.

Attempts were made to decompose succinic acid by means of uranyl succinate, but so far it has been impossible to effect such a decomposition.

Uranyl succinate is described in Watts' Dictionary as being made from uranyl nitrate and acid sodium succinate by evaporation to dryness. This method was tried, but the uranium salt obtained was so nearly insoluble in water that it was not suited for the experiments. Some of the salt obtained was dissolved in a dilute solution of succinic acid, and this solution exposed to the direct sunlight for some days showed no tendency to change. Various other methods were tried for the purpose of making uranyl succinate, but they were not successful. Solutions of uranyl nitrate and succinic acid can be evaporated to crystallization, but they crystallize separately. It was also hoped to get it from barium succinate and uranyl sulphate. These salts were brought together in molecular proportions, but part of the barium was changed into sulphate and part into the insoluble barium uranate.

As it was desired to study the decomposition of succinic acid in the presence of uranyl succinnate, the experiments were carried on further.

Seekamp[1] found that succinic acid decomposes in the sunlight in the presence of uranyl nitrate into carbon dioxide and propionic acid. This was verified qualitatively. The action takes place rather slowly, and as this work could be carried on only during the winter and early spring months, it was not carried further. Seekamp believed the green precipitate in this case to be uranous succinate. A small amount of this substance was obtained and analyzed for uranium, but the percentage did not agree with that required for uranous succinate.

It is necessary to do much more work on the precipitates obtained in these decompositions as they are difficult to obtain in a pure state, and, from analyses made of precipitates from other acids, they do not appear to be the simple reduction-product.

Decomposition of Tartaric Acid.

When tartaric acid and uranyl nitrate are exposed to the sunlight, the clear yellow solution gradually turns to a deep green color, and after a few hours there is a precipitation of a light green salt. No gas is given off in the reaction. Several solutions were attached to nitrometers containing mercury, but there was no change in the volume, although the solutions were under much reduced pressure. Heat facilitates the precipitation very greatly. Some of the green solution from which the precipitate had been removed was placed on a water-bath, when there was a complete precipitation in a few minutes. The precipitate is most readily formed when one molecule of uranyl nitrate is exposed with one molecule of tartaric acid. If the solution in which the precipitate has been formed is allowed to stand in the sunlight for several weeks, the green-colored salt passes into solution forming an amber-colored liquid.

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[1] Ann. Chem. (Liebig), **133**, 253.

For analysis the green salt was dried between filter-paper and then over solid potassium hydroxide. It gave the following results:

I.

0.2631 gram gave 0.1529 gram U_3O_8
0.2631 " " 0.0555 " H_2O
0.2631 " " 0.1396 " CO_2

II.

0.2949 gram gave 0.1713 gram U_3O_8
0.2949 " " 0.0684 " H_2O
0.2949 " " 0.1662 " CO_2

	Calculated for $U_6H_{12}O_{16}$.	Found. I.	II.
Uranium........	49.58	49.3	49.31
Hydrogen.......	2.48	2.34	2.57
Carbon	14.87	14.46	15.3

The nature of the above precipitate cannot be learned from the above results, and the formula suggested has no significance at present. It may be possible to isolate the organic portion of the salt, but until this has been done it would be useless to speculate in regard to the nature of the precipitate.

Decomposition of Isobutyric Acid.

Wisbar[1] has studied the action of sunlight on butyric acid in the presence of uranium salts, and found that it is decomposed into propane and carbon dioxide. It was thought desirable to know whether the other acids of this series undergo a similar decomposition, and accordingly a study was made of isobutyric, propionic, and acetic acids. The study of isobutyric acid was taken up first, as it was found to work readily, giving off gas freely when exposed to the sunlight with uranyl nitrate.

Experiments were first made to see whether any definite relations existed between the gases given off. Carbon dioxide was shown to be present by its ready absorption by potassium hydroxide, and the residual gas was burnt from the capillary tube of the nitrometer in which it was collected. It burned with a smoky flame, showing it to be a hydrocarbon.

It was believed that the isobutyric acid would decompose in

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[1] Ann. Chem. (Liebig), **262**, 232.

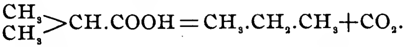
the same way as the butyric acid, giving equal volumes of propane and carbon dioxide. This was found to be the case as is shown by the following experiment:

I. For the purpose of collecting the gases the solutions were exposed in small test-tubes 13 × 120 mm. connected by means of a capillary tube to a nitrometer filled with mercury. The acid to be used was weighed directly into the tube, and a weighed portion of uranyl nitrate was added. Water was now added to bring the solution to the required height in the tube.

2.0201 grams isobutyric acid and 0.3365 gram uranyl nitrate were dissolved in 30 cc. water and exposed to the sunlight. Gas begins to be given off about fifteen minutes after the exposure is made. After being exposed for nearly an hour the lower half of the solution becomes cloudy, and small drops of a dark green, viscous liquid soon appear, which gradually collect in the bottom of the test-tube. Most of the gas evolved seems to come from this large drop. This dark-green, heavy liquid is, however, not always formed, and its formation depends on conditions which have not as yet been learned. A precipitate, however, is always formed—either this liquid or a light green powder.

The exposure was continued for several days when all action ceased. All of the uranium was precipitated.

The total volume of gas was 30 cc. and of this 14.8 cc. were absorbed by caustic potash, which shows half the volume of gas to be carbon dioxide. This also shows that the total decomposition of the acid was approximately 30 per cent. of that calculated for the equation,



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!>CH.COOH = CH_3.CH_2.CH_3 + CO_2.$$

At the end of the first day's exposure 21.5 per cent. of the decomposition had taken place.

II. This experiment was carried on precisely as the preceding, except that, after the reaction had begun, a tube filled with warm water was placed around the tube containing the solution. This increased the reaction very much, and it was found that by this method large quantities of the gases can be collected in a very short time. Of 27 cc. gas collected 13.6 cc. were absorbed by caustic potash.

III. In this experiment much larger quantities of acid and uranyl nitrate were used for the purpose of securing a pure specimen of the hydrocarbon for analysis. After 25 cc. of the gas had been collected, it was removed from the nitrometer so as to get rid of any oxygen or nitrogen, possibly held in solution by the water. This was repeated several times before a sample of the gas was collected for analysis.

The gas was removed by having it under pressure by means of the pressure-tube connected with the nitrometer, and then opening the glass stop-cock of the nitrometer only a little way. The stop-cock was closed before all of the gas had escaped, thus making sure that no air could enter. By this means it was found possible to collect the evolved gas. On absorption exactly half of the volume was shown to be carbon dioxide. The remaining portion was then transferred to a eudiometer and exploded with oxygen.

Volume of original gas.......	21.3 mm.	= 1 volume.
Volume after addition of oxygen	400.7 "	= 18.81 "
Volume after explosion.......	335.9 "	= 15.76 "
Contraction		= 3.05 "

The calculated contraction for C_3H_8 is three volumes. This shows the hydrocarbon to be propane, and the reaction is to be represented by the equation,

$$C_4H_8O_2 = C_3H_8 + CO_2.$$

Decomposition of Propionic Acid.

Uranyl nitrate and propionic acid, when exposed to sunlight decompose very readily, giving off gas in a few minutes after exposure is made. It was found best to use a rather strong solution of the acid. The gas is given off evenly and continues until nearly all of the acid is decomposed. The gas was collected and analyzed in the same manner as described under isobutyric acid.

I.	32.4 cc. of gas gave	15.8 cc. CO_2.
II.	30.5 " " " "	15.1 " "
III.	26.4 " " " "	13.2 " "

These figures show that approximately half the volume of the gas is carbon dioxide.

The residual portion was run into a eudiometer and exploded with oxygen.

Volume of original gas........	19.97 mm.	= 1 volume.
Volume after addition of oxygen	201.12 "	= 10.07 "
Volume after explosion	147.44 "	= 7.38 "
Contraction..................		2.69 "
Calculated contraction for C_2H_6		2.5 "

This shows the hydrocarbon to be ethane, and the decompositian of propionic acid is to be represented by the equation,

$$C_2H_5.COOH = C_2H_6 + CO_2.$$

Decomposition of Acetic Acid.

Various attempts were made to decompose acetic acid in the same manner as propionic, and isobutyric acid, but it was decomposed only with difficulty. The only proportions which were found to give off gas was when 15 cc. glacial acetic acid and 5 cc. strong solution of uranyl acetate were exposed. From this solution gas was given off, but only extremely slowly. The exposure was made in April and May, about six weeks being required to give enough for analysis. The clear yellow solution did not to any extent change to the green, so characteristic in all the other cases. There was a slight green color, but it was not marked.

Analysis of gas—

13.4 cc. of gas gave 6.4 cc. CO_2.

Volume of original gas	13.2 mm.	= 1 volume.
Volume after addition of oxygen	108.24 "	= 8.2 "
Volume after explosion	80.52 "	= 6.1 "
Contraction............................		2.1 "

Calculated contraction for CH_4 is two volumes, while that found is 2.1 volumes, which shows the gas to be methane, and the decomposition is to be represented by the equation,

$$CH_3.COOH = CH_4 + CO_2.$$

It is interesting to note that the power of decomposition ceases with acetic acid, which breaks down under the influence of light only with difficulty. The power is apparently lost in formic acid, and it has been impossible so far to effect any decomposition of this acid by light in the presence of uranium salts.

Comparison of the Rates of Decomposition of Propionic, Butyric, and Isobutyric Acids.

For the purpose of comparing the relative rates of decomposition of these three acids, tenth-normal solutions of each were made, and varying quantities of the acid were exposed with varying quantities of uranyl nitrate. It was decided to use propionic acid as the standard in determining the best conditions possible. The following table shows the comparison between two solutions of propionic acid exposed under exactly similar conditions.

No. of days.	Hours of exposure.	Amount of gas collected. No. 1.	No. 2.	Condition of weather.
1	2	0.8	0.6	Clear.
2	7½	2.8	2.8	"
3	7½	3.4	4.8	"
4	7½	4.0	7.2	"
5	15	4.3	9.2	"

Solution No. 1 contained 10 cc. of one-tenth normal nitrate, $UO_2(NO_3)_2.6H_2O$ and 10 cc. one-tenth normal propionic acid.

Solution No. 2 contained 15 cc. one-tenth normal propionic acid and 5 cc. one-tenth normal nitrate, $UO_2(NO_3)_2.6H_2O$.

It will be seen that the solution containing the larger amount of acid acted the more rapidly. The comparison is not exactly fair, as the precipitate which is formed some time after the decomposition begins has some effect, as will be seen in the following table, in which is given a comparison of propionic, butyric, and isobutyric acids. Each solution contains 15 cc. one-tenth normal acid and 5 cc. one-tenth normal nitrate, $UO_2(NO_3)_2.6H_2O$.

No. of days.	Propionic.	Amount of gas collected. Isobutyric.	Butyric.
1	1.2	1.4	1.0
2	2.5	3.0	2.5
3	4.0	4.7	3.6
4	5.3	5.7	4.3
5	5.3	5.7	4.3

No. of days.	Amount of gas collected. Propionic.	Isobutyric.	Butyric.
6	6.5	6.4	4.9
10	7.6	7.4	5.8
11	8.8	8.4	....
12	10.2	9.5	....
13	12.0	10.6	9.0
14	13.6	11.4	9.6
15	15.0	12.4	10.5
16	15.8	12.8	11.2
17	16.3	13.0	11.2

It will be seen that on the sixth day the amount of gas collected from the propionic acid and the isobutyric acid is practically the same. Up to this time there was only slight cloudiness in the solutions, but after three days of rain a precipitate was found in the solution containing isobutyric acid. From this time on it will be seen that there is a gradual gain in the amount of gas collected from the propionic acid over the amount collected from the isobutyric acid.

As the weather was unfavorable for carrying these comparisons any further, the subject was dropped at this point, but it is believed that interesting comparisons can be obtained by working during the summer months.

Summary.

It has been shown that the precipitate in the solution of uranyl oxalate and oxalic acid is formed in two stages: (1) formation of uranous oxalate, (2) formation of the purplish-brown precipitate from the uranyl oxalate left in solution. The nature of the latter has not been cleared up, but it is shown to contain carbon, and consequently cannot be the hydrated oxide as supposed. The formic acid found when oxalic acid is decomposed must come from the oxalic acid itself, as all attempts to build it up from water and carbon monoxide in presence of uranium salts, has failed.

Tartaric acid, when exposed with uranium salts to the sunlight, forms an insoluble precipitate with uranium, the nature of which has not been cleared up.

It has finally been shown that acetic, propionic, and isobutyric acids, decompose into the hydrocarbons corresponding to the acids and into carbon dioxide.

A REVIEW OF SOME RECENT WORK ON DOUBLE HALIDES.

By Charles H. Herty.

The field of the double halides has long been an inviting one for those eager to prepare new compounds with a comparatively small outlay of trouble or thought. This has been due to two causes; first, the ease of formation of the compounds; second, the old idea of molecular combination, according to which any analytical results could be interpreted by the usually accepted formulas. In this way no check was placed upon the work and the result was the description of a large number of compounds and very little effort to deduce any general conclusions bearing upon the constitution of the compounds. More recently chemists have realized that the former so-called explanation, molecular combination, was a mere matter of words sufficing only to cloak ignorance. The realization of this has led to a more careful study of the compounds previously described, and generalizations have been attempted in the line of explanation according to our present conception of valence. Chief among these was the conception of two halogens playing the part of a linking oxygen atom. This theory, though advanced many years ago, received little attention until the recent able paper of Remsen.[1] He found, however, several salts described, whose composition could not be explained in this way. This led to a very careful revision of some of the work of previous investigators, and it was shown that many of the compounds described were incapable of existence, in fact that they were really impure and that little trouble had been taken to purify them.

More recently, Wells[2] has devoted a great deal of time to the systematic determination of the full number of double halides which can be prepared. This work has been characterized by extreme care and wide variations in the conditions of experiment.

Furthermore, many workers have obtained substances by mixing together salts containing different halogens, for example, antimony chloride and potassium bromide. Such substances have been analyzed and formulas deduced. My

[1] This Journal, **11**, 291.

[2] Am. Jour. Sci., **16**, 121. etc.

own work[1] has shown that probably in all cases the so-called mixed double halides containing two halogens are really isomorphous mixtures of different double halides containing only one halogen.

This reaction in the method of work has proved wholesome and has resulted in bringing some order into the chaotic field. But quite recently the old erroneous methods of work seemed to be creeping in again, so that now we find the literature on this subject very confused. It has seemed advisable, therefore, to call attention to the character of some recent work in the hope that further complications may not arise from the acceptance of work which is undeniably bad.

The particular portion of the field to which I desire to call attention is that of the double halides of lead and the alkalies. The French seemed to monopolize this field for many years, during which time a large number of compounds were prepared by Boullay, Ditte, Berthelot, André and others. Working under the direction of Professor Remsen of Johns Hopkins University, I undertook, seven years ago, a revision of the work on the double iodides of lead and potassium. After two years constant work I was able to announce the preparation of only one double iodide of lead and potassium, $KPbI_3.2H_2O$, although all possible variations of conditions of experiment had been made. This reduced the number of compounds of this class from five previously described to one. Soon afterwards, Schreinemakers[2] published a lengthy article on the conditions of equilibrium of solutions of double salts. In this article he accepted Ditte's formula, $PbI_2.2KI$, but changed the amount of water of crystallization. He made no determinations of lead, potassium or iodine in the compound. As soon as his attention was called to the work done by Remsen and me,[3] he made a complete analysis of the compound with which he had been working and found it to be under all conditions $KPbI_32H_2O$,[4] thus confirming our work.

Wells[5] next took up the subject and succeeded in preparing

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[1] This JOURNAL, **15**, 81, and **16**, 490; and J. Am. Chem. Soc., **18**, 130.

[2] Ztschr. phys. Chem., **9**, 57.

[3] This JOURNAL, **14**, 107.

[4] Ztschr. phys. Chem., **10**, 467.

[5] Am. Jour. Sci., **45**, 121.

only the salt $KPbI_3.2H_2O$, confirming again our work.

In spite of the accumulated evidence on this point, articles continue to appear giving other results. Lenher,[1] in an article on the sulphiodide of lead, speaks of the presence in solution of the salts $PbI_2.2KI$ and $PbI_2.4KI$. No proof of their existence is furnished. As a matter of fact such expressions are simply the result of ignorance of the literature of the subject. No one attempts to defend either of the above formulas at the present day.

Again, Mosnier[2] has published a preliminary notice of some work upon compounds of lead iodide with metallic or organic iodides. Among other compounds he claims to have prepared the salts $3PbI_2.4KI$, $3PbI_2.4NH_4I$, $PbI_2.2NaI$, etc. He gives only general statements upon the conditions of experiment, method of preparation and method of analysis. Furthermore constant reference is made to the work of Boullay, Berthelot, and Ditte, while not a single reference is made to the work of Wells, Schreinemakers, or Remsen and myself. In spite of the very general directions for preparation of the compounds, I have endeavored as nearly as possible to repeat some of the experiments. It was deemed unnecessary to repeat the work upon the salt $3PbI_2.4KI$, for it has been shown repeatedly of late that no such compound is capable of existence. In order to prepare the salt $3PbI_2.4NH_4I$, I followed Mosnier's directions as accurately as possible, and obtained a crystal-mass which by the naked eye was seen to contain a considerable quantity of free ammonium iodide. Inspection under the microscope confirmed this, so that an analysis was deemed superfluous. It has also been found impossible to obtain a specimen of $PbI_2.2NaI$ sufficiently pure for analysis, large quantities of sodium iodide crystallizing out each time with the double iodide. In his article Mosnier states that the details of his experiments will be published later. A year has elapsed, but no details have as yet appeared.

Finally, still another article has appeared, which demands attention. Miss Eleanor Field,[3] as a result of her work, proposed the formulas $3PbI_2.4NH_4I$ and $3PbI_2.4KI$, accurate

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[1] J. Am. Chem. Soc., 17, 511.

[2] Compt. Rend., 120, 444.

[3] J. Chem. Soc., 1893, 540.

directions being given for the preparation of the salts. As has been stated above, it was deemed unneccessary to repeat the work upon the potassium compound, but the work upon the ammonium compound has been repeated, following the directions to the letter. Crystals were obtained, which under the microscope, seemed very pure. Analysis showed:

	Found.		Calculated for
	I.	II.	$NH_4PbI_3.2H_2O$.
Pb	32.06		32.25
I	59.52		59.32
NH_4	2.68	2.67	2.82
H_2O	5.76		5.61
Total	100.02		100.00

Evidently the salt obtained is $PbI_2.NH_4I.2H_2O$. To show more clearly the incorrectness of Miss Field's formula, I have in the table below placed side by side the analytical data obtained by Miss Field and those obtained by me. As Miss Field analyzed only the salt thoroughly dried at 100°, I have reduced my results also to an anhydrous basis for the sake of comparison. It will be noticed that the total percentage of the elements found by Miss Field in the anhydrous salt is only 96.79, an error of 3.21 per cent.

	Found.	Found by Miss Field.	Calculated for	
			NH_4PbI_3.	$(NH_4)_4Pb_3I_{10}$.
Pb	34.02	29.90	34.17	31.65
I	63.16	64.05	62.85	64.67
NH_4	2.84	2.84	2.98	3.68
Total	100.02	96.79	100.00	100.00

By mixing lead iodide and potassium chloride in stated proportions, Miss Field obtained the compound PbICl. Again, from a mixture of lead chloride and potassium iodide she obtained a substance which she called a "double salt," and to which she ascribed the formula $PbI_2.3PbCl_2$. This work I have repeated, following the directions to the letter; in both cases crystals were obtained corresponding exactly to those described by Miss Field. Analytical results show plainly that these substances are not true chemical compounds, but isomorphous mixtures of lead iodide and lead chloride.

	Found by Miss Field.	Found by me.	Found by Miss Field.	Found by me.
Pb	54.80	55.69	64.04	70.18
I	33.70	34.24	18.16	8.10
Cl	9.80	9.61	16.00	21.65
Total	98.30	99.54	98.20	99.93
Atomic ratio Pb : (I + Cl)	1 : 2.05	1 : 2.01	1 : 1.92	1 : 1.99

Retgers[1] has also pointed out that these substances were probably isomorphous mixtures, but no experimental evidence was given.

In conclusion two pressing needs are evident for all work on double halides: first, more care in the preparation of pure compounds; second, more accuracy in analytical work. Surely it is not unreasonable to expect good analyses of such stable compounds as the above with our excellent methods for determining lead, iodine, chlorine and ammonia. Should we not hesitate to deduce a formula from an analysis which sums up only 96.8?

UNIVERSITY OF GEORGIA,
Feb. 10, 1896.

Contribution from the Laboratory of Analytical Chemistry of the University of Michigan.

ON THE QUANTITATIVE DETERMINATION OF HYDROGEN BY MEANS OF PALLADOUS CHLORIDE.

BY E. D. CAMPBELL AND E. B. HART.

In the methods heretofore proposed for the quantitative determination of hydrogen in the presence of methane and other paraffins, this element has been estimated from the contraction after complete combustion by explosion with oxygen, or by partial combustion with air and palladium asbestos, or by direct absorption with spongy palladium.

In some cases, where a large amount of gas is available, the mixed hydrogen and paraffins are burned in presence of red-hot copper oxide, the resulting water and carbon dioxide being collected and weighed in the usual manner.

In 1894, F. C. Phillips[2] proposed the use of palladous chlo-

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[1] Ztschr. phys. Chem., **16**, 600.

[2] This JOURNAL, **16**, 256.

ride, either dry or in solution, as a reagent for the qualitative detection of hydrogen. Phillips has also shown[1] that palladous chloride is reduced by the olefins and by carbon monoxide, which must therefore be removed before testing for hydrogen. The paraffins, he has further shown,[2] have no action upon palladous chloride, so that hydrogen can be easily detected in their presence. Dr. Phillips proposes the use of dry palladous chloride for the determination of hydrogen, but has not up to the present time overcome the difficulties which he mentions.[3]

Thinking it not unlikely that under proper conditions complete absorption of hydrogen might be obtained by means of a suitable solution of palladous chloride, the authors have devised a method based upon this principle, which they have found very satisfactory. This, with Dr. Phillips' permission, they describe below.

A solution of palladous chloride was prepared as follows: 5 grams of palladium wire were dissolved in 30 cc. of hydrochloric acid, to which was added 1–2 cc. of nitric acid. After solution, this was evaporated just to dryness on the water-bath, redissolved by adding 5 cc. of hydrochloric acid (sp. gr. 1.20) and 25–30 cc. of water, and warming till solution is complete. The solution so obtained was then diluted to 750 cc., giving a nearly neutral solution, containing about 1 per cent. of palladous chloride. This strength of solution was found to be well adapted to the work and was adopted in our subsequent determinations.

The pipette used in the absorption was the ordinary single Hempel absorption pipette, the only modification being in the clamps which fastened the pipette proper to the stand. In place of the small brass bands generally used for holding the glass portion in position, three pairs of small screws were substituted, so that the pipette could be easily slipped from between these when desirable, or firmly retained in position by small wires twisted between each pair of screws. In operating, the amount of solution necessary to fill the pipette is first determined and then introduced into the pipette in the usual manner. The gas to be analyzed, from which every-

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[1] *Ibid*, 265–269, and 272.

[2] *Ibid*, 262–265.

[3] *Ibid*, 262.

thing but hydrogen, paraffins, and nitrogen had been removed by the usual methods, is then passed into the pipette and followed up by sufficient water to fill the capillary completely. The pipette is then disconnected, after first closing the top with a pinch-cock, removed from the stand, and placed in a water-bath for two hours, at the end of which time absorption will be found complete, unless the amount of hydrogen exceeds 65 cc., or the pipette has been previously used, in which case a longer time will be required, as will be seen from the experiments cited below.

A pipette should not be used for the absorption of more than about 100 cc. of hydrogen before refilling with fresh solution. After absorption is complete, the residual paraffins and nitrogen are passed back, when the residual volume may be measured and paraffins determined by addition of oxygen and explosion in the usual manner. After the pipette has been used for the absorption of about 100 cc. of hydrogen, the remaining solution of palladous chloride containing precipitated palladium is rinsed into a casserole and then evaporated just to dryness on the water-bath, 5–6 cc. of hydrochloric acid and 4–5 drops nitric acid and a little water are then added and evaporation repeated. The dry palladous chloride so produced is then dissolved by adding 2 cc. of hydrochloric acid and warming with a small amount of water, and the whole diluted with water to a volume necessary for 1 pipette full. This solution is then returned to the stock bottle, to be used again when needed.

The accuracy of the above method may be judged from the following experiments. In these experiments all volumes of gases given are those found after reducing to standard conditions 0° C. and 760 mm. pressure.

Experiment 1.

Volume of hydrogen taken = 18.7 cc.
" " nitrogen " = 80.3 "

The mixture was passed over 1 per cent. palladous chloride, heated to 50° C. over night; absorption was complete, residue showing 80.3 cc.

Experiment 2.

Volume of hydrogen taken = 53.7 cc.
" " nitrogen " = 23.8 "

1 per cent. palladous chloride was used, and heated in water-bath one hour and thirty minutes. Residue = 23.8 cc. Absorption complete.

Experiment 3. To the residue of nitrogen from experiment 2 was added 26.4 cc. of hydrogen, and the mixed gases returned to the same solution as was used in experiment 2. Heated in the water-bath one hour and thirty minutes, it still showed 6.2 cc. of unabsorbed hydrogen. On again returning the gas to the pipette and allowing it to stand over night in the water-bath, absorption was complete, residue again showing 23.8 cc.

Experiment 4.

Volume of hydrogen taken = 1.07 cc.
" " nitrogen " = 52.23 "

Heated over 1 per cent. palladous chloride in water-bath one hour and thirty minutes, showed absorption of 0.68 cc. On standing over night in water-bath the absorption was 1.21 cc.

Experiment 5.

Volume of hydrogen taken = 1.27 cc.
" " nitrogen " = 70.8 "

This was passed over nearly neutral 2 per cent. palladous chloride and heated on water-bath over night, showing an absorption of 1.23 cc.

Experiment 6.

Volume of hydrogen taken = 60.2 cc.
" " nitrogen " = 18.2 "

Passed over nearly neutral 2 per cent. palladous chloride, and heated in water-bath one hour and thirty minutes. Residue = 18.2 cc.

Experiment 7. Residue from experiment 6 taken, and 64.4 cc. of hydrogen added. Mixture returned to same solution as that used in experiment 6, and again heated in water-bath one hour and thirty minutes. 4.4 cc. of hydrogen still remained unabsorbed, but, on returning the gas to the pipette the second time and allowing it to stand overnight, absorption was complete, the residue measuring 18.2 cc.

From experiments 5, 6, and 7 it will be seen that a 2 per cent. solution of palladous chloride has very little advantage over a 1 per cent. solution. Further experiments showed that with strongly acid solutions absorption was retarded.

The most satisfactory results have been obtained by using a fresh 1 per cent. nearly neutral solution for each determination; absorption is then complete in two hours. The pipette can be easily refilled with fresh solution, the one which has been used being evaporated down and redissolved and diluted again. 750 cc. of solution will be found to be plenty to keep two pipettes in use, the amount necessary for filling an ordinary pipette being about 160 cc.

ANN ARBOR, MICH., Feb. 11. 1896.

Contributions from the Chemical Laboratory of Harvard College.

XCIII.—ON THE BEHAVIOR OF CERTAIN DERIVATIVES OF BENZOL CONTAINING HALOGENS.[1]

BY C. LORING JACKSON AND SIDNEY CALVERT.

INTRODUCTION.

It is a well known fact that in substituted aromatic compounds the firmness with which atoms of halogen are attached to the benzol ring is diminished by the presence of nitro groups in certain positions, so that these atoms can be replaced by reagents, which would have no effect on them if the nitro groups had been absent. It has also been shown that certain other negative radicals exert a similar loosening effect: these are the two oxygen atoms in substituted quinones—chloranil and bromanil are very reactive bodies—the hydroxyl groups in phenols,[2] and especially in substituted resorcin,[3] and also probably carboxyl.[4] The object of the research described in the present paper was to determine

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[1] Presented to the American Academy of Arts and Sciences, May 9, 1894.

[2] Armstrong and Harrow, J. Chem. Soc., 1886, 447.

[3] Jackson and Dunlap, This JOURNAL, 18, 117.

[4] Rahlis, Ann. Chem. (Liebig), 198, 112.

whether such a loosening effect could be produced by less negative radicals, and for this purpose we have taken up the study of derivatives of benzol, in which the substituting radicals are halogens only, so that both the radicals removed and those which make the removal possible belong to this same class, and the latter are distinctly less negative than any of those enumerated above. The amount of work already done in this field is meagre. Balbiano[1] found that paradibrombenzol was converted into parabromphenetol, brombenzol, and a little benzol, when it was heated to 190° with sodic ethylate. The same substance with sodic methylate at 150° gave according to Blau[2] parabromphenol, parabromanisol, and a little hydroquinone dimethylether. Blau[3] also found that symmetrical tribrombenzol gave with sodic methylate at 130° symmetrical dibromphenol and the corresponding anisol as principal products. These results indicate that the atoms of bromine in these di- and tribrombenzols exert some loosening effect, as monobrombenzol must be heated to 200° before it reacts with sodic methylate;[4] but all these actions take place in sealed tubes, and even the maximum difference between their temperatures of reaction and that of monobrombenzol is not very great, only 70°. We decided therefore, in taking up the subject, to try to obtain reactions in open vessels, that is, under conditions which have prevented all action with monobrombenzol, and to do this it was obvious that we must increase the number of atoms of halogen which are to produce the loosening effect. We selected for our first experiment accordingly the tribromiodbenzol having the constitution Br.H.Br.I.Br.H, as in this compound we have iodine as the element to be removed, and this is usually less strongly attached to the ring than bromine or chlorine, and the three atoms of bromine which are to produce the loosening effect are in the most favorable positions for this purpose (two ortho and one para). Trichloriodbenzol would probably have been better, because chlorine is more negative than bromine, but we preferred the bromine compound on account of the great difficulty of preparing the trichloraniline in quantity.

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[1] Gazz. Chim., **11**, 401.

[2] Monatsh f. Chem., **7**, 627.

[3] *Ibid*, 630.

[4] *Ibid*, 636.

Upon trying a variety of reagents with the unsymmetrical tribromiodbenzol, we obtained negative results with all except two, sodic ethylate and sodic methylate. These converted it into symmetrical tribrombenzol, melting-point 119°, by replacing the iodine with hydrogen, the sodic ethylate acting to some extent even in the cold, more freely when the solution in alcohol and benzol was boiled under a return condenser, while the sodic methylate did not act in the cold, and only to a limited extent boiling. The unsymmetrical tetrabrombenzol Br.H.Br.Br.Br.H, which differs from the preceding compound only in having an atom of bromine in place of the iodine, was also partially converted into symmetrical tribrombenzol by boiling with sodic ethylate, but there was much less action than with the iodine compound, the tetrabrombenzol undergoing about as much substitution when the solution was boiling, as was the case with the tribromiodbenzol in the cold. The tribromchlorbenzol Br.H.Br.Cl.Br.H, on the other hand, was entirely unaffected by a solution of sodic ethylate in open vessels. These experiments show that the presence of the three bromine atoms exercises a loosening effect similar to to that exhibited by nitro groups, although much weaker in degree. They also furnish an additional case in which the stability of the aromatic compounds of the different halogens increases in the order iodine, bromine, chlorine. This is worth noting, because Körner[1] states that the halogens are removed from dinitrohalogenbenzols (X 1, NO_2 2, NO_2 4) in exactly the reverse order; that is, chlorine most and iodine least easily.

We next turned our attention to the tetrabrombenzol melting at 174–175°, which has been proved by work done in this laboratory to have the symmetrical constitution Br.Br.H.Br.Br.H, as in this substance only two of the bromine atoms are in the positions to the one to be removed (ortho and para) which had proved effective in the unsymmetrical compound. This, however, did not affect the result materially, as this tetrabrombenzol was converted into tribrombenzol (unsymmetrical Br 1, Br 2, Br 4) by the boiling solution of sodic ethylate to about the same extent as the unsymmetrical

[1] Gazz. Chim., 4, 323, note.

tetrabrombenzol. In separating the small quantity of tribrombenzol formed from the large amount of unaltered tetrabrombenzol we have obtained excellent results in both the cases just mentioned by exposing the mixture for a long time to the lowest temperature at which anything sublimes. The sublimate thus obtained, if not the pure tribrombenzol, could be converted into it by a single repetition of this rough fractional sublimation.

An arrangement of the bromine atoms entirely different from the effective ortho para positions is found in the symmetrical tribrombenzol Br.H.Br.H.Br.H, as here all the halogen atoms are in the meta position to each other, but, as has been already mentioned, Blau found that one of the atoms of bromine was removed by the action of sodic methylate at 130°. As our work just described has shown that sodic ethylate is more active than the methylate, we thought this might act even in open vessels, and on trying the experiment have found that sodic ethylate in boiling alcoholic solution removes from symmetrical tribrombenzol a portion of its bromine. The organic products of the partial reaction were oily, but, as the object of our experiment was to determine whether a reaction took place, and not what its products were, no attempt was made to examine them. This is not the only case in which one of three radicals in the symmetrical position has been removed, as Lobry de Bruyn[1] has converted symmetrical trinitrobenzol into dinitranisol or dinitrophenetol by the action of the sodic alcoholates in open vessels. The work of Blau and Lobry de Bruyn, therefore, establishes this as a general behavior of symmetrical compounds, and such replacements are the more remarkable, because a single negative radical has no effect upon one other in the meta position.

In the work with unsymmetrical tetrabrombenzol, mentioned above, it was only the fourth atom of bromine (in the diortho para position to the others) that was replaced by hydrogen, but in some work upon the corresponding dinitro compound $C_6Br_4(NO_2)_2$, done some years ago by W. D. Bancroft and one of us, this atom of bromine remained obstinately

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[1] Rec. d. Tr. Chim., **9**, 208; **13**, 149.

unattacked when other atoms of bromine were removed;[1] in the same way the reduction of tetrabromdinitrobenzol with tin and hydrochloric acid gave monobromphenylene diamine, so that in these cases the symmetrical atoms of bromine alone were removed, and the action was exactly the reverse of that obtained with tetrabrombenzol and sodic ethylate. This difference is explained by the facts that in the tetrabrombenzol the three atoms of bromine in the trimeta position are the loosening radicals, whereas in the tetrabromdinitrobenzol they are those which are loosened. In this connection we decided to try the action of sodic ethylate on tetrabromdinitrobenzol, as this experiment had not been included in the previous work of W. D. Bancroft and one of us, and we found that tetrabromdinitrobenzol ($Br.NO_2.Br.NO_2.Br.Br.$) was converted by the action of a cold solution of sodic ethylate into the tribromnitroresorcine diethylether melting at 101°, and first obtained by W. H. Warren and one of us[2] by the action of sodic ethylate on tribromtrinitrobenzol. This substance has the formula $C_6Br_3NO_2(OC_2H_5)_2$, and must have been formed in this case by the replacement of one nitro group and the fourth atom of bromine by ethoxy groups, just as it was formed from the tribromtrinitrobenzol by the replacement of two nitro radicals by ethoxyls. If the action with the tetrabrom body is analogous to that with the trinitro compound, there should be formed at the same time by a parallel reaction a substituted phloroglucine, in this case dinitrobromphloroglucine or its ethers; but although we have found indications that such a substance is formed, we have not succeeded in isolating it.

The principles governing the replacement of radicals attached to the benzol ring, which we have brought forward in this introduction, make it possible to explain the strange behavior of tribromtrinitrobenzol with sodic ethylate. This action consists in the two following reactions, which take place side by side.[3]

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[1] This JOURNAL, **12**, 289. Sodium malonic ester gave the compound $C_6HBr_2(NO_2)_2CH(COOC_2H_5)_2$; reduction of this gave bromamidoxindol; aniline gave $C_6Br(NO_2)_2(C_6H_5NH)_3$.

[2] This JOURNAL, **13**, 184.

[3] This JOURNAL, **15**, 619. Tetrabromdinitrobenzol acts in the same way, as just stated, but for the sake of simplicity of expression, the explanation has been confined to the trinitro body, although it applies equally well to the tetrabrom compound.

$C_6Br_3(NO_2)_3 + 3C_2H_5ONa = C_6(OC_2H_5)_3(NO_2)_3 + 3NaBr.$
$C_6Br_3(NO_2)_3 + 2C_2H_5ONa = C_6Br_3NO_2(OC_2H_5)_2 + 2NaNO_2.$

In this substance we seem to have two zones of action, one consisting of the three symmetrically disposed bromine atoms, the other of the three nitro groups also symmetrically disposed, and the action in each molecule is confined to one of these zones, if it is carried on in the cold. In the first or bromine zone the atoms of bromine are submitted to two loosening influences: (*a*) that of the three nitro groups, in the diortho and para positions to each bromine atom, and (*b*) that of the trimeta bromine atoms on each other. In the second or nitro zone also we have two loosening influences: (*c*) that of the three bromine atoms diortho and para to each nitro group, and (*d*) the loosening effect of the three symmetrical nitro groups on each other. Of these loosening influences (*a*) is by far the strongest, and (*b*) the weakest; it seems therefore that the combined effect of (*c*) and (*d*), of intermediate strength, is about equal to that of (*a*) and (*b*) together; consequently each of these zones of action lies about equally open to the attack of the sodic ethylate, and the two reactions take place simultaneously. When the solvent is alcohol alone, they run to about the same extent. If the repellant action of the three symmetrical nitro groups (*d*) is removed, that is, if tribromdinitrobenzol is used instead of the trinitro body, the nitro groups should be much less loosened than the bromine atoms, and as a matter of fact there has been observed in this case no tendency to remove the nitro groups, the action being confined to the bromine zone, causing the formation of $C_6Br(OC_2H_5)_2(NO_2)_2H$ or $C_6H(OC_2H_5)_2(NO_2)_2H$.

The work described in this paper has furnished us with 3 additional cases, in which atoms of halogens have been replaced by hydrogen under the action of sodic ethylate, but even with these we do not feel that enough facts are known to make it possible to deduce a general rule in regard to the conditions, which produce this curious reaction. The collection of such facts will be continued in this laboratory.

We also tried the action of fuming nitric acid on unsymmetrical tribromiodbenzol, and found that iodine was set free, and the organic product was the tribromdinitrobenzol melting at 192°, and having the constitution $Br.NO_2.Br.NO_2.Br.H$.

A few statistics which we have collected about the removal of radicals from substituted benzols may be given here. By far the greater number of such removals are those in which a negative radical stands in the ortho position to the radical removed. Of these we have counted over 60 cases, in only 9 of which the negative radical is a halogen. Of the cases of removal, where there is no negative radical in the ortho position, we have found 4 in which a negative radical is in the para position to the radical removed; these are $C_6H_4Br_2$, $C_6H_4ClNO_2$, $C_6H_4BrNO_2$, and $C_6H_4(NO_2)_2$; and to these perhaps should be added five of the nine cases mentioned above, in which the ortho radical is a halogen, as in all of these there is a nitro group in the para position to the radical removed.[1] In no case is a radical removed which is only in the meta position to a single negative radical;[2] but if there are 2 negative radicals in meta positions to the radical attacked (symmetrical tricompound), there are 2 cases in which substitution has been observed, $C_6H_3Br_3$ and $C_6H_3(NO_2)_3$.

EXPERIMENTAL PART.

Behavior of Tribromiodbenzol.

The tribromiodbenzol (I 1, Br 2, Br 4, Br 6) was made from symmetrical tribromaniline by replacing the amido group by an atom of iodine. Silberstein,[3] who discovered this substance, made it from the nitrate of diazotribrombenzol. We have preferred to use the sulphate, and, as our method seems to give a better result than Silberstein's to judge from his statement, we give it in detail. Ten grams of symmetrical tribromaniline were mixed with moderately dilute sulphuric acid in such proportion that there was one molecule of the acid to each molecule of the tribromaniline; the calculated amount of sodic nitrite was then added in small quantities at a time,

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[1] In the other cases where a radical was removed, which was ortho only to halogens, these halogens were in the diortho position, and therefore probably were sufficient to cause the removal.

[2] The conversion of meta and para nitranisol into the corresponding nitranilines were not counted, because they took place at such a high temperature, 200°; but perhaps they should be added to the list given above.

[3] J. Prakt, Chem. [2], **27**, 119.

shaking the loosely corked flask after each addition until the red fumes were absorbed. The mixture after standing over night was filtered, and then treated with hydriodic acid till there was no further action. The slightly brown precipitate was washed with water, and purified by crystallization from a mixture of benzol and alcohol, when it showed a melting-point of 104°. Silberstein gives 103°.5. For greater safety it was analyzed with the following result:

0.3374 gram of the substance gave 0.6119 gram of a mixture of argentic bromide and iodide.

	Calculated for $C_6H_2Br_3I$.	Found.
Iodine and Bromine	83.24	83.32

We find the solubilities of the substance the same as those given by Silberstein, but we do not agree with him when he says it sublimes easily, as we have found that it sublimes much less easily than symmetrical tribrombenzol.

To study the action of sodic ethylate on tribromiodbenzol, 6 grams of it were dissolved in anhydrous benzol, and mixed with 40 cc. of an alcoholic solution of sodic ethylate, containing 2 grams of sodium, that is, more than enough to remove all the halogen atoms present. The mixture was then heated on the steam bath under a return condenser for one hour, when the liquid had taken on a dark color, and a brownish precipitate had appeard; the liquid was now evaporated and the residue treated for half an hour with a large quantity of water, filtered and washed, when it weighed 4.1 grams. Upon subliming this residue, 2 grams of sublimate were obtained in small white needles which melted at 119–120°, the melting-point of symmetrical tribrombenzol. An analysis of the sublimate gave the following result.

0.2612 gram of the substance gave by the method of Carius 0.4695 gram of argentic bromide.

	Calculated for $C_6H_3Br_3$.	Found.
Bromine	76.18	76.51

There can be no doubt, therefore, that the substance is tribrombenzol, formed by the replacement of the atom of iodine in the tribromiodbenzol by hydrogen. The residue which did not sublime was a brownish yellow powder, containing many black specks. It did not melt at 300°, but melted with blackening when held over the free flame. It was not completely soluble in any of the common solvents, and all our efforts to obtain from it a body fit for analysis have proved fruitless.

The experiment was next repeated under the same conditions, except that the mixture was not heated, but allowed to stand three days at the ordinary temperature. At the end of this time it had turned dark brown, in fact a pale brown color appeared almost as soon as the materials were mixed ; the solvents were then allowed to evaporate spontaneously, and the residue treated with water as in the previous experiment, when the aqueous filtrate gave a strong test with starch paste and chlorine water for iodine. The residue insoluble in water was sublimed at a very gentle heat, and crystals of symmetrical tribrombenzol were obtained recognized by their melting-point, 119–120°. The residue, which did not sublime at this gentle heat, was crystalline and of a reddish white color, very different from the amorphous brown product obtained under the same conditions from the action of hot sodic ethylate. The crystalline residue after three recrystallizations from a mixture of benzol and alcohol, showed the melting-point 104°, and was therefore unaltered tribromiodbenzol. It seems, therefore, that cold sodic ethylate behaves like hot, but the acton is less complete.

An alcoholic solution of sodic hydrate, after being warmed for ten minutes with a solution of tribromiodbenzol in benzol, converted it into tribrombenzol with elimination of iodine. This, therefore, acted in the same way as the hot solution of sodic ethylate, but the yield seemed to be larger, and the residue from the sublimation was lighter in color (yellow) and free from black specks. It did not, however, prove to be more manageable than that previously obtained. These differences may be due to the shorter heating, ten minutes in this case instead of an hour when the ethylate was used. Several attempts were made to detect the aldehyde which it seemed probable was formed as the secondary product in the replacement of the iodine by hydrogen, but these led to no definite results.

Sodic methylate when boiled with a benzol solution of tribromiodbenzol for over an hour gives a result similar to that obtained from cold sodic ethylate; that is, tribrombenzol was formed, but there was a large amount of undecomposed tribromiodbenzol. The two substances were separated by careful sublimation and recognized by their melting-points. Cold sodic methylate, on the other hand, gave no action even after standing three days. This was proved by testing the aqueous washings for halogens with negative results, and recovering essentially all of the tribromiodbenzol used.

The following reagents had no effect on the tribromiodbenzol: sodic phenylate in alcoholic solution boiling, sodic hydrate in aqueous solution boiling, sodic carbonate in aqueous solution boiling, zincic oxide and water in a sealed tube at 200° for twelve hours, argentic acetate in aqueous solution boiling, aniline boiling, tin and hydrochloric acid, sodic malonic ester both cold and hot. The proof that no action had taken place in these experiments was obtained either by the recovery of the unaltered tribromiodbenzol, or by tests for a salt of the halogens which gave negative results. In most cases both methods of proof were applied.

To determine whether the removal of the iodine was due to the loosening effect of the three atoms of bromine or to the slight attraction of iodine alone for carbon, iodbenzol was treated with sodic ethylate under the same conditions which had produced an action on the tribromiodbenzol; but after heating the mixture for an hour and a half no test for sodic iodide could be obtained, showing that there had been no action.

Action of Fuming Nitric Acid on Tribromiodbenzol.

When tribromiodbenzol was treated with fuming nitric acid, it lost its white crystalline appearance even in the cold, and became converted into a yellow powder. If the mixture was allowed to stand at ordinary temperatures over night, and then water added to it, iodine appeared both in scales and in the form of vapor, as a great amount of heat was given off. The identity of the iodine was also established by the smell and the violet color of its solution in carbonic disulphide. If now the insoluble portion was washed with cold alcohol until free from iodine, and then recrystallized several times from a mixture of benzol and alcohol, it showed the constant melting-point 191°, which indicated that the substance was tribromdinitrobenzol, and this was confirmed by the following analysis:

0.3375 gram of the substance gave by the method of Carius 0.4740 gram of argentic bromide.

	Calculated for $C_6HBr_3(NO_2)_2$.	Found.
Bromine	59.26	59.78

The somewhat high results may be due to a trace of a substance containing iodine. If the mixture of tribromiodbenzol and fuming nitric acid was boiled, the organic product was the same, but no free iodine was obtained.

Behavior of Unsymmetrical Tetrabrombenzol Melting at 98°.

The action of sodic ethylate on this substance was selected for study, because that reagent had given the best results in the work on tribromiodbenzol just described. To prepare the unsymmetrical tetrabrombenzol, 20 grams of tribromaniline were dissolved in 180 cc. of hot glacial acetic acid, about 80 cc., that is, a considerable excess of a distilled solution of hydrobromic acid (boiling-point 125°) added, and, disregarding any precipitate formed, the mixture treated with sodic nitrite in the proportion of a molecule and a half or two molecules to each molecule of the tribromaniline. For this purpose the finely powdered nitrite was slowly sifted, with vigorous stirring, into the solution, which had previously been cooled so that it felt barely warm to the hand. The white crystals which were suspended in it gradually changed into a dirty brown solid, much of which dissolved even in the cold. The mixture was then heated for two or three hours on the water bath; the solid matter at first went into solution, but later the tetrabrombenzol, as it formed, separated, principally in long white needles, or sometimes in part as a semi-liquid brown mass. The needles were separated mechanically, and were usually found to be pure. The semi-liquid portion solidified in a short time, and was purified by dissolving it in a little hot benzol, and pouring this solution into alcohol. The tetrabrombenzol precipitated in this way had a slight reddish color, while the mother liquid was of a dark claret-red. The precipitate was easily obtained white by one or two recrystallizations from a large volume of alcohol, to which it was well to add a little benzol. In this way 20 grams of the tribromaniline gave 22 grams of tetrabrombenzol, instead of the 23.88 grams required by theory, a yield of 92 per cent.

Eight grams of the tetrabrombenzol were mixed with an alcoholic solution of sodic ethylate, made from 2 grams of sodium and 50 cc. of absolute alcohol, and a little benzol to assist the solution of the tetrabrombenzol. The mixture was heated to boiling under a reverse condenser for two days, when it had taken on a blackish green color; it was then evaporated to dryness and washed with water. The wash water gave a good test for sodic bromide. The residue insoluble in water was sublimed at the lowest possible temperature, when a small amount of white needles was obtained, which melted at 119°, the melting-point of symmetrical tribrombenzol. The residue which had not sublimed at the very low temperature used made up the principal bulk of the product, and was chiefly unaltered tetrabrombenzol. This method of fractional sublimation has also yielded us excellent results in another similar case, which will be described later in this paper. The sodic ethylate, therefore, acts on the tetrabrombenzol in the same way that it does on the tribromiodbenzol, replacing by hydrogen the bromine atom occupying the same position as the atom of iodine, but the action takes place with more difficulty, and is less complete.

Behavior of Unsymmetrical Tribromchlorbenzol.

The tribromchlorbenzol was prepared by a method similar to that used for the tetrabrombenzol. Upon adding the hydrochloric acid to the solution of tribromaniline in glacial acetic acid a precipitate of the chloride was formed, but this went into solution as the amido was converted into the diazo compound. Twenty grams of tribromaniline yielded 15 grams of tribromchlorbenzol melting at 82°. Two grams of this substance were heated for four hours with an alcoholic solution of sodic ethylate, prepared from half a gram of metallic sodium; when upon evaporation to dryness and washing with water only a very faint test for halogens could be obtained from the wash water, and the residue, which consisted of unaltered tribromchlorbenzol, weighed nearly 2 grams. A similar experiment with the tetrabrombenzol, in which the mixture was boiled for only three hours, gave a strong test for sodic bromide and a small amount of tribrombenzol. The chlortribrombenzol, therefore, if effected at all by sodic ethylate, is much less susceptible to the action than either the corresponding iod or brom compound.

Behavior of Symmetrical Tetrabrombenzol.

Tetrabrombenzol, melting at 174–175°, which has been proved by work done in this laboratory to have the symmetrical constitution (1, 2, 4, 5), was boiled for over twelve hours with an alcoholic solution of sodic ethylate; the brown liquid thus obtained, with some long, rather dark colored crystals, which were deposited as it cooled, was evaporated to dryness and the residue washed with water. The wash waters gave a good test for sodic bromide. The residue insoluble in water was then extracted with a mixture of alcohol and benzol, filtered to remove a brown insoluble substance, and the filtrate concentrated, when it deposited crystals which melted at 174–175°, and were therefore the unaltered tetrabrombenzol. The mother liquor was evaporated to dryness and cautiously sublimed at as low a temperature as possible; the crude sublimate melted at 42-43°, and upon resubliming it with the same care its melting-point rose to 44°, the melting-point of unsymmetrical tribrombenzol (1, 2, 4), which must be formed if one of the atoms of bromine is removed from this tetrabrombenzol. Only a small portion of the substance, however, reacts with the sodic ethylate, by far the greater part remaining unaltered.

Experiment with Symmetrical Tribrombenzol.

Blau[1] states that tribrombenzol is converted by sodic methylate into the symmetrical dibromphenol, when the substances

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[1] Monatsh. f. Chem., 7, 630.

are heated together in methyl alcohol solution for two or three days at 120–130°. We accordingly tried an experiment to see whether sodic ethylate would have a similar action in open vessels, as we had used this reagent in the preceding work. Ten grams of tribrombenzol were boiled with a solution of the necessary amount of sodic ethylate in about 200 cc. of alcohol for somewhat more than seventy hours; the aqueous wash waters from the product gave a good test for sodic bromide, and in addition to a large amount of unaltered tribrombenzol we obtained a very little of an oil, probably the dibromphenol ethylether, which is a liquid. As this result, which it will be observed confirms Blau, had given us all the information about the reaction which we wished, we did not pursue the work further.

Hexabrombenzol gave when boiled with sodic ethylate a good test for sodic bromide. The organic product was an oil, and a great deal of unaltered hexabrombenzol was recovered. Hexachlorbenzol gave a similar result.

Action of Sodic Ethylate on Tetrabromdinitrobenzol.

In the experiments described in this paper the fourth atom of bromine was removed from tetrabrombenzol by sodic ethylate, while in the work by W. D. Bancroft and one of us[2] upon the tetrabromdinitrobenzol, the fourth atom of bromine was not removed by aniline or sodium malonic ester. It seemed of interest, therefore to try the tetrabromdinitrobenzol with sodic ethylate, and see whether it behaved like the tetrabrombenzol with this reagent or in the same way that it had behaved with the other reagents mentioned above. For this purpose 10 grams of tetrabromdinitrobenzol were dissolved in benzol, and treated with an alcoholic solution of the sodic ethylate made from 2 grams of sodium. The solution became claret-colored as soon as the sodic ethylate was added, but this color changed later to a reddish brown. There was no perceptible evolution of heat. The mixture was allowed to stand at ordinary temperatures for two days, after which it was evaporated spontaneously. The residue, after being washed with water, was recrystallized from alcohol until it

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[2] This JOURNAL, **12**, 289.

showed the constant melting-point 100° to 101°. This showed that it must be the tribromnitroresorcine diethylether made by Warren and one of us[1] from tribromtrinitrobenzol. This substance must have been formed by the replacement of one nitro group, and the fourth atom of bromine by two ethoxy radicals. To confirm this the wash waters of the original product were tested for a bromide and a nitrite, and good results obtained in both cases. If in this case the reaction has run as with tribromtrinitrobenzol,[2] which we should infer from the isolation of tribromnitroresorcine diethylether, the secondary product should be bromdinitrophloroglucin, or its ethers. As a matter of fact, an oil having the properties of a phenol was obtained by acidifying the aqueous wash waters from the first of the reaction, but all our attempts to bring it into a form fit for analysis have failed, and we have been prevented from continuing work on this substance by the departure of one of us from Cambridge.

Contributions from the Chemical Laboratory of Cornell University.

THE CIS AND TRANS MODIFICATIONS OF BENZENE HEXABROMIDE.

W. R. Orndorff and V. A. Howells.

Benzene hexabromide ($C_6H_6Br_6$), seems to have been obtained first by Mitscherlich,[3] about 1837, by the action of bromine on benzene in the sunlight. This addition-product of benzene, when heated with an alcoholic solution of potassium hydroxide, gave an oily tribrombenzene, which Laurent afterwards obtained in crystals by the evaporation of its ethereal solution.

But little else was known of this substance until 1887, when Meunier,[4] after having carefully studied the hexachlor addition-product of benzene, and shown that it existed in two modifications, which he termed α- and β-, turned his attention very naturally to Mitscherlich's benzene hexabromide, in order to see if it did not exist in two isomeric forms, and also to determine to which of the hexachlorides it corresponded. The method of preparation of the hexabromide was improved

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[1] This Journal, **13**, 184.

[2] *Ibid.*, **15**, 619.

[3] Ann. der Phys. Pogg., **35**, 374.

[4] Ann. chim. phys. [6], **10**, 269.

by Meunier, and the complete crystallographic study of the substance, undertaken at his request by Des Cloizeaux, established the isomorphism, and consequently the identity of chemical constitution between this hexabromide and the α-hexachloride of benzene. This conclusion was further supported by the complete analogy shown by the two substances in their chemical conduct. Regarding an isomeric hexabromide corresponding to the β-hexachloride Meunier says nothing.

Friedel,[1] in 1891, published a very interesting paper in which he discusses the constitution of the two hexachlorides of benzene in the light of the stereochemical hypothesis. To the β-modification he assigns the cis formula, because the higher symmetry of the cis structure might account for its comparative stability, higher melting-point and greater specific gravity. As the α-hexachloride crystallizes in the monoclinic system and is always formed in much greater quantity than the β-product, he regards it as a trans compound. He then shows that the cis formula has an hexagonal symmetry and that the β-hexachloride really crystallizes in the hexagonal system being in fact pseudo-regular.

In 1892 Matthews[2] showed that benzene hexabromide could be made by passing air saturated with bromine through a layer of benzene floating on a dilute solution of sodium hydroxide, a method similar to that by which he had previously made the two benzene hexachlorides so readily. Later he found that a better method was to mix benzene and bromine in the presence of water or dilute caustic soda solution. In regard to the product formed by this method he says, "I have not as yet investigated the benzene hexabromide thus produced, but it will be of interest to see whether it is a simple substance or a mixture. Meunier has already examined the hexabromide produced by other processes and finds it to be homogeneous."

It will be seen from this brief survey of the work done on benzene hexabromide that it corresponds with the α- or trans benzene hexachloride and also that the β- or cis modification

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[1] Bull. Soc. chim. (Paris), [3], **5**, 130. See also This JOURNAL, **13**, 356.

[2] J. Chem. Soc., **61**, 110.

of benzene hexabromide, predicted by the stereochemical theory and corresponding to the cis hexachloride, has not yet been made. It seemed of interest, therefore, to see if this variety of the hexabromide could be prepared and, if so, to study it in the light of the stereochemical theory and of the facts stated by Friedel regarding the two benzene hexachlorides.

Experimental.

Benzene hexabromide was first made following Meunier's method exactly, by treating boiling benzene with bromine in the direct sunlight. Hydrobromic acid was evolved in large quantities from the beginning of the operation. The crystals remaining after the excess of bromine and benzene had evaporated off spontaneously, were washed with water, dried, and then repeatedly extracted with boiling alcohol, in which the bromine substitution-products of benzene dissolve readily, while the addition-products are only sparingly soluble. The yield of the crude hexabromide by this method was only 20 grams, though we used 250 grams of benzene and 550 of bromine. Meunier states that he obtained 85 grams of the hexabromide from the above amounts of benzene and bromine. He used the method of sublimation to free his material from substitution-products, however, which may account for the difference between his results and ours.

In our experiments quite a large quantity of paradibrombenzene was formed, but as this substance is soluble in alcohol no difficulty was experienced in separating it from the hexabromide.

The crude benzene hexabromide thus made was then subjected to very careful fractional crystallization, using chloroform as a solvent. Friedel used this method and solvent to separate the cis and trans benzene hexachlorides and obtained excellent results, but notwithstanding all our care we found it impossible to obtain a substance with any higher or lower melting-point than that of Meunier's hexabromide. The crystals in the different fractions were always homogeneous and all had the same melting-point (212–215° C.). The method used by Matthews to separate the two benzene hexachlorides, (distillation in steam, the α or trans product alone being volatile), was next tried, but without success, nothing being volatilized with the steam after ten hours treatment.

As it seemed not improbable, that, at the temperature at which the hexabromide was prepared, the cis compound, if any were formed, might have been transformed into the more stable trans modification, we next made the benzene hexabromide by the method proposed by Matthews, taking care to keep the temperature in the neighborhood of 0° C. 100 grams of benzene were floated on 300 cc. of a one per cent. solution of sodium hydroxide and 650 grams of bromine were added (50 grams daily), from a dropping-funnel. The bromine dissolved in the benzene, forming a heavy red oil, which fell to the bottom of the flask. After the addition of each 50 grams of bromine fresh sodium hydroxide solution was employed. When all the bromine had been added the watery layer was removed and the oil allowed to stand in an open flask in a hood for about eight weeks. There then remained in the flask a mass of beautiful, large crystalline plates together with some benzene, bromine, and monobrombenzene. The contents of the flask were then placed in an open dish and the volatile portion allowed to evaporate spontaneously. The crystals left were ground to powder, extracted with cold alcohol, (to remove bromine monobrombenzene and *o*-dibrombenzene), and then boiled several times with alcohol to remove substitution-products of benzene. This process removed all but 20 grams of the crystals which melted at 205–210° C. The material recovered from the alcohol melted at 85–90° C. and was shown to be principally paradibrombenzene. The product insoluble in alcohol was then put into a paper shell and extracted with chloroform, using a Soxhlet fat-extractor for this purpose. At the end of this operation there was left in the paper shell 0.6 gram of crystals, which melted at 249–252° C. but which after being recrystallized from boiling benzene had a melting-point of 253° C., turning brown and giving off some hydrobromic acid at this temperature. The crystals obtained from the chloroform solution melted at from 205–217° C. After several recrystallizations from benzene, however, they melted at 212–215° C., and probably contained a very small amount of the higher melting compound. The only other successful attempt to make the crude hexabromide containing enough of the higher melting product to isolate was carried out in exactly the same manner and with the same quantity of materials as the one above described, except that water was used in place of the solution of sodium hydroxide. After removing the substitution-products with alcohol and extracting with chloroform, 0.5 gram of the higher melting substance was obtained. None of this product melting at 253° C. was formed when the bromine and benzene were mixed dry and indeed but little of the hexabromide itself was formed under these conditions. When the bromine was added to the benzene and sodium hydroxide solution or water in the direct sunlight and no precautions were taken to keep the mixture cold, substitution-products mostly resulted, and from the small amount of hexabromide formed no higher melting product could be isolated.

As both these products were prepared from pure benzene directly and both were undoubtedly addition-products, from their chemical conduct, it was not deemed necessary to make complete analyses, so only a determination of the amount of bromine each contained was made. The following are the results obtained by the Carius method.

α-Product Melting at 212–215° C.

0.2182 gram gave 0.4404 gram AgBr.

	Found.	Calculated for $C_6H_6Br_6$.
Bromine	85.91	86.01

β-Product Melting at 253° C.

0.2500 gram gave 0.5032 AgBr.

	Found.	Calculated for $C_6H_6Br_6$.
Bromine	85.65	86.01

These results indicate that both of these substances are hexabrom addition-products of benzene.

Molecular weight determinations were next made with the α-product melting at 212–215° C., using the boiling-point method and the apparatus[1] recently described by one of us for this purpose. The following are the results[2] obtained:

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[1] This JOURNAL, 17, 517.

[2] These determinations were made for us by Mr. C. L. Bliss, to whom we wish here to express our thanks.

α-Benzene Hexabromide, $C_6H_6Br_6 = 558$.

Solvent: *Benzene.*

Boiling-point 79.6° at 744.5 mm. barometric pressure.

Molecular elevation for 100 grams 26.6°.

	Grams solvent.	Grams substance.	Concentration in 100 grams.	Observed elevation.	Barometer mm.	Molecular weight.
1	118.71	1.4083	1.1863	0.060°	739.9	526
2	"	2.6126	2.2008	0.109	739.7	537
3	"	3.4914	2.9411	0.132	739.7	593
4	"	4.3077	3.6287	0.160	739.5	605

Average of all determinations,	565
Molecular weight at infinite dilution,	545

Barometer 740–739.5 mm.

These results show that the molecular weight of the α-product, melting at 212–215° C. is 558 and that the formula of the substance is $C_6H_6Br_6$. Unfortunately it was impossible to determine the molecular weight of the higher melting β-benzene hexabromide as we did not have enough of the material left to give satisfactory results. Owing to the high molecular weight of this substance it requires over a gram, nearly a gram and a half, to give a rise of *six hundredths* of a degree. It seems almost certain, however, from the method of preparation, the analyses and the analogy of the hexabromides with the hexachlorides of benzene that both these addition-products have the same molecular weight and that they are stereoisomers.

Professor A. C. Gill, of the Mineralogical Department of this University, made a complete crystallographical examination of these two substances for us and, since his results with the α-product melting at 212–215° C. differ somewhat from those given by Des Cloizeaux and Des Cloizeaux's measurements vary considerably from the calculated values in some cases, they are given here complete for both substances. The material melting at 212-215° C. was carefully recrystallized several times from chloroform and was undoubtedly much purer than that examined by Des Cloizeaux. The higher melting β-product was crystallized both from benzene and from xylene, in which it is much more soluble.

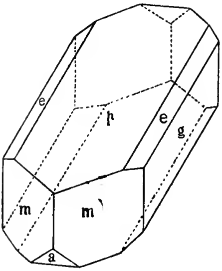
"Two modifications of benzene hexabromide were examined.

The α-hexabromide was found to agree, in general, with the description given by J. Meunier.[1] The angles, however, were found to be somewhat different from the figures given by Des Cloizeaux, and they also agree rather better with each other. Crystals from chloroform, xylene, and from a mixture of the two, were measured. Those from chloroform were brilliant, clear, and colorless. The crystals obtained by a second crystallization from chloroform gave the best results; *viz*:

Monoclinic; $\beta = 69°22'$; $a : b : c = 0.9938 : 1 : 0.5268$ Faces observed; $p = 0P(001)$; $g = \infty P\grave{\infty}\ (010)$; $m = \infty P\ (110)$; $a = +2P\bar{\infty}\ (\bar{2}01)$; $e = P\grave{\infty}\ (011)$; and, on one or two crystals, $b = +P\ (\bar{1}11)$; and $h = \infty P\bar{\infty}\ (100)$.

In the following table are given some of the more important angles, with the results of Des Cloizeaux for comparison.

			Des Cloizeaux.	
	Observed.	Calculated.	Observed.	Calculated.
p : m	75° 3′		75° 8′	
p : a	122° 16′		120° 33′	122° 25′
m : a	63° 47′			
p : a′	57° 46′	57° 44′	57° 35′	
m : m	85° 57′	85° 51′	86° 36′	87° 14′
m : m′	94° 12′	94° 9′	92° 50′	92° 46
p : e	26° 14′	26° 18′	26° 3′	
g : e	63° 48′	63° 42′	64° 10′	63° 57′
g : m	47° 8′	47° 4′ 30″	46° 23′	
b : a	37° 16′	37° 16′		
p : h	69° 27′	69° 22′		



A common shape of the crystals from chloroform is seen in the accompanying figure, though the development of the clinozone is frequently much less than here shown.

The β-hexabromide of benzene crystallizes in the regular system. Only octahedral planes were measured (on the stage of the microscope), though the rhom-

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[1] *Loc. cit.*

bic dodecahedron appears also to be quite frequent in occurrence. Unlike the corresponding hexachloride, the crystals show no trace of double refraction."

Regarding the α-hexabromide, melting at 212–215° C., Meunier's statements were confirmed in every particular.

As to the β-product so small a quantity of the material was left after the analysis that but little could be learned of its properties and chemical conduct. It has a higher melting-point (253° C.), and is less soluble in chloroform, benzene, toluene, and *m*-xylene than the corresponding α-benzene hexabromide. In alcohol and ether it is almost insoluble. It is decomposed quantitatively into hydrobromic acid and the unsymmetrical tribrombenzene when heated with an alcoholic solution of potassium hydroxide.

That the α-benzene hexabromide is the trans compound seems quite certain from the larger amount formed, the system in which it crystallizes, the lower melting-point and the complete analogy of this substance with the trans hexachloride. The smaller amount of the β-compound formed, the crystal form and the higher melting-point, all indicate the cis stereo formula for this modification of the benzene hexabromide. It is worthy of note here, however, that this β-hexabromide is actually regular in its crystal form, while the corresponding hexachloride is hexagonal, being pseudo-regular, as first shown by Friedel, and confirmed by an examination made by Dr. Gill of some of the crystals.

CORNELL UNIVERSITY,
ITHACA, N. Y., January, 1896.

SILICIDE OF CALCIUM.

BY G. DE CHALMOT.

When making silicides of different metals in an electric furnace, I have often used a flux in order to make the mixture that was used more liquid. In cases where I used lime as a flux, I have often found that the resulting silicide contains considerable amounts of calcium. I have thus introduced calcium in copper, silver, iron, and manganese silicide. I tried to obtain pure calcium silicide by putting into the furnace a mixture of silica, calcium oxide and carbon. I have found that if these ingredients are mixed in such proportions as to give the compound $CaSi_2$, mainly carbide of calcium is obtained, which, however, contains some silicide. If silica is used in excess and the amount of carbon is reduced, a calcium silicide of metallic appearance can be obtained, especially if a direct current of low voltage (25 volts and 225 amperes) is used. This silicide often contains some carbide as can be ascertained by the formation of acetylene gas. It also contains much more silicon and much less calcium than corresponds to the formula $CaSi_2$. All my specimens, moreover, contain some iron. The iron is derived from the furnace, the pencils and the silica (powdered quartz). All the iron which is present accumulates in silicide, because iron silicide is much more readily formed than calcium silicide.

Different samples contained:

	Calculated for $CaSi_2$.	Found.			
		I.	II.	III.	IV.
Si	58.33	71.19	62.48	81.65	91.99
Ca	41.67	19.75	28.41	15.61	5.60
Fe		3.74	2.74	3.61	0.92

Specimens I and II contain calcium carbide, II contains lead colored crystals imbedded in a more or less crystalline matter. III is silver white, homogenous and of crystalline structure. IV has much the same appearance, but is of darker color and contains some graphite. It is remarkable that sample IV was found on the anode, which was the upper pole in this special test. All specimens are hard enough to scratch glass.

The reactions which Wöhler describes[1] for calcium silicide, $CaSi_2$, were obtained with all the specimens.

With cold water some hydrogen is formed, more with warm water. Dilute hydrochloric acid forms a yellow silicic acid, and stronger hydrochloric acid forms a more orange colored acid. Dilute hydrochloric acid and sulphur dioxide form a red compound. I also found that if hydrochloric acid is brought into contact with finely divided silicide, hydrogen silicide is sometimes formed, which is self-igniting, and when burning leaves little white flakes of silica.

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[1] Dammer: Anorganische Chemie, [2], 2, 327.

In these specimens calcium silicide, $CaSi_2$, and silicon are mixed. When they are boiled with hydrochloric acid, the calcium silicide is decomposed and crystals of silicon remain. A part of Sample III, which is apparently homogenous, was thus treated. The insoluble residue of silicon and silicic acid was washed by decantation, and the silicic acid was dissolved with hot sodium carbonate solution. The remaining black crystals contained Si 95.88, and Fe 4.25 per cent.

This shows that these crystals contain, in addition to silicon, most of the iron silicide which is only little attacked by boiling hydrochloric acid.

When calcium carbide is heated in an electric furnace with an excess of sand, some crystals are formed, which contain in addition to silicon some calcium silicide that can be detected by the hydrochloric acid reaction.

WILLSON ALUMINUM COMPANY, SPRAY, N. C.

THE CONDUCTIVITY OF YTTRIUM SULPHATE.

BY HARRY C. JONES AND CHARLES R. ALLEN.

The yttrium sulphate used was prepared from a portion of the material previously employed by one of us in determining the atomic weight of yttrium.[1] This is probably the purest yttrium compound thus far obtained containing, according to Rowland, not over, and probably much less than one-half per cent. of impurities. The details of the purification are given in full in the article cited above.

At the end of the atomic weight determinations the yttrium was left in the form of the sulphate with which some of the oxide had been mixed. This mixture was dissolved in a little dilute nitric acid, the yttrium precipitated as oxalate and the oxalate ignited to the oxide.

The oxide thus obtained was treated in small portions with an excess of pure sulphuric acid, and the product evaporated to dryness in an air-bath. It was then heated to constant weight in the same bath, at a temperature a little above the boiling-point of sulphuric acid. The sulphate thus obtained was perfectly soluble in water, and solutions prepared from it were used in the measurements described below.

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[1] Jones: This JOURNAL, **17**, 154.

200 cc. of a solution of yttrium sulphate containing 0.011957 gram to the cc. were used as the starting-point. The molecular weight of the yttrium sulphate was taken as 466.08, and the volumes were calculated on the basis of one-sixth of this number, or 77.68.

The water used was prepared from ordinary distilled water by redistilling, first from potassium permanganate containing a little sulphuric acid, and then from alkaline permanganate. This water contained no detectable trace of acid or alkali, and gave a conductivity value far less than the probable experimental error of the work.

The Kohlrausch form of apparatus, as recommended by Ostwald,[2] was used. The dilutions were made by withdrawing one-half the contents of the cell and adding an equal quantity of water, using a carefully calibrated pipette.

To reduce the accumulative error which is unavoidably connected with this method of dilution, the process described above was repeated only a limited number of times. Measured volumes of the original solution were then taken, and diluted directly in measuring flasks. Each of the solutions thus prepared, was used as a starting-point for a new series of dilutions made with the pipette.

The values given are the mean of two complete series of conductivity measurements for the various concentrations. Owing to the limited amount of material available, it was necessary to use small volumes in making up the solutions, and to repeat the process of dilution with the pipette more frequently than is compatible with extreme accuracy; hence the results are subject to an error that may possibly amount to one per cent.

In determining the cell-constant we used two $\frac{n}{50}$ potassium chloride solutions made up from different samples. Ostwald's value for μ_v at 25° (129.7) was taken. The cell-constant was redetermined from time to time during the work. The samples of potassium chloride had each been recrystallized six times, and their flame reactions were those of perfectly pure potassium salts.

The results of the conductivity measurements are given in

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[2] Lehrb. Bd., **2**, 631-633.

the following table. The column headed v gives the number of liters which contains a one-sixth gram molecular weight of yttrium sulphate. That headed μ_v, the molecular conductivities at the volumes v.

Owing to the extreme dilutions, the values in determinations 13, 14 and 15 must be regarded as only roughly approximate.[1]

No. of determination.	v.	μ_v.
1	6.49	23.2
2	12.98	27.8
3	25.96	32.5
4	51.92	38.5
5	103.84	36.9
6	207.68	54.0
7	415.36	66.6
8	830.72	78.8
9	1661.44	102.6
10	3322.88	123.8
11	6645.76	152.6
12	13291.52	192.9
13	26583.00	240.7
14	53166.00	333.3
15	106332.00	601.1

JOHNS HOPKINS UNIVERSITY,
CHEMICAL LABORATORY.

THE PRACTICAL USE IN THE CHEMICAL LABORATORY OF THE ELECTRIC ARC OBTAINED FROM THE LOW POTENTIAL ALTERNATING CURRENT.

BY MILO S. WALKER.

In this paper the author does not claim to have discovered any action of the electric arc that is not already known to chemists, but he will attempt to give a few suggestions as to the way in which the highest temperature at our command can be obtained and used in every chemical laboratory supplied with a fixture for incandescent lighting. Many colleges and secondary schools are equipped with these fixtures, and others can obtain them at but little cost. There is no practical reason why they should not be used for some experi-

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[1] The material was purified and the original solution was made up by Jones; the conductivity determinations by Allen.

ments that cannot be performed with a Bunsen burner or a blow-pipe.

The alternating current of about 50 volts and 1 to 5 amperes, now generally used for incandescent lighting, furnishes an excellent arc for chemical experimentation. It is very efficient and can be handled easily and safely even by beginners in laboratory work.

The apparatus required consists of an iron or wooden stand, a screw clamp like those used for holding burettes, insulated copper wire, some electric light carbons, and a rheostat.

A piece of the so-called 10-ampere flexible lamp-cord may be connected at one end with a plug set into the socket intended for an incandescent lamp. The two parts at the other end of the twisted cord are left free. Besides the lamp-cord two pieces of ordinary insulated copper wire of medium size, (about No. 20) and 70 cm. long will be needed. These wires can be supplied and fixed as directed by any dealer in electrical supplies.

The rheostat is the most important part of the apparatus. Any commercial rheostat capable of carrying 12 amperes will answer all ordinary purposes. It may be necessary in large buildings where one transformer supplies 100 lights or more, to use an additional resistance. About 40 feet No. 13 German silver wire has been found very satisfactory in a building where 175 lights are used.

The adjustable rheostat is essential to the proper control of the current, and to prevent too high heating of the wires and consequent melting of the safety fuses when the arc is started. All the experiments are started with a high resistance which is lessened until the proper arc light is obtained.

The assorted carbons are $\frac{1}{4}$ to $\frac{1}{2}$ inch in diameter. The cored carbons are much better than the ordinary uncored ones. For obvious reasons "coppered" carbons should not be used. Carbons differ much in quality. Some contain considerable quantities of carbides and carbonates of metals. Those manufactured for use in optical projection usually contain less of these substances and give the best results.

The operator should not touch any metallic fixtures connected with the earth while he is working with the apparatus, as serious shocks may be received if the transformer is not properly insulated, a defect not uncommon in electrical work. It is better to work at a table on which there are no gas or water fixtures. Gas should be conducted to the table by a rubber tube connected with a gas-cock so far removed that there is no danger of touching any part of the apparatus and the gas-cock at the same time. There seems to be no other danger in working with the 50-volt alternating current. The students working in this laboratory sometimes receive shocks, but they generally consider shocks less disagreeable than accidental burns incident to work in general chemistry.

The electric arc can be used for the following purposes:

1. To show the effect of high temperatures upon difficultly fusible and "non volatile" substances.
2. For reduction of oxides of metal.
3. As a partial substitute for the blow-pipe in qualitative analysis.
4. For the synthetic preparation of some compounds of carbon from the elements.

There is a wide range of experiments showing the effect of the electric arc upon substances almost infusible by other means.

The apparatus can be arranged in a variety of ways depending upon the experiment. For general use it may be arranged thus: Fasten a cored carbon about 10 × 1 cm. in a vertical position so that the lower end is about 10 cm. from the top of the table. Connect by wrapping with insulated copper wire, stripped where contact is made with the carbon. Bore a conical shaped cavity 4 or 5 mm. deep in one end of another piece of cored carbon 4 × 1 cm. Fix into a wooden clamp and connect with insulated wire like the other carbon. On account of the heat an iron clamp with insulated handle is better for some experiments. Connect all wires so that the circuit will be completed if the carbons are allowed to touch each other. As the light is intense the eyes should be protected by a dark or blue glass. The longer carbon is stationary. The movements of the shorter carbon are controlled like a test tube and holder. The rheostat should be adjusted so that an arc $\frac{1}{16}$ to $\frac{1}{8}$ inch long can pass between the lower end of the longer carbon and the edge of the conical cavity in the smaller carbon. A small piece of the substance to be tested can be placed in the cavity. Most minerals and common metals fuse easily. A piece of quartz 2 × 1 mm. fuses completely. A piece the size of a pea fuses on one side.

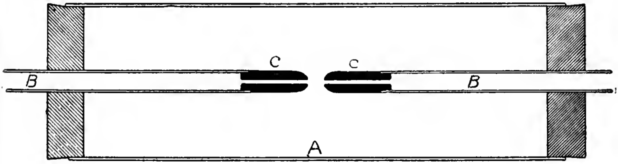
As this contribution is intended only to show how the electric arc can be obtained and used in a chemical laboratory, a description of experiments is omitted except where they show the method of working. The apparatus has not been in use long enough to show all its possible applications or even a small part of them. But it has been shown that many of the remarkable experiments of Moissan can be repeated on a smaller scale by this simple apparatus. His work suggests much that can be done in the ordinary chemical laboratory lighted by "incandescent lamps."

If iron, copper or manganese ores are placed in the conical cavity, the metals are formed containing small quantities of carbides.

For reduction of oxides it is better to substitute for the solid upper carbon, a carbon tube made by removing the core from the "cored carbon" 3 or 4 cm. long. This tube is then fastened into a brass tube of about the same outside diameter, but with a large bore. The joint can be made gas-tight by a paste of pure graphite and water. The brass tube is fixed and connected with wire like the upper carbon in the other apparatus. The end of the carbon tube should occupy the position of the lower end of the larger carbon as indicated above. Now a gas can be passed through the carbon tube so that it will strike a substance in the cavity of the small carbon, while the arc is passing. Hydrogen or coal gas may thus be conveniently used to prevent oxidation of metals while cooling, and seem to assist in reducing oxides and chlorides while the arc is passing. If carbon dioxide is used, carbon monoxide is formed with apparent increase in the reduction of oxides. In all these experiments a crater is gradually formed, and the arc generally passes from the inside of the carbon tube, thus giving maximum efficiency. When oxygen is used, the crater forms rapidly and enlarges to the full diameter of the carbon. Carbon monoxide is the main product of the quite rapid combustion, and acts as a powerful reducing agent upon an oxide in the cavity of the other carbon. By reducing with carbon monoxide in this way and cooling in hydrogen, quite pure manganese has been obtained from pure manganese dioxide. Similar experiments with oxides of other metals will be tried as soon as pure materials are secured.

Experiments with the electric arc are particularly interesting to the student, because he is able to get quick, sharp and definite results. The manipulation is so easy that young students can obtain beads of copper, iron or manganese after a few minutes practice. The electric arc has been used in this laboratory as an aid in qualitative analysis and a partial substitute for the blow-pipe, but the method will not be described at present because it has not been sufficiently tested. A special apparatus has been used in which the electric arc is inside a partially closed glass tube, and the volatile constituents of the substance to be treated are collected and partially separated on the sides of the glass. The results so far obtained are very satisfactory.

Some experiments on the synthesis of the hydrocarbons from their elements have been tried. Thus acetylene is easily prepared by the method of Berthelot[1] modified by Dewar.[2] The apparatus may be made as follows :



Fit a gas tight cork into each end of a straight lamp chimney. Pass brass tubes 1 cm. diameter and 15 cm. long through each cork. Into one end of each tube fix a tube of carbon 3 cm. long, prepared and fitted as shown under experiments for reduction of oxides. The joints of carbon and brass tubes should be gas tight.

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[1] Compt. Rend., **54**, 640.

[2] Proc. Roy. Soc., **29**, 188.

Fit the corks and brass tubes so that the ends of the carbon tubes are nearly together, test the apparatus for gas leakage, turn on the current and again test after the heat has reached a maximum. If air-tight pass a stream of hydrogen through the brass and carbon tubes. After the oxygen in the apparatus has been consumed it may be necessary to increase the current.

As there is nitrogen from the air in the apparatus small quantities of hydrocyanic acid are formed at first along with acetylene. The yield of acetylene is not large, but the method seems to be fully as satisfactory as the usual laboratory method of preparation of this gas from coal gas by burning it in an insufficient supply of air. This is recommended as a laboratory method for students. It is the only experiment showing synthesis of carbon and hydrogen from the elements, and the construction and manipulation of apparatus are not too difficult for any one who has had a few weeks' experience in a laboratory.

CHEMICAL LABORATORY, RACINE HIGH SCHOOL,
RACINE, WISCONSIN.

THE PREPARATION OF ALLYLENE, AND THE ACTION OF MAGNESIUM UPON ORGANIC COMPOUNDS.

BY EDWARD H. KEISER.

As described in a previous paper[1] metallic magnesium at a low red heat acts energetically upon the vapors of the alcohols. The metal glows and is converted into a black coherent mass. This black residue, when put into water, evolves a gas which consists chiefly of hydrogen and allylene. The evolution of gas becomes very rapid if a few drops of ammonium chloride solution are added to the water. The hydrogen and allylene can be readily separated from one another by conducting the mixed gases through a series of wash-bottles containing an ammoniacal solution of silver nitrate; the allylene is thereby converted into the insoluble silver allylide, AgC_3H_3, while the hydrogen passes through unchanged.

The best yield of allylene in the earlier experiments was

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[1] Journal of the Franklin Institute, January, 1895.

obtained from the magnesium that had been heated in the vapors of propyl or of allyl alcohols. Recent experiments have shown that a more advantageous method of preparing the hydrocarbon is to heat magnesium powder in the vapor of acetone and to decompose the black mass thus obtained with water. In the method of preparation now adopted a layer of magnesium powder is put into a thin-walled iron tube, which is as long as the combustion furnace that is to be subsequently employed for heating it. The iron tube is closed with asbestos stoppers, and through these stoppers glass tubes are passed ; so that the acetone vapor may be conducted in at one end of the iron tube and the gases formed during the reaction may be drawn off at the other end. The acetone is converted into vapor by boiling the liquid in a flask which is connected with one end of the iron tube containing the magnesium. After the air is driven out of the apparatus the iron tube is heated in the combustion furnace. At a low red heat the action begins ; the magnesium becomes red hot and finally the glowing extends throughout the entire mass of the metal. When this has taken place the contents of the tube are allowed to cool down in the acetone vapor ; the black mass is then removed from the tube and, since the moisture of the air acts upon it, it is best to preserve it in a tightly stoppered bottle. To obtain allylene from this residue it is only necessary to put it into a flask containing water to which a few drops of ammonium chloride solution have been added. The gas given off consists mainly of allylene and hydrogen ; the latter gas being obtained from the magnesium that has remained unacted upon.

In order to throw light upon the nature of the reaction that takes place when magnesium acts upon the alcohols and upon acetone, the gases that escaped from the tube while the magnesium was glowing, were collected in gasometers over water. These gases were analyzed and the results of the analyses are given in the following table :

Alcohols.	CO_2.	CO.	Unsaturated hydrocarbons.	Saturated hydrocarbons.	Hydrogen.
Methyl	0.8	0.6		19.7	78.9
Ethyl		0.4	14.0	11.1	74.5
Propyl		3.5	17.8	19.9	58.8
Isopropyl		0.2	12.2	15.4	72.2
Isobutyl		0.5	11.4	14.4	73.7
Amyl	1.0		20.4	22.3	56.3
Tertiary amyl (*a*)			24.3	17.5	58.2
" " (*b*)	0.2		22.4	17.9	59.3
Secondary octyl (*a*)		0.5	26.0	24.5	49.0
" " (*b*)	0.6	1.6	25.2	25.8	46.8

From the very small quantities of oxides of carbon in these gases it seems probable that the magnesium combines with the oxygen of the alcohols; hydrogen and hydrocarbons are thereby formed, and at the elevated temperature of the reaction a portion of the magnesium unites with the carbon and hydrogen of these compounds forming magnesium allylide. The black residue contains, besides the magnesium oxide and magnesium allylide, a quantity of free carbon. Attempts have been made to extract the allylide by means of solvents, but thus far it has not been possible to obtain a solvent for it. That magnesium allylide is present in the black mass is shown not only by the action of water upon it, whereby allylene is evolved which has been transformed into the silver, the mercury and the copper compounds which characterize this hydrocarbon; but also by the fact that it contains from 0.3 to 0.4 per cent. of hydrogen, as has been found by burning weighed quantities of it in a stream of oxygen. Further experiments have shown that when the magnesium is heated in an atmosphere containing no hydrogen, as, for instance, in carbon monoxide or carbon dioxide, and the residue thus obtained is decomposed by water, the gas evolved gives scarcely any precipitate with ammoniacal silver solution. The small traces of silver allylide thus obtained being formed from the hydrogen which is occluded in the metallic magnesium.

The black mass consisting of magnesium oxide, carbon, and magnesium allylide obtained by the glowing of magnesium in the vapors of acetone and of the alcohols was in each case treated with water, and the gases evolved were conducted through an ammoniacal solution of silver nitrate. The silver precipitates were removed by filtration and, after washing and drying, were analyzed. The following table contains the results of the analyses :

Magnesium allylide from		Analyses of silver precipitates.		
		Wt. taken.	Wt. AgCl found.	Per cent. Ag.
Acetone		0.1617	0.1577	73.40
Methyl alcohol		0.1292	0.1270	73.97
Ethyl “	(*a*)	0.1163	0.11365	73.53
	(*b*)	0.0979	0.09615	73.89
Propyl “		0.15605	0.1522	73.39
Isopropyl “	(*a*)	0.27308	0.26802	73.58
	(*b*)	0.10244	0.10114	74.31
Allyl “	(*a*)	0.16705	0.1620	72.97
	(*b*)	0.17185	0.16735	73.27
Isobutyl “		0.1301	0.1289	74.56
Amyl “	(*a*)	0.18156	0.17933	74.34
	(*b*)	0.1365	6.13767	75.90
Tertiary amyl “		0.08509	0.08374	74.07
Calculated for AgC_3H_3				73.45

The comparatively close agreement of these results with the theoretical value for silver in silver allylide indicates that the silver precipitates were most probably pure compounds. The copper allylide was made by conducting the gases from the evolution flask through an ammoniacal solution of cuprous chloride. The greenish yellow precipitate was filtered and washed thoroughly with water and, after drying in desiccators, was analyzed.

Found 62.1 and 62.2 per cent. of Cu.
Calculated for CuC_3H_3, 61.98 per cent.

The mercury allylide has also been prepared. When first formed it is a white flocculent precipitate. It was purified by dissolving it in boiling alcohol. On cooling it crystallized out in the form of slender needles. These crystals possessed the properties of the mercuric allylide described by Kutscheroff.[1]

Experiments have also been made to determine the yield of allylene obtained by this method of preparation. If it be assumed that the magnesium acts upon the acetone vapor according to the following equation :

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[1] Ber. d. chem. Ges., **17**, 26.

$$2C_3H_6O + 3Mg = 2MgO + Mg(C_3H_3)_2 + 6H.$$

then the residual magnesium mass should contain 3.3 per cent. of hydrogen. Determinations of hydrogen by combustion gave on an average 0.37 per cent.; so that the yield would be about 0.1 of the theoretical amount. Further, 10 grams of the magnesium residue gave about 0.7 gram silver precipitate.

Further experiments with the allylene are in progress. The gas is readily absorbed by concentrated sulphuric acid. It is probable that a sulphonic acid is thus formed. The sulphuric acid, after having absorbed a large volume of the gas, was diluted with water and neutralized with barium carbonate. After filtration the clear solution on evaporation gave a deposit of a crystalline barium salt. The composition of this compound is now being determined.

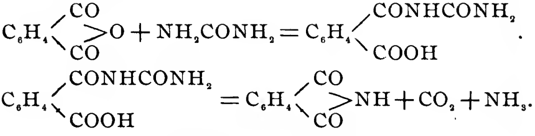
In conclusion, I desire to express my thanks to Miss Mary B. Breed and Miss Lucy Francisco for their careful work in making the analyses and in assisting me in the experiments described in this paper.

BRYN MAWR COLLEGE CHEMICAL LABORATORY,
March, 1896.

THE ACTION OF UREA AND SULPHOCARBANILIDE ON CERTAIN ACID ANHYDRIDES.

By FREDERICK L. DUNLAP.

In 1882, Piutti,[1] in an article on "urea and thiourea derivatives of phthalic acid," showed that phthaluric acid was the product of the reaction of urea on phthalic anhydride when equal molecules were heated to 110–120°. At a higher temperature he found that the phthaluric acid decomposed into phthalimide with the liberation of carbon dioxide and ammonia. The two stages in the formation of the imide are shown in the following equations:



$$C_6H_4{<}\begin{matrix}CO\\CO\end{matrix}{>}O + NH_2CONH_2 = C_6H_4{<}\begin{matrix}CONHCONH_2\\COOH\end{matrix}.$$

$$C_6H_4{<}\begin{matrix}CONHCONH_2\\COOH\end{matrix} = C_6H_4{<}\begin{matrix}CO\\CO\end{matrix}{>}NH + CO_2 + NH_3.$$

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[1] Ann. Chem. (Liebig), **214**, 20.

I have found that the reaction passes directly through both stages to the formation of phthalimide if the temperature of the mixture of phthalic anhydride and urea be raised at once to 150°, the imide thus obtained being nearly pure.

Phthalimide.—Ten grams of urea (1 molecule) and 25 grams of phthalic anhydride (1 molecule) were heated in a half liter flask, in an oil-bath, until the bath showed a temperature of 150°. At this temperature the contents of the flask became entirely liquid, and ammonia and carbon dioxide were evolved. After heating at this temperature for several minutes, the contents of the flask suddenly solidified. The solid contents of the flask were then treated with boiling water, to free the phthalimide from any unchanged urea or phthalic anhydride. The phthalimide thus prepared was perfectly white and melted without further purification at 227°. When pure, phthalimide melts at 229° (uncorrected) and upon analysis gave the following results:

0.2058 gram substance gave 0.4915 gram CO_2 and 0.0656 gram H_2O.

	Calculated for $C_8H_5O_2N$.	Found.
C	65.31	65.12
H	3.40	3.54

Obviously, this method is a good one for making phthalimide, as the product obtained is practically pure, and only a few minutes are necessary for its preparation. A 90 per cent. yield was obtained.

In hopes that a new and general method for the preparation of imides could be obtained by the action of urea upon anhydrides, this action of urea was studied further upon dichlormaleïc anhydride, dibrommaleïc anhydride and succinic anhydride.

Dichlormaleïnuric Acid.—When a mixture of equal molecules of dichlormalëic anhydride was heated in a bath to 70°, the mixture began to melt. When the temperature of the bath was raised to 90–95° and held constant for about five minutes the liquid mixture of anhydride and urea solidified. This temperature of 90–95° was maintained for twenty minutes. The solid product thus obtained was washed with a small quantity of cold water and then recrystallized from alcohol. It recrystallized from alcohol in transparent prisms having truncated ends, and had a melting-point of 158°. When this pure product—dichlormaleïnuric acid—melts, it gives off gas and again solidifies in the melting-point tube, remelting at 179°, the melting-point of dichlormaleïnimide. It is very sparingly soluble in all the ordinary solvents except water, in which it dissolves when heated. Nearly a 50 per cent. yield was obtained.

0.1917 gram substance gave 0.2415 gram AgCl.

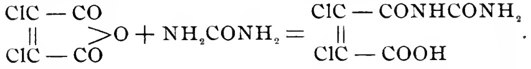
	Calculated for $C_5H_4O_4N_2Cl_2$.	Found.
Cl	31.28	31.15

Dichlormaleïnimide.—Five grams of dichlormaleïc anhydride and 3 grams of urea (equal molecules) were heated in a flask, the temperature of the oil-bath being raised to 110–115°. The contents of the flask were liquid at this temperature, and ammonia and carbon dioxide were freely evolved. After heating for fifteen minutes at this temperature the contents of the flask were allowed to cool, and the solid product washed with a small quantity of cold water. One gram of dichlormaleïnimide remained after this washing. When pure, the dichlormaleïnimide melted at 179°, and upon analysis gave the following results :

0.2136 gram substance gave 0.3700 gram AgCl.

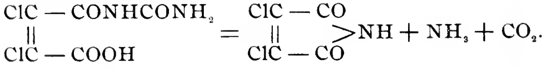
	Calculated for $C_4Cl_2O_2NH$.	Found.
Cl	42.78	42.83

We have here, in the formation of dichlormaleïnimide from dichlormaleïc anhydride and urea, a reaction exactly similar to the one in which phthalimide is formed. The first stage of the reaction consists first in the addition of urea to dichlormaleïc anhydride to produce dichlormaleïnuric acid.



$$\begin{array}{l}\mathrm{ClC-CO}\\ \Vert \qquad >\mathrm{O}\\ \mathrm{ClC-CO}\end{array} + \mathrm{NH_2CONH_2} = \begin{array}{l}\mathrm{ClC-CONHCONH_2}\\ \Vert\\ \mathrm{ClC-COOH}\end{array}.$$

This dichlormaleïnuric acid, upon being heated to its melting-point, loses ammonia and carbon dioxide with the formation of dichlormaleïnimide,



$$\begin{array}{l}\mathrm{ClC-CONHCONH_2}\\ \Vert\\ \mathrm{ClC-COOH}\end{array} = \begin{array}{l}\mathrm{ClC-CO}\\ \Vert \qquad >\mathrm{NH}\\ \mathrm{ClC-CO}\end{array} + \mathrm{NH_3} + \mathrm{CO_2}.$$

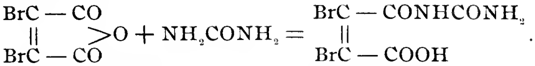
Dibrommaleïnuric Acid.—A mixture of equal molecules of urea and dibrommaleïc anhydride were heated in an oil-bath. When the bath registered 90° the contents of the flask began to melt. The temperature was raised to 100–105°, at which point it was kept until the liquid contents of the flask had become solid again. After cooling, this solid product was washed with water and purified by recrystallization from alcohol. When pure it is perfectly white and melts at 191° with gas evolution. After melting, the liquid contents of the tube resolidified and again melted at 221°, which is 4° low for the melting-point of dibrommaleïnimide. This low melting-point is explained by the fact that the dibrommaleïnuric acid, upon melting, does not entirely break down into ammonia, carbon dioxide, and dibrommaleïnimide, as is seen by the darkening of the contents of the melting-point tube. The presence of impurities would naturally tend to lower the melting-point of the dibrommaleïnimide. Nearly a 50 per cent. yield of dibrommaleïnuric acid was obtained. If crystallized in bunches of small prisms having doubly truncated ends.

0.2117 gram substance gave 0.2512 gram AgBr.

	Calculated for $C_6H_4Br_2N_2O_4$.	Found.
Br	50.63	50.51

I found this acid to be readily soluble in acetone ; tolerably soluble in chloroform and ether ; insoluble in ligroïn, benzol, carbon bisulphide and water.

Dibrommaleïnuric acid corresponds exactly to dichlormaleïnuric acid, being formed by the addition of urea and dibrommaleïc anhydride.



$$\begin{array}{l}\mathrm{BrC-CO}\\ \| \qquad >\mathrm{O}\\ \mathrm{BrC-CO}\end{array} + \mathrm{NH_2CONH_2} = \begin{array}{l}\mathrm{BrC-CONHCONH_2}\\ \|\\ \mathrm{BrC-COOH}\end{array}.$$

Dibrommaleïnimide.—When equal molecules of dibrommaleïc anhydride and urea were heated up gradually to 135°, the mass turned very dark in color and ammonia and carbon dioxide were evolved. After the evolution of gas had ceased, the then solid contents of the flask were extracted with hot alcohol, filtered from the insoluble portion, treated with boneblack, and then evaporated to small bulk, and the dibrommaleïnimide allowed to crystallize out. It was further purified by crystallization from alcohol. No analysis of this dibrommaleïnimide was made, because its crystalline form, melting-point and method of formation were definite enough for identification. A twenty-four per cent. yield was obtained.

The formation of dibrommaleïnimide from dibrommaleïc anhydride and urea is exactly similar to the formation of dichlormaleïnimide when urea and dichlormaleïc anhydride are used, therefore no new equations are necessary to represent this imide formation.

Succinimide.—Ten grams of succinic anhydride and 6 grams of urea were heated in a distilling-flask. As the temperature rose the contents of the flask melted and, finally, began to darken, ammonia and carbon dioxide being freely evolved. As the temperature was raised a slightly yellowish distillate, boiling above 280°, was obtained. This distillate immediately solidified and was further purified by recrystallization from anhydrous acetone. It had a melting-point of 124° and was perfectly white. A 40 per cent. yield of succinimide was obtained. Upon analysis it gave the following result:

0.2099 gram substance gave 0.3751 gram CO_2 and 0.1019 gram H_2O.

	Calculated for $C_4H_5O_2N$.	Found.
C	48.49	48.73
H	5.05	5.39

Pike, who first made succinuric acid,[1] states that it melts with complete decomposition. In hopes of finding succinimide as one of these products of decomposition, succinic acid was prepared according to Pike's method, and upon purification was found to have a melting-point of 211–211°.5, and not 203–205°, as Pike gives it. When pure succinuric acid was subjected to distillation it acted as did the mixture of succinic anhydride and urea. The succinuric acid melted with the evolution of ammonia and carbon dioxide, and turned quite dark. A distillate, boiling above 280°, was obtained, which was easily identified as succinimide.

Having obtained succinimide from succinuric acid, this shows us how the succinimide is formed by the action of urea upon succinic anhydride. When this mixture is heated succinuric

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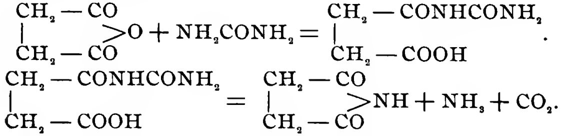
[1] Ber. d. chem. Ges., 6, 1104.

acid is first formed. This breaks down at a higher temperature with succinimide, carbon dioxide, and ammonia as its products. The formation of succinimide is represented by the following equations :

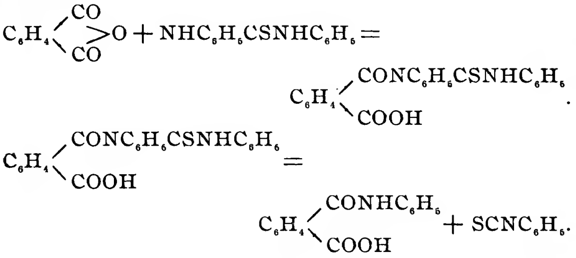


$$\left.\begin{array}{l}CH_2-CO\\ \vert\\ CH_2-CO\end{array}\right>O + NH_2CONH_2 = \begin{array}{l}CH_2-CONHCONH_2\\ \vert\\ CH_2-COOH\end{array}.$$

$$\begin{array}{l}CH_2-CONHCONH_2\\ \vert\\ CH_2-COOH\end{array} = \left.\begin{array}{l}CH_2-CO\\ \vert\\ CH_2-CO\end{array}\right>NH + NH_3 + CO_2.$$

Action of Sulphocarbanilide on Phthalic Anhydride.

The action of a substituted urea, sulphocarbanilide, on phthalic anhydride was next studied. It was hoped that a diphenylthiophthaluric acid might be obtained in this way, and the evidence goes to show that it was formed, but that decomposition ensued immediately at the temperature of the reaction. I found as product of the reaction at 125–130°, phthalanilic acid and phenyl mustard oil. The formation of the phthalanilic acid can best be explained by the following equations :



$$C_6H_4\left<\begin{array}{l}CO\\ CO\end{array}\right>O + NHC_6H_5CSNHC_6H_5 = C_6H_4\left<\begin{array}{l}CONC_6H_5CSNHC_6H_5\\ COOH\end{array}\right..$$

$$C_6H_4\left<\begin{array}{l}CONC_6H_6CSNHC_6H_6\\ COOH\end{array}\right. = C_6H_4\left<\begin{array}{l}CONHC_6H_5\\ COOH\end{array}\right. + SCNC_6H_5.$$

At 170–175° phthalanil, carbonic oxysulphide, and aniline are the products.

Phthalanilic Acid.—Five grams of phthalic anhydride and 7.7 grams of sulphocarbanilide, equal molecules, were heated in an oil-bath until the bath showed a temperature of 125–130°. The contents of the flask liquified, and, after a few minutes heating, began to solidify. The heating was carried on at 125–130° for twenty minutes more. During this heating a very small amount of carbonic oxysulphide was evolved.

The solid product was then washed with a small amount of cold alcohol and the product thus obtained purified by recrystallization from alcohol. The pure product melted at 169–169°.5, and then gave off gas, resolidifying in the melting-point tube, and remelting at 204°, the melting-point of phthalanil. The first alcoholic washings contained quantities of phenyl mustard oil, which was identified by its boiling-point and other properties. After the first treatment with alcohol the product was perfectly white and nearly pure. A 60 per cent. yield was obtained. The phthalanilic acid so prepared crystallized from alcohol in small prisms, and upon analysis gave the following results:

0.2090 gram substance gave 0.5366 gram CO_2 and 0.0865 gram H_2O.

	Calculated for $C_{14}H_{11}O_3N$.	Found.
C	69.71	70.03
H	4.56	4.60

Phthalanilic acid is insoluble in benzol and chloroform; very sparingly soluble in acetone; insoluble in ligroïn and ether; practically insoluble in cold water, but slightly soluble in boiling water, from which it separates upon cooling.

Phthalanil.—Five grams of phthalic anhydride and 7.7 grams of sulphocarbanilide were heated upon an oil-bath to 170–175°. This mixture at first melted, resolidified and remelted with the evolution of carbonic oxysulphide. After heating at 170–175° for ten or fifteen minutes the gas evolution had practically ceased. After cooling, the product was washed with cold alcohol and practically pure phthalanil was obtained. The yield was 93 per cent.

Phthalanil crystallizes from alcohol in long slender prisms and melts at 204°. Laurent and Gerhardt[1] give its melting-point at 203°, and Döbner as 205°.[2]

The first alcoholic washings contain aniline in considerable amount. Upon analysis, phthalanil gave the following results:

0.2464 gram substance gave 0.6790 gram CO_2, and 0.0952 gram H_2O.

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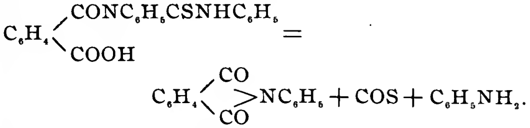
[1] Jsb., 1847-48, 605.

[2] Ann. Chem. (Liebig), **210**, 267.

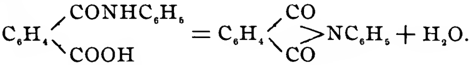
	Calculated for $C_{14}H_9O_2N$.	Found.
C	75.34	75.16
H	4.04	4.29

Phthalanil is formed in two ways in this reaction, one of which doubtless depends upon the formation of an unstable diphenylthiophthaluric acid, which breaks down at the temperature of the reaction, as follows :



$$C_6H_4\left\langle\begin{matrix}CONC_6H_5CSNHC_6H_5\\COOH\end{matrix}\right. = C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle NC_6H_5 + COS + C_6H_5NH_2.$$

The second reaction in which phthalanil is formed depends upon the production of phthalanilic acid by the action of the phthalic anhydride on sulphocarbanilide. The phthalanilic acid so formed breaks down, upon heating, into phthalanil and water.



$$C_6H_4\left\langle\begin{matrix}CONHC_6H_5\\COOH\end{matrix}\right. = C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle NC_6H_5 + H_2O.$$

The phthalanil seems to be formed mostly according to the equation in which carbonic oxysulphide and aniline are by-products.

Laurent and Gerhart[1] first obtained phthalanilic acid by the action of ammonia on phthalanil. They give its melting-point at 192°, at which temperature phthalanil is formed. Zincke and Cooksey[2] obtained phthalanilic acid by the action of alkalies on phthalanil. They found its melting-point to be 158°, at which temperature the phthalanilic acid decomposed with the formation of phthalanil.

Recently, F. Thorp[3] obtained phthalanilic acid by the action of hydroxylamine upon orthobenzoylbenzoic acid. Thorp also gives its melting-point as 191–193°, at which temperature he too finds that phthalanilic acid is converted into phthalanil. Phthalanilic acid made by the interaction of phthalic anhydride and sulphocarbanilide, has, according to my observation, a melting-point of 169–169°.5, at which temperature

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[1] Jsb., 1847-48, 605.

[2] Ann. Chem. (Liebig), **255**, 375.

[3] Ber. d. chem. Ges., **26**, 1262.

water vapor is given off, the contents of the melting-point tube resolidifying and remelting at 204°, the melting-point of phthalanil.

I have repeated the work of Laurent and Gerhardt, and the melting-point of phthalanilic acid, prepared according to this method, I find not to be 192° but 169–169°.5. Phthalanilic acid was also prepared according to Anschütz's[1] method, by dissolving molecular quantities of aniline and phthalic anhydride in dry chloroform and allowing the mixture to stand, phthalanilic acid separating in a short time from this solution. Prepared according to this method, I find that phthalanilic acid has the melting-point 169–169°.5.

Action of Sulphocarbanilide on Succinic Anhydride.

Succinanil.—Five grams of succinic anhydride and 11.4 grams of sulphocarbanilide (equal molecules) were heated in an oil-bath until the bath registered a temperature of 150–155°. The contents of the flask liquified, and a regular evolution of carbonic oxysulphide took place. After heating at this temperature for 30 to 35 minutes, the contents of the flask had become practically solid. This solid product was then washed with cold alcohol to free it from the aniline which was formed as a by-product. It was then heated with boiling alcohol, and the difficultly soluble portion filtered off. Upon cooling, succinanil separated from the filtrate. A yield of 90 per cent. of succinanil was obtained. The difficultly soluble portion had a melting-point of 226°. When pure, the succinanil melted at 150°, which agrees with the melting-point obtained by Hübner.[2] Upon analysis it gave the following results:

0.2043 gram substance gave 0.5156 gram CO_2 and 0.1031 gram H_2O.

	Calculated for $C_{10}H_9O_2N$.	Found.
C	68.58	68.84
H	5.14	5.60

When succinic anhydride and sulphocarbanilide reacts at 130–135°, succinanil and the compound melting at 226° are formed, phenyl mustard oil being formed at the same time. At this temperature, the yield of succinanil was small. If,

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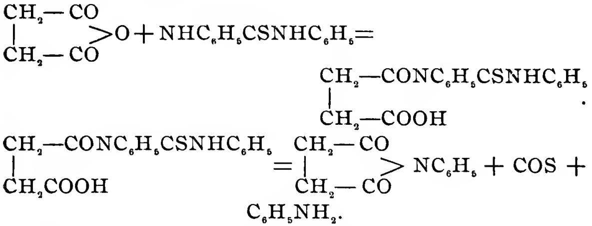
[1] Ber. d. chem. Ges., **20**, 3214.

[2] Ann. Chem. (Liebig), **209**, 373.

however, the reaction is carried on at 150–155°, succinanil, carbonic oxysulphide, and aniline are practically the sole products. The formation of succinanil at this temperature is doubtless parallel to the formation of phthalanil from phthalic anhydride and sulphocarbanilide. The formation of succinanil may be explained by the following equations :



$$\begin{array}{l}CH_2-CO\\ |\qquad\quad >O\\ CH_2-CO\end{array} + NHC_6H_5CSNHC_6H_5 = \begin{array}{l}CH_2-CONC_6H_5CSNHC_6H_5\\ |\\ CH_2-COOH\end{array}.$$

$$\begin{array}{l}CH_2-CONC_6H_5CSNHC_6H_5\\ |\\ CH_2COOH\end{array} = \begin{array}{l}CH_2-CO\\ |\qquad\quad >NC_6H_5\\ CH_2-CO\end{array} + COS + C_6H_5NH_2.$$

Succinanilic acid has not as yet been isolated, and I have been as yet unable to identify the compound melting at 226°.

I shall study further the action of urea, sulphourea, sulphocarbanilide, and other substituted ureas upon acid anhydrides.

THE KENT CHEMICAL LABORATORY OF YALE UNIVERSITY.

REVIEWS.

ELECTROCHEMIE. IHRE GESCHICHTE UND LEHRE. BY W. OSTWALD. Large 8vo. 1151 pp. Veit and Comp. Leipzig: 1895. Price, 28 marks.

The recent completion of Ostwald's large work upon Electrochemistry adds an important contribution to scientific literature, for in it we find combined the historical studies and much of the independent research of a man whose fruitful scientific activity has been largely in electrochemical domain. The general plan pursued in the construction of the work is most admirable, for it aims at giving an account of the development of one particular branch of science as a matter of history, and the presentation is made vivid by the incorporation of copious extracts from the original papers in which the results of investigation have appeared. The treatment is therefore a comprehensive one and makes a large book.

The opening chapter is concerned with the slight chemical effects produced by frictional electricity, such as the decomposition of water and of metallic oxides and the formation of nitric acid in moist air. Observations of this kind were made in the latter half of the eighteenth century. This general introduction leads to the "animal electricity" of Galvani (1791), and the construction by Volta in 1800 of the voltaic pile; and we then find treated the development of electrometry up to the invention of Coulomb's tension balance, the first proposition of a "chemical theory" of electrical action by Ritter, the experimental study of electrolytic decompositions and the discovery of the alkali metals, and the electrochemical theories of Davy and Berzelius. The electromagnetism of Oersted (1820), the thermoelectric currents of Seebeck (1821), and Ohm's law next appear upon the program; and they are followed in turn by the long conflict between the contact theory and the chemical theory of the pile, and by the brilliant experimental researches of Faraday. The next strikingly important feature of the history is the appearance of the energy method in physical science about the middle of this century, with the accompanying discoveries of Joule, W. Thomson and Helmholtz; and the reader then passes to the systematic progress which was slowly made in the study of the electrical conductivities of solutions, and in that of the electromotive forces of voltaic combinations. The hypothesis of an electrolytic dissociation and the application made of it in the development of a theory of the cell close the work. These matters are all treated in a clear and vigorous way, the comment made upon the details of historical development are everywhere acute and lucid, (a delightful illustration of this is the review of Kekulé's work upon the electrolysis of the salts of organic acids, p. 1052), and the flowing style of the writing makes the book readable to a degree. This latter characteristic is not, however, always present in the interspersed quotations, as is amusingly apparent in a passage on p. 418, where we meet an astonishing sentence of one hundred and twenty-six words.

Now this book, notwithstanding its many excellent features, presents some serious defects, and the most prominent of these is a lack of balance in the treatment of material. When at the outset all possible details seem drawn into the text and the literature is abstracted with a completeness nothing less than remarkable the reader is caused to anticipate a most satisfying thoroughness of historical exposition in what is to follow. And this anticipation is strengthened by the appearance of no less than forty-two very large pages (Chapter VIII) devoted to the divining rod and similar affairs. After such preparation it is disappointing to find the immensely instructive and important work of Willard Gibbs represented by little more than a single extract from Gibbs' paper, with entire omission of the mathematical formation of his theory; and to find a little later the classical papers of Helmholtz of about the same date treated in a similarly superficial manner. One might think that a detailed consideration of the progress due to these two men should seem fully as important as a like treatment of galvanic cures, and of the literature of the divining rod.

And, again, it is constantly insisted upon throughout the text that the osmotic pressure theory of the voltaic cell is as quantitative theory the one thing to which the entire discussion leads, for the sake of which even some of Helmholtz's exact work is omitted (p. 1005), and that it is to be regarded as the fit culmination of a century of effort. We are told plainly (p. 1140) that this "Complete theory of the galvanic phenomena . . . corresponds everywhere to the facts, and in the entire range of observations in this much cultivated domain has left almost nowhere an essential residue." In view of the fact that the osmotic theory holds only qualitatively for any practical cell in ordinary use it seems unfortunate that the reader should be referred to another book (p. 1140) for its detailed exposition and therefore for the quantitative confirmation upon which our author's confidence must rest. The present osmotic theory is beyond question a great step in advance, but it is certainly not the ultimate achievement which Ostwald claims it to be.

Objection might also be made to Ostwald's attitude towards the energy doctrine, for the reason that his conception of the substantiality of energy falls so far short of the wider view that the energy doctrine is in essence a scientific *method*, but his position has already been attacked in the current literature with such vigor that this passing reference is sufficient. The book as a whole is an able production and is sure to be of great service; in most respects it is an authoritative work, and no one who takes electrochemical matters at all seriously can afford to be without it.

J. E. TREVOR.

THE DILUTION LAW.

It is a well known fact that the dissociation of electrolytes in solution increases with the dilution. If an expression could be found for the relation between dissociation and dilution, this would enable us to calculate the amount of dissociation of any substance, at any dilution, in a given solvent, knowing the dissociation of that substance at any other dilution in the same solvent. The importance attached to the discovery of such a relation is self-evident.

The dilution law of Ostwald[1] is an attempt to state just this relation. That the significance of the law may be seen, it is necessary to follow the more important steps which led to its

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[1] Ztschr. phys. Chem., 2, 36 and 278.

deduction. If water solutions of electrolytes are dissociated, and obey the gas laws, then the laws which hold for *dissociating* gases must apply to solutions. If a gas molecule dissociates into two molecules, and the temperature is constant and neither product of the decomposition is present in excess, the following equation holds good :[1]

$$\frac{p}{p_1^2} = C \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{I.}$$

This means that the pressure p, of the undecomposed parts, bears a constant relation to the square of the pressure of the decomposition products p_1. The case with solutions, which is strictly analogous to the above process of dissociation in a gas, is that of a binary electrolyte dissociating into an equal number of anions and cations.

At a given temperature the pressure of a gas is proportional to its mass u, and inversely proportional to its volume v. For the gas pressure we can substitute the osmotic pressure of solutions, which, for the same number of molecules in a given space, is equal to it. For solutions we have then p proportional to $\frac{u}{v}$, and p_1 to $\frac{u_1}{v}$. Substituting these values for p and p_1 in I, we have

$$\frac{uv}{u_1^2} = C \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{II.}$$

The amount of dissociation in a solution, represented by u_1, is the ratio between the conductivity when the dissociation is complete, $\mu\infty$, and the conductivity at any given dilution, μv.

$$u_1 = \frac{\mu v}{\mu\infty}.$$

The non-dissociated portion of the electrolyte in the solution is represented by u.

$$u = 1 - \frac{\mu v}{\mu\infty}.$$

Substituting these values of u and u_1, for u and u_1, in equation II, we obtain,

$$\frac{\mu\infty\,(\mu\infty - \mu v)}{\mu v^2}\, v = C \ldots\ldots\ldots\ldots\ldots \text{III.}$$

This last equation can be simplified by expressing $\frac{\mu v}{\mu\infty}$ by α, whence it becomes

$$\frac{\alpha^2}{(1-\alpha)v} = C,$$

which is the Ostwald dilution law. In this expression, α is

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[1] Ostwald's Lehrb., 1st Edition, 2, 723.

the amount of dissociation in any given solution of an electrolyte; v is the volume in liters of that solution, which contains a gram molecular (or gram equivalent) weight of the electrolyte, and C is a constant.

Having deduced the law theoretically, it remained to apply it to the experimental facts. This was done by Ostwald in his extensive study of the conductivity of solutions of organic acids,[1] involving between two and three hundred compounds. A few of Ostwald's results are given in the following table.

μv is the molecular conductivity.

$\frac{\mu v}{\mu \infty} = \alpha$ is the amount of the dissociation in percentage.

Acetic Acid.

v.	μv.	$\frac{\mu v}{\mu \infty}$	C.
8	4.34	1.193	0.00180
16	5.10	1.673	0.00179
32	8.65	2.38	0.00182
64	12.09	3.33	0.00179
128	16.99	4.68	0.00179
256	23.82	6.56	0.00180
512	32.20	9.14	0.00180
1024	46.00	12.66	0.00177

$\mu \infty = 364.$

o-Amidobenzoic Acid.

v.	μv.	$\frac{\mu v}{\mu \infty}$	C.
64	7.21	2.03	0.00066
128	10.73	3.02	0.00074
256	16.11	4.54	0.00084
512	23.52	6.62	0.00092
1024	33.51	9.44	0.00096

$\mu \infty = 355.$

The values obtained for C, for most of the acids studied, approached a constant, as is seen in the results for acetic acid; yet, deviations of very considerable dimensions are frequently to be found, as is observed in the case of *o*-amidobenzoic acid. It may, however, be said in general, that the law holds approximately for the organic acids, which, in comparison with the inorganic acids, bases and salts, are weakly dissociated compounds.

The dilution law acquires new interest from this work of Ostwald, in that the constant is a characteristic of the compound in question; the numerical value of this constant giving us an insight into many of the properties of the acid. For details on this point the reader must consult the original papers.

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[1] Ztschr. phys. Chem., 3, 170, 241, 369.

The work of Bredig[1] on the conductivity of ammonia, the amines and other weakly dissociated bases, shows the applicability of Ostwald's formula to somewhat more than thirty of these compounds. A few examples are given below:

Ammonia.		*Trimethylamine.*		*Piperidine.*	
v.	*C.*	*v.*	*C.*	*v.*	*C.*
8	0.0023	8	0.0069	8	0.157
32	0.0023	32	0.0075	32	0.162
64	0.0023	64	0.0076	64	0.150
256	0.0024	256	0.0074	256	0.152

The values for C, for each compound, are rather nearer a constant in the work of Bredig on the weak bases, than in that of Ostwald on the organic acids.

While the dilution law as deduced by Ostwald holds thus fairly well for weakly dissociated compounds, it does not apply at all satisfactorily to the strongly dissociated electrolytes—the strong acids and bases, and salts of these acids and bases. A satisfactory reason for this failure on the part of the law, has not yet been furnished.

A very interesting contribution to this subject came recently from Rudolphi.[2] A study of the conductivity of solutions of silver nitrate, of varying concentrations, brought out the following suggestive relations. Representing again by v, the volume of the solution in liters, which contains a gram molecular weight of the salt, and by C, the constant in the Ostwald equation, the following values were found:

When $v = 16$, $C = 0.26$
" $v = 64$, $C = 0.13$
" $v = 256$, $C = 0.065$

At a glance, these figures will show that a constant would be obtained for C, if the individual values of C were multiplied by the square root of v, in each case thus:

$$0.26 \times \sqrt{16} = 0.13 \times \sqrt{64} = 0.65 \times \sqrt{256}.$$

We must substitute then for v in the Ostwald expression the square root of v, when the equation becomes

$$\frac{\alpha^2}{(1 - \alpha)\sqrt{v}} = C.$$

To show how well the facts fit in with this formula in this particular case, some of Rudolphi's figures for silver nitrate at different temperatures are given. The letters v and C have the same significance as in Ostwald's results.

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[1] Ztschr. phys. Chem., **13**, 289.

[2] Ztschr. phys. Chem., **17**, 385.

T = 25°.		T = 40°.		T = 60°.	
v.	*C.*	*v.*	*C.*	*v.*	*C.*
16	1.00	16	1.03	16	1.11
32	1.08	32	1.18	32	1.15
64	0.96	64	1.07	64	1.14
128	1.03	128	1.05	128	1.16
256	1.05	256	1.19	256	1.16
512	1.07	512	1.27	512	1.15

This table shows that the value of C is nearly a constant, depending slightly, if at all, upon the volume and the temperature.

Rudolphi applied his equation to between fifty and sixty strongly dissociated compounds, calculating in each case the value of α from the conductivity measurements of Kohlrausch, Ostwald and others. The values found for C for the different dilutions of any one substance, approached a constant. A few results will suffice to illustrate the point.

Hydrochloric Acid.		*Potassium Sulphite.*		*Potassium Acetate.*	
v.	*C.*	*v.*	*C.*	*v.*	*C.*
2	4.36	2	0.453	2	1.24
4	4.45	8	0.454	100	1.19
8	5.13	32	0.455	1000	1.18
16	5.13	128	0.544	10000	1.03

Deviations from a constant value for C are not wanting; yet, Rudolphi's equation gives for most of the strongly dissociated substances as near a constant for the different dilutions as Ostwald's equation, when applied to the less dissociated organic acids.

Rudolphi has shown further that this equation holds for different temperatures:

Magnesium Sulphate.

T = 18°.		T = 50°.3.		T = 99°.4.	
v.	*C.*	*v.*	*C.*	*v.*	*C.*
4	0.096	4	0.073	4	0.058
16	0.103	16	0.078	16	0.060
64	0.124	64	0.091	64	0.070

The *numerical value* of the constant for any given compound depends, however, somewhat upon the temperature.

We thus seem to have two expressions for the relation between the dissociation of electrolytes and the dilution of the solutions; first, that of Ostwald,

$$\frac{\alpha^2}{(1-\alpha)v} = C,$$

applying to the weakly dissociated electrolytes; second, that of Rudolphi,

$$\frac{\alpha^2}{(1-\alpha)\sqrt{v}} = C,$$

holding for those substances which are most strongly dissociated. The physical significance of the $\sqrt{v}$ in Rudolphi's equation, instead of v in that of Oswald, is at present unexplained.

Rudolphi's expression has undergone still further modification very recently in the hands of van't Hoff.[1] If in Ostwald's equation, we write instead of α, its value $\frac{\mu v}{\mu\infty}$, the equation becomes,

$$\frac{\left(\frac{\mu v}{\mu\infty}\right)^2}{\left(1-\frac{\mu v}{\mu\infty}\right)v} = \text{const.}$$

$\frac{\mu v}{v\mu\infty}$ is the concentration of the ions $= C_i$.

$\frac{1-\frac{\mu v}{\mu\infty}}{v}$ is the concentration of undecomposed salt $= C_m$.

If Rudolphi's expression is changed to

$$\frac{\left(\frac{\mu v}{\mu\infty}\right)^{\frac{3}{2}}}{\left(1-\frac{\mu v}{\mu\infty}\right)\sqrt{v}} = \text{const., or } \frac{\left(\frac{\mu v}{\mu\infty}\right)^3}{\left(1-\frac{\mu v}{\mu\infty}\right)^2 v} = \text{const.}$$

and we substitute in the last form C_i and C_m for their respective values, we obtain the very simple relation:

$$\frac{C_i^3}{C_m^2} = \text{const.}$$

The physical meaning of this expression is as little known as that of Rudolphi's expression. Van't Hoff, however, calls attention to the greater simplicity of his equation, and shows by a number of examples, that it agrees a little more nearly with the facts, for strongly dissociated compounds than does the equation of Rudolphi.

Kohlrausch[2] has still further simplified, algebraically, the last very simple expression in the following manner. If we write this in the form, $\frac{C_i}{C_m} = \frac{\text{const.}}{C_m^{\frac{1}{3}}}$ observing that $C^{\frac{1}{3}}$ is the linear concentration of the molecules, and its reciprocal, $C^{-\frac{1}{3}}$, the mean distance of the molecules, we see that $\frac{C_i}{C_m} = \text{const. } r_m$, in which $r = C^{-\frac{1}{3}}$.

This, as Kohlraush observes, "would be, without doubt, a surprisingly simple relation."

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[1] Ztschr. phys. Chem., 18, 300.

[2] Ztschr. phys. Chem., 18, 662.

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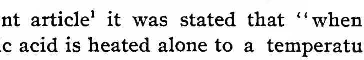
TRANSFORMATIONS OF PARASULPHAMINEBENZOIC ACID UNDER THE INFLUENCE OF HEAT.

By Ira Remsen and A. M. Muckenfuss.

In a recent article[1] it was stated that "when parasulphaminebenzoic acid is heated alone to a temperature near its melting-point it is completely transformed into other substances." The object of the investigation, the results of which are here presented, was to study these transformations carefully and to determine as far as possible their nature. As will be seen, the reactions which take place are of an unusual character, and they suggest further study in other groups. The point of chief interest is that, under the influence of heat, the nitrogen of the parasulphaminebenzoic acid passes from the sulphur atom, or, at least, from the sulphamine group to the carbon atom in the carboxyl. It appears highly probable that at 285° the principal reaction is that indicated below:



$$C_6H_4<\begin{matrix}CO.OH\\SO_2NH_2\end{matrix} \rightarrow C_6H_4<\begin{matrix}CO.NH_2\\SO_2OH.\end{matrix}$$

At lower temperatures, however, products are obtained that are not easily soluble in water, and among them, an acid isomeric with parasulphaminebenzoic acid, and a compound isomeric with the diamide of parasulphobenzoic acid,

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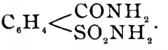
[1] This Journal, 18, 151.



$C_6H_4<\begin{matrix}CONH_2\\SO_2NH_2\end{matrix}$. The properties of these substances have been carefully studied, but, up to the present, no plausible hypothesis as regards their constitution has suggested itself. It is hoped, however, that further investigation may lead to a solution of the problem.

Method of Heating.

A cylindrical air-bath is surrounded with asbestos, so that by the use of one Bunsen burner the temperature within can be raised to 300°. The bath is covered with a glass plate, in the center of which is a hole for the insertion of a cork holding a thermometer. The temperature is regulated by means of a screw-clamp on the tubing of the burner. The parasulphaminebenzoic acid to be heated is ground very fine and placed in a small evaporating dish. The dish is covered with a watch glass, in the center of which is a small hole for the insertion of a thermometer. The bath is first heated to the desired temperature, and the flame regulated so that the temperature remains constant ; then the dish is lowered to the shelf in the bath. The temperature of fusion can thus be accurately observed, as well as changes in color.

Changes at 285°.

If parasulphaminebenzoic acid is kept at 285° for three hours the resulting mass is somewhat colored, and is completely and easily soluble in water and in alcohol, but insoluble in benzene, ether, and ligroïn. The opaque water solution was treated with bone-black, filtered and evaporated to crystallization, when, on cooling, crystals filled the liquid. These had the appearance of acid ammonium parasulphobenzoate, and were easily identified as such by comparing them with some of the salt made from parasulphaminebenzoic acid by treating it with hydrochloric acid in a sealed tube to 200°. On treating the solution of the salt with barium chloride, the acid barium salt of parasulphobenzoic acid was formed, and easily identified by the aid of its characteristic properties, and by its analysis :

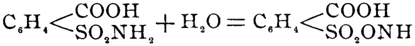
0.3845 gram barium salt lost 0.035 gram H_2O, and gave 0.1493 gram $BaSO_4$.

	Calculated for $(C_6H_4<^{COOH}_{SO_2O})_2Ba.3H_2O$.	Found.
H_2O	9.11	9.10
Ba	23.10	22.83

The mother-liquor from the acid ammonium salt was evaporated after the addition of barium chloride, and on cooling, seed-like crystals were deposited in very small quantity. It is evident from the above that at 285° parasulphaminebenzoic acid is practically completely transformed into a substance which, when dissolved in water, is in turn transformed into acid ammonium parasulphobenzoate. The first change takes place without loss in weight, as was shown by a series of experiments, the results of which are recorded in the table below:

No.	Weight in grams of acid heated.	Weight in grams of acid after heating.	Temperature of heating.	Time of heating in hours.
I.	10.992	10.9655	220°	8
II.	4.56	4.525	225°	6
III.	4.8395	4.8475	235°	3
IV.	4.0235	4.026	235°	4
V.	3.9339	3.922	285°	3
VI.	5.001	5.886	285°	8

The facts observed show conclusively that the acid ammonium salt obtained cannot be formed in the first stage of the reaction, but that it must be formed when the first product is treated with water. In order to pass from parasulphaminebenzoic acid to acid ammonium parasulphobenzoate the addition of a molecule of water is obviously necessary:



$$C_6H_4<^{COOH}_{SO_2NH_2} + H_2O = C_6H_4<^{COOH}_{SO_2ONH_4}.$$

Now, this water is not formed at the expense of a part of the acid, and in consequence of a deep-seated reaction, for practically the only product formed is the one yielding the acid ammonium salt. Further, considering (1) that there is no loss in weight caused by the heating; (2) that the product is very easily soluble in water; and (3) that, as has been shown in a previous communication,[1] the nitrogen of the sulphamide group easily passes to the carbon of the carboxyl, it appears

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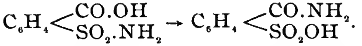
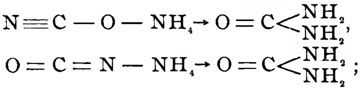
[1] This JOURNAL, 18, 150.

not improbable that the first effect of heating parasulphaminebenzoic acid to 285° is to cause the amido group and the hydroxyl groups to exchange places :



$$C_6H_4\textless\begin{matrix}CO.OH\\SO_2.NH_2\end{matrix} \rightarrow C_6H_4\textless\begin{matrix}CO.NH_2\\SO_2OH\end{matrix}.$$

According to this view, the first product is benzaminesulphonic acid. This being a sulphonic acid would probably be easily soluble in water and in alcohol. On the other hand, we have no means of judging whether a substance of this composition would take up water readily and yield the acid ammonium salt of parasulphobenzoic acid, but such a reaction would be quite analogous to others which are well known. The change in the position of the nitrogen atom suggested above is in some respects similar to that which takes place in the well known transformation of ammonium cyanate to urea, and in the reaction studied by Beckmann, and commonly called Beckmann's transformation. In the former case there is a shifting of the nitrogen atom from oxygen to carbon or from nitrogen to carbon :

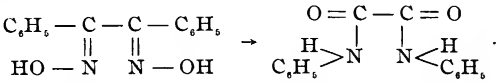


$$N \equiv C - O - NH_4 \rightarrow O = C\textless\begin{matrix}NH_2\\NH_2\end{matrix},$$

or,

$$O = C = N - NH_4 \rightarrow O = C\textless\begin{matrix}NH_2\\NH_2\end{matrix};$$

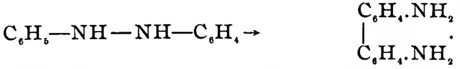
and there is shifting of nitrogen from oxygen to carbon in Beckmann's reaction, as illustrated in the change of benzildioxim to oxanilide :



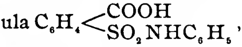
$$\begin{matrix}C_6H_5 - C - C - C_6H_5\\ \quad\| \quad\;\; \|\\ HO - N \quad N - OH\end{matrix} \rightarrow \begin{matrix}O = C - C = O\\ \quad | \qquad\; |\\ \overset{H}{\underset{C_6H_5}{}}\!\!>N \quad N\!<\!\overset{H}{\underset{C_6H_5}{}}\end{matrix}.$$

The transformation of diazoamidobenzene to amidoazobenzene, and that of hydrazobenzene to benzidine are also illustrations of this same tendency :

$$C_6H_6 - N = N - NH.C_6H_5 \rightarrow C_6H_5 - N = N - C_6H_4.NH_2;$$



$$C_6H_5-NH-NH-C_6H_4 \rightarrow \begin{matrix}C_6H_4.NH_2\\ |\\ C_6H_4.NH_2\end{matrix}.$$

Experiments are now in progress in this laboratory on the action of heat on metasulphaminebenzoic acid, and these have already made it appear highly probable that the first change effected consists in an exchange of the amido group for hydroxyl, as suggested above. It is proposed, further, to study other cases as, for example, the sulphanilido acids of the formula  $C_6H_4<\begin{matrix}COOH\\SO_2NHC_6H_5\end{matrix}$, and similar substances. It may in some cases be possible to isolate the intermediate products, and thus secure more satisfactory evidence in regard to the shifting of the nitrogen atoms.

Changes at 220° to 235°.

The lowest temperature at which a change takes place in parasulphaminebenzoic acid is 220°. If the temperature is kept between this point and 235°, a product insoluble in water, and quite different from parasulphaminebenzoic acid was obtained in varying qnantities, according to the temperature. As shown in the table below, the lower the temperature the larger the yield of the insoluble product :

No.	Weight in grams of substance heated.	Grams of insoluble material formed.	Per cent. formed of insoluble material.	Temperature of heating.	Length of heating in hours.
I.	10.962	2.512	22.91	220°	8
II.	5.557	1.1338	20.4	223°	8
III.	4.56	0.8645	18.95	225°	6
IV.	6.132	1.1609	18.93	225°	6
V.	4.023	0.4825	11.98	235°	4

None of the original acid remained in any of these experiments.

Preparation of the Insoluble Product.—For the purpose of preparation the following method was found to be most satisfactory : Heat parasulphaminebenzoic acid at 220° for eight hours ; after cooling, powder the mass thus obtained. Treat with water, boil, and set the liquid aside over night, then filter, and wash with cold water. Dissolve the substance in cold caustic soda, treat with bone-black in the cold, and after the solution has stood for a short time with occasional stirring, filter with the aid of a pump. Treat the filtrate at once with a slight excess of hydrochloric acid, when the product is deposited in characteristic crystalline form. Filter and wash free from hydrochloric acid.

When first formed the substance is in very finely divided condition, and, if filtration is attempted at once after treating the powdered mass with water, some of the undissolved product will pass through the filter. If, however, the mass is boiled with water, and allowed to stand for twelve hours, filtration is easy, and nothing is deposited from the filtrate on cooling.

The compound thus obtained is neutral toward litmus, is not dissolved by alkaline carbonates, is slightly soluble in boiling water, insoluble in cold and hot alcohol, and is infusible. It gives off ammonia copiously when boiled with a caustic alkali, and slowly even at low temperatures. It was analyzed with the following results:

I. 0.2118 gram gave 0.3264 gram CO_2, and 0.09 gram H_2O.

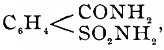
II. 0.1855 gram gave 0.286 gram CO_2, and 0.0709 gram H_2O.

III. 0.2455 gram gave 29.8 cc. of nitrogen at 18.4° and 762 mm.

IV. 0.2102 gram gave 25.96 cc. of nitrogen at 19.8° and 762 mm.

V. 0.1761 gram gave 0.2028 gram $BaSO_4$ (Carius method).

	Calculated for $C_7H_8SN_2O_3$.			Found.		
		I.	II.	III.	IV.	V.
C	42	42.02	42.04	....	....	....
H	4	4.51	4.25	....	....	....
N	14	....	....	14	14.14	....
S	16	....	....	....	....	15.9

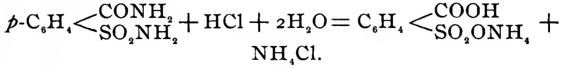
The substance has, therefore, the same composition as the diamide of parasulphobenzoic acid,  $C_6H_4<\begin{matrix}CONH_2\\SO_2NH_2\end{matrix}$, and it was at first supposed to be this, but further investigation showed conclusively that the two substances are not identical, and in the absence of clear evidence as to the relation between the two, the product obtained by heating parasulphaminebenzoic acid is here called the *infusible diamide.* This infusible diamide can be crystallized from water, but it is so difficultly soluble, even in boiling water, that this does not commend itself as a method of purification. It does not dissolve in benzene, ligroïn, chloroform, or ether. Sodium hydroxide, as already stated, decomposes it even at low temperature, but neither boiling hydrochloric nor boiling nitric acid changes it. It dissolves readily even in cold concentrated sulphuric acid, and this solution can be heated to 200° without decomposition. On cooling and pouring into water, the characteristic crystals again appear. The crystals consist of small plates. If an excess of acid is added to a dilute alkaline solution, the minute plates appear slowly, and occasionally arrange themselves in rows forming needle-shaped crystals, which when disturbed break up into plates again. Even phosphorus pentachloride does not affect it easily; for, when heated with this reagent at 200° for several hours, the diamide was recovered unchanged.

Action of Concentrated Hydrochloric Acid on the Infusible Diamide at 200°.—The heating was continued for six hours. After the acid was evaporated, most of the residue dissolved easily in water, though there was a very small quantity of an insoluble substance left—too small for investigation. The soluble substance proved to be a mixture of acid ammonium parasulphobenzoate and ammonium chloride. The former was identified by its crystalline form and solubility, and the ease with which it yielded acid barium parasulphobenzoate. The barium salt was analyzed with the results below recorded:

0.2455 gram lost 0.0221 gram H_2O at 200°, and gave 0.0957 gram $BaSO_4$.

	Calculated for $\left(C_6H_4<\begin{smallmatrix}COOH\\SO_2O\end{smallmatrix}\right)_2Ba.3H_2O$.	Found.
H_2O	9.11	9.00
Ba	23.10	22.92

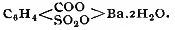
The reaction with hydrochloric acid is represented by the following equation:



$$p\text{-}C_6H_4<\begin{smallmatrix}CONH_2\\SO_2NH_2\end{smallmatrix} + HCl + 2H_2O = C_6H_4<\begin{smallmatrix}COOH\\SO_2ONH_4\end{smallmatrix} + NH_4Cl.$$

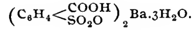
Action of Sodium Hydroxide on the Infusible Diamide.—In order to determine what proportion of the nitrogen is given off as ammonia when the infusible diamide is treated with sodium hydroxide, the following experiment was made: 1.005 grams of the substance were placed in a small flask, about 20 cc. dilute sodium hydroxide added, and the ammonia distilled into an excess of dilute sulphuric acid of known strength. Titration showed that the weight of the ammonia given off was 16.9 per cent. of the weight of the substance taken, while, if all the nitrogen should be given off in this reaction, the weight of the ammonia would be 17 per cent. of that of the original substance. The solution left in the flask was neutralized, evaporated to dryness, and extracted with methyl alcohol. It was thus shown to contain the neutral sodium salt of parasulphobenzoic acid, which was converted in turn into the neutral barium salt and the acid barium salt, both of which were analyzed. The neutral salt gave these results:

0.7798 gram lost 0.0751 gram H_2O at 150°, and gave 0.484 gram $BaSO_4$.

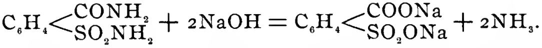
	Calculated for  $C_6H_4<^{COO}_{SO_2O}>Ba.2H_2O$.	Found.
H_2O	9.65	9.63
Ba	36.73	36.50

The acid salt gave these results:

0.5113 grhm lost 0.0466 gram H_2O at 200°, and gave 0.2001 gram $BaSO_4$.

	Calculated for  $(C_6H_4<^{COOH}_{SO_2O})_2Ba.3H_2O$.	Found.
H_2O	9.11	9.11
Ba	23.10	23.01

Sodium hydroxide, therefore, easily drives out all the nitrogen from the infusible diamide, the reaction being represented by the equation:



$$C_6H_4<^{CONH_2}_{SO_2NH_2} + 2NaOH = C_6H_4<^{COONa}_{SO_2ONa} + 2NH_3.$$

Experiments were next made with the object of determining whether half the nitrogen could be eliminated, and an intermediate product formed, but without success. If decomposition takes place at all, it is complete as far as it goes. A portion of the infusible diamide was allowed to stand for two months in strong hydrochloric acid, and another portion dissolved in concentrated sulphuric acid was allowed to stand for the same time, but no change was observed in either case. A weighed quantity was then boiled with a solution containing only half enough potassium hydroxide to drive off all the nitrogen, but it was found that part of the diamide was converted into neutral potassium parasulphobenzoate, while the rest remained unchanged. It was also found to be impossible to obtain an intermediate product by letting the infusible diamide stand in sodium hydroxide solution. Even at temperatures below 0° only a short time was required to drive out all the nitrogen.

Preparation and Properties of the Fusible or Normal Diamide of Parasulphobenzoic Acid.

The properties of the infusible diamide described in the preceding section make it difficult to believe that it is the normal diamide of parasulphobenzoic acid. Substances containing the sulphamide group, SO_2NH_2, do not easily give up the nitrogen of this group in the form of ammonia, nor, indeed, is the group $CO.NH_2$, as it usually presents itself, easily decomposed by acid or by alkali. Attempts were accordingly made to prepare the normal diamide by means of the ordinary reactions. First, parasulphaminebenzoic acid was converted into the acid ammonium salt of parasulphobenzoic acid by heating with hydrochloric acid to 200° in a sealed tube. From the acid ammonium salt, the neutral potassium salt was made, and this converted into the dichloride by phosphorus pentachloride. The dichloride can be crystallized from benzene in stout, transparent plates. By treating it with ammonia it is converted into the diamide. This proved, however, to be quite different from the infusible diamide. After crystallization from water it was found to have the properties of a pure substance, and it was analyzed with the results given below:

I. 0.2064 gram gave 0.0815 gram H_2O and 0.318 gram CO_2.

II. 0.3327 gram gave 0.1226 gram H_2O and 0.5132 gram CO_2.

III. 0.1846 gram gave 22.4 cc. of nitrogen at 20° and 773.1 mm.

IV. 0.1361 gram gave 16.75 cc. of nitrogen at 20° and 763.65 mm.

V. 0.1701 gram gave 0.1982 gram $BaSO_3$ (Carius).

	Calculated for $C_6H_4<\begin{matrix}CO.NH_2\\SO_2NH_2\end{matrix}$	Found. I.	II.	III.	IV.	V.
C	42	42.01	42.09	....	....	....
H	4	4.39	4.20	....	....	....
N	14	....	....	14.10	14.12	....
S	16	....	....	....	....	16.01

As was to be expected from the method of formation, the substance is the diamide. That it is entirely different from the infusible diamide will appear from the account of its properties. Like the infusible substance, it is neutral and insoluble in alkaline carbonates, and it gives off ammonia when boiled with the caustic alkalies. But, while the infusible diamide is extremely difficultly soluble in boiling water, the new compound dissolves readily in boiling water, and is deposited in needles from the solution on cooling. Again, the infusible compound is insoluble in alcohol, while the fusible isomer is soluble. It melts sharply at 230°. Both substances dissolve in caustic soda. From this solution the infusible diamide is precipitated by acids in minute, lustrous plates, the fusible in milky form.

Action of Acids on the Fusible Diamide.—When heated at 200° in a sealed tube for six hours, with hydrochloric acid, the fusible diamide is completely transformed into acid ammonium parasulphobenzoate and ammonium chloride, just as the infusible compound is. The ammonium salt was transformed into the acid barium salt, and this was analyzed.

0.5298 gram lost 0.0483 gram H_2O at 200°, and gave 0.2073 gram $BaSO_4$.

	Calculated for $(C_6H_4<\begin{matrix}COOH\\SO_2O\end{matrix})_2Ba.3H_2O$.	Found.
H_2O	9.11	9.11
Ba	23.10	23.00

Only ammonium chloride was found in the mother-liquor from the acid ammonium salt.

Action of Sodium Hydroxide on the Fusible Diamide.—When the fusible diamide is boiled with sodium hydroxide, ammonia is readily given off. If the boiling is continued as long as ammonia is evolved, the solution obtained gives a copious precipitate with hydrochloric acid. This proved to be easily soluble in sodium carbonate, insoluble in cold water, and difficultly soluble in hot water, from which it crystallized in needles melting at about 280°. This is parasulphaminebenzoic acid, as is clearly shown by the facts stated, and, further, by the properties and analysis of the barium salt. This crystallized in spherical clusters, as described by Remsen[1] and by Noyes.[2] It was analyzed with the results given below:

0.2145 gram of salt lost 0.0313 gram H_2O at 160°, and gave 0.0789 gram $BaSO_4$.

	Calculated for $\left(C_6H_4<\begin{smallmatrix}COO\\SO_2NH_2\end{smallmatrix}\right)_2Ba.5H_2O$.	Found.
H_2O	14.35	14.59
Ba	21.85	21.64

Even in the cold, sodium hydroxide affects this decomposition, though much more slowly than in the case of the infusible diamide. At 18° two weeks were required, but at 0° two months were necessary. The precipitate obtained in these cases on acidifying proved to be parasulphaminebenzoic acid.

While, therefore, the infusible diamide readily gives up all of its nitrogen as ammonia when treated with an alkali, the fusible diamide gives up only half of its nitrogen, the other half remaining in combination in the form of the stable sulphamide group, SO_2NH_2. In other words, the fusible diamide conducts itself as we should expect it to, if it has the constitution represented by the formula $C_6H_4<\begin{smallmatrix}CONH_2\\SO_2NH_2\end{smallmatrix}$, while the infusible diamide of the same composition does not so conduct itself.

Special experiments showed that when the fusible diamide is boiled with sodium hydroxide, the sulphamide group is not at all affected, no parasulphobenzoic acid being formed.

Preparation of the Fusible Diamide from Parasulphaminebenzoic Acid.—Parasulphaminebenzoic acid was converted into the chloride by treating the potassium salt with phosphorus

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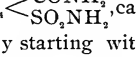
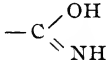
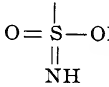
[1] Ann. Chem. (Liebig), **178**, 302.

[2] This Journal, **7**, 147.

pentachloride, extracting with anhydrous ether, and passing dry ammonia into the ethereal solution. In this way a compound was obtained having the properties of the diamide described in the preceding section. It crystallized in the same way and melted at 230°. It gave off ammonia when boiled with caustic soda, and the solution thus formed gave a precipitate of parasulphaminebenzoic acid when acidified. It was only after many experiments that the above method was devised. At first, the product formed with phosphorus pentachloride was treated with water, and the insoluble material, after filtering and washing, was treated with aqueous ammonia. On acidifying this solution, only parasulphaminebenzoic acid was obtained.

Preparation of the Fusible Diamide from Ethyl Parasulphaminebenzoate.—The ethyl salt of parasulphaminebenzoic acid was prepared by treating the chloride of the acid with alcohol and by the usual method. In order to convert it into the corresponding amide, it was treated with aqueous ammonia. It dissolved at once, and, on acidifying, only parasulphaminebenzoic was precipitated. Next, some of the ethereal salt was dissolved in absolute alcohol, the solution saturated with dry ammonia, and the whole heated in a sealed tube at 100° for a day, but the ethereal salt was recovered unchanged. Finally some of the dry ethereal salt was kept at 100° in a flask, and dry ammonia passed over it, but no change took place until the temperature was raised to 170°, when decomposition set in. The mass was charred but, nevertheless, it was extracted with hot water. In this way some of the ethereal salt was recovered unchanged, and a little of the amide was also obtained. The difficulty with which this change of the ethereal salt to the amide takes place is remarkable.

Comparison of the two Diamides.

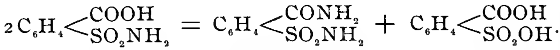
The work above described shows conclusively that two substances of the composition of the diamide,  $C_6H_4<\begin{matrix}CONH_2\\SO_2NH_2\end{matrix}$, can be obtained from parasulphobenzoic acid. By starting with this acid we have passed through the chloride to the diamide. This loses one of its nitrogen atoms easily and gives parasulphaminebenzoic acid; and the latter can be reconverted into the diamide by means of the usual reactions. There is no reason for supposing that the diamide thus formed is anything but the normal compound, containing the ordinary carbamide group and the ordinary sulphamide group. But what is the isomeric compound, the so-called infusible diamide? There is no room for doubt in regard to its composition. It is unquestionably isomeric with the fusible or normal diamide. It may contain the group $CONH_2$, identical with that contained in the normal diamide; though this does not appear probable in view of the ease with which it gives up all of its nitrogen; but it cannot contain the ordinary sulphamide group, SO_2NH_2, which, as is well known, is extremely stable. The compound is a derivative of parasulphobenzoic acid, as appears from the ease with which it can be converted into salts of this acid. The facts thus far established plainly do not suffice to enable us to draw a conclusion in regard to the relation between the two diamides. Stereochemistry appears to be of no avail in this case, and, while it is possible to write different structural formulas for compounds of this composition, that would not be a profitable occupation without further data. One would be inclined to suspect some rearrangement of the constituents of each of the two groups, $CO.NH_2$ and $SO_2.NH_2$. These might become respectively  $-C\begin{smallmatrix}\diagup OH\\ \diagdown\!\!\diagdown NH\end{smallmatrix}$ and  $O=\overset{|}{\underset{\underset{NH}{\|}}{S}}-OH$; but, as it will be extremely difficult to test these ideas by experiment, they are worth practically nothing.

It has not been found possible to change one diamide into the other. The fusible substance was heated for some time just above its melting-point, but no trace of the isomer could be found in the product. Some of the infusible substance was heated with water alone in a sealed tube, but no change was effected through comparatively wide ranges of temperature.

Isoparasulphaminebenzoic Acid.

The filtrates from the infusible diamide (see p. 353), obtained by heating parasulphaminebenzoic acid at 220–235°, were collected, purified by means of bone-black, and evaporated to crystallization. Six successive deposits were obtained. The first three were alike. The other three were small in quantity, appearing to consist chiefly of an acid that formed an insoluble barium salt crystallizing in fine, voluminous needles. The final mother-liquor was evaporated to dryness, and found to contain very little nitrogen. Three different substances were thus obtained. The first was found to be acid ammonium parasulphobenzoate. After many experiments, it is safe to say that, when parasulphaminebenzoic acid is heated at 220–235°, about 25 per cent. of it is changed in the same way that nearly all of it is changed at 285°, so that, on treating it with water, it yields acid ammonium parasulphobenzoate.

The final residue referred to above as containing very little nitrogen proved to be free parasulphobenzoic acid, which was identified by means of the characteristic acid barium salt. The quantitiy of this acid formed differed in different experiments. Its formation may be accounted for by supposing that it runs parallel with the formation of the diamide as indicated in the equation :



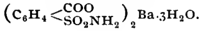
$$2\,\mathrm{C_6H_4}{<}\begin{matrix}\mathrm{COOH}\\ \mathrm{SO_2NH_2}\end{matrix} = \mathrm{C_6H_4}{<}\begin{matrix}\mathrm{CONH_2}\\ \mathrm{SO_2NH_2}\end{matrix} + \mathrm{C_6H_4}{<}\begin{matrix}\mathrm{COOH}\\ \mathrm{SO_2OH}\end{matrix}.$$

The intermediate product above mentioned as yielding a barium salt that crystallizes in fine, voluminous needles proved to be a compound of special interest. It is this to which the name *isoparasulphaminebenzoic acid* is given for reasons that will appear. In order to prepare the substance, it is best to proceed thus : After heating parasulphaminebenzoic acid at 220° for eight hours, pulverize the product and extract with hot alcohol. A flocculent substance will then be deposited from the filtrate on cooling. When its solution in water is treated with barium chloride, the characteristic needles of the barium salt are formed. The salt was recrystallized from hot water and analyzed with the following results :

I. 0.2182 gram salt lost 0.0137 gram H_2O at 150°, 0.0202 gram H_2O at 200°, and gave 0.086 gram $BaSO_4$.

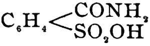
II. 0.1916 gram salt gave 8.2 cc. of nitrogen at 18° and 749.45 mm.

III. 0.1342 gram salt gave 0.103 gram $BaSO_4$ (Carius).

	Calculated for  $(C_6H_4{<}\substack{COO\\SO_2NH_2})_2Ba.3H_2O$.	Found.		
		I.	II.	III.
$2H_2O$	6.09	6.28	....	....
$3H_2O$	9.14	9.21	....	....
Ba	23.18	23.17	....	....
N	4.73	....	4.86	....
S	10.82	....	....	10.54

It will be seen that the salt is derived from an acid isomeric with parasulphaminebenzoic acid. When dissolved in water, it crystallizes out on cooling in exceedingly fine needles so intricately interwoven that, when the salt is deposited from a saturated solution, the vessel containing it can be inverted without loss of material, though the saturated solution contains only 1 per cent. of the salt.

Free isoparasulphaminebenzoic acid is very soluble in water. Several of its salts were made, but only the ammonium and barium salts are at all well characterized. The former crystallizes in short, stout, transparent prisms, quite different from the glistening aggregates of needles formed by ammonium parasulphaminebenzoate. The calcium, strontium, zinc, magnesium, and lead salts of the two isomeric acids were made, and compared side by side. Those of parasulphaminebenzoic acid are well defined, the zinc salt being especially beautiful, while those of the iso acid are amorphous, and all except the lead and barium salts are very easily soluble. The analytical results obtained, except in the case of the barium salt, were quite variable and unsatisfactory. The mercury and silver salts were made also, but they are equally uninviting.

Action of Potassium Hydroxide on Isoparasulphaminebenzoic Acid.—The fact that the free acid is easily soluble in water, and isomeric with parasulphaminebenzoic acid led to the suspicion that it might be benzaminesulphonic acid  $C_6H_4{<}\substack{CONH_2\\SO_2OH}$. But experiment showed that this view is highly improbable. It has already been shown that the carbamine group readily gives up its nitrogen as ammonia under the influence of alkalies. This acid, however, gives up its nitrogen with great difficulty. No ammonia was given off on boiling with a concentrated solution of potassium hydroxide, and it was not until the hydroxide was practically free from water, and the temperature high enough to drive out the sulphonic acid group that ammonia was detected. The product formed under these circumstances is parahydroxybenzoic acid, as was shown by the melting-point and other properties.

Effect of Heating Isoparasulphaminebenzoic Acid with Hydrochloric Acid at 270°.—The acid is not as easily changed by heating with hydrochloric acid as is parasulphaminebenzoic acid. A temperature of 270° seemed to be necessary to effect anything like a complete change. For the purpose of the experiment, the barium salt was used instead of the free acid. After precipitating the barium from the solution, a very small quantity of a substance appeared in flocculent form, but the quantity was so small as to render an investigation impossible. Almost all of the material left, after heating with hydrochloric acid and evaporating to dryness, is soluble in cold water. This proved to be nothing but the acid ammonium salt of parasulphobenzoic acid, the same product that is formed under similar circumstances, though at lower temperature, from parasulphaminebenzoic acid.

Attempt to Prepare the Amide of Isoparasulphaminebenzoic Acid.—In the thought that the amide of isoparasulphaminebenzoic acid might be identical with one or the other of the two diamides described in the early part of this article, an attempt was made to prepare it, but this was unsuccessful. The dried salt of the acid was thoroughly mixed with an equivalent quantity of phosphorus pentachloride, and the mass gently warmed. Reaction took place easily, and, on the addition of water, a white substance separated. This was found to contain chlorine and to be free from phosphorus. It was quite insoluble in every solvent tried. On boiling with an alkali, it passed into solution, and, on acidifying and cooling, no precipitate was formed ; but, on rendering the solution slightly alkaline with ammonia, and adding barium chloride, a precipitate was formed. On crytallizing this from water it proved to be the barium salt of isoparasulphaminebenzoic acid. When the chlorine derivative of the iso acid is treated with aqueous ammonia it dissolves at once; and when this solution is acidified a gelatinous mass is precipitated much like aluminic hydroxide.

Lack of material prevented further investigation of the isoparasulphamine acid and its derivatives; and we are entirely at a loss to form any conception in regard to the relations existing between it and the ordinary parasulphaminebenzoic acid. In this connection, it should be mentioned that, in their study of metasulphaminebenzoic acid, Limpricht and Uslar[1] isolated two acids isomeric with their sulphamine acid, one very soluble in water the other insoluble and amorphous. They succeeded in transforming the amorphous acid into the ordinary variety by heating it with water in a sealed tube to 170–180°. A similar experiment was made with free isoparasulphaminebenzoic acid, but apparently no change took place.

Further efforts will be made to discover the nature of the curious and, at present, inexplicable compounds described in this article.

CHEMICAL LABORATORY,
JOHNS HOPKINS UNIVERSITY,
March, 1896.

THE HEAT OF ELECTROLYTIC DISSOCIATION OF SOME ACIDS.[2]

BY F. L. KORTRIGHT.

The heat of electrolytic dissociation of a number of acids has been determined by Arrhenius[3] and Jahn,[4] but in each case it has been with acids which do not obey the Ostwald dilution law or else belong to one particular class of organic acids. It has therefore seemed desirable that measurements should be made on a number of acids of different but allied constitution, and thus a study made of the effect of constitution upon the heat of electrolytic dissociation.

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[1] Ann. Chem. (Liebig), **106**, 43.

[2] The measurements for the above were made at the suggestion of Professor Trevor during the summer of 1894, but were not published at that time in the hope that they might be further extended.

[3] Ztschr. phys. Chem., **4**, 96; **9**, 360.

[4] Ztschr. phys. Chem., **16**, 72.

The conductivity measurements were made by means of the well-known Ostwald-Kohlrausch method described in Ostwald's Handbuch fur physiko-chemische Messungen, page 266, using the Arrhenius resistance cell (Fig. 176 of the above book).

A wooden pail having an inside diameter of 6 inches, a depth of 10 inches, and walls an inch thick, was employed as a thermostat. It was kept immersed in a larger pail of ice water. The inner pail was filled with a slush of clean finely pulverized ice, which gave a very constant temperature of 0°. A thermometer divided into tenths of a degree placed near the resistance cell never showed over 0.03° variation from 0° at the time of taking the bridge reading.

The water employed was taken from a spring, carefully distilled through block tin condensers from alkaline permanganate into phosphoric acid, and then into a carboy. The carboy had previously contained ammonium hydroxide, but before using it was carefully washed out with hydrochloric acid and then with running water for several days. The water thus prepared gave a specific conductivity at 0° of 1.7×10^{-6}.

The conductivities of the salt solutions were corrected by subtracting the molecular conductivity of the water from that of the salt solution; with the acids no correction was applied.

The potassium salts of the various acids were prepared by running a standard solution of potassium hydroxide (made from metallic potassium and carefully kept from carbon dioxide) upon the solid acid until the color of phenolphthalein appeared, and then adding a small amount of solid acid to cause the color to disappear, thus guarding against the presence of any excess of potassium hydroxide. This salt was then diluted to a concentration of one mol in 32 liters of water.

The concentration of the acid solution was determined in each case by titrating with a standard solution of barium hydroxide, using phenolphthalein as an indicator. The barium hydroxide solution was standardized by titrating against carefully purified, dried, and weighed portions of succinic acid.

In order to obtain μ_∞ for the acids by use of the formula $\mu_{\infty\ \text{acid}} = \mu_{\infty\ \text{HCl}} - \mu_{\infty\ \text{KCl}} + \mu_{\infty\ \text{KR}}$, which seems to be the most nearly correct of anything we have at present, it is necessary to know the conductivity at infinite dilution and at 0° of hydrochloric acid, potassium chloride, and the potassium salt of the acid in question. The μ_∞ for potassium chloride at 0° was obtained from the extrapolation formula of Déguisne,[1]

$$\mu_t = \mu_{18}[1 + \alpha\,(t - 18) + \beta\,(t - 18)^2]$$

where $\mu_{\infty\ 18^\circ} = 123$,[2] and for 1 mol in about 20,000 liters of water $\alpha = 2194 \times 10^{-5}$, and $\beta = 324 \times 10^{-7}$. This gave 77.7, while direct measurements by R. W. Wood[3] gave 77.8. μ_∞ for hydrochloric acid at 0° obtained from Déguisne's formula where $\mu_{\infty\ 18^\circ} = 353$, and for 1 mol in 10,000 liters of water $\alpha = 1660 \times 10^{-5}$ and $\beta = 92 + 10^{-7}$, is 248.5. Kohlrausch[4] gives 208 as the migration velocity of hydrogen at 0° and, since the transference number of chlorine in potassium chloride is nearly independent of the temperature, *i. e.*, 0.510 according to Hittorf, $77.7 \times 0.510 = 39.6$ is the migration velocity of chlorine. Therefore, $208 + 39.6 = 247.6$ is the μ_∞ of hydrochloric acid at 0° according to Kohlrausch. The mean of these two values is about 248, which is adopted as the μ_∞ for hydrochloric acid at 0°. The μ_∞ at 0° of the potassium salts of the acids was obtained by determining the conductivity of the salts prepared as above at dilutions of 1 mol salt in 32, 64, 128, 256, 512, and 1024 liters of water, and adding to these values of μ_v the proper increment as given from $\mu_\infty - \mu_v = n_1 n_2 C$. Where n_1 and n_2 are the valences of the ions, and C is a constant for constant volume and temperature. The various values for C were taken from Wood's[5] table for the conductivity of potassium chloride at 0°, and checked against the values of C at 25° given by Breidig.[6] The μ_∞ for the potassium salt calculated from the μ_v of the salt at different concentrations was very nearly constant and a suitable average of these values gives a very

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[1] Temperatur-Coëfficienten des Leitvermögens sehr verdünnter wässriger Lösungen. Inaug. Dissert., p. 14.

[2] Kohlrausch, Ann. Phys. (Wiedeman), **50**, 406, 1893.

[3] Ztschr. phys. Chem., **18**, 322.

[4] Ztschr. phys. Chem., **14**, 326.

[5] *Loc. cit.*

[6] Ztschr. phys. Chem., **13**, 198.

nearly correct value for the μ_∞ of the various potassium salts. Therefore, by taking

$$\mu_{\infty\,\text{acid}} = 248 - 77.7 + \mu_{\infty\,\text{KR}},$$

we obtain the μ_∞ for the various acids, and from the measurements of their conductivities their affinity constants may be calculated.

Very pure acids were employed for the measurements; the butyric, malonic, maleïc, fumaric, mesaconic, citraconic, ortho- and metaphthalic acids were kindly furnished me by Professor Trevor and were from the preparations used by him in his work on the measurement of small degrees of dissociation.[1] The monobromacetic acid was obtained specially pure from Kahlbaum. The benzoic, succinic, and monochloracetic acids were several times recrystallized.

In the following tables, under v is the number of liters solution containing 1 mol. of acid; μ_∞ is, as usual, the conductivity at infinite dilution; μ_v the conductivity at a dilution v; $100\,\alpha$ the percentage of electrolytic dissociation of the acid; $100\,k$ the affinity constant calculated according to the Ostwald dilution law; Kt.K is the most probable affinity constant of the acid at 0° from my measurements; Ost.K is the most probable affinity constant at 25° as given by Ostwald.

Monochloracetic Acid.—$\mu_\infty = 229$.

v.	μ_∞.	$100\,a$.	$100\,k$.
32	48.88	21.34	0.181
64	65.21	28.47	0.177
128	85.21	37.21	0.172
256	109.4	47.77	0.170
512	135.9	59.34	0.169
1024	162.6	71.00	0.170

Kt.K = 0.181 Ost.K = 0.155

Monobromacetic Acid.—$\mu_\infty = 229$.

32	45.79	19.99	0.156
64	61.13	26.69	0.152
128	80.66	35.22	0.150
256	103.91	45.37	0.147
512	130.24	56.87	0.146

Kt.K = 0.156 Ost.K = 0.138

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[1] Ztschr. phys. Chem., **10**, 321.

Malonic Acid.—$\mu_\infty = 240$.

16	32.93	13.72	0.136
32	44.69	18.61	0.133
64	59.83	24.93	0.129
128	78.92	32.90	0.126
256	102.14	42.56	0.123

Kt.K = 0.136 Ost.K = 0.158

Butyric Acid.—$\mu_\infty = 225$.

16	3.64	1.618	0.00166
32	5.17	2.298	0.00169
64	7.34	3.262	0.00171
128	10.34	4.595	0.00172
256	14.48	6.435	0.00172

Kt.K = 0.00166 Ost.K = 0.00149

Benzoic Acid.—$\mu_\infty = 225$.

64	13.76	6.12	0.00623
128	19.34	8.60	0.00632
256	26.93	11.97	0.00631
512	37.05	16.47	0.00634
1024	50.85	22.60	0.00644

Kt.K = 0.00632 Ost.K = 0.00600

Orthophthalic Acid.—$\mu_\infty = 236$.

64	56.51	23.94	0.118
128	74.77	31.68	0.115
256	97.00	41.10	0.112
512	122.20	51.78	0.109
1024	149.04	63.15	0.105

Kt.K = 0.118 Ost.K = 0.121

Metaphthalic Acid.—$\mu'_\infty = 236$.

626	70.31	29.79	0.0202
1252	94.04	39.85	0.0211
2504	124.70	52.83	0.0236

Kt.K = 0.0202 Ost.K = 0.0287

Succinic Acid.—$\mu_\infty = 238$.

32	9.547	4.01	0.00523
64	13.24	5.56	0.00511
128	18.51	7.77	0.00511
256	25.69	10.79	0.00510
512	35.62	14.95	0.00513
1024	49.25	20.69	0.00527

Kt.K = 0.00511 Ost.K = 0.00665

Maleïc Acid.—$\mu_\infty = 239$.

32	107.49	44.97	1.14
64	132.31	55.36	1.07
128	156.44	65.45	0.97
256	179.71	75.19	0.89
512	198.55	83.07	0.80
1024	212.30	88.82	0.69

Kt.K = 1.14 Ost.K = 1.30

Fumaric Acid.—$\mu_\infty = 240$.

32	35.48	14.78	0.0801
64	48.42	20.17	0.0796
128	65.36	27.23	0.0796
256	86.75	36.14	0.0799
512	113.01	47.09	0.0818
1024	143.45	59.77	0.0867

Kt.K = 0.0800 Ost.K = 0.093

Mesaconic Acid.—$\mu_\infty = 237$.

64	45.95	19.38	0.0729
128	62.11	26.20	0.0727
256	82.23	34.70	0.0720
512	106.24	44.83	0.0711
1024	134.17	56.61	0.0721

Kt.K = 0.0729 Ost.K = 0.0790

Citraconic Acid.—$\mu_\infty = 235$.

64	89.85	38.23	0.369
128	113.84	48.44	0.355
256	139.55	59.38	0.339
512	164.42	69.96	0.318
1024	185.99	79.15	0.293

Kt.K = 0.369 Ost.K 0.340

Since the rate of change of the affinity constant with the temperature is given by the van't Hoff equation,

$$\frac{\partial \log K}{\partial T} = \frac{J q}{R T^2}$$

where K is the affinity constant, T the absolute temperature, q the heat of electrolytic dissociation, J the mechanical equivalent of heat, and R the gas constant, we may by integrating and solving for q obtain the value for the heat of electrolytic dissociation. Integrating the above equation between K_1 and K_2 under the assumption that q is independent of the temperature which is not far from correct for small temperature differences, we get

$$\log K_2 - \log K_1 = \frac{J q}{R} \cdot \frac{T_2 - T_1}{T_1 T_2}.$$

Solving for q and substituting the values for J, R and the factor for changing natural logarithms to the base 10, gives

$$q = \frac{4.56\ (\log_{10} K_2 - \log_{10} K_1)\ T_1\ T_2}{T_2 - T_1}$$

where positive q is heat absorbed if the process takes place without outside work.

The heats of electrolytic dissociation, calculated from the above formula by substituting the values of K_1 from the above tables, K_2 from Ostwald's measurements at 25° and the proper temperature values, appear in the following table:

Acid.	Formula.	q 12.5°.		
Acetic	CH_3COOH	—428	cal.	J[1]
Monochloracetic	$CH_2ClCOOH$	—999	"	
Monobromacetic	$CH_2BrCOOH$	—790	"	
Dichloracetic	$CHCl_2COOH$	—2924	"	A
Malonic	$CH_2(COOH)_2$	+966	"	
Butyric	C_3H_7COOH	—696	"	
Benzoic	C_6H_5COOH	—335	"	
Orthophthalic	$C_6H_4(COOH)_2$	+162	"	
Metaphthalic	$C_6H_4(COOH)_2$	+2260	"	
Succinic	$C_2H_4(COOH)_2$	+1697	"	
Maleïc	$C_2H_2(COOH)_2$	+846	"	
Fumaric	$C_2H_2(COOH)_2$	+970	"	
Mesaconic	$C_3H_4(COOH)_2$	+518	"	
Citraconic	$C_3H_4(COOH)_2$	—522	"	

The above table confirms the result of Arrhenius and Jahn that the monobasic acids dissociate electrolytically with an evolution of heat; it also shows that the evolution of heat is increased by the introduction of a halogen, and that the effect of a second halogen is greater than that of the first. On the other hand, the introduction of a carboxyl group into the acid causes an absorption of heat, and the further the carboxyl groups are removed from each other the greater the absorption of heat.

[1] The value of q marked J is taken from Jahn's table at 18°, that marked A from Arrhenius table at 21.5°.

CORNELL UNIVERSITY, March, 1896.

Contribution from the Laboratory of General Chemistry, University of Michigan.

ON THE EXISTENCE OF PENTAETHYL NITROGEN.

BY ARTHUR LACHMAN.

There is *a priori* no reason why nitrogen in its pentavalent state cannot combine with five *like* atoms or radicals, just as in its trivalent state it unites with three like atoms. And there is, further, no reason known why in pentavalent nitrogen compounds, the atoms or radicals attached to the nitrogen must consist of two groups, strongly contrasted (*e. g.*, $H_4\equiv N-Cl$, $(CH_3)_3\equiv N=ICl$, $C_6H_5-N\equiv O_2$). The existence of a compound NX_5, therefore, is not contradicted by anything but experience; and it seemed well worth the effort to attempt its preparation. The pentachloride, NCl_5, was not to be thought of; the hydrogen compound, NH_5, presented no point of attack; but for the pentaethyl compound, $N(C_2H_5)_5$, one method in particular suggested itself, which has been very frequently employed in the carbon series, and which had been successful in the one case where it was tried with (trivalent) nitrogen.

This method is the action of zinc alkyl on alkyl halogen substitution products of the hypothetical compound, NH_6. Tertiary butyl iodide,[1] $(CH_3)_3CI$, reacts immediately with zinc ethyl, and tetraethylammonium iodide, $(C_2H_5)_4NI$, seems to be structurally analogous. Triethylamine dibromide,[2] $(C_2H_5)_3NBr_2$, appears to present even a more favorable case, as Tscherniak[3] had successfully prepared triethylamine by the action of zinc ethyl on ethyldichloramine, $(C_2H_5)NCl_2$. The experiments were confined to these two substances.

Action of Zinc Ethyl on Tetraethylammonium Iodide.

Strange to say, tetraethylammonium iodide and zinc ethyl do apparently react. The action is very slow; heating on the water-bath for several hours produces no effect, nor does standing at ordinary temperature for ten days. But if, after standing from four to six weeks, a mixture of the substances in question (slightly diluted with ether to give fluidity to the mass) is poured into water and filtered from the

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[1] Ann. Chem. (Liebig), **165**, 107.

[2] The kindness of Dr. J. F. Norris enabled me to use this compound instead of the more difficultly accessible $(CH_3)_3NICl$.

[3] Ber. d. chem. Ges., **9**, 143.

zinc hydrate,[1] the solution possesses a *strongly alkaline* reaction. It slowly turns yellow, and then a finely crystalline red precipitate separates. This precipitation is not hastened by carbon dioxide; in the experiment that was carefully controlled it required a day and a half for completion.

10 grams tetraethylammonium iodide, 5 grams zinc ethyl, and 15 cc. ether stood for 43 days at the ordinary working temperature, and yielded 0.61 gram of the red substance. This red substance, by properties and analysis, seems to be tetraethylammonium triiodide, $(C_2H_5)_4NI_3$. (Found 73.4 per cent. iodine, calculated 74.5 per cent.; the crude product was analyzed directly).

I am at a loss to explain this curious reaction. The formation of an alkaline[2] substance is in itself peculiar. The alkaline body could not be isolated nor in any way identified owing to the very small quantity formed; in evaporating the solution saturated with carbon dioxide, the alkaline reaction disappeared. The precipitation of tetraethylammonium triiodide from an *alkaline* solution, which could not have contained any free iodine, is quite inexplicable.

Action of Zinc Ethyl on Triethylamine Dibromide.[3]

This reaction presented three possibilities:

I. $(C_2H_5)_3NBr_2 + Zn(C_2H_5)_2 = (C_2H_5)_5N + ZnBr_2$.

II. $(C_2H_5)_3NBr_2 + Zn(C_2H_5)_2 = (C_2H_5)_4NBr + Zn(C_2H_5)Br$.

III. $(C_2H_5)_3NBr_2 + Zn(C_2H_5)_2 = (C_2H_5)_3N + C_2H_5Br + Zn(C_2H_5)Br$.

Reactions I and II would represent actual syntheses; reaction III would involve reduction. Experiment showed that reaction III took place, to the exclusion[4] of the others. It seems superfluous to give the details of work which has no preparative value; but every product of the action was iden-

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[1] It was impossible to determine satisfactorily whether this zinc hydrate contained basic zinc iodide, and thus ascertain whether the zinc ethyl had reacted in the usual manner. The hydrate retained tetraethylammonium iodide so tenaciously that even after washing for several days with water and alcohol, the filtrate still gave a distinct reaction with silver nitrate.

[2] It is not impossible that this alkaline substance is really pentaethyl nitrogen, but alkalinity is hardly a property it would be expected to possess.

[3] This was prepared according to Remsen and Norris. This JOURNAL, 18, 90.

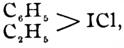
[4] A minor reaction, represented by the equation $(C_2H_6)_3NBr_2 + Zn(C_2H_6)Br = (C_2H_6)_3N + C_2H_5Br + ZnBr_2$, also took place.

tified. As a matter of fact, in some cases where the mixture of zinc ethyl and the dibromide (always diluted with considerable chloroform) was allowed to stand several hours, as much as 33 per cent. of the total nitrogen employed was obtained as tetraethylammonium bromide; but this was due to a secondary action,—the addition of ethyl bromide to triethylamine—for, if the mixture was examined shortly after its preparation, no quaternary ammonium compound could be found.

No synthesis whatever, then, had been accomplished. Triethylamine dibromide, in its action toward zinc ethyl, behaves merely as a mixture of triethylamine and bromine. It will be interesting to learn from Dr. Norris whether it behaves thus in every case. In this connection, it may be remarked that ethyl dichloramine, which reacts normally with zinc ethyl, acts like free chlorine in some instances.[1]

Perhaps pentaethyl nitrogen will be prepared by some one more fortunate, by means at present undiscernible. The experiments just sketched will not be continued.

Action of Zinc Ethyl on Phenyl Iodide Chloride.

This may be the place to briefly give an account of the action of zinc ethyl on phenyl iodide chloride, $C_6H_5I.Cl_2$, which possesses some analogy to triethylamine dibromide, and the study of which I took up for that reason. Both are halogen addition-products, a sort of half-way station between the more stable derivative of elements exhibiting two valencies. One might reasonably expect to obtain, in this case, a semi-aliphatic analogue,  $\begin{matrix}C_6H_5\\C_2H_5\end{matrix}{>}ICl$, of the very stable iodonium compounds of Hartmann and Victor Meyer. The reaction, however, is exactly analogous to that of the dibromide: phenyl iodide, ethyl chloride, zinc chloride, and zinc oxychloride are the final products. There are indications that an unstable intermediate addition-product is formed. It was possible to show analytically that almost exactly half of the total chlorine was regained as zinc chloride (and oxychloride); the other half could not be accurately traced: the phenyl

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[1] Ber. d. chem. Ges., 16, 1047.

iodide was recovered unaltered, and in practically theoretical quantity, but only a small percentage of ethyl chloride could be isolated.

ANN ARBOR, MICH.

THE CONDUCTIVITY OF SOLUTIONS OF ACETYLENE IN WATER.[1]

BY HARRY C. JONES AND CHARLES R. ALLEN.

Keiser[2] has shown by his work on the metallic compounds of acetylene, that both the hydrogen atoms possess acid properties, being capable of substitution by some metals. The compounds of silver and copper are formed by the substitution of two univalent metallic atoms for the two hydrogen atoms in the acetylene, and have the composition indicated by the formulas Ag_2C_2 and Cu_2C_2, respectively. In these cases the acetylene conducts itself like a weak dibasic acid.

As the behavior of acetylene in forming these compounds is that of an acid, it might be expected that it would exhibit, at least to some extent, the conductivity phenomena shown by that class of substances. It appeared, therefore, that the investigation of the molecular conductivity of acetylene might be of interest.

For the cuprous acetylide, from which the acetylene was obtained, we are indebted to Prof. Keiser. The acetylene was liberated from the cuprous acetylide by heating it in a flask, on the water-bath, with a solution of potassium cyanide, as directed by Keiser. The gas was passed into water, which had been redistilled from acid and alkaline potassium permanganate and condensed in a tube of block tin. The conductivity of the water used was determined and found to be negligible. This solution was tested for cyanogen, which might have passed over in some way, by boiling a portion of it with an alkali and ferrous sulphate, neutralizing the alkali with an acid, and adding a ferric salt. No trace of a blue color was obtained. The usual tests for copper, with ammonia or ammonium sulphide also gave negative results, thus showing the absence of all possible impurities. Solutions of

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[1] Solutions were prepared by Jones; the conductivity measurements were made by Allen.

[2] This JOURNAL, 14, 285 and 15, 535.

acetylene thus prepared and tested were used in the conductivity determinations.

Soon after the work was begun it was found that the solutions gave off the acetylene gas very rapidly, even in glass-stoppered bottles, and at temperatures only a little above zero. It was impossible to retain even dilute solutions at a constant concentration for any considerable time. After a number of trials, the following method was adopted as introducing the least error. The thermostat-bath of the Kohlrausch–Ostwald conductivity apparatus was replaced by a vessel containing much finely powdered ice and a little water, giving a temperature which was approximately zero. The acetylene solution of unknown concentration, was cooled nearly to zero by placing it in a glass-stoppered bottle and immersing the bottle in a freezing-mixture. A portion of this solution was then poured into the resistance cell, (which was already in the ice-bath described above), and the position of equilibrium on the bridge determined as rapidly as possible. A known volume of the solution in the cell was then at once drawn off in a pipette, and the amount of acetylene present determined as follows: A standard tenth-normal solution of silver nitrate and an exactly equivalent solution of potassium chloride were used. The gas was brought into combination by running in an excess of the silver nitrate solution. An equal volume of the potassium chloride solution was then run in, a few drops of a solution of potassium chromate, serving as an indicator, added, and the excess of potassium chloride titrated with the silver nitrate. As there was no loss of acetylene from the solution after the first addition of silver nitrate, the only loss of gas, affecting the results was that which took place during the interval between the conductivity measurement and the first addition of silver nitrate, which was, on an average, only two or three minutes. Since the solutions of acetylene were very dilute and the analyses, of necessity, made with a comparatively small volume, the standardization of the solutions must be regarded as only roughly approximate. The results of the conductivity measurements of the acetylene solutions, are given in the following table. The column headed v gives the volume in liters, which contains a one-half gram-molecular weight of the gas; μ_v are the molecular conductivities at the volumes v.

	v.	μv.
1.	417	29.0
2.	833	41.0
3.	1111	50.0
4.	2502	77.0

Although these results are necessarily affected by considerable error, due to the causes indicated above, yet they undoubtedly show that solutions of acetylene in water are somewhat dissociated, and that this dissociation increases with the dilution, results which would be expected from the weakly acid character of the compound.

CHEMICAL LABORATORY, JOHNS HOPKINS UNIVERSITY.

THE USE OF PHENOLPHTHALEÏN IN ILLUSTRATING THE DISSOCIATING ACTION OF WATER.

BY HARRY C. JONES AND CHARLES R. ALLEN.

The fact that an alcoholic solution of phenolphthaleïn is not colored red by ammonia or triethylamine, but is so colored by potassium, sodium, or barium hydroxide was observed by Menschutkin.[1] He stated that if phenolphthaleïn is added to alcohol, it does not show an alkaline reaction on the addition of triethylamine or ammonia, and he concluded that "the alkalinity of the triethylamine had disappeared, alcohol decomposing the compound of phenolphthaleïn with triethyamine, even when the latter is present in a large excess.

Without knowing of this work of Menschutkin, we observed facts of the same kind in connection with an investigation which is being carried out in this laboratory by Mr. Mackay. Not only an alcoholic solution of ammonia did not show an alkaline reaction with phenolphthaleïn, but when a few drops of a water solution of ammonia were added to several cubic centimeters of alcohol, this solution also failed to give an alkaline reaction with alcoholic phenolphthaleïn. If, however, a considerable volume of water was added to this solution the red color appeared.

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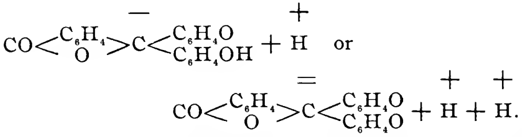
[1] Ber. d. chem. Ges., **16**, 315.

When potassium or sodium hydroxide was substituted for ammonia the red color appeared at once, without the addition of water, as stated by Menschutkin. There is thus a marked difference between the action of sodium and potassium hydroxides on the one hand, and that of ammonium hydroxide on the other.

It would be difficult to interpret these facts without the aid of the dissociation theory, unless we were content simply to say that potassium and sodium hydroxides are *stronger* bases than ammonium hydroxide, which really explains nothing. This difficulty becomes the more apparent in that Menschutkin was compelled to seek an explanation in the decomposition of the compound of phenolphthaleïn with triethylamine, by alcohol. In the light of the dissociation theory, however, the facts become intelligible.

In a solution prepared by adding a few drops of aqueous ammonia to several cubic centimeters of alcohol, little or no dissociation of the ammonium hydroxide is effected. The addition of water to this solution dissociates the base, the degree of dissociation depending on the amount of water, with respect to alcohol present. The presence of the ions $\overset{+}{N}H_4$ and $\overset{-}{O}H$, into which the ammonium hydroxide dissociates, will cause the phenolphthaleïn to dissociate into :



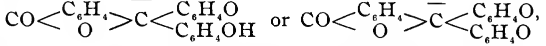
$$CO<^{C_6H_4}_{O}>\overset{-}{C}<^{C_6H_4O}_{C_6H_4OH} + \overset{+}{H} \quad \text{or}$$

$$CO<^{C_6H_4}_{O}>\overset{=}{C}<^{C_6H_4O}_{C_6H_4O} + \overset{+}{H} + \overset{+}{H}.$$

The complex anion is colored and gives the characteristic color to the solution in which it is present as an ion. When this colored anion is combined with the colorless cation, hydrogen, to form a molecule, the solution of these molecules is nearly colorless. When the dissociation of the phenolphthaleïn indicated above is effected, its cation $\overset{+}{H}$ would combine with the anion $\overset{-}{O}H$ from the ammonium hydroxide, forming water, since these ions cannot, to any appreciable extent, remain uncombined in the presence of each other.

It may be, however, that the actual course of the reaction is slightly different from that above described, in that the ammonium may, first, combine with the phenolphthaleïn in the alcoholic solution. The addition of water would then dissociate this compound, liberating the colored anion referred to above.[1]

In either case the cause of the color is the presence of the anion,



$$CO<\substack{C_6H_4 \\ O}>\overline{C}<\substack{C_6H_4O \\ C_6H_4OH} \quad \text{or} \quad CO<\substack{C_6H_4 \\ O}>\overline{\overline{C}}<\substack{C_6H_4O, \\ C_6H_4O}$$

and the dissociation of the compound yielding this colored anion is effected by the water which is present. The dissociation theory furnishes this explanation. It remains to determine whether the explanation is true. If it is, then a solution formed by adding a little aqueous ammonia to a considerable volume of alcohol should show little or no dissociation, and the amount of dissociation should increase with the addition of water. Solutions of potossium or sodium hydroxide in mixtures of alcohol and water should be more dissociated than corresponding solutions of ammonium hydroxide. Indeed, a solution of sodium or potassium hydroxide in alcohol alone, should manifest some dissociation, since, as stated above, it gives the color reaction with phenolphthaleïn.

All of these points can be tested experimentally by the conductivity method. We have carried out such measurements as seemed desirable, and give the results in the following tables. Table I contains the results for ammonium hydroxide. The conductivity of a known volume of a standard solution of aqueous ammonia was at first determined. A measured volume of this solution was then removed, an equal volume of absolute alcohol added, and the conductivity again determined. This process was repeated until nearly all of the water had been removed, the solvent being nearly pure alcohol.

The values under v are the number of liters which would contain a gram molecular weight of the ammonium hydroxide at the particular dilution of the solution used. The column μv gives the molecular conductivities at the volume v

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[1] Long (this JOURNAL) 11, 84, has shown that when strong aqueous ammonia is allowed to set on phenolphthaleïn for a considerable time, phenoldiimidophthaleïn, a colorless substance is apparently formed. If this compound should be formed to some extent in the alcoholic solutions under discussion, its presence would not affect the color reactions of the solutions in question, since it is soluble even in alkalies without color.

and at 25° C. That portion of the solution which was withdrawn in each case after the conductivity reading had been made, was placed in a Nessler tube, treated with some phenolphthaleïn, and the strength of the red color observed approximately. These observations are recorded in the column headed color. No correction is introduced in the results for the conductivity of the water used, since this was tested, and for water which had been redistilled from acid and alkaline permanganate, was so slight that it was quite negligible.

The corresponding measurements for potassium hydroxide are given in table II.

Table I.

v.	μ_v.	Parts water.	Parts alcohol.	Color.
11	4.8	100	0	strong
22	2.2	50	50	slight
44	1.0	25	75	none, or trace
88	1.1	12.5	87.5	none

Table II.

v.	μ_v.	Parts water.	Parts alcohol.	Color.
8.8	214	100	0	strong
17.6	77	50	50	"
35.2	26	25	75	"
70.4	20	12.5	87.5	"

The conductivity of a standardized solution of potassium hydroxide in pure alcohol alone, was determined with the following results :

v.	μ_v.	Color.
8	15	strong.

The appearance of the red color when water is gradually added to an alcoholic solution of phenolphthaleïn containing ammonia is not sudden. As the results show, it requires the addition of a considerable volume of water before any trace of red can be detected, then a delicate pink color appears, gradually shading off into red, in the presence of more and more water. This would also be expected, if the color is a function of the dissociation, since the latter increases gradually with the increase in the water present. The results thus appear to confirm at all points the deductions from the dissociation theory.

This experiment furnishes a very satisfactory lecture demonstration of the dissociating action of water. A few drops of an alcoholic solution of phenolphthaleïn are placed in a glass cylinder and diluted to, say 50 cc., by the addition of alcohol. A few drops of an aqueous solution of ammonia are then added. A red color may appear where the aqueous ammonia first comes in contact with the alcoholic phenolphthaleïn, but this will disappear instantly on shaking the cylinder, leaving the solution with a yellowish tint, possibly due to the formation of the ammonium salt of phenolphthaleïn. Water is then gradually added to the cylinder, when the red color appears, first faint, then stronger as the amount of water increases. When the red color has become intense, add a considerable volume of alcohol and the entire color will disappear, leaving a solution which is slightly yellow. The experiment serves then not only to illustrate the dissociating action of water, but also the driving back of the ions into molecules by alcohol.

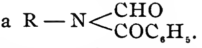
CHEMICAL LABORATORY.
JOHNS HOPKINS UNIVERSITY.

Contribution from the Sheffield Laboratory of Yale University.

THE ACTION OF ACID CHLORIDES ON THE SILVER SALTS OF THE ANILIDES.

BY H. L. WHEELER AND B. B. BOLTWOOD.

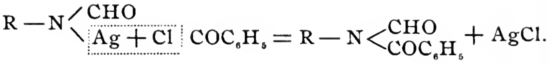
In this paper we shall describe the action of benzoyl chloride on silver formanilide, on silver 2-4, dichlorformanilide and on silver formorthotoluide. We shall show that these reactions resulted in the formation of diacid anilides and a diacid toluide, and that these diacid derivatives have the structure represented by the general formula



$R - N\begin{matrix} CHO \\ COC_6H_5 \end{matrix}$.

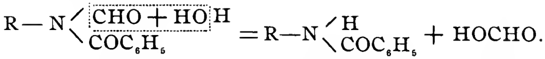
Some experiments on the action of chlorcarbonic ethylester on the silver salts of formanilide and formorthotoluide are also given.

If the reactions with benzoyl chloride are viewed as direct double decompositions, the following general equation will represent the formation of the diacid anilides, provided the silver salts have the metal joined to nitrogen :



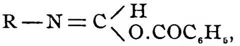
$$R-N\begin{matrix}\diagup CHO \\ \diagdown \boxed{Ag + Cl}\end{matrix} COC_6H_5 = R-N<\begin{matrix}CHO \\ COC_6H_5\end{matrix} + AgCl.$$

This view seems to be confirmed by the action of alkali or acids on the diacid anilides and toluide. This action consists in the removal of the formyl group, leaving the benzoyl radical attached to the $R-N<^{H}$ group, and shows that the structure of the diacid anilides is best represented by the formula used above. It may be represented by the following equation:



$$R-N\begin{matrix}\diagup \boxed{CHO + HO}H \\ \diagdown COC_6H_5\end{matrix} = R-N\begin{matrix}\diagup H \\ \diagdown COC_6H_5\end{matrix} + HOCHO.$$

On the other hand, if the diacid anilides were oxygen derivatives, and if they had the structure



$$R-N=C\begin{matrix}\diagup H \\ \diagdown O.COC_6H_5,\end{matrix}$$

corresponding to the pseudoform of the anilide, it would be difficult to see how the formyl group could be removed, leaving the benzoyl radical attached to the group $R-N\begin{matrix}\diagup H, \\ \diagdown\end{matrix}$ as shown above.

From the above considerations, we are led to believe that the diacid anilides are nitrogen derivatives. It follows then that the silver salts of the anilides behave with benzoyl chloride as if they had the structure $R-N\begin{matrix}\diagup CHO \\ \diagdown Ag\end{matrix}$, that is, as if the silver was joined to nitrogen. This behavior is remarkable, since the results obtained by the study of the action of alkyl halides on these salts are in direct opposition to this view. The work of Comstock,[1] with Kleeburg,[2] Wheeler[3] and Clapp[4] has shown that these salts give imido ethers with alkyl halides. It was therefore concluded that the silver in these compounds is joined to oxygen, their structure being represented by the formula $R-N=C\begin{matrix}\diagup H \\ \diagdown OAg\end{matrix}$ and the gen-

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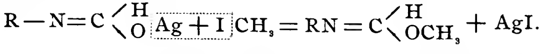
[1] Ber. d. chem. Ges., **23**, 2274.

[2] This JOURNAL, **12**, 493.

[3] *Ibid*, **13**, 514.

[4] *Ibid*, **13**, 525.

eral reaction represented as a direct double decomposition as follows:



$$R-N=C\begin{matrix}\diagup H\\ \diagdown O\end{matrix}\boxed{Ag+I}CH_3 = RN=C\begin{matrix}\diagup H\\ \diagdown OCH_3\end{matrix} + AgI.$$

It is not our intention to discuss in this article the probable structure of the silver salts, but to call attention to the fact that these salts react as if they were derivatives of both the normal and pseudoform of the anilide. In other words, if we consider the double decomposition or substitution theory alone, these salts behave as if they had two structures. Questions of this nature, of so-called tautomeric reactions have received considerable attention from Nef[1] and his co-workers in recent years. Nef has plainly shown in his series of elaborate researches on tautomerism that reactions of this nature involve not alone a double decomposition or substitution, but also an intermediate addition. We refer especially to his last article on this subject,[2] and also to his work published in 1892, where he refers to the different behavior of the sodium and silver salts of the anilides with alkyl halides, and decides that it is very improbable that these salts differ in their constitution, and that, in one case, an addition must take place.[3]

It is now evident that although in the action of alkyl halides or of acid chlorides on the silver salts, a double decomposition may take place, such cannot be the case in both. Evidently in one case, and possibly in both an intermediate addition is involved. The experimental evidence thus far obtained, indicates that in the reactions described in this paper, the acid chloride first forms an addition-product with the silver salt. This addition-product then separates silver chloride with the formation of the diacid anilide. That a silver salt can add hydrogen chloride and hydrogen sulphide without immediate separation of silver chloride or sulphide has been shown in the beautiful work of Nef on silver fulminate.[4] The addition of benzoyl chloride to the silver salts of the anilides seem to be another example of this peculiar union.

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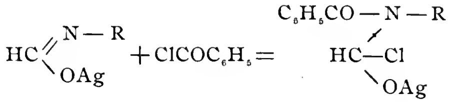
[1] This JOURNAL, **11**, 1; **12**, 379; **13**, 422. J. prakt. Chem. [2], **42**, 161. Ann. Chem. (Liebig), **266**, 52; *Ibid.*, **270**, 267; *Ibid.*, **276**, 200; *Ibid.*, **277**, 59 and 162; *Ibid.*, **280**, 263 and 291.

[2] Ann. Chem. (Liebig), **287**, 269.

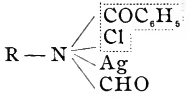
[3] Proc. Amer. Acad., May, 1892, 102; and Ann. Chem. (Liebig), **270**, 293.

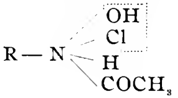
[4] Ann. Chem. (Liebig), **280**, 313.

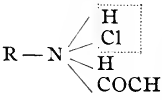
If this is indeed the case, it does not necessarily favor the assumption that the silver salts of the anilides are derivatives of the pseudoform of the anilide, nor that addition takes place as follows:



For it is to be noticed that the addition of acid chloride to a silver salt of an anilide might well take place to the nitrogen entirely, the resulting product then being analogous to the hypochlorous acid addition first noticed by Witt,[1] and also to the salts of the anilides with the halogen acids.[2] The compounds being pentavalent nitrogen derivatives as follows:[3]







That the structure of the silver salts of the anilides can not be decided by their final reaction-products is shown by the above considerations, and it is again shown in the work that we have done so far with chlorcarbônic ethyl ester and silver formanilide. We shall show in the latter part of this paper that these substances gave both the oxygen derivative, phenylformimidoethyl ether or ethylisoformanilide, and the nitrogen compound formylphenylurethane from which we isolated phenylurethane. The action with silver formorthotoluide appears to be similar.

Work on the action of acid chlorides on other salts of the anilides is now in progress in this laboratory, and it is also intended to continue the present work on the silver salts, this having been interrupted by the departure of one of us from this laboratory.

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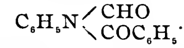
[1] Ber. d. chem. Ges., **8**, 1226.

[2] Knorr: Ann. Chem. (Liebig), **245**, 375; Wheeler and Walden: This JOURNAL, **18**, 87.

[3] Pictet explains the formation of benzanilide from benzoyl chloride and form— or acetanilide, etc., by means of a similar addition of the acid chloride to the anilide. Ber. d. chem. Ges., **23**, 3011.

Experimental Part.



Formylbenzanilide, $C_6H_5N\begin{cases}CHO \\ COC_6H_5\end{cases}$. — When dry silver formanilide[1] is suspended in a small amount of benzene and one molecular proportion of benzoyl chloride is added, the first evidence of a reaction begins with a slight warming. On stirring, the mass thickens until it becomes almost semi-solid, it then becomes more fluid and the odor of benzoyl chloride disappears. The action can be hastened by warming. On filtering and concentrating the benzene solution, silver chloride frequently separates, although the extract filters at first perfectly clear. The residue consists of an oil which on standing solidifies. When this mass is crystallized from alcohol, more silver chloride separates along with beautiful colorless needles of the diacid anilide. It sometimes takes several crystallizations from alcohol to free these crystals completely from silver. Attempts were made to isolate this supposed addition product which apparently is formed here, and which would explain the persistency with which silver chloride contaminates the product, but the reaction took place too rapidly to permit of the isolation of an addition-product suitable for analysis, even at the melting-point of benzene. The yield of formylbenzanilide is practically quantitative. Analysis of the diacid anilide dried over calcium chloride gave:

	Found.	Calculated for $C_{14}H_{11}NO_2$.
C	74.33	74.67
H	4.92	4.88
N	6.46	6.14

Formylbenzanilide is readily soluble in benzene and chloroform, less so in ether and alcohol, and difficultly in water. It melts at 112°. When it is treated with sodium hydroxide the formyl group is removed and benzanilide melting at 162° is obtained. A mixture of benzanilide and formylbenzanilide can readily be distinguished when crystallized from alcohol. The former separates at first in needles, the latter forms a supersaturated solution, and on shaking deposits plates.

2-4 Dichlorformanilide, $C_6H_3Cl_2NH.CHO$.—This was pre-

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[1] This was prepared according to the directions of Comstock and Kleeburg, *loc. cit.*

pared from acetanilide by chlorinating according to the method of Beilstein and Kurbatow.[1] From the pure dichloracetanilide thus obtained the acetyl group was replaced by the formyl in the usual manner. 2-4 dichlorformanilide crystallizes from alcohol in colorless needles, which melt at 153°.

	Found.	Calculated for $C_7H_5NOCl_2$.
C	44.15	44.22
H	2.71	2.63

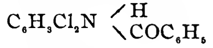
Silver 2-4 Dichlorformanilide, $C_6H_3Cl_2NAgCHO$, was obtained from the sodium salt in the same manner as silver formanilide. It separates as a white amorphous bulky precipitate, and as regards the action of light, it is the most stable silver salt of the anilides that we are familiar with. It was washed with water and dried over sulphuric acid.

	Found.	Calculated for $C_6H_3Cl_2NAgCHO$.
Ag	36.48	36.36

2-4 Dichlorformylbenzanilide, 
$C_6H_3Cl_2N\left\langle\begin{matrix}CHO\\COC_6H_5\end{matrix}\right.$. — To prepare this, the above silver salt was mixed with benzoyl chloride in proportion to their molecular weights, the operation being carried out as before in dry benzene. When the benzene solution was filtered and evaporated, an oil remained. This was taken up in 95 per cent. alcohol. This left a residue apparently of silver chloride. On letting the alcoholic solution stand, more silver chloride separated ; then the diacid anilide, first as an oil, and finally in bunches of colorless acicular prisms. These, on crystallizing from alcohol, melted at 77°. Analysis gave :

	Found.	Calculated for $C_{14}H_9Cl_2NO_2$.
C	57.09	57.14
H	3.17	3.06
N	4.83	4.76

2-4 Dichlorformylbenzanilide is readily soluble in benzene and in hot alcohol, but difficultly soluble in water.

2-4 Dichlorbenzanilide, 
$C_6H_3Cl_2N\left\langle\begin{matrix}H\\COC_6H_5\end{matrix}\right.$. —This was

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[1] Ann. Chem. (Liebig), 196, 215.

formed when 2-4 dichlorformylbenzanilide was boiled with dilute hydrochloric acid, the resulting product was crystallized from strong alcohol. It melted sharply at 117°. Analysis gave :

	Found.	Calculated for $C_{13}H_9NOCl_2$.
N	5.11	5.26

2-4 Dichlorbenzanilide is only sparingly soluble in hot water, difficultly in cold alcohol, readily in hot, and easily in ether.

Formylbenzorthotoluide,  $C_6H_4CH_3N\begin{matrix}\diagup CHO\\ \diagdown COC_6H_5\end{matrix}$. — The preparation of this from silver formorthotoluide and benzoyl chloride was precisely the same as we have described in the two preceding cases. The product showed the same tendency to retain silver. It was obtained from the benzene solution as an oil. This was dissolved in alcohol and the solution allowed to stand, when beautiful, thick, apparently rectangular plates, diagonally striated, separated. These on crystallizing from alcohol melted at 92°. Analysis gave :

	Found.	Calculated for $C_{15}H_{13}NO_2$.
C	75.12	75.31
H	5.64	5.43
N	5.87	5.85

Formylbenzorthotoluide is readily soluble in benzene and in warm alcohol, but difficultly soluble in water. Some of the analyzed material was treated with dilute sodium hydroxide, and the product then crystallized from dilute alcohol, when benzorthotoluide was obtained in colorless needles melting at 142°.

A comparison of the melting-points of the diacid derivatives, described in this paper, with those of the mono acid anilides and toluides shows no strict regularity, except that the melting-points of the di-derivatives are lower than those of the benzoyl compounds. This will be seen from the following list:

	M. P.		M. P.
Formanilide	46°.	Formorthotoluide	62°.
Formylbenzanilide	112°.	Formylbenzorthotoluide	92°.
Benzanilide	163°.	Benzorthotoluide	142°.

	M. P.
2-4 Dichlorformanilide	153°.
2-4 Dichlorformylbenzanilide	77°.
2-4 Dichlorbenzanilide	117°.

Action of Chlorcarbonic Ethylester on Silver Formanilide and on Silver Formtoluide.

Silver formanilide and chlorcarbonic ester were mixed in benzene solution in molecular proportions; the reaction took place rapidly and carbonic acid gas was given off. To complete the reaction, the whole was warmed on the water-bath. On filtering from silver chloride and evaporating the benzene solution, an oil was obtained; this was distilled at a pressure of 18 mm., when a small amount of phenylformimidoethyl ester or ethylisoformanilide[1] was obtained, which boiled at about 106° under these conditions. This substance was identified by its action with aniline, and also on standing alone exposed to the air. In both cases diphenylformamidine was obtained, melting at 136°. For comparison this imidoether was made from the silver salt of formanilide with ethyl iodide. This product was found to be identical with that obtained from the chlorcarbonic ester reaction.

Phenyl 2-4 dichlorphenylformamidine,  $HC\begin{matrix}\diagup NC_6H_5 \\ \diagdown NHC_6H_3Cl_2\end{matrix}$.—This was formed when the above imidoether was mixed with 2-4 dichloraniline. It crystallizes from benzene in bunches of minute colorless plates, which melt at 159°.

	Found.	Calculated for $C_{13}H_{10}N_2Cl_2$.
N	10.59	10.57

The residue left after the distillation of the imido ether was treated with dilute hydrochloric acid and alkali, and then crystallized from ligroïn. This gave phenylurethane melting at 52°. On extracting the silver chloride residue with water, diphenylformamidine hydrochloride was obtained.

In another experiment 30 grams of silver salt were taken, and an excess of chlorcarbonic ester was unintentionally used. In this experiment we succeeded in isolating phenylurethane in addition to the imido ether and the amidine. The approxi-

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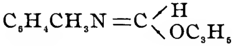
[1] Described by Comstock and Clapp, *loc. cit.*

mate quantities of these substances formed were as follows: 0.9 gram of diphenylformamidine hydrochloride, 5.0 grams of imido ether and 14 grams of oil, which we did not succeed in purifying. A small quantity of isonitril was formed, probably in the distillation. The oil evidently consisted of the expected formylphenyl urethane, since, on warming with dilute sodium hydroxide and then crystallizing the product from ligroïn, phenylurethane was obtained, melting at 52°. The latter was positively identified by analysis:

	Found.	Calculated for $C_9H_{11}NO_2$.
C	65.60	65.45
H	6.74	6.66

Experiments with the silver salt of formorthotoluide and chlorcarbonic ethyl ester, conducted in the same manner as the preceding, gave orthotolylformimidoethyl ester, *s*-ditolyl urea, and a residue, presumably formyltolyl urethane, but we did not succeed in purifying this for analysis.

Orthotolylformimidoethyl Ester,



$C_6H_4CH_3N{=}C\begin{cases}H\\OC_3H_5\end{cases}$.—

This is an aromatic oil boiling at 101°, at 12 mm. pressure. Analysis gave:

	Found.	Calculated for $C_{10}H_{13}NO$.
C	73.19	73.62
H	7.94	7.91

From the high-boiling fractions of the imido ether a crystalline colorless substance separated. This was washed with ligroïn and analyzed.

	Found.	Calculated for $C_{15}H_{16}N_2O$.
C	74.44	74.37
H	7.11	7.43
N	11.06	11.57

Its melting-point, 256°, and the above analysis show that this substance was *s*-orthoditolyl urea.

Contribution from the Sheffield Laboratory of Yale University.

ON THE EXISTENCE OF TWO ORTHOPHTHALIC ACIDS.

BY W. T. H. HOWE.

INTRODUCTION.

The melting-point of orthophthalic acid, as given by different investigators, varies from 175° to 213°. Lossen[1] obtained phthalic acid by oxidizing naphthalene with potassium permanganate and determined the melting at 184°. Weith[2] obtained, by oxidizing orthotoluic acid, an acid crystallizing in colorless prisms and melting from 182° to 195°. Piccard[3] obtained phthalic acid from the same source, but gave as its melting-point 180°, while Carius[4] gave the melting-point as low as 175°–180°. Ador[5] declared these melting-points as too low, since phthalic acid obtained by boiling the anhydride with water gave 203° for the finely pulverized, and 213° for the crystallized acid, although he says that the acid precipitated from its salts apparently does melt at 180°. Graebe,[6] in a revision of the previous work, assumed that the higher melting-points given by Ador were due to too rapid heating, and that the 184 degree melting-point of Lossen was the correct one.

The present investigation has shown that two orthophthalic acids exist, one melting at 184°, the other at 203°. The variations in melting-point found by previous observers have, therefore, been due, not alone to the formation of the low melting anhydride, but to the fact that under the varying conditions of preparation, these two different acids have been obtained or mixtures of them. Very probably, certain low melting-points have been due to an admixture of an acid salt which is precipitated together with the acid under certain conditions of concentration.

The acid melting at 203° will be called the α-acid, while that melting at 184° will be designated as the β-compound. The higher melting-point has usually been the accepted one.

The two acids are identical in composition, molecular weight and molecular refraction, but they differ (1) in melt-

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[1] Ann. Chem. (Liebig), **144**, 78.

[2] Ber. d. chem. Ges., **7**, 1057.

[3] Ber. d. chem. Ges., **19**, 579.

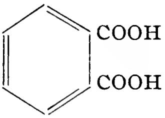
[4] Ann. Chem. (Liebig), **148**, 62.

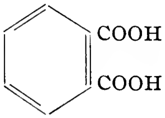
[5] Ann. Chem. Liebig), **164**, 230.

[6] Ann. Chem. (Liebig), **238**, 321.

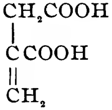
ing-points, (2) in electrical conductivity, (3) in solubility, (4) in the properties of their salts with organic and inorganic bases, (5) in their reduction products. The β-acid is converted into the α-body simply by boiling with water, while the reverse change takes place by the action of strong acids or alkalies.

It is possible to explain the existence of two orthophthalic acids by the single and double bond isomerism required by Kekulè's benzene formula, as follows :

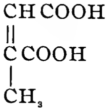




The existence of this form of isomerism has never been definitely established, and indeed its absence has been considered as a strong argument against Kekulé's formula, but it seems possible from the analogous behavior of citra- and itaconic acids, which are believed to have single and double bonds between the carbons to which the carboxyls are attached, thus :



$$\begin{array}{l} CH_2COOH \\ | \\ C\,COOH \\ \| \\ CH_2 \end{array}$$



$$\begin{array}{l} CH\,COOH \\ \| \\ C\,COOH \\ | \\ CH_3 \end{array}$$

Furthermore, the single and double bond isomerism is plausible from the behavior of the β-acid on reduction as compared with that of the α-acid as studied by Baeyer.[1] The β-acid yields a new dihydrophthalic acid when reduced under the same conditions as used by Baeyer with the α-acid.[1] This product is much more unstable than the $\Delta^{3.5}$ body obtained by Baeyer from the α-acid. It differs from that compound by reducing a cold silver nitrate solution and by being reduced by sodium amalgam at a low temperature to two tetrahydro-orthophthalic acids. Upon the basis of Baeyer's exhaustive work, the new dihydro acid seems to be the $\Delta^{1.3}$ compound,

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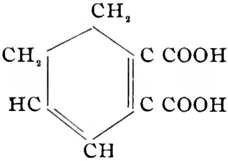
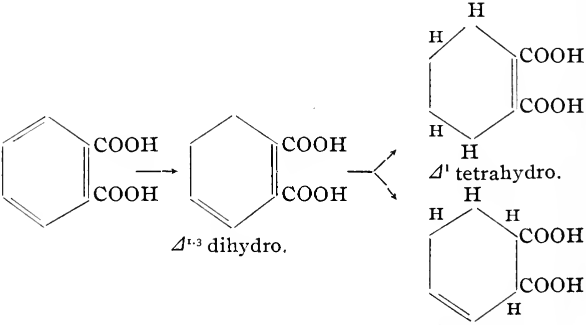
[1] Ann. Chem. Liebig, **269**.



this being the only one, previously unknown, considered by Baeyer as stable enough to exist, and he predicted that this would be rather unstable.

Of the two tetrahydro acids obtained from the reduction of the new dihydro acid, one agrees in its melting-point and that of its anhydride, as well as in its solubility with the Δ^1 compound obtained by an indirect process by Baeyer, and it is doubtless that compound. The other is a new tetrahydro acid, and since, according to Baeyer's theory, only the cis and trans Δ^3 compounds have been lacking, this should be one of those acids. If this proves to be the case, the double bond should occur between the carboxyls in the β-acid, as may be seen from the following formulæ:



Δ^3 tetrahydro.

It is an important fact that Baeyer did not obtain the Δ^1 tetrahydro acid by the direct reduction of any dihydro compound, because it shows a marked difference in the behavior

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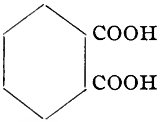
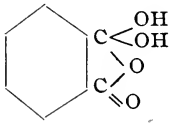
[1] The β-acid yields a new dihydrophthalic acid when reduced under the same conditions as used by Baeyer with the α-acid.

of the β-orthophthalic acid, and shows the probable position of the double bond.

Other explanations of the existence of two orthophthalic acids seem less satisfactory than the one according to Kekulè's formula suggested above. An isomerism depending upon the symmetrical and asymmetrical arrangement of the hydroxyls, as follows:



and



has the arguments against it that the second form would apparently be very unstable, and moreover, the identical molecular refraction of the two isomers does not allow of this assumption.

EXPERIMENTAL PART.

Method for Preparing the Two Acids in a Pure Condition.

α-Orthophthalic Acid.—Commercial phthalic acid is usually a mixture of the two acids, but if an aqueous solution of it or of the anhydride, be boiled for 3 to 4 hours, an acid crystallizes out on cooling, which, filtered and dried for an hour at 100°, melts in a finely pulverized condition at 203–4°. It was shown by Graebe that if the bath be kept at 183–4° for some time the acid melts. But this is due simply to the decomposition of the acid into its anhydride. This may be effected at as low a temperature as 160°.

To prepare the pure β-acid, the anhydride is dissolved in cold dilute sodium hydroxide, the solution cooled to 0°, slowly precipitated with hydrochloric acid and dried over sulphuric acid. Phthalic anhydride appears to be the anhydride of the β-acid, for it yields this on dissolving in alkali, precipitating and drying as stated above. This cannot be due to the isomerizing influence of the alkali, since the pure α-acid, dissolved in alkali, precipitated at 0° and dried over sulphuric acid, melts at 199–201°. Furthermore, the anhydride reduced with zinc dust and acetic acid according to Wislicenus[1] yields

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[1] Ber. d. chem. Ges., **17**, 2180.

the same hydrodiphthalyl as obtained in the present work by the reduction of the β-acid.

The α-acid is converted into the β-isomer by boiling with a 30 per cent. sodium or potassium hydroxide solution for four to five hours, then precipitating and drying as mentioned above. Strong acids also partially change the α- into the β-acid.

The β-acid is extremely sensitive to warm water and readily changes in part into the ordinary acid. This may be caused even by the heat generated in precipitating the acid at ordinary temperatures from its alkali salt solutions, and the slightly moist acid cannot be dried at 80° without a considerable change taking place. Thus, the β-acid, precipitated from its sodium salt solutions and dried at 80°, melted at 184–195°, but precipitated at 0° and dried over sulphuric acid, it melted at 183–4°. To effect a complete change, however, of the β into the α-acid, three to four hours boiling is required as stated above.

Light seems to have no effect upon the β-acid, moist or dry, since two portions of the same preparation, one dried in the dark, the other exposed to sunlight, both melted at 184°.

Melting-points lower than that of the β-acid, such as 175–180°, observed by previous investigators, as noticed above, appear to have been due to an inter-mixture of an acid salt with the acid. The pure β-acid is precipitated by acidifying dilute solutions, but from concentrated alkaline solutions a white crystalline precipitate is thrown down. This is identical in appearance with the pure acid, but it melts at 175–180°, and upon drying and extracting with absolute alcohol, a residue of an acid salt remains.

Analytical results for the two orthophthalic acids :

	Calculated for $C_8H_6O_4$.	Found.	
		α-acid.	β-acid.
C	57.84	57.38	57.42
H	3.62	3.86	3.82

The molecular weights were determined by Beckmann's method in absolute alcohol solution :

α-Orthophthalic Acid.

Weight of solution	17.5119 grams.
" " "	1.2364 "
Rise of boiling-point	0.49 "
Molecular rise for alcohol	11°.5

Molecular weight = 165.4.

β-Orthophthalic Acid.

Weight of solution	23.7301 grams.
" " "	1.2369 "
Rise in boiling-point	0.365 "
Molecular rise for alcohol	11°.5

Molecular weight = 164.

Molecular weight calculated for $C_8H_6O_4 = 166$.

Molecular refraction:

	Obtained.	Calculated by Ostwald.
α-Orthophthalic acid	40.42 40.79	39.26
β- " "	40.47	39.26

The *electrical conductivity* for the α-acid was determined by Ostwald,[1] as follows:

v.	μ.	100 M.	100 K.
64	85.9	24.3	0.121
128	114.2	32.3	0.121

In the present work the following results were obtained for the same acid:

v.	μ.	100 M.	100 K.
18.5	49.07	13.87	0.121
37.0	67.33	19.02	0.121
74.0	90.95	25.69	0.120

The greater conductivity of the β-acid as follows shows it to be the stronger of the two:

v.	μ.	100 M.	100 K.
23.63	58.29	16.46	0.137
47.3	78.00	22.04	0.137

$$\mu\infty = 354.$$

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[1] Ztschr. phys. Chem., **3**, 376.

The Relative Solubilities of α- and β-Orthophthalic Acids, Determined according to V. Meyer's Method in Absolute Alcohol.

α-Orthophthalic Acid.

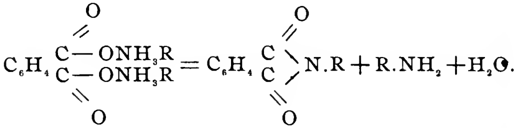
At 20°, 100 parts of solvent dissolved 11.74 parts acid.
" 23° " " " " " 14.08 " "

β-Orthophthalic Acid.

At 20°, 100 parts solvent dissolved 14.12 parts acid.
" 23° " " " " 16.18 " "

To avoid the tendency of alcohol to isomerize the β- into the α-acid, great care was used in not heating too long or much above the temperature for determination.

Salts with Organic Bases.—The aniline, naphthylamine and quinoline salts of both the acids were prepared by adding to the alcoholic solution of the acid the calculated quantity of the base. Warm alcohol or an excess of the base quickly changes the salt of the β- to that of the α-acid. In a dry condition the salts of the β-acid are perfectly stable, and furthermore, can be boiled in a benzene solution for several hours without effecting any change. If, however, an alcoholic solution of the aniline or naphthylamine salts of either the α- or β-acid be boiled for six or eight hours, water and the free base split off and phenyl or naphthylphthalimide is obtained. Thus:



$$C_6H_4\begin{matrix}\overset{O}{\overset{/\!/}{C}}-ONH_3R\\ \underset{O}{\underset{\backslash\backslash}{C}}-ONH_3R\end{matrix} = C_6H_4\begin{matrix}\overset{O}{\overset{/\!/}{C}}\diagdown\\ \underset{O}{\underset{\backslash\backslash}{C}}\diagup\end{matrix}N.R + R.NH_2 + H_2O.$$

To prepare the *brucine salts* the calculated quantity for two molecules of brucine was dissolved in dry benzene, and one molecule of α- or β-acid added. On cooling, the α-salt crystallized out in beautiful, doubly-terminated prisms, the β-salt in clusters of needles. By recrystallizing the β-salt several times from hot alcohol the pure brucine salt of the α-acid is obtained.

A Comparison of the Salts of the Two Phthalic Acids.

	α-Orthophthalic Acid.	*β-Orthophthalic Acid.*
Aniline,	plates M. P. 160°	plates M.P. 147–8°
α-Naphthylamine,	doubly terminated prisms M. P. 163°	needles M.P. 155°
Quinoline,	plates M. P. 98	needles M. P. 92°
Brucine	brilliant, doubly-terminated prisms, M.P. 228°	needles M.P. 212-3°

The aniline salt is the only one previously known. This was obtained by Beamer and Clarke,[1] and melted at 145–6°. This was undoubtedly the β-salt, although no source or method of preparation for the acid was given :

Analytical Results.

Aniline salts :

	Calculated for $C_{20}H_{20}N_2O_4$.	Found.	
		α-salt.	β-salt.
C	66.30	65.92	66.01
H	5.53	5.72	5.63

α-Naphthylamine salts :

	Calculated for $C_{28}H_{24}N_2O_4$.	Found.	
		α-salt.	β-salt.
C	73.34	74.22	74.15
H	5.21	5.42	5.51

Quinoline salts :

	Calculated for $C_{26}H_{20}N_2O_4$.	Found.	
		α-salt.	β-acid.
C	73.57	73.13	73.28
H	4.71	4.86	4.93

Brucine salts :

	Calculated for $C_{54}H_{58}N_4O_{12}$.	Found.	
		α-acid.	β-acid.
C	78.81	72.22	72.35
H	6.52	6.82	6.89

Reduction of β-Orthophthalic Acid.

The β-acid was submitted to reduction under the following conditions : 20 grams of acid and 32.8 grams of sodium acetate were dissolved in 200 cc. of water, and while cooled with ice and constantly stirred, 400 grams of 3 per cent. so-

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[1] Ber. d. chem. Ges., **12**, 1066.

dium amalgam were added, 40 grams at a time, and each time 6 cc. of 50 per cent. acetic acid. The solution was thus kept acid throughout the operation, and at no time did the temperature rise above 6°. After the reduction was completed, sodium sulphate was separated by the addition of 50 cc. of dilute sulphuric acid and an acid was precipitated by acidifying with dilute sulphuric acid, which crystallized repeatedly from hot water, with the addition of animal charcoal, separated in colorless prisms, melting at 195°. Dried at a constant weight over sulphuric acid, the compound gave analytical numbers for a dihydrophthalic acid.

	Calculated for $C_8H_8O_4$.	Found. I.	 II.
C	57.14	57.20	56.92
H	4.76	4.88	4.93

For the preparation of the anhydride, the finely pulverized dihydro acid was treated with ten times its volume of acetic anhydride and permitted to stand for twenty-four hours, when solution occurred. Upon evaporating the solution in a vacuum over soda-lime, the anhydride crystallized out in long needles, which purified from benzene or chloroform, melted at 126°. The anhydride dissolved in hot water regenerated the original acid.

Under the same conditions, Baeyer obtained from α-orthophthalic acid, a dihydro acid with a melting-point of 210°, and its anhydride melting at 101-3°, while the new dihydro acid melts at 195° and its anhydride at 126°. Furthermore, the new dihydro acid showed decided chemical differences from the $\Delta^{3.5}$ dihydro compound obtained from the α-orthophthalic acid. The new dihydro acid instantly reduces a silver nitrate solution in the cold, while for the $\Delta^{3.5}$ acid to act, warming on the water-bath is required. The new dihydro acid is readily reduced in the cold to two tetrahydro acids, while the $\Delta^{3.5}$ acid is not acted on under such conditions. Furthermore, on boiling the two dihydro acids with copper acetate, the new acid precipitates cuprous oxide, while the $\Delta^{3.5}$ requires the addition of acetic acid to effect such a reaction. The above differences may be tabulated as follows :

	$\Delta^{3.5}$ Acid.	*New Dihydro Acid.*
M. P.	210°	195°
M. P. of anhydride	101–3°	126°
Toward cold solution of $AgNO_3$	no reaction	reduces
Toward sodium amalgam in cold	no reaction	reduces to tetrahydro acids
Toward $Cu(C_2H_3O_2)_2$	precipitation of cuprous oxide on addition of acetic acid	precipitation of cuprous oxide without acetic acid

The new dihydro acid behaves identically with the $\Delta^{3.5}$ acid in instantly decolorizing a permanganate solution and in being converted by boiling alkalies into the most stable dihydroorthophthalic acid, $\Delta^{2.6}$.

Reduction of the New Dihydro Orthophthalic Acid.

10 grams of the new dihydro acid were dissolved in 18 grams of sodium acetate and 125 cc. of water. After cooling the solution with ice, a small excess of the calculated amount of 3 per cent. sodium amalgam was added in ten gram portions, and with each addition of amalgam, 3 cc. of 50 per cent. acetic acid. After the amalgam had been added, an acid was isolated, according to the method used with the dihydro compound, which was rather insoluble in cold water and crystallized from hot water in long doubly terminated prisms, melting at 206° with a partial change into its anhydride. The filtrate from the acid melting at 206° yielded a small amount of a very soluble acid, crystallizing in plates, and melting at 120°. This formed an anhydride at the temperature of the water-bath, melting at 78°.

Dried over sulphuric acid the two compounds gave the following analytical results :

	Calculated for $C_8H_{10}O_4$.	Found.	
		I. M. P. 206°.	II. M. P. 120°.
C	56.37	56.24	56.31
H	5.88	6.01	5.90

These analyses show both I and II to be tetrahydrophthalic acids. No. II from its melting-point and that of its anhydride and its easy solubility in water, would seem to be the

Δ' tetrahydroorthophthalic acid obtained by Baeyer[1] by an indirect process.

There is no tetrahydrophthalic acid known that agrees with No. I in the melting-point or that of its anhydride. It reduces a silver nitrate solution on warming for some time on the water-bath, and decolorizes a cold potassium permanganate solution. This tetrahydro acid is not acted upon by acetyl chloride, for, upon boiling a portion of the acid with fifteen times its volume of acetyl chloride for an hour, the chloride distilled, leaving the acid unchanged. If, however, the acid be boiled with ten times its volume of acetic anhydride for ten minutes, and evaporated in a vacuum over soda-lime, the anhydride crystalizes out in short needles which recrystallized from chloroform or benzene, melts at 112–3° and regenerates the original acid from hot water.

Baeyer,[2] in his study of the reduction of α-orthophthalic acid, obtained, among his by-products, a compound giving analytical percentages and chemical behavior of hydrodiphthalyl, but melting at 250° instead of 228°, the melting-point assigned by Wislicenus,[3] who first obtained the compound by reducing phthalic anhydride. Later Hasselbach[4] believed the hydrodiphthalyl melting at 228° to be slightly impure, since the compound obtained by him and melting at 250° was perfectly white, while his hydrodiphthalyl, melting at 228°, was always slightly colored.

A hydrodiphthalyl was isolated in the present investigation from the reduction of β-orthophthalic acid. This compound could be obtained perfectly colorless from glacial acetic acid and melted at 228°. On boiling with sodium hydroxide, hydrodiphthalyllactonic acid was obtained, melting at 198°. From this it would seem that there are two hydrodiphthalyls corresponding to the α- and β-orthophthalic acids. The relation between the two is being studied in this laboratory.

Metallic Salts of α- and β-Orthophthalic Acids.—A considerable number of metallic salts of the two orthophthalic acids have been prepared. In many cases they differ in form and in water of crystallization. In every case the α-salt is the

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[1] Ann. Chem. (Liebig), **258**, 203.

[2] Ann. Chem. (Liebig), **269**, 155.

[3] Ber. d. chem. Ges., **17**, 2180.

[4] Ann. Chem. (Liebig), **243**, 265.

stable one, and the β-salt is converted into this by boiling with water. It is expected that a description of these salts with their crystallographic relations will be given in a future article. Further work also will be done on the reduction products and on the substituted phthalic acids.

It should be stated that the variability in the melting-point of orthophthalic acid, came to the notice of the author while engaged in work under the direction of Dr. F. L. Dunlap at Harvard University in the summer of 1894. Most of the investigation, however, has been carried out in this laboratory.

The author takes pleasure in expressing his thanks to Prof. H. L. Wells of this laboratory for valuable advice, and also to Dr. A. J. Wakeman for assistance in connection with the physical determinations.

THE REDUCTION OF PERMANGANIC ACID BY MANGANESE SUPEROXIDE.

BY H. N. MORSE, A. J. HOPKINS AND M. S. WALKER.

One finds in the literature of analytical chemistry very contradictory statements regarding the stability of solutions of potassium permanganate, and probably many have noticed that while solutions made from one specimen of the salt may exhibit a gratifying stability, those made from material of different origin decompose with rapidity. Many observations point to the conclusion that this difference is due to the presence or absence of manganese superoxide in the specimens of permanganate from which the solutions are made; in other words, that the decline in concentration results from a reduction of the permanganic acid by the oxide with the evolution of oxygen in the free state.

Experiments designed to test the fact of such reduction and to discover the quantitative relations involved in it have been in progress in this laboratory for several years. During that time hundreds of determinations of manganese and oxygen have been made, and a great mass of evidence has been secured which points to certain well-defined conclusions. This evidence has already been utilized, in part, in theses for the doctor's degree. It is too voluminous to present in detail, and we shall therefore give only so much of it as may be thought necessary to establish the conclusions arrived at. For the sake of clearness and brevity, we shall also depart from the usual custom by giving the principal conclusions before presenting the evidence on which they are based.

The work upon the reduction of permanganic acid by manganese superoxide has led to the investigation of another question closely related to it, namely the instability of the superoxide itself when prepared in the wet way. But the facts developed in this direction are, in the main, reserved for another paper.

I.

Potassium Permanganate and Permanganic Acid in Solution are Reduced by Precipitated Superoxide of Manganese with Evolution of Free Oxygen.

a. Solutions of permanganate which have been filtered through asbestos are, as a rule, much more stable than the same solutions unfiltered. Again, filtered solutions which remain undisturbed in stoppered bottles are more stable than the same solutions in use. In the latter case, the solutions probably acquire, in consequence of the exposure to which they are subjected, the oxide required for the initiation of the reduction.

b. In solutions of permanganate containing large quantities of suspended oxide, there is often, even at ordinary temperatures, a visible evolution of gas, which gas is found, on examination, to be oxygen. If the temperature of the solution is raised, the evolution of gas becomes more rapid.

c. A solution of permanganate which has once begun to lose strength declines in concentration with increasing rapidity, owing apparently to the increasing quantity of suspended oxide.

d. If a solution in which considerable oxide is suspended is heated to its boiling-point, it loses its color after a time; while a solution of equal concentration which has been filtered through asbestos is only slightly altered under the same conditions. That this change is attended by the loss of oxygen is easily proved by determining the oxidizing power of the solution before and after heating.

e. The following is a form of the above experiment which is frequently employed in this laboratory for the purpose of emphasizing the necessity of keeping standard solutions of permanganate free from suspended oxide, as well as for the purpose of illustrating the need of certain precautions in determining manganese by the method of Volhard.

The relation of a dilute solution of manganese sulphate to a standard solution of potassium permanganate having been determined by the method of Volhard, a measured portion of the former is prepared for precipitation in the usual manner, and to it is added twice the required volume of permanganate. The body of the flask is then immersed in boiling water until the color of the permanganate disappears, after which the total active oxygen remaining in the liquid is determined by means of oxalic acid and permanganate and compared with the quantity introduced. The time required for decolorization is usually from two to five hours, and depends very much upon the exact temperature of the water-bath.

If the remaining oxygen is determined immediately after the disappearance of the color, it is found that quite exactly three-tenths of the total active oxygen in the permanganate has been lost. This relation indicates a reduction of the half of the permanganate which is not concerned in the precipitation of the manganese of the sulphate in accordance with the following equation:

$$2HMnO_4 + MnO_2 = H_2O + 3MnO_2 + 3O.$$

The correctness of the explanation has also been demonstrated by the determination of the oxygen evolved.

If the heating of the flask is continued for some time after the disappearance of the color, the remaining oxygen is found to be somewhat less than that required by the equation, showing that the precipitated oxide also loses oxygen at the temperature of boiling water.

The facts enumerated above are sufficient to demonstrate the very decided reducing action of manganese superoxide on permanganic acid. It appears improbable to us that some of them should have escaped the notice of analytical chemists, nevertheless we were unable to discover in the available records more than two references to the possibility of such a reduction and these were somewhat obscure. Thenard in 1856,[1] states that manganese dioxide may act upon potassium permanganate either as a reducing agent, in which act the dioxide is converted into a manganate, or its influence may be catalytic causing an evolution of oxygen. Again in 1858,[2] Mulder ascribes the decomposition of permanganate solutions to the presence of potassium manganate. It is certain that the importance of this reduction in its bearings upon the stability of permanganate solutions is not generally appreciated; for nowhere do we find the necessity for the careful filtration of these solutions emphasized. On the other hand, one often finds the deterioration of the solutions ascribed to the dust acquired through exposure to the air. It may safely be asserted that the reduction actually accomplished by dust is insignificant as compared with that accomplished by the oxide produced by the dust.

f. The following experiments are given to illustrate the effect of the presence of suspended oxide upon solutions of potassium permanganate at ordinary temperatures. The oxide used was prepared by pouring a hot dilute solution of manganese sulphate into a hot solution of potassium permanganate. The latter solution contained an excess of the salt and had been acidified with nitric acid. To obtain the oxide in weighable form, it was dried at 65°. We have found that the ratio of oxygen to manganese in oxide precipitated in this way is invariably 2 : 1 if analyzed immediately after the removal of the excess of permanganate and while it is still wet. If, on the other hand, the analysis is delayed for a few hours, or if the oxide is dried at any temperature above that of the air, the proportion of oxygen is found to be smaller. It appears to be impossible for the precipitated oxide to retain the full proportion of oxygen except in the presence of permanganic acid. If, however, an oxide which has lost oxygen by standing or by drying is again placed in a solution of per-

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[1] Compt. Rend., **42**, 382.

[2] Jahresbericht, p. 581.

manganate, it soon recovers the full amount of the oxygen it has lost.

It might be inferred from these facts, which have often been verified, that the reduction of permanganic acid by the superoxide consists in the simple restoration of the oxygen which the oxide loses spontaneously. The explanation, however, appears to be inadequate, since the oxide, in the absence of permanganic acid, is reduced much more slowly than is the permanganic acid in the presence of the oxide.

It will be seen that in all the experiments described some allowance is to be made for a slight reduction of the permanganate due to the deficit of oxygen in the oxide employed. The reduction from this cause is, however, slight as compared with the total observed reduction.

1. *June 14, 1892.*—Placed 250 cc. of permanganate solution which had been filtered through glass wool in a dark place. Concentration equivalent to 5.278 milligrams of iron per cc.

Oct. 14, 1892.—The solution was analyzed and found to have declined in strength 0.72 per cent.

2. Dates and solution the same as in No. 1. The bottle, however, was kept in mildly diffused light. On analysis the decline in concentration was found to be 0.72 per cent.

3. Dates the same as in Nos. 1 and 2. The solution was filtered through glass and kept in a dark place. Its concentration was equivalent to 14.379 milligrams of iron per cc. On analysis it was found to have lost 1.71 per cent. of the active oxygen.

4. Dates and solution the same as in No. 3. The bottle containing the solution, however, was, like No. 2, kept in mildly diffused light. The loss in strength was 2.41 per cent. The above experiments are not believed to be a satisfactory test of the stability of a permanganate solution which is entirely free from suspended oxide. It is thought, rather, that owing to the imperfect filtration through glass wool, all of the solutions contained traces of suspended oxide. In the subsequent experiments bearing on the stability of pure solutions, greater pains were taken to secure a perfect filter.

5. *Dec. 10, 1892.*—Placed four bottles containing permanga-

nate solution in a dark place. The solutions were filtered with great care through asbestos into the thoroughly cleansed bottles and precautions were taken to prevent contamination from the air during and after filtration. Two of the bottles contained a solution equivalent to 5 milligrams of iron per cc., and the other two a solution having twice that strength. The solution in one of each pair of bottles was examined Dec. 24, 1892, May 31, 1893, Oct. 4, 1893, and March 16, 1894, while the contents of the second bottle of each pair were left undisturbed until March 17, 1894. In no case could any decline in concentration be detected.

6. Experiment No. 5 was paralleled in every particular except one. The solutions were kept in mildly diffused light instead of in darkness. As in the preceding case, all of the solutions were found after fifteen months to have the same strength as when put away.

It appears from Experiments 5 and 6 that carefully filtered and properly protected solutions of permanganate exhibit a high degree of stability. A pure solution may, however, easily become contaminated while in use ; it is therefore to be recommended that standard solutions be refiltered from time to time into clean bottles and that the portions left in burettes should never be returned to the main supply without filtration. Such a practice, together with other precautions which readily suggest themselves, renders a frequent redetermination of the concentration of permanganate solutions unnecessary.

It has long been known that direct sunlight exerts a deleterious influence upon solutions of potassium permanganate. The following experiment was undertaken with a view of determining approximately how great that influence may be.

7. *Dec. 10, 1892.*—Place four bottles containing filtered solutions of permanganate in a window facing to the south. The solution in two of the bottles had a concentration equivalent to 5 milligrams of iron per cc., while that in the other two was twice as strong. The contents of one of each pair of bottles was analyzed at intervals, as stated below, while the remaining bottle of each pair was undisturbed until after the last analysis of the contents of its mate had been made.

Percentage Decline in Concentration.

	Equiv. 5 mgs. Fe.		Equiv. 10 mgs. Fe.	
Dec. 24, 1892	1.1		0.68	
May 31, 1893	14.5		8.92	
Oct. 4, 1893	29.8		20.10	
March 16, 1894	42.4	10.8	30.70	8.1

It will be noticed that in both cases the loss of strength was smaller in those bottles which were undisturbed until the expiration of the period of observation. The explanation of this is probably to be found in the fact that the interior of the bottles on the side toward the sun was covered with a film of oxide, which, in the case of the undisturbed bottles, remained intact, while in those from which portions were withdrawn from time to time for analysis, the film was to a great extent detached from the glass. In other words, it is supposed that the solutions were protected in varying degrees by this film from the influence of the direct rays of the sun.

The preceding experiments (1–7) were made with solutions from which the oxide had been carefully excluded, while in those which follow (8–12) weighed quantities of the oxide were added to the solutions of permanganate. As already explained, it was necessary to dry the oxide at a low temperature in order to obtain it in a weighable condition; and, since a precipitated oxide so dried loses some oxygen which is recovered in contact with permanganate, a small portion of the observed loss in concentration is to be ascribed to the reoxidation of the suspended oxide.

8. *June 14, 1892.*—Added to 250 cc. of permanganate solution which had been filtered through glass wool 0.5 gram of manganese oxide. The concentration of the solution was equivalent to 5.278 milligrams of iron per cc. The bottle was kept in mildly diffused light until Oct. 14, 1892, and then analyzed. The loss in strength amounted to 34.62 per cent. This experiment is to be compared with Nos. 1 and 2.

9. Dates, volume of solution, quantity of oxide, and relation to light the same as in No. 8, but the concentration of the solution was equivalent to 14.379 milligrams of iron per cc. The loss of strength was 78.86 per cent. This experi-

ment is to be compared with Nos. 3 and 4, in which solutions of the same concentration, but without oxide, were placed in darkness and diffused light.

It should, perhaps, be explained that the summer of 1892, during which experiments 1, 2, 3, 4, 8, and 9 were made, was one of unusually high temperature in this locality, and that the observed quantitative effects are therefore not strictly comparable with those recorded in connection with other experiments.

10. *Dec. 10, 1892.*—Placed in darkness four bottles, each containing one liter of permanganate solution which had been filtered through asbestos, and to each of which had been added 0.5 gram of oxide. The solution in two of the bottles had a concentration equivalent to 5 milligrams of iron per cc., while that in the other two was twice as strong. The solution in one of each pair of bottles was analyzed on the dates given below, but the remaining bottles were not disturbed until the date of the last analysis.

Percentage Decline in Concentration.

	Equiv. 5 mgs. Fe.		Equiv. 10 mgs. Fe.	
May 31, 1893	11.5		5.9	
Oct. 4, 1893	13.2		7.0	
Mar. 16, 1894	14.8	11.9	7.6	6.8

It will be seen that the absolute reduction in the solutions of different concentration was approximately the same, though the solutions which were unopened, lost less of their active oxygen than those from which liquid was withdrawn from time to time. The relatively large reduction which occurred prior to May 31, may be explained, in part at least, by the loss suffered in restoring oxygen to the oxide.

11. Dates, solutions, and quantities of oxide the same as in the preceding experiment. The bottles, however, were placed in diffused light.

Percentage Decline in Concentration.

	Equiv. 5 mgs. Fe.		Equiv. 10 mgs. Fe.	
May 31, 1893	11.3		6.1	
Oct. 4, 1893	13.0		6.9	
March 16, 1894	14.9	12.1	7.6	7.0

Experiments 10 and 11, are comparable with Nos. 5 and 6. On comparing the first two with each other, it appears that it makes little difference as regards stability whether a solution of permanganate is kept in darkness or in diffused light.

12. Dates, solutions, and quantities of oxide the same as in Nos. 10 and 11, but the bottles were placed in a window facing to the south.

Percentage Decline in Concentration.

	Equiv. 5 mgs. Fe.		Equiv. 10 mgs. Fe.	
May 31, 1893	29.4		16.9	
Oct. 4, 1893	50.6		30.2	
March 16, 1894	67.4	22.9	41.5	14.7

Here, as in No. 7, a great difference is to be observed between the reduction accomplished in bottles from which liquid was withdrawn from time to time, and in those which were undisturbed until the date of the last analysis. The only obvious cause of this difference has been referred to in connection with experiment No. 7. If the results of this experiment are compared with those of No. 7, it will be seen that, though a solution of permanganate free from oxide is decomposed by sunlight, this decomposition is accelerated by the addition of oxide.

It appears from the results obtained in experiments 10 and 11, that when a permanganate solution is reduced by suspended oxide in darkness or in diffused light, the amount of the reduction is probably nearly, if not quite, independent of the concentration of the solution. On the other hand, an observation previously referred to, namely, that solutions which have once begun to lose strength decline in concentration with increasing rapidity, made it appear probable that the rate of decomposition stands in some direct relation to the quantity of the oxide. The following experiment (13) bears upon this question.

13. *Feb. 11, 1893.*—Placed in diffused light half-liter portions of permanganate solution (concentration equivalent to 4.96 mgs. Fe per cc.). One of these (No. 1) contained no oxide, while to the others were added quantities of oxide as

follows: No. 2, 0.25 gram; No. 3, 0.5 gram; No. 4, 1 gram; No. 5, 2 grams; No. 6, 4 grams. The solutions were analyzed Oct. 5, 1893, and the losses expressed in percentage of original concentration were found to be as follows:

No. 1 (no oxide)	0.00
No. 2 (0.25 gram oxide)	4.29
No. 3 (0.5 gram oxide)	14.45
No. 4 (1.00 gram oxide)	29.26
No. 5 (2.00 grams oxide)	59.44
No. 6 (4.00 grams oxide)	entirely decomposed

Except in the case of No. 2, the reduction is nearly proportional to the quantity of oxide.

Another series of bottles containing a solution of equal concentration and volume and the same quantities of oxide respectively, were placed in sunlight and analyzed on the same dates. The losses observed were:

No. 1 (no oxide)	26.64 per cent.
No. 2 (0.25 gram oxide)	30.95 “ “
No. 3 (0.50 gram oxide)	31.80 “ “
No. 4 (1.00 gram oxide)	39.75 “ “
No. 5 (2.00 grams oxide)	61.34 “ “
No. 6 (4.00 grams oxide)	entirely decomposed

We have frequently had occasion, in the course of this and other work closely related to it, to determine the ratio of active oxygen to manganese in the oxide resulting from the decomposition of potassium permanganate in solution; and we have invariably found that the ratio, so long as any unreduced permanganate remained, is 1 : 1, just as it is when an oxide is prepared by adding manganous sulphate to an excess of potassium permanganate, both solutions being hot and the latter having been acidified with nitric acid. The following record of analytical results is given in confirmation of the statement:

	Calculated ratio for MnO_2.	Ratio found.
No. 1	1 : 1	1 : 0.999
No. 2	“	1 : 1.000
No. 3	“	1 : 1.000
No. 4	“	1 : 0.999
No. 5	“	1 : 1.001
No. 6	“	1 : 0.999

On the other hand, analyses of the precipitated oxide, made at varying periods after the disappearance of the permanganate color, have indicated a smaller proportion of active oxygen. Considering the precipitates in question as consisting of manganese and oxygen only, the ratios found would give formulas ranging between $MnO\ 90\ MnO_2$ and $MnO\ 40\ MnO_2$.

The liquid which remains after the complete reduction of potassium permanganate in solution has a neutral reaction, indicating that all of the potassium of the permanganate is in combination with the oxide. The liquid is yellow in color, has a very slight oxidizing power, and when it is evaporated, a minute residue is obtained which, on heating and moistening with water, gives an alkaline reaction. These properties of the liquid—the color, etc. — are, however, believed to be due to the suspended oxide rather than to substances in solution which differ in composition from the precipitate, since by repeated filtration through asbestos, a colorless liquid may be obtained which has no oxidizing power, and which leaves no appreciable residue on evaporation. These facts have an important bearing on a method recently published in this journal[1] for the mutual standardization of potassium permanganate and sulphuric acid, for they are believed to show that the presence of free alkali in a carefully filtered solution of the commercial salt is not to be feared.

II.

When Permanganic Acid is Reduced by Precipitated Superoxide of Manganese, Three-fifths of the Active Oxygen in the Former Compound is Evolved in the Free State.

In other words, the reduction is in accordance with the equation:

$$2HMnO_4 + XMnO_2 = H_2O + (X + 2)\ MnO_2 + 3O.$$

Some evidence of the correctness of this interpretation of the reduction has already been given under I, *e*. In the experiments which follow, the attempt is made to test the quantitative aspects of the reaction by means of a measurement of the oxygen liberated.

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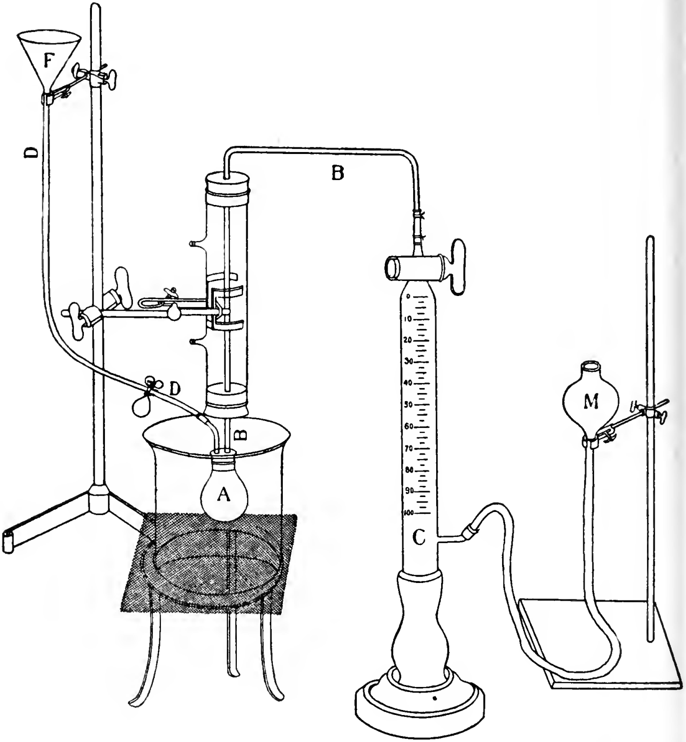
[1] Vol. 18, 236.

The apparatus which was used is represented in the accompanying figure. It consisted of

(1) A flask, A, of about 50 cc. capacity, which was closed with a doubly perforated rubber stopper. Through one hole of the stopper passed

(2) A small glass tube, BB, running about 40 cm. above the flask and then bending to two right angles. The longer limb was surrounded by a condenser, while the shorter one was connected with



(3) A Schiff's azotometer, C, filled with mercury. In use it was found better to have a small quantity of water above the mercury column.

(4) Through the second hole of the rubber stopper passed a short piece of glass-tubing, bent obliquely to clear the lower end of the condenser. This was connected with the funnel, F, by means of the rubber tube, DD.

The method of work was as follows:

The reservoir M was raised to fill C and the stop-cock closed. F and DD were filled with water, and the latter closed at a point near the flask by a pinch-cock, after which F was lowered to give a descending curve to the rubber tube.

A, containing the material to be experimented upon, was placed in position and the stop-cock of the azotometer opened.

After heating the flask in a water-bath kept at the boiling point until it was desired to ascertain how much oxygen had been evolved, water was allowed to run into it through F and DD, and to force all of the gas in A and BB, into the azotometer.

The volume of the gas having been measured, the oxygen in it was determined by absorption in a Hempel pipette, filled either with phosphorus or with an alkaline solution of pyrogallol.

Finally, in order to ascertain what proportion of this oxygen belonged with the residual nitrogen as a constituent of the air in A and BB at the beginning of the experiment, a determination of the oxygen in the atmosphere of the laboratory was made with the same azotometer.

Since the reduction of potassium permanganate by the superoxide in a neutral solution is too slow for convenient observation, all the solutions in the experiments recorded below were mildly acidified with tenth-normal nitric acid. In each case, however, the quantity of acid which was added bore some definite numerical-molecular ratio to the permanganate in solution.

In every experiment, three sets of apparatus like that described, were employed, all the flasks of which were immersed in the same water-bath, in order to secure like conditions of temperature.

No. I contained a weighed quantity of the superoxide and a measured volume of tenth-normal nitric acid.

No. II contained measured volumes of a standard solution of potassium permanganate and of tenth-normal nitric acid.

No. III contained measured volumes of the same permanganate and nitric acid as No. II, and, in addition, the same weight of oxide as No. I.

The contents of all the flasks were diluted with water to the same volume.

The quantities of acid were, in general, so regulated as to produce the same degree of acidity in the three flasks, supposing one molecule of nitric acid to be neutralized by the potassium of a molecule of permanganate. This rule was rigidly adhered to with respect to Nos. I and III, but sometimes departed from in the case of No. II.

The object of thus associating Nos. I and II with No. III was to ascertain whether, under the given conditions, either the superoxide or the free manganic acid separately can yield an appreciable quantity of free oxygen. It was thought that the evolution of a larger volume in No. III must be interpreted as the direct effect of the reducing action of the superoxide upon the permanganic acid.

We give by way of illustration a brief account of the first experiment; but, since the subsequent ones did not differ from this in any essential particular, we present the conditions and results of later experiments in tabular form:

Flask No. I.

Weight of superoxide, 150 mgs.

Tenth-normal nitric acid, 14.28 cc. (equivalent to Mn in $KMnO_4$ in No. II or No. III).

Water, 27.12 cc. (total volume of solution, 41.40 cc.).

Flask No. II.

Potassium permanganate solution, 20 cc. containing 112.48 mgs. $KMnO_4$.

Tenth-normal nitric acid, 7.14 cc. (equivalent to K in $KMnO_4$).

Water, 14.26 cc. (total volume of solution, 41.40 cc.).

Flask No. III.

Potassium permanganate, 20 cc. containing 112.48 mgs. $KMnO_4$.

Tenth-normal nitric acid, 21.40 cc. (equivalent to K + Mn in $KMnO_4$).

Weight of superoxide, 150 mgs.

The nitric acid remaining free in No. III after the neutralization of the potassium in the permanganate was equal to that free in No. I, while No. II may be supposed to contain only free permanganic acid.

The three flasks were immersed to the same depth in the bath and the water in the latter was kept boiling for three hours. During this time a diminished pressure equal to about 50 mm. of mercury was maintained as nearly as possible by lowering from time to time the reservoirs connected with the azotometers.

No evolution of gas could be observed, either in No. I or in No. II. In No. III, on the other hand, a visible evolution of gas began as soon as the flask was lowered into the hot water, and within five minutes the deep purple color of the permanganate had given place to a delicate pink which persisted for about ten minutes, when it also disappeared. Immediately after the disappearance of the color, the liquid was seen to be filled with a brown oxide which remained suspended for about thirty-five minutes, when it subsided, leaving a perfectly clear supernatant solution. During this subsidence of the oxide a slight increase in the volume of gas in the azotometer was noticed, but after fifty minutes the volume of the gas appeared to remain stationary.

Results.

	I. cc.	II. cc.	III. cc.
Total air and oxygen, =	42.60	52.40	60.60
Nitrogen after absorption of oxygen, =	34.00	40.90	37.80
Oxygen, =	8.60	11.50	22.80
Air = 79.8 per cent. nitrogen, 20.2 per cent. oxygen,			
Oxygen of air = nitrogen found × $\frac{20.2}{79.8}$ =	8.60	10.353	9.57
Oxygen obtained, =	0.0	1.147	13.23

Temperature = 21° C.
Barometer = 737 mm.
Oxygen obtained at normal, = 0 1.033 11.913
The 20 cc. $KMnO_4$ = 112.48 mg
1 atom of oxygen = 7.967 cc.
Atoms oxygen found from one molecule $KMnO_4$, = 0 0.129 1.496

In the table which follows are presented the results of a series of twenty-three determinations made exactly as described in the foregoing example. The first column under each of the three designations—Flask I, Flast II, and Flask III,—gives the quantity of liberated oxygen expressed as atoms per molecule of the permanganic acid in No. II or No. III, while the second column under the same headings gives the number of molecules of nitric acid per molecule of the same permanganic acid.

Three-hour Determinations.

	Flask I.		Flask II.		Flask III.	
	MnO_2 (150 mg.)	$\frac{N}{10}$ HNO_3 No. of molecules.	$KMnO_4$ 20 cc. = 112.48 mg.	$\frac{N}{10}$ HNO_3 No. of molecules.	$KMnO_4$ 20 cc. = 112.48 mg.	$\frac{N}{10}$ HNO_3 No. of molecules.
1	0.00	2	0.13	1	1.495	3
2	0.00	2	?	1	1.493	3
3		2	0.13	3	1.532	3
4	0.00	2	0.21	3	1.466	3
5	0.03	2	0.10	3	1.467	3
6	0.02	2	0.25	3		3
7	0.06	2	0.08	3	1.526	3
8	0.04	2	0.15	3	1.527	3
9	0.04	2	0.11	3	1.504	3
10		2	0.20	3	1.504	3
11	0.03	2	0.14	3	1.516	3
12	0.00	2	0.18	3	1.524	3
13	0.03	2	0.25	3	1.559	3
14	0.05	2	0.26	3	1.574	
15	0.02	1	0.32	2	1.552	2
16	0.03	1	0.31	2	1.583(?)	2
17	0.04	1	0.31	2	1.512	2
18	0.01	1	0.32	2	1.466	2
19	0.00	1	0.18	2	1.412	2
20	0.01	1	0.36	2	1.411	2
21	0.06	1	0.22	2	1.402	2
22	0.00	1	0.30	2	1.495	2
23		2	0.08	3	1.469	3
				Average	1.4995	

The small quantities of oxygen obtained in flask No. II indicate that permanganic acid is somewhat unstable under the conditions of the work, but it does not appear that its instability is materially increased by the presence of a moderate amount of free nitric acid.

The oxygen obtained in flask No. III, ranges from 1.402 (Exp. 21) to 1.574 (Exp. 14) with an average of 1.4995 atoms per molecule of permanganic acid. These numbers approximate sufficiently to the value 1.5 (three-fifths of the active oxygen of $HMnO_4$), to show that the reduction is probably in accordance with the equation previously given.

There are, however, two sources of error in all of these experiments, but, since they tend in opposite directions, the results are vitiated only by their difference. In the first place, the oxide which was used in the reduction, contained less oxygen, as has already been explained, than is normal to the superoxide, and the lacking oxygen is recovered in the presence of permanganic acid. The effect of this reaction is, of course, to diminish the quantity of oxygen liberated. On the other hand, the oxide itself loses some oxygen when, as in all the cases covered by the table, the period of heating is extended beyond the time of the disappearance of the color of the permanganic acid, and thus some of the oxygen lost in the first instance is regained. How perfectly the two sources of error balance each other could be ascertained only by determining the oxygen, both in the oxide employed for the reduction and in the oxide resulting from the reduction. But, as will be seen, we have ascertained in another way that our results are not greatly vitiated by the causes in question.

In this connection, it seemed to us important to establish the fact that the oxide does lose oxygen when, as in the experiments recorded, the heating is continued beyond the time of the disappearance of the color. It has already been stated that the color of the permanganate disappeared within fifteen minutes, leaving the oxide in a state of suspension, and that within the next thirty-five minutes the oxide subsided, leaving the supernatant liquid clear. Since during this subsidence of the oxide an increase in the volume of the gas was observed, it was interpreted as an evidence of the reduction of the oxide. We therefore made a series of experiments in every respect like the preceding ones, except that the liberated oxygen was determined after heating for fifteen minutes in the bath. The results are given below:

Fifteen Minute Determinations.

	Flask I.		Flask II.		Flask III.	
	MnO_2 (150 mg.)	$\frac{N}{10}$ HNO_3 No. of molecules.	$KMnO_4$ 20 cc. = 112.48 mg.	$\frac{N}{10}$ HNO_3 No. of molecules.	$KMnO_4$ 20 cc. = 112.48 mg.	$\frac{N}{10}$ HNO_3 No. of molecules.
1	0.05	1	0.08	2	1.340	2
2	0.04	1	0.05	2	1.325	2
3	0.06	1	0.05	2	1.335	2
4	0.00	1	0.00	2	1.347	2
5	0.03	1	0.03	2	1.412	2
6	0.02	2	0.02	3	1.363	3
7	0.02	2	0.06	3	1.377	3
8	0.00	2	0.02	3	1.363	3
				Average	1.358	

The difference between 1.358 (the average number of atoms of oxygen per molecule of permanganic acid, which was obtained in the above series of experiments) and 1.5 (three-fifths the number of atoms of active oxygen in a molecule of permanganic acid), is believed fairly to represent the loss of the permanganic acid in restoring to the oxide the oxygen it had lost in drying.

Still another series of determinations were made in order to ascertain whether all the oxygen conveyed to the oxide by the permanganic acid is liberated during the subsidence of the oxide which follows the disappearance of color. Since the liquid lost color and became clear within fifty minutes, the period of heating was limited to that time:

Fifty Minute Determinations.

	Flask I.		Flask II.		Flask III.	
	MnO_2 (150 mg.)	$\frac{N}{10}$ HNO_3 No. of molecules.	$KMnO_4$ 20 cc. = 112.48 mg.	$\frac{N}{10}$ HNO_3 No. of molecules.	$KMnO_4$ 20 cc. = 112.48 mg.	$\frac{N}{10}$ HNO_3 No. of molecules.
1	0.04	1	0.06	2	1.564	2
2	0.04	1	0.11	2	1.491	2
3	0.05	1	?	2	1.512	2
4	0.03	1	0.05	2	1.532	2
				Average	1.525	

It appears from the above results that all of the oxygen which was lost by the permanganic acid in the higher oxidation of the oxide used for the reduction is again liberated during the subsidence of the oxide after the disappearance of the color. In other words, the two sources of error which were mentioned as affecting our work were of nearly equal magnitude, and therefore neutralized each other quite exactly.

Summary.

1. Permanganic acid and potassium permanganate are reduced by precipitated superoxide of manganese with liberation of three-fifths of the active oxygen of the permanganic acid.

2. To this cause is to be ascribed the observed instability of standard solutions of potassium permanganate. Such solutions should, therefore, be carefully filtered through asbestos and thereafter protected.

3. Solutions of potassium permanganate which are free from suspended oxide exhibit a high degree of stability whether kept in darkness or in diffused light. Even pure solutions are, however, decomposed in direct sunlight.

4. The oxide resulting from the complete reduction of a neutral solution of potassium permanganate contains all of the potassium of the original salt, and the supernatant liquid is, therefore, neutral.

5. Whether the precipitated superoxide is formed by the slow decomposition of a neutral solution of potassium permanganate or by the addition of manganese sulphate to an acidified solution of permanganic acid, the ratio of oxygen to manganese in it remains normal (*i. e.*, 2 : 1) only so long as there is present unreduced permanganate or permanganic acid. In the absence of permanganic acid or its salt, the oxide loses oxygen even at ordinary temperatures.

6. In the presence of permanganate or permanganic acid, the lost oxygen is restored.

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REVIEWS AND REPORTS.

A REVIEW OF SOME IMPROVEMENTS IN CHEMICAL INDUSTRY.

In the earlier numbers of this JOURNAL there appeared a series of papers on the technical applications of chemistry, by Prof. J. W. Mallet. Ten years later, in 1889, Prof. S. B. Newbury contributed several articles upon the advances made in this direction during the interval.

In these pages the writer will endeavor to show a few of the notable improvements introduced during the past five or six years, with an occasional reference to some of the failures, and to the more promising inventions which may be developed in the future.

Heavy Chemical Manufactures.

Sulphur.—Sicily continues to furnish the larger part of the world's supply of sulphur, although many of the mines are now idle. The industry has suffered a period of great depression since 1890, and the price in 1895 had fallen to about $16 per ton for seconds and $15 for thirds. A few operators have attempted to introduce more modern appliances for mining, the better to meet low prices, but in most cases this has only been done after a struggle against native prejudice, even resulting in riots at the mines.

In the methods of extracting sulphur from the gangue little advance has been made since the papers of Professors Mallet[1] and Newbury[2] were published. The "calcerone" is most generally employed, though melting out the sulphur by the use of solutions of calcium chloride[3] is used to some extent. Extraction by means of carbon disulphide has made little progress.

Japanese sulphur has become a considerable competitor with the Sicilian, and in these mines are found many modern improvements and economical working. Late statistics show that 84 mines were in operation in 1894. A new sulphur deposit of probable future importance is being developed on the island of Tanna, New Hebrides. A rich ore, with cheap labor and fuel at hand may make this even a more formidable rival of Sicily.

Our domestic production has fallen until it scarcely deserves notice, but little more than 400 tons being produced in 1894. An innovation recently introduced in the Nevada mines, is a plant for hydraulic mining to remove the overlaying surface earth. The method of extraction employed in

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[1] J. W. Mallet: This JOURNAL, 1, 273.

[2] S. B. Newbury: *Ibid*, 11, 124.

[3] Vincent: Bull. Soc. Chim., 40, 528.

this country is the Dubois[1] process of distillation with steam in rotary retorts. The deposits of Louisiana and Texas have not been developed.

Of the several recovery processes for sulphur from the tank waste of the Leblanc soda industry, only the Chance-Klaus[2] method has proved practical on a large scale. This can be so managed that a large part of the product is obtained as "flowers of sulphur," which finds a ready sale because of its purity and attractive appearance. But the process has not apparently met the original expectations of its promoters, for in 1894 England imported 20,100 tons of sulphur besides their imports of pyrites. Apparently about 12,000 or 15,000 tons are now recovered annually, though exact figures have not been obtainable. In 1893 the United States imported about 10,000 tons of sulphur from Great Britain, of which a considerable part was probably recovered sulphur.

The manufacture of wood-pulp by the sulphite process has stimulated the demand for sulphur within the past few years in this country.

Pyrites.—The use of pyrites for sulphuric acid is constantly increasing, but owing to the very low price of brimstone for the past two years, a few acid makers who had not destroyed their old brimstone burners, returned to the use of sulphur. Mr. K. F. Stahl[3] presented the relative merits of brimstone and pyrites, in a paper published about three years ago, and figured a difference of three cents per ton of 50°Bé acid, in favor of brimstone; but he based his estimate on pyrites at $6 per long ton. E. W. Parker[4] shows, however, that the actual cost of pyrites in 1893, was less than $3.50 per long ton and pyrites acid of 50°Bé really cost $5 per ton, against $6.25 for brimstone acid. Since our native pyrites are nearly free from arsenic and contain but little copper, there appears to be no good reason for the continued use of brimstone, except for a special acid free from all traces of arsenic, copper or zinc. Even at the present price of brimstone, the other items remaining the same, a decided advantage remains with the pyrites acid.

Improvements in the business have resulted in the production from pyrites of an iron oxide containing only 1 to 2 per cent. of sulphur. This now finds a somewhat restricted use in the arts and as an iron ore. Residues from Spanish pyrites containing copper are of course valuable ores for that metal.

Sulphuric Acid.—The chief advances in sulphuric acid making have been in the improvement of details rather

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[1] J. Soc. Chem. Ind., *1887*, 439, 442; *1889*, 696.

[2] J. Soc. Chem.. Ind., *1888*, 163

[3] J. Anal. Appl. Chem., *1892*, 690.

[4] Mineral Resources of U. S., *1893*, 745.

than in radical changes of apparatus or system. Mechanical furnaces have been introduced in some works recently, and generally give good results. They seem to be particularly good for burning "fines," since they allow no excessive introduction of air during raking. Muffle furnaces of the Spence type of mechanical burners have proved successful for roasting zinc blende, the muffle being heated by generator gas. The waste heat of the fire is utilized to heat the air by which the blende is oxidized. The ore is charged through a hopper into the top shelf of the burner and raked down by mechanical rakes from one shelf to the next. Some recent kilns of this kind will roast about 42 tons of ore carrying 28½ per cent. sulphur, in twenty-four hours, not more than 1 per cent. sulphur being left in the roasted ore. For making sulphuric acid, the gases from blende-roasting are treated in much the same way a those from pyrites. Since the amount of sulphur in blende is not sufficient to support the combustion, the roasting is accomplished by the aid of external application of heat to the muffles.

The Lunge-Rohrmann perforated plates are generally considered unsuitable for use in the Glover tower (though the inventors did not recommend them for this purpose),[1] because the high temperature would cause them to crack and impure gases might clog the openings. But placed in towers between the chambers they undoubtedly are effective. Their great cost, together with the fact that they offer considerable resistance to the movement of the gases, hinder their more general use. The "pipe columns" of Gilchrist[2] and Hacker have been introduced in several acid works in this country but in one case, at least, proved a failure. In other cases, however, under different conditions they seem to give very satisfactory results. Their chief advantage appears to be a more thorough mixing of the gases as they pass from one chamber to the next. The cause of the one failure above mentioned is attributed to improper placing of the towers, on the theory that their chief function is to *cool* the gases.

In some acid works, instead of steam jets in the outlet pipes, fans are used to assist in the movement of the gases, and give better results.

The more modern form of Glover tower has a steel frame and is lined with acid-resisting brick on tile. Quartz is still in favor as packing for these towers.

The general trend of improvement appears to be in the direction of smaller chambers and increased tower capacity. One of the latest ideas of this kind is embodied in Barbier's

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[1] J. Soc. Chem. Ind., *1893*, 232.

[2] J. Soc. Chem. Ind., *1894*, 1142.

Tower System,[1] in which the lead chambers are entirely abolished and a system of towers substituted for making the acid. The scheme has hardly advanced beyond the experimental stage as yet, but gives promise of future importance. In this system the gases from sulphur or pyrites burners are led into a series of towers, five or six in number, connected by flues from the top of one tower to the bottom of the one adjacent. Beneath each tower is a pan for collecting the acid formed. These pans are set *en cascade*, so that the overflow is by gravity from one to the next, and all are set over a flue leading from a fire grate at the lower end of the series; or they may be heated by the sulphur dioxide gas on its way from the burners to the towers. The towers are filled with perforated pottery vessels of acid-resisting material, thus affording a large surface exposure. A sprinkler at the top of each tower supplies the dilute nitric acid needed. The last tower of the series is a Gay Lussac for absorbing the nitrogen oxides. As it is formed, the acid collects in the pans beneath the towers and flows from one to the next, always approaching the fire and becoming more concentrated in each pan, the denitration being accomplished at the same time. The water vapor and nitrogen gases pass off from the pans and immediately back into the towers. The final concentrating pan is set directly over the fire and not under any tower, and in it the acid reaches a gravity of about 60° Bé.

The advantages claimed for this system are, a more concentrated pan acid, free from nitrogen; larger yield per cubic meter of tower space compared with the cubic capacity of chambers; adaptability to use in both warm and cold climates, the temperature in the tower being high, (about 90°C); the cost of construction not exceeding one-half that for a chamber plant of the same daily output; and a much smaller ground area to be occupied.

While this particular apparatus may not prove entirely successful,[2] there seems no doubt that the tower system is in many ways superior to the chamber process and will probably be much developed in the near future.

Among improvements in the methods of concentration of the acid is to be noted that much of this is now done in the Glover tower, which is so constructed and managed that acid of 62° to 66° Bé may be obtained directly. In some cases two towers are in series, the one next the chambers being the denitrating tower and part of the acid from it is sent through the tower next the burners, by which the acid is concentrated

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[1] P. de Boissieu: Bull. Soc. Chim., **11**, 726. U. S. Patent No. *535882*, March 19, 1895.

[2] Unsatisfactory results with this apparatus are reported from Italy. J. Soc. Chem. Ind., *1895*, 698.

up to 64° or 66° Bé, the steam passing along with the sulphur gases into the denitrating tower.

Kessler's[1] apparatus, in more or less modified form, is also being introduced for the concentration of acid. This is a continuous surface heating system used in connection with platinum or iron stills which are fired with generator gas or oil, and the waste fire gases passed over the surface of the acid contained in lead-lined iron tanks.

Cast iron stills are replacing platinum to a great extent, the acid being concentrated to about 64° Bé in the Glover tower and finished in the iron still. The results are very satisfactory and the life of a still is from two to six months.

Gold-lined platinum stills are used to some extent, but their great cost acts as a bar to a more extended application.

Another new idea is the abolition of the "acid-egg," a system of air-lifts similar to those used for raising water from artesian wells, being substituted.

Hydrochloric Acid.—This acid has been the main support of the Leblanc soda process for some years, because of its use in generating the chlorine necessary for making bleaching powder. But few improvements in the manufacture or condensation of hydrochloric acid as derived from the salt-cake process, have been made within recent years. The Lunge-Rohrman plate tower is found quite effective in condensing the acid but when the draught is strong it seems necessary to supplement it with a small coke tower.[2]

Recovery of hydrochloric acid from the waste calcium chloride liquors of the ammonia-soda process has apparently not proved successful on a commercial scale, as yet.

Methods depending upon the decomposition of magnesium chloride by water vapor, have been proposed for use in connection with a modified ammonia-soda process, and also to be applied to the magnesium chloride residues, obtained in the Stassfurt salt works; but though they have been given experimental trials, none of these processes appear to have met with commercial success. Most investigators have attempted only the direct production of chlorine from these residues, and some of these processes will be considered in a subsequent paper.

Nitric Acid.—The old form of iron retort with exposed ends is being replaced by the newer apparatus of Guttman.[3] In this the entire retort is surrounded by flame and furnace gases, thus ensuring nearly equal temperature in all parts, the retort

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[1] J. Soc Chem. Ind., *1892*, 434. and *1895*, 156.

[2] Lasche: Ztschr. angew. Chem., *1894*, *1895*, 610; 374.

[3] J. Soc. Chem. Ind., *1892*, 349: *1893*, 203; Ztschr. angew. Chem., *1893*, 37.

being heated to such a high degree that the acid has very little action on the iron. Two of these retorts are usually joined to one condensing apparatus of Guttman's design.

This condenser has found much favor with acid makers and is generally used in more advanced plants. It consists of a series of some twenty vertical pipes of thin-walled earthenware, joined in pairs at the top by elbows and opening at the bottom into a horizontal collecting pipe; this is divided by diaphragms into a series of chambers connected by U tubes passing beneath the diaphragms. The condensing pipes are about two and one-half meters high, twelve cm. diameter, and eight mm. thickness of wall. Air cooling is used in this apparatus. Because of the diaphragms in the horizontal pipe, the acid vapors must pass up one vertical tube and down the next, in order to pass through the system. The condensed acid accumulates in the chambers and passes into a suitable collecting vessel. To absorb the nitrous gases, the uncondensed vapors pass into a Lunge-Rohrmann plate tower through which water or sulphuric acid of 150° Twaddell is trickling.

The condenser is provided with a hot-air injector by which the uncondensed nitrous acid is brought in contact with moisture and air at 76° C, and is converted into nitric acid. The injector also improves the draught through the apparatus, hastening the distillation and removal of the gases from the retort. So little nitrogen peroxide is formed in this apparatus, that the acid needs but very little or no "bleaching" for market, and its strength may reach 40° Bé. About 95 per cent. of the vapors condense in the pipes and 5 per cent. in the Lunge tower. A modification of the apparatus consists of five or six pipes, cooled by a water jacket. In these about 98 per cent. of the vapor condenses. The liquid condensed contains about 96 per cent. of nitric acid and 1 per cent. of nitrogen peroxide. The apparatus is gradually replacing the old system with "bombons" for condensation.

Hart's tube condenser[1] has been introduced in some works and appears to be giving good results. The apparatus is constructed of glass and earthenware tubes, placed above the brick arch over the retort, thus occupying very little floor space. It is simple, easily repaired and needs so little attention that one man can attend to several retorts. The system is based on the theory that nitrogen peroxide, which colors the acid and causes loss to the manufacturer, is produced by too prolonged heating of the acid vapors, and the more rapidly the vapors pass from the retort and are condensed, the

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[1] J. Soc. Chem. Ind., *1894*, 1197; J. Am. Chem. Soc., *1895*, 576.

lighter colored will the product be. Among other advantages claimed for the system, is an increased yield of light-colored, concentrated acid with small consumption of condensing water.

FRANK H. THORP.

OSTWALD'S KLASSIKER DER EXAKTEN WISSENSCHAFTEN. Engelmann: Leipzig.

NO. 68. DAS NATÜRLICHE SYSTEM DER CHEMISCHEN ELEMENTE. L. Meyer and D. Mendelejew. 2.40 marks.

NO. 69. UEBER FARADAY'S KRAFTLINIEN. J. C. Maxwell. 2.00 marks.

NO. 70. MAGNETISCHE POLARISATION DER METALLE UND ERZE DURCH TEMPERATUR-DIFFERENZ. T. J. Seebeck. 2.00 marks.

NO. 72. CHEMISCHE ANALYSE DURCH SPECTRALBEOBACHTUNGEN. G. Kirchhoff and R. Bunsen. 1.40 marks.

NO. 74. UNTERSUCHUNGEN UEBER DIE GESETZE DER VERWANDSCHAFT. C. L. Berthollet. 1.80 marks.

Among the recent issues of Ostwald's neat and inexpensive reprints of classical papers are the very important ones cited above. The four famous papers by Lothar Meyer (1864–1869) and Mendelejew (1869–1871) are edited and annotated by Karl Seubert; Maxwell's first paper (1856) on Faraday, from the Cambridge Transactions, is translated and discussed by Boltzmann in a truly magnificent manner; the early work on the electrochemistry of thermocurrents, Seebeck (1823), is edited by von Oettingen; and the remaining volumes are issued by Ostwald. The first of them comprises the two papers by Kirchhoff and Bunsen (1860), announcing the discovery of spectrum analysis and its first great results, among which the discovery of caesium and rubidium are prominent; while the other is a translation of the brilliant and very inaccessible original paper of Berthollet (1801) on chemical affinity. The annotations and biographical notes are in every case of the greatest interest.

J. E. T.

REVIEW OF AMERICAN CHEMICAL RESEARCH. ARTHUR A. NOYES, Editor.

Attention is here called to an important literary undertaking of interest to chemists. Dr. Noyes, of the Massachusetts Institute of Technology, conceived the idea of bringing together abstracts of all articles embodying the results of original work done in America in the field of chemistry, and publishing them regularly in the *Technology Quarterly*. In a preliminary note the Editor says: "The purpose of this publication, which is hereafter to appear serially in this JOURNAL, is to present in a concise form a review as complete as possible of all original work having a chemical bearing, published in the United States after the beginning of the year 1895. It is believed that such a compilation will prove of more than usual value in the case of the research work of this country, by reason of the fact that so large a proportion of it is published in other than chemical journals, and thus fails to become incorporated with the rest of the science, and also because the abstracts of American chemical literature published in foreign journals are very incomplete."

The execution of the plan has been made possible by the coöperation of members of the instructing staff of the Institute of Technology.

Three instalments of the Review have been issued and an examination shows that the work thus far has been carefully done. I. R.

ORGANIC CHEMISTRY. THE FATTY COMPOUNDS. By R. LLOYD WHITELEY, F. I. C., F. C. S., Principal of the Municipal Science School, West Brunswick; Late Lecturer and Demonstrator in Chemistry in University College, Nottingham. London: Longmans, Green & Co. and New York: 1895. 291 pp.

This book calls for very little comment. It is clearly written and may prove useful to some students, but there are better books available about as advanced as this. The fatty compounds are here treated in 290 pages. Nothing is said in the Preface indicating that the aromatic compounds are to be treated in a subsequent volume, and the question may fairly be raised—Of what use is a small book on the fatty compounds? Is it possible that there are schools in which a course on these compounds is given and the aromatic compounds neglected? The author's reasoning is not always satisfactory, and does not, therefore, give the student a correct conception of the character of the evidence upon which the prevailing ideas regarding the structure of compounds rest. As an illustration, the reasoning on page 55 in regard to the structure of ethylene may be mentioned. This would not carry conviction to the mind of a thinking student. Some errors have been noted: In the first equation on page 60 the composition of the cuprous compound of acetylene is represented by the formula, $C_2Cu_2H_2O$. This is not correct. Keiser has proved that the compound has the formula C_2Cu_2. On page 7 "Henniger" is given instead of "Henninger." Under Lactic Acid, p. 227, it is stated that the inactive and the dextro-rotatory varieties are known, and no mention is made of the laevo-rotatory acid discovered by Schardinger.

It is, however, hardly fair to emphasize the slight shortcomings of the book. On the whole, it is probably as free from errors as most others and, in many respects, it is worthy of praise.

THE CHEMISTRY OF POTTERY. BY KARL LANGENBECK, Superintendent of the Mosaic Tile Company, Zanesville, O., formerly Superintendent of Rookwood Pottery, Chemist of the American Encaustic Tiling Company, etc. Easton, Pa.: Chemical Publishing Co. 1895. 197 pp. Price, $2.00.

The object of this book is thus stated by the author: " While to many of our chemists, engaged in developing the natural resources of the country, the clays found on every side have seemed to offer a fruitful field for investigation, the information at command concerning the chemical needs of the potter has been so meager, that their efforts have been practically abortive. The thousands of analyses published are mostly worthless, because they do not go far enough or because unaccompanied by essential physical tests and practical trials.

" It is hoped that this little treatise will supply information that will turn future labors in this channel to good account.

"The writer is well aware that in confining the subject matter to the results of his personal experience, the shortcomings of the treatise are numerous and manifest; but he believes as such it is a more direct expression of the practical needs of the working potter, and therefore of more immediate value, than a compilation of the published work of European chemists on their ceramic industries."

The book is made up of fifteen chapters with the following titles: 1. Analysis of Pottery Materials and Products; 2. Physical and Empirical Tests; 3. Pyrometry; 4. Classification of Ceramics; 5. Pottery Glazes; 6. Red Ware; 7. Rockingham and Yellow Ware; 8. Stoneware; 9. Raw Materials of White-Ware Bodies; 10. White Granite and Cream-colored Ware; 11. Majolica and Enameled Tile; 12. White Enameled Brick; 13. Floor Tile and Terra Cotta; 14. Refractory Materials; 15. Burning the Ware.

In view of the extensive experience of the author there can be no doubt of the value of this book.

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ON THE SPECIFIC GRAVITIES OF MIXTURES OF NORMAL LIQUIDS.

By C. E. Linebarger.

I.

The molecular masses of substances being established by getting them into the gaseous or dissolved state and then comparing their density or concentration in the light of the hypotheses of Avogadro and van't Hoff, with that of a standard substance, it is not allowable without experimentation along other lines to affirm that the molecular mass of a liquid or solid is the same as that it possesses when vaporized. When a gas is condensed into a liquid, or the solvent is removed from a dissolved substance which we assume to be liquid, it is conceivable that the pure liquid may have a greater, the same, or a smaller molecular mass than it does in the gaseous or dissolved state; it may be made up of "associated," "normal," or "dissociated" molecules.

Now, all experimental evidence indicates that substances in the gaseous state present the simplest phenomena and relationships; also, high temperatures necessary for the maintenance of the vaporous state are inimical to molecular complexity. It may be conceded then that the molecular condition of a substance in the gaseous state is simpler than in the liquid state, and that no dissociation occurs when a gas, made up of molecules remaining of the same size throughout considerable ranges of temperature, condenses into a liquid.

But can vapors on condensing to liquids preserve their molecular size unaltered? And is the difference between the gaseous and liquid state to be alone attributed to a difference between the mutual attractions of the molecules? The work of Guye, Ramsay and Shields, and others, interpreted as it has been, indicates that these questions can often be answered in the affirmative; there exist many compounds which suffer no change in molecular condition in passing from the one state of aggregation into the other; the number of "normal liquids" is legion.

But there also exist numerous compounds which undergo more or less radical changes in passing from the one state of aggregation into the other. There are some—the alcohols, for example—which possessing normal molecules in the gaseous state suffer polymerization on liquifying; and there are others, for instance, the acids, that made up even in the gaseous state of polymerized molecules, experience comparatively slight changes in their degree of polymerization on assuming the liquid state.

Now, it happens that the more commonly occurring liquids are those which exhibit an intricate molecular structure, and, in the investigations of the properties of liquids, such have naturally enough been employed. But, their molecular structure being so complex, it is no wonder that so few general results have been obtained, for an associated liquid cannot be considered as a type, and all determinations of its behavior in the pure or mixed state are merely individual and cannot be taken as characteristic of the liquid state in general. If, however, the disturbing factor of molecular complexity be removed, and "normal liquids" be investigated, it is legitimate to expect more uniformity and generality of results, and the examination of a few simple liquids may give us a comprehensive insight into the nature of liquid structure.

Among the important physical properties of liquids is that of volume, and, although much has been done on the subject, much remains to be done. Such questions as these arise: What changes of volume occur when liquids are mixed? Will the mixing of normal liquids be accompanied with an increase or decrease of volume, or will it, since no change in the number of molecules occurs, occasion no change of volume? Does the contraction or expansion that may supervene depend upon the chemical characteristics or the physical properties of the normal liquids mixed?

The object of this paper is to attempt a partial theoretical and experimental elucidation of these and kindred questions.

II.

Historical and Critical.

If the degree of molecular association of liquids be taken as a basis of classification, three classes of binary mixtures may be distinguished.

1. The liquids mixed are normal;
2. One liquid is normal, the other associated;
3. Both liquids are associated.

Of course, there is nothing fixed or absolute in these classes, since there may occur every degree of association in liquids from carbon bisulphide in which it is hardly detectable even at low temperatures to sulphuric acid which has been found probably to consist of more than thirty simple molecules. Still it is convenient for reference and discussion to make such a classification.

Without doubt, the mixtures of the first class may be expected to exhibit the simplest behavior in respect to their physical properties, and, indeed, all determinations of density which have been made upon mixtures of normal liquids have shown such to be the case. Thus, Bussy and Buignet[1] in the course of their investigations on the change of temperature brought about by the mixing of liquids determined the changes of volume occurring from the mixing. In the absence of any experimental particulars, it is impossible to judge of the accuracy of their determinations or of the purity of the liquids employed. Only two mixtures of normal liquids (and one of these, carbon bisulphide, is slightly associated) were examined, about which the authors write the following:

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[1] Bussy and Buignet; Recherches sur les changements de temperature produits par le mélange des liquides de nature differente. Comptes rendus, **59**, 671 (1864); and Annales de chimie et de physique (4 ser.) **4**, 5 (1865).

"*Ether et sulfure de carbone*—Le changement de volume qui accompagne le mélange de ces deux liquides est très-peu marqué. Il consiste en une contraction qui, pour le mélange ou elle atteint un maximum, n'excède guere 2 millièmes de volume théorique total."

"*Chloroforme et sulfure de carbone*—Le mélange de ces deux liquides donne toujours lieu à une augmentation de volume. ....Le maximum correspond au mélange formé par 3 équivalents de sulfure de carbone pour en seul équivalent de chloroforme ; il represente un peu plus des 6 milliemes du volume théorique total."

Also, Frederick D. Brown[1] has very carefully determined at temperatures in the vicinity of 20° the densities of mixtures of carbon bisulphide with carbon tetrachloride, of benzene with dichlorethane, dibromethane, and carbon tetrachloride, and of toluene and carbon tetrachloride, all except carbon bisulphide being normal liquids. The volume relations of these mixtures to their components were found to be very simple in comparison with those obtained with mixtures containing associated liquids. His data, which may be regarded as very accurate, will be reproduced and discussed later on.

Recently, E. Paternò and C. Montemartini[2] have determined the densities at 20° of mixtures of benzene with methyl, ethyl, isopropyl, isobutyl, and caproic alcohol ; with acetic and isobutyric acids, and anethol. All of these liquids, with the exception of benzene, are more or less associated ; the mixtures, accordingly, belong to the second of the classes mentioned above, and, as might be expected, more deviation from simplicity is to be found in their determinations than in those made by Brown.

A number of isolated determinations of the densities of mixtures of liquids of the second class might be cited, but it is unnecessary, as they are for the most part of doubtful accuracy and are outside of the domain of our subject.

When we consider mixtures of the third class, we find the

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[1] On the Distillation of Mixtures of Carbon Disulphide and Carbon Tetrachloride: Transactions of the Chemical Society, **39**, 304 (1881).

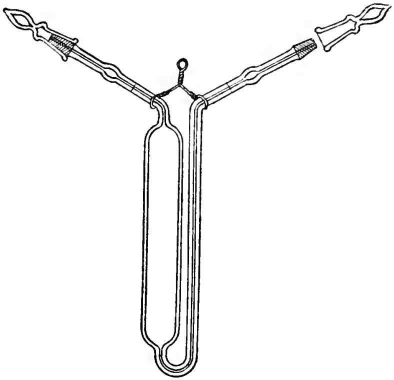
[2] Sulle variazioni di volume nei miscugli dei liquide in relazione al comportamente crioscopico. Gazzetta chimica italiana. Vol. II, anno XXIV, 179–190 (1894).

differences between the densities calculated by the rule of mixtures, and those determined by direct experiment to be considerably greater than those found in the previous two classes. The possibility of ascertaining the composition of mixtures of liquids of commercial importance, as of water and alcohol, water and acids, etc., etc., most of which are associated liquids, by means of a determination of their specific gravities, an operation of great simplicity, especially if the convenient hydrometer be used, and yet of considerable accuracy, has led to the investigation of the densities of mixtures of a number of such liquids. But the volume relations of these mixtures exhibit many irregularities, due, no doubt, to the amount of association becoming altered through the mixing. For illustration, in every one of the possible mixtures of ethyl alcohol and water, there must be a definite number of simple and a definite number of associated molecules, of the latter of which there may be several different kinds. The decomposition of the complex molecules brought about by the successive addition of either constituent to any mixture may be continuous or possibly discontinuous, and for certain mixtures there may be maxima or minima of density. When such mixtures possess an approximately simple stoichiometrical composition, it has been claimed that definite molecular compounds have been formed, the so-called "hydrates." But it is remarkable that only such liquids as possess a considerable complexity of molecular structure have a tendency towards the formation of "hydrates" and it seems probable that this very intricacy of structure is the cause of the "breaks" in the continuity of the curves representing the relation between specific gravity and composition, and that it is only pure accident that such "breaks" occur at points, which, by a liberal allowance for experimental errors, may be regarded as integral stoichiometrical ratios, and so indicating the presence of "hydrates." Also, it is an experimental fact that the number and position of these breaks varies with the temperature; the higher the temperature, the less pronounced and distinct the "hydrates." This fact, which has been speciously claimed to be due to the breaking up of "hydrates" under the influence of heat, more rationally can be said to be due to the decomposition of the more complex into simpler molecules through rise of temperature; and the simpler the molecules, the simpler the relationships.

III.

Experimental Details.

For the determination of the specific gravities of the liquids and their mixtures, pycnometers having the form represented in Fig. 1 were employed. Three of them were used, having capacities of about 15 cc., 25 cc., and 40 cc., respectively. Every precaution was taken to prevent any alteration in their capacity. They were never exposed to temperatures far removed from 25°, the temperature at which the determinations were made, for it is a well established fact that glass vessels, when subjected to considerable changes of temperature, suffer temporary and even permanent changes of capacity. Their content of water was often determined during the course of the investigation, but its variation was never found to be greater than that due to unavoidable experimental errors, so that their capacity may be said to have remained unchanged. A slight loss was found to have occurred in the weight of the empty pycnometers, due to "wear and tear," probably from the putting on and taking off of the glass caps; this loss,



however, was very slight, amounting, in the case of the pycnometer used the most, to but 0.0013 gram after the performance of more than 100 determinations; as the pycnometers were weighed empty after every dozen or so of experiments, account could be taken of this slight loss.

Plenty of time was always given for the liquid or mixture to acquire the temperature of the bath in which it was immersed; after the weighing of the pycnometer and its contents it was again placed in the bath, and if the liquid did not assume exactly the same volume as at first, the determination was repeated; this was found, however, to be necessary in only a very few cases.

The weighings were carried out with a balance capable of indicating a tenth of a milligram with accuracy, and the same set of weights, which had been carefully tested, was always employed.

The thermostat was an enamelled iron kettle holding about thirty quarts of water. As the temperature of the room in which the experiments were made could be kept within a degree or so of 25°, the water in the bath, which was stirred continuously by an automatic device, could be kept from that temperature by not more than 0°.01 to 0°.02 for an hour or so.

The thermometer used was graduated in tenths of degrees, and permitted of the pretty accurate estimation of fiftieths of degrees; it had been tested by the "Physikalische Reichsanstalt," and had been found to be "ohne merklichen Fehler" from 20°.0 to 30°.0.

Notwithstanding my efforts to push the degree of accuracy in densimetric work as far as possible, I cannot claim that my determinations are accurate to more than a few units of the fifth decimal place; still in many cases there is no doubt that the results are more accurate than this, but, on an average, only the above claim is justifiable.

IV.

Purification of Liquids and Preparation of Mixtures.

Although desirable, it is not absolutely necessary to employ in the investigation of the volume relations of mixtures of liquids, material that has been subjected to the most careful preparation. The presence of the amount of impurity contained in the preparations furnished by reputable makers as "chemically pure" is of vanishing influence in the results, inasmuch as these are relative and not absolute. Brown (*loc. cit.*) was also of this opinion, being led to it by a consideration of his results obtained with samples of dibromethane of different degrees of purity. The main thing in an investigation of this sort is the accuracy of the experimental work. For example: It was found that a mixture containing 47.322 per cent. of toluene and 52.678 per cent. of ethyl benzoate had a specific gravity of 0.94937, while the specific gravity as calculated by the rule of mixtures, was 0.94806, the difference, accordingly being 0.00131; the specific gravity of the ethyl benzoate contained in this mixture was 1.04843. In another mixture containing 51.249 per cent. of toluene and 48.751 per cent. of another sample of ethyl benzoate, whose specific gravity was 1.05455, a specific gravity of 0.94445 was found, differing by 0.00134 from the calculated specific gravity 0.94311. We have then two mixtures of nearly the same percentage composition having differences of specific gravity measured and calculated, 0.00131 and 0.00134, while the samples of ethyl benzoate employed differed by 0.00612 in their specific gravities. In the data communicated later some similar results may be found.

I have not, accordingly, used in every case liquids of the greatest purity, and, although the employment of material of different degrees of impurity may introduce a little confusion, the certainty of the results is in nowise lessened.

In the following paragraphs are indicated briefly the methods of purification adopted, together with some physical properties of the liquids serving as criteria of their degree of purity.

Benzene I.—About three pounds of benzene, labelled chemically pure and free from thiophene, were treated with sulphuric acid to remove last traces of thiophene; the liquid was then subjected to fractional crystallization until a little over a pound was obtained melting at 5°.3 (uncorr.). The whole was distilled over a little sodium, most of it boiling at 80°.1 (uncorr.) under a pressure of 756 mm. of mercury.

Benzene II.—About five pounds of "chemically pure" benzene were treated many times with sulphuric acid and crystallized repeatedly. It was then distilled over some pieces of sodium, the whole of it boiling at 80°.12 (corr.) under a pressure of 757.3 mm. of mercury. The distillate was collected in three portions of somewhat more than a pound each, and their melting-points determined by means of a thermometer graduated in hundredths of degrees; these were found to be 5°.39 (corr.), 5°.40 (corr.) and 5°.42 (corr.) This sample can hence be regarded as of a very high degree of purity.

Toluene I.—Of the quantity of toluene taken for purification (about two pounds) more than four-fifths distilled at 109°.8 to 110°.1 (uncorr.), an indication that the commercial article was nearly pure. After a couple of distillations over a little sodium, more than a pound was obtained boiling almost constantly at 110°.1 (uncorr.) under a pressure of 758 mm. of mercury.

Toluene II.—Five pounds of toluene (Merck's chemically pure boiling at 110°–112°) were fractionally distilled a half dozen times or so until the larger portion boiled almost constant. Three fractions of nearly a pound each were taken boiling: *a* at 109°.90–109°.94; *b* at 109°.94–110°.00, and *c* at 110°.00–110°.03 under a pressure of 757.7 mm. The specific gravities at 25°.0 referred to water at the same temperature were: *a* 0.85678; *b* 0.85681, and *c* 0.85680; that is, they were practically the same.

Monochlorbenzene.—A couple of pounds of commercially pure benzene monochloride was fractionally distilled until nearly half of it boiled at 131°.8 to 131°.9 (uncorr.) under a pressure of 757 mm. of mercury.

Nitrobenzene.—The commercial article was repeatedly crystallized in fractions until an almost colorless product was obtained, which when solidified showed the same temperature during the remelting, *viz.*, 3°.6 (uncorr.).

Ethyl Ether.—Five pounds of ordinary ether were washed a couple of dozen times with small portions of water, dried over fused calcium chloride, allowed to stand over mercury for a few days and finally distilled over sodium. Almost the total quantity distilled within 0°.1 degree. The portion which was found to boil at an almost constant temperature was distilled over phosphoric anhydride, and the distillate collected in two portions. Their specific gravities at 25°.0 referred to water at 25°.0 were found to be 0.70940 and 0.70944, respectively, almost identical results.

Acetic Ether I.—A kilogram of C. P. ethyl acetate was fractionally distilled until about a third of it was found to boil within a few tenths of a degree.

Acetic Ether II.—Five pounds of commercial acetic ether were dried for several days over fused calcium chloride, and after filtration from this salt, were allowed to stand for several days over phosphoric anhydride. It was then distilled, the distillate being collected in two portions, one of which boiled at 71°.0–71°.3 (uncorr.), the other at 71°.3–71°.4 (uncorr.). Each of these distillates was then distilled over about half a pound of phosphoric anhydride, when they were found to boil throughout the distillations at identical temperatures. The specific gravity of one sample at 25° referred to water at the same temperature was determined to be 0.89155; that of the other under similar conditions, 0.89157.

Carbon Bisulphide.—Several different preparations of carbon bisulphide were used in the work, all of which had practically identical properties. The method of purification adopted was distillation over mercury and dehydrated copper sulphate. As this compound decomposes somewhat on exposure to light, it was redistilled before the preparation of each series of mixtures.

Turpentine.—The sample used was kindly furnished me by Prof. J. H. Long, of the Northwestern University, who had had it prepared in his laboratory by the distillation of pure spruce gum. It had been rectified over sodium and boiled at 156°.5–157° (uncorr.) under a pressure of 745 mm. of mercury.

Ethyl Benzoate.—This ester was prepared by the action of hydrochloric acid gas on a mixture of benzoic acid and absolute alcohol in the customary way. It was repeatedly rectified, and two different distillates used: I, boiling at 210°.3–210°.8 (uncorr.), and II, boiling at 210°.8–212°.8 (uncorr.), under a pressure of 758 mm. of mercury.

Ethyl Iodide.—The ethyl iodide was made by the action of iodine and red phosphorus on absolute alcohol, and after a couple of fractional distillations a constant boiling portion was obtained. This portion was again distilled and the distillate collected in two equal portions. The specific gravity of the first portion at 25°.0 referred to water at the same temperature was 1.93012, that of the second under the same conditions was 1.93015.

Chloroform.—The chloroform had been fractionated to constant boiling-point, and was finally distilled over phosphoric anhydride; its boiling-point was 61°.3 (uncorr.) under a pressure of 759 mm. of mercury.

Carbon Tetrachloride.—The sample had been fractionally distilled over phosphoric anhydride, after preliminary treatment with concentrated sulphuric acid, and boiled at 76°.7 (uncorr.) under a pressure of 754 mm. of mercury.

The mixtures were prepared by weighing the liquids to less than half a milligram in a bottle or flask; the corked flask was tared, the less volatile liquid poured in and weighed, and then the more volatile. As from forty to one hundred grams of the mixture were weighed out, its composition was known to a ten-thousandth, at least. The mixtures were preserved in bottles or flasks fitted with the finest corks, and stored in a dry, cool, dark closet. Invariably, their specific gravities were determined immediately after their preparation, although it was found in all the cases that were tried that their specific gravities did not change even when they had been made up for more than a year.

V.

Experimental Results.

In the following tables are recorded the experimental data obtained. In the first two columns are given the composition of the mixtures in percentages; in the third and fourth the composition in molecular percentages. The fifth column gives the theoretical specific gravities of the mixtures as calculated from those of their component liquids by means of the formula,

$$D = \frac{dd_1(p + p_1)}{pd_1 + p_1 d},$$

wherein p and p_1 represent the weights of the two liquids, and d and d_1 their respective specific gravities. In the sixth column are placed the specific gravities of the liquids and their mixtures as actually determined. All of the specific gravities are referred to water at the same temperature, no reductions to 4° or a vacuum being made; the data then are quite independent of any reduction formulas or constants, but are simply the direct results of experiment.

In the seventh column, finally, are shown the differences between the observed and calculated values; a plus sign before a number indicates that the observed value is less than the calculated one, while a minus sign shows the opposite. I do not think it necessary to represent the data in a graphical form, as the curves, which I constructed in each case, are remarkably uniform, and the numbers in the seventh column show almost as well as a curve the trend of the phenomena.

It might seem as if it were advisable to communicate the following data in the form of specific volumes as well as specific gravities. The advantage claimed for the first mode being, however, only of algebraical nature, and it being easy enough to obtain specific volumes from the specific gravities, the data for the last were thought sufficient.

TABLE I.

Specific Gravities of Mixtures of Benzene II. and Ethyl Ether.

Temperature, 25°.0.

Percentage composition.		Molecular percentage composition.		Calculated specific gravity.	Observed specific gravity.	Differences.
C_6H_6	$C_4H_{10}O$	C_6H_6	$C_4H_{10}O$			
0.000	100.000	0.000	100.000		0.70942	
28.576	71.424	27.502	72.498	0.74971	0.75369	—0.00398
56.924	43.076	55.627	44.373	0.79455	0.79972	—0.00517
75.691	24.309	74.709	25.291	0.82728	0.83179	—0.00451
100.000	0.000	100.000	0.000		0.87390	

TABLE II.

Specific Gravities of Mixtures of Benzene I. and Acetic Ether II.

Temperature, 25°.0.

Percentage composition.		Molecular percentage composition.		Calculated specific gravity.	Observed specific gravity.	Differences.
C_6H_6	$C_4H_8O_2$	C_6H_6	$C_2H_8O_2$			
0.000	100.000	0.000	100.000		0.89663	
15.594	84.406	17.250	82.750	0.89346	0.89285	+0.00061
51.404	48.596	54.411	45.589	0.88625	0.88506	+0.00116
80.803	19.197	82.605	17.395	0.88038	0.87982	+0.00056
100.000	0.000	100.000	0.000		0.87661	

TABLE III.

Specific Gravities of Mixtures of Benzene I. and Carbon Tetrachloride.

Temperature, 20°.0 (Brown).

Percentage composition.		Molecular percentage composition.		Calculated specific gravity.	Observed specific gravity.	Differences.
C_6H_6	CCl_4	C_6H_6	CCl_4			
		0.000	100.000		1.59742	
		10.074	89.926	1.53049	1.53059	—0.00010
		20.363	79.637	1.46099	1.46116	—0.00017
		30.216	69.784	1.39331	1.39363	—0.00032
		40.748	59.252	1.31974	1.32004	—0.00030
		50.422	49.578	1.25101	1.25120	—0.00019
		60.437	39.563	1.17796	1.17825	—0.00029
		70.585	29.415	1.10408	1.10420	—0.00012
		80.533	19.467	1.02971	1.02983	—0.00012
		90.511	9.489	0.95380	0.95388	—0.00008
		100.000	0.000		0.88038	
Temperature, 23°.0 (Linebarger).						
0.000	100.000	0.000	100.000		1.59156	
13.728	86.273	23.860	76.140	1.43202	1.43214	—0.00012
40.779	59.221	57.550	42.450	1.19579	1.19598	—0.00019
58.600	41.400	73.599	26.401	1.07861	1.07868	—0.00007
100.000	0.000	100.000	0.000		0.87847	
Temperature, 25°.0 (Linebarger).						
0.000	100.000	0.000	100.000		1.58828	
13.727	86.273	23.860	76.140	1.42942	1.42956	—0.00014
40.779	59.221	57.550	42.450	1.19328	1.19339	—0.00011
58.600	41.400	73.599	26.401	1.07632	1.07642	—0.00008
100.000	0.000	100.000	0.000		0.87661	

TABLE IV.

Specific Gravities of Mixtures of Benzene I. and Chloroform.

Temperature, 25.°0.

Percentage composition.		Molecular percentage composition.		Calculated specific gravity.	Observed specific gravity.	Differences.
C_6H_6	$CHCl_3$	C_6H_6	$CHCl_3$			
0.000	100.000	0.000	100.000		1.48069	
6.970	93.030	10.291	89.709	1.41613	1.41203	+0.00410
23.011	76.989	31.410	68.590	1.27788	1.27568	+0.00220
72.780	27.220	80.370	19.630	0.98619	0.98485	+0.00134
85.830	14.171	90.289	9.711	0.93042	0.92965	+0.00077
100.000	0.000	100.000	0.000		0.87661	

TABLE V.

Specific Gravities of Mixtures of Benzene I. and Nitrobenzene.

Temperature 25.°0.

Percentage composition.		Molecular percentage compositiou.		Calculated specific gravity.	Observed specific gravity.	Differences.
C_6H_6.	$C_6H_5NO_2$.	C_6H_6	$C_6H_5NO_2$.			
0.000	100.000	0.000	100.000		1.20200	
14.394	85.606	20.956	79.044	1.14105	1.14200	—0.00095
37.610	62.390	48.735	51.265	1.05477	1.05620	—0.00143
80.053	19.947	86.355	13.645	0.92664	0.92764	—0.00100
100.000	0.000	100.000	0.000		0.87661	

TABLE VI.

Specific Gravities of Mixtures of Benzene I. and Carbon Bisulphide.

Temperature, 19°.80 (Brown).

Percentage composition.		Molecular percentage composition.		Calculated specific gravity.	Observed specific gravity.	Differences.
C_6H_6.	CS_2.	C_6H_6.	CS_2.			
0.000	100.000	0.000	100.000		1.26642	
5.327	94.673	5.198	94.802	1.23751	1.23459	+0.00292
17.201	82.799	16.835	83.165	1.17758	1.17184	+0.00574
20.195	79.805	19.780	80.220	1.16338	1.15700	+0.00638
27.537	72.463	27.022	72.978	1.12996	1.12241	+0.00755
34.613	65.387	34.027	65.973	1.09952	1.09132	+0.00820
38.980	61.020	38.364	61.636	1.08153	1.07250	+0.00903
49.612	50.388	48.963	51.037	1.04012	1.03126	+0.00886
59.039	40.961	58.409	41.591	1.00596	0.99868	+0.00728
60.581	39.419	59.959	40.041	1.00059	0.99354	+0.00705
75.074	24.926	74.585	25.415	0.95274	0.94744	+0.00530
87.366	12.634	87.077	12.923	0.91561	0.91307	+0.00254
100.000	0.000	100.000	0.000		0.88034	

Temperature, 25°.0 (Linebarger).

Percentage composition.		Molecular percentage composition.		Calculated specific gravity.	Observed specific gravity.	Differences.
C_6H_6.	$C_4H_{10}O$.	C_6H_6.	$C_4H_{10}O$.			
0.000	100.000	0.000	100.000		1.25958	
8.872	91.127	8.675	91.325	1.21257	1.20897	+0.00360
34.858	65.142	34.270	65.730	1.09314	1.08494	+0,00820
75.886	24.114	75.409	24.591	0.94607	0.94176	+0.00431
100.000	0.000	100.000	0.000		0.87661	

TABLE VII.

Specific Gravities of Mixtures of Benzene I. and Toluene I.

Temperature, 25°.0.

Percentage composition.		Molecular percentage composition.		Calculated specific gravity.	Observed specific gravity.	Differences.
C_6H_6.	C_7H_8.	C_6H_6.	C_7H_8.			
0.000	100.000	0.000	100.000		0.86288	
10.990	89.010	12.720	87.280	0.86446	0.86434	+0.00012
30.558	69.412	34.229	65.771	0.86712	0.86635	+0.00072
51.920	48.080	56.020	43.980	0.87002	0.86920	+0.00082
66.433	33.567	70.000	30.000	0.87197	0.87140	+0.00057
66.576	33.424	70.240	29.760	0.87198	0.87143	+0.00055
91.556	8.444	92.750	7.250	0.87549	0.87528	+0.00021
100.000	0.000	100.000	0.000		0.87661	

TABLE VIII.

Specific Gravities of Toluene II. and Turpentine.

Temperature, 25°.0.

Percentage composition.		Molecular percentage composition.		Calculated specific gravity.	Observed specific gravity.	Differences.
C_7H_8.	$C_{10}H_{16}$.	C_7H_8.	$C_{10}H_{16}$			
0.000	100.000	0.000	100.000		0.85970	
6.791	93.209	9.724	90.276	0.85955	0.85948	+0.00007
20.654	79.346	24.464	72.536	0.85910	0.85838	+0.00072
53.701	46.299	63.162	36.838	0.85815	0.85682	+0.00133
75.091	24.909	89.884	20.116	0.85801	0.85654	+0.00147
100.000	0.000	100.000	0.000		0.85680	

TABLE IX.

Specific Gravities of Mixtures of Toluene II. and Ethyl Benzoate I.

Temperature, 25°.0.

Percentage composition.		Molecular percentage composition.		Calculated specific gravity.	Observed specific gravity.	Differences.
C_7H_8.	$C_9H_{10}O_2$.	C_7H_8.	$C_9H_{10}O_2$.			
0.000	100.000	0.000	100.000		1.04843	
15.282	84.718	22.726	77.274	1.01378	1.01458	—0.00080
47.322	52.678	59.450	40.550	0.94806	0.94937	—0.00139
76.170	23.830	83.918	16.082	0.89580	0.89667	—0.00087
100.000	0.000	100.000	0.000		0.85680	

Specific Gravities of Mixtures of Toluene II. and Ethyl Benzoate II.

0.000	100.000	0.000	100.000		1.05455	
51.249	48.751	63.152	36.848	0.94311	0.94445	—0.00136
100.000	0.000	100.000	0.009		0.85680	

TABLE X.

Specific Gravities of Mixtures of Toluene I. and Nitrobenzene.

Temperature, 25°.0.

Percentage composition.		Molecular percenlage composition.		Calculated specific gravity.	Observed specific gravity.	Differences.
C_7H_8.	$C_6H_5NO_2$.	C_7H_8.	$C_6H_5NO_2$.			
0.000	100.000	0.000	100.000		1.20200	
15.400	84.600	19.566	80.434	1.13334	1.13523	—0.00189
37.410	62.590	44.406	55.594	1.04795	1.05084	—0.00289
70.957	29.043	76.554	23.446	0.93991	0.94240	—0.00249
87.796	12.204	90.579	9.421	0.89365	0.89478	—0.00143
100.000	0.000	100.000	0.000		0.86288	

TABLE XI.

Specific Gravities of Mixtures of Toluene I. and Monochlorbenzene.

Temperature, 25°.0.

Percentage composition.		Molecular percentage composition.		Calculated specific gravity.	Observed specific gravity.	Differences.
C_7H_8.	C_6H_5Cl.	C_7H_8.	C_6H_5Cl.			
0.000	100.000	0.000	100.000		1.10362	
19.756	80.244	23.290	76.710	1.04704	1.04768	—0.00064
53.364	46.636	58.181	41.819	0.96061	0.96159	—0.00098
77.713	22.287	81.010	18.990	0.90695	0.90787	—0.00092
79.578	20.422	82.643	17.357	0.90310	0.90399	—0.00087
100.000	0.000	100.000	0.000		0.86288	

TABLE XII.

Specific Gravities of Mixtures of Toluene I. and Carbon Bisulphide.

Temperature, 25°.0.

Percentage composition.		Molecular percentage composition.		Calculated specific gravity.	Observed specific gravity.	Differences.
C_7H_8.	CS_2.	C_7H_8.	CS_2.			
0.000	100.000	0.000	100.000		1.25958	
7.269	92.731	6.082	93.918	1.21888	1.21783	+0.00105
37.992	62.008	33.605	66.395	1.07229	1.06759	+0.00470
63.242	36.758	58.699	41.301	0.97587	0.97217	+0.00370
100.000	0.000	100.000	0.000		0.86288	

TABLE XIII.

Specific Gravities of Mixtures of Toluene II. and Acetic Ether II.

Percentage composition.		Molecular percentage composition.		Calculated specific gravity.	Observed specific gravity.	Differences.
C_7H_8.	$C_4H_8O_2$.	C_7H_8.	$C_4H_8O_2$.			
0.000	100.000	0.000	100.000		0.89156	
15.708	84.292	15.129	84.871	0.88592	0.88588	+0.00006
45.301	54.699	44.202	55.798	0.87546	0.87529	+0.00017
71.255	28.745	70.335	29.665	0.86652	0.86636	+0.00016
100.000	0.000	100.000	0.000		0.85680	

TABLE XIV.

Specific Gravities of Mixtures of Acetic Ether II. and Carbon Bisulphide.

Percentage composition.		Molecular percentage composition.		Calculated specific gravity.	Observed specific gravity.	Differences.
$C_4H_8O_2$.	CS_2.	$C_4H_8O_2$.	CS_2.			
0.000	100.000	0.000	100.000		1.25958	
16.359	83.641	14.451	85.549	1.17990	1.16956	+0.01034
39.246	60.754	35.811	64.189	1.08498	1.06877	+0.01621
66.413	33.587	63.069	36.931	0.98856	0.97681	+0.01175
100.000	0.000	100.000	0.000		0.89156	

TABLE XV.

Specific Gravities of Mixtures of Acetic Ether II. and Ethyl Iodide.

Percentage composition.		Molecular percentage composition.		Calculated specific gravity.	Observed specific gravity.	Differences.
$C_4H_8O_2$.	C_2H_5I.	$C_4H_8O_2$.	C_2H_5I.			
0.000	100.000	0.000	100.000		1.93015	
21.799	78.201	33.073	66.927	1.53925	1.52760	+0.01265
64.427	32.573	78.585	21.415	1.08104	1.07553	+0.00551
100.000	0.000	100.000	0.000		0.89156	

TABLE XVI.

Specific Gravities of Mixtures of Ethyl Ether and Carbon Bisulphide.

Percentage composition.		Molecular percentage composition.		Calculated specific gravity.	Observed specific gravity.	Differences.
$C_4H_{10}O$.	CS_2.	$C_4H_{10}O$.	CS_2.			
0.000	100.000	0.000	100.000		1.25959	
13.100	86.900	13.407	86.593	1.14342	1.14280	+0.00062
34.367	65.633	34.969	65.031	0.99455	0.99380	+0.00075
62.759	37.241	63.380	36.620	0.84725	0.84689	+0.00036
100.000	0.000	100.000	0.000		0.70942	

TABLE XVII.

Specific Gravities of Mixtures of Carbon Tetrachloride and Carbon Bisulphide.

Percentage composition.		Molecular percentage composition.		Calculated specific gravity.	Observed specific gravity.	Differences.
CCl_4.	CS_2.	CCl_4.	CS_2.			
Temperature, 20°.0. (Brown.)						
		0.000	100.000		1.26583	
		9.840	90.160	1.31527	1.31269	+0.00258
		19.474	80.526	1.35857	1.35430	+0.00427
		29.676	70.324	1.39976	1.39430	+0.00546
		39.974	60.026	1.43718	1.43102	+0.00616
		49.976	50.024	1.47009	1.46410	+0.00599
		59.161	40.839	1.49773	1.49216	+0.00457
		69.779	30.221	1.52698	1.52232	+0.00466
		80.231	19.769	1.55331	1.55005	+0.00326
		88.471	11.529	1.57253	1.57057	+0.00196
		100.000	0.000		1.59742	
Temperature, 25°.0. (Linebarger.)						
0.000	100.000	0.000	100.000		1.25958	
28.271	71.729	16.285	83.715	1.33803	1.33397	+0.00406
57.150	42.850	39.942	60.058	1.42857	1.42298	+0.00559
85.772	14.228	74.844	25.156	1.53178	1.52729	+0.00449
100.000	0.000	100.000	0.000		1.58828	

TABLE XVIII.[1]

Specific Gravittes of Mixtures of Carbon Bisulphide and Acetic Ether.

Percentage composition.		Molecular percentage composition.		Calculated specific gravity.	Observed specific gravity.	Differences.
$C_4H_8O_2$.	CS_2.	$C_4H_8O_2$.	CS_2.			
0.000	100.000	0.000	100.000		1.25958	
16.359	83.641	14.451	85.549	1.17990	1.16956	+0.01034
39.246	60.754	35.811	64.189	1.08498	1.06877	+0.01621
66.413	33.587	63.069	36.931	0.98856	0.97681	+0.01175
100.000	0.000	100.000	0.000		0.89156	

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[1] The mixture containing 16.359 per cent. of acetic ether separated out into layers when cooled a little below 25.0.°

TABLE XIX.

Specific Gravities of Mixtures of Chloroform and Carbon Bisulphide.

Percentage composition.		Molecular percentage composition.		Calculated specific gravity.	Observed specific gravity.	Differences.
$CHCl_3$.	CS_2.	$CHCl_3$.	CS_2.			
0.900	100.000	0.000	100.000		1.25958	
28.696	71.304	20.940	79.060	1.31598	1.30877	+0.00721
62.557	34.443	51.518	48.482	1.38938	1.37919	+0.01019
79.361	20.639	70.976	29.024	1.42895	1.42130	+0.00765
93.909	6.091	90.749	9.251	1.46503	1.46197	+0.00316
100.000	0.000	100.000	0.000		1.48069	

TABLE XX.

Specific Gravities of Mixtures of Carbon Tetrachloride and Chloroform.

Percentage composition.		Molecular percentage composition.		Calculated specific gravity.	Observed specific gravity.	Differences.
CCl_4.	$CHCl_3$.	CCl_4.	$CHCl_3$.			
0.000	100.000	0.000	100.000		1.48069	
19.269	80.731	15.663	84.337	1.50018	1.49872	+0.00146
53.446	46.554	47.118	52.882	1.53820	1.53344	+0.00476
57.277	42.723	50.989	49.011	1.56805	1.56489	+0.00316
100.000	0.000	100.000	0.000		1.58828	

TABLE XXI.

Specific Gravities of Mixtures of Nitrobenzene and Acetic Ether I.

Percentage composition.		Molecular percentage composition.		Calculated specific gravity.	Observed specific gravity.	Differences
$C_6H_5NO_2$.	$C_4H_8O_2$.	$C_6H_5NO_2$.	$C_4H_8O_2$.			
0.000	100.000	0.000	100.000		0.89663	
22.896	77.104	17.530	82.470	0.95202	0.95669	—0.00467
56.100	43.900	47.770	52.230	1.04568	1.05318	—0.00760
75.530	24.470	68.870	31.130	1.10911	1.11618	—0.00707
100.000	0.000	100.000	0.000		1.20200	

TABLE XXII.

Specific Gravities of Mixtures of Toluene and Carbon Tetrachloride.

Temperature, 20.°0. (Brown.)

Molecular percentage composition.		Calculated specific gravity.	Observed specific gravity.	Differences.
C_7H_8.	CCl_4.			
0.000	100.000		1.59712	
20.706	79.294	1.43408	1.43447	—0.00039
40.594	59.406	1.28277	1.28442	—0.00165
47.661	52.339	1.23156	1.23202	—0.00047
50.540	49.460	1.21055	1.21090	—0.00035
60.166	39.834	1.14113	1.14130	—0.00017
70.231	29.769	1.06988	1.07013	—0.00025
79.920	20.080	1.00256	1.00265	—0.00009
100.000	0.000		0.86684	

TABLE XXIII.

Specific Gravities of Mixtures of Dichlorethane and Benzene.

Temperature, 20°.0. (Brown.)

Molecular percentage composition.		Calculated specific gravity.	Observed specific gravity.	Differences.
C_6H_6.	$C_2H_4Cl_2$.			
0.000	100.000		1.25105	
20.477	79.523	1.16809	1.16587	+0.00222
39.527	60.473	1.09440	1.09139	+0.00301
59.900	40.100	1.01906	1.01622	+0.00284
79.522	20.478	0.94968	0.94790	+0.00178
100.000	0.000		0.88036	

TABLE XXIV.

Specific Gravities of Mixtures of Benzene and Dibromethane I.

Temperature, 20.°0. (Brown.)

Molecular percentage composition.		Calculated specific gravity.	Observed specific gravity.	Differences.
C_6H_6.	$C_2H_4Br_2$.			
0.000	100.000		2.17053	
27.001	72.999	1.81638	1.81277	+0.00361
49.185	50.815	1.52864	1.52467	+0.00397
58.287	41.713	1.41142	1.40776	+0.00366
67.289	32.711	1.29597	1.29269	+0.00328
82.199	17.801	1.10577	1.10384	+0.00193
100.000	0.000		0.88036	

Specific Gravities of Mixtures of Benzene and Dibromethane II.

0.000	100.000		2.17626	
39.378	60.622	1.65811	1.65460	+0.00351
66.084	33.916	1.31256	1.30942	+0.00314
100.000	0.000		0.88036	

VI.

Discussion of Results.

If any amount of a pure liquid be mixed with any other amount of it under identical conditions of temperature and pressure, the volume of the resulting mixture is equal to the sums of the volumes of the amounts mixed, and all physical properties of the unmixed liquids persist in the mixture. If, however, two liquids of different chemical composition—be the difference ever so slight, and be the similarity of the physical properties of the liquids ever so great—are mixed, the resulting mixture does not necessarily have a volume equal to the sum of the volumes of its own components, although, in certain instances, this may be the case; generally there will occur a contraction or expansion in volume. It is interesting to seek an explanation for this behavior.

The simplest case that can perhaps be considered is this: two liquids, *A* and *B*, have no appreciable specific action upon one another; the attractions between the like molecules is of the same order as those between the unlike. The molecular actions being thus supposed to be independent of the chemical nature of the liquids, these might be expected to behave similarly to gases, and, when mixed, not to undergo any change in volume, were it not for the fact that the analogy fails in a most essential particular. A distinguishing feature between gases and liquids is the possession by the latter of a definite surface, and the exhibition of the so-called capillary phenomena. The cause of this surface and the capillary phenomena is to be found in the internal pressure, due to the interaction of the molecules and acting normally to the surface. This pressure it is, which determines the density of a liquid at any temperature, and its amount as well as the density, decreases in most cases with rise of temperature. Since the internal pressure is due to the attractions of the molecules of a liquid, any circumstance tending to diminish this action, occasions a falling off in the amount of the internal pressure. Rise of temperature lessens molecular attraction, and, as just stated, the internal pressure also ; a dilution of the liquid by another without specific action in like manner reduces the molecular attraction and the internal pressure correspondingly. If, then, to the liquid *A* a small proportion of the liquid *B* be added, the number of molecules of *A* in the unit of surface or volume becomes smaller, so that the molecular attraction and internal pressure also become smaller; a decrease in the density or an increase in volume is the effect measurable by the experimental means at our command. As more and more of the liquid *B* is added to the liquid *A*, the internal pressure and the density becomes less and less. Now, entirely similar effects are caused by the addition of *A* to *B* ; hence the minimum of internal pressure and density should be reached when about equal quantities of both liquids are mixed. It is to be concluded then that the mixing of normal liquid decreases the specific gravity.

Similar conclusions are arrived at by the introduction and use of the conception of osmotic pressure. When a small proportion of *A* is mixed with *B*, the molecules of *A* are in a way freed from their internal pressure, and behave as if in the gaseous state ; they accordingly exert osmotic pressure, which acts against the internal pressure, so that the latter becomes reduced in amount. As *A* in *B*, so does *B* in *A* exert an osmotic pressure, the maximum of which is attained when about equal numbers of molecules of each liquid are contained in the mixture. But as osmotic and internal pressure are in inverse proportion, it follows that the mixture with the maximum osmotic presure must have the minimum internal pressure.

It is doubtful if there exist two liquids which are without appreciable specific action upon each other. The above considerations, then, as applying to an ideal state of affairs, can lead only to approximate results. But an examination of the data given in the previous section shows that in the majority of cases the calculated density is greater than that found experimentally. The differences are generally small and have their maximum value when the mixture in question is made up of about equal proportions of its constituents ; in no case do points of inflection occur. This is quite in accordance with the developments of the foregoing paragraphs.

Some mixtures there are, however, that do not behave in this normal way ; in them a contraction of volume attends the mixing and their densities are found to be greater than those calculated. It may seem natural to attribute this behavior to some specific actions between the molecules of the liquids mixed. Still, certain mixtures, as that of toluene and monochlorbenzene, are made up of such chemically similar liquids, that it seems that recourse should not be had to assumptions of specific molecular attractions. In other mixtures, however, it seems quite allowable to make such assumptions. Thus, if benzene, toluene, or acetic ether be mixed with nitrobenzene, the density of the resulting mixture is greater than that calculated by the rule of mixtures, although any of the three first mentioned liquids when mixed with another of them shows the normal behavior, *viz.*, expansion. In this case, then, there seems to reside in the nitrobenzene a power of drawing the molecules of mixtures of which it is a component closer together.

In a mixture of benzene or toluene with carbon tetrachloride, the observed density is very slightly greater than the theoretical. Yet when the last-named liquid is mixed with chloroform, the observed densities are relatively considerably less than those calculated. It would appear that these liquids are so normal and so similar physically and chemically that in their mixtures the normal behavior would be found ; it may be called to mind that these very liquids—chloroform and carbon tetrachloride—were found to behave somewhat irregularly in the vapor tensions of their mixtures[1] and in the heat phenomina attendant upon their mixing.[2] The remark of Brown[3] is applicable here, who, in discussing his results,

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[1] See my paper "On the Vapor Tensions of Mixtures of Volatile Liquids." J. Am. Chem. Soc., **17**, 690, (1895).

[2] See my paper "On the Heat Effect of Mixing Liquids." The Physical Review, 1896.

[3] *Loc. cit.*

obtained with mixtures of benzene and toluene with carbon tetrachloride, writes: "The numbers form a remarkable confirmation of the supposition that these changes are dependent on the chemical character of the molecules, and entirely independent of such physical properties as vapor-tension, molecular volume, etc." It is indeed remarkable that the differences between the calculated and observed values of mixtures of carbon tetrachloride with either benzene or toluene are almost the same, as is clearly shown by the curves that Brown has published.[1]

It must be concluded that with our present meager data very few generalities can be drawn as to a connection between the chemical or physical properties of liquids and their changes of volume when mixed.

A point which it may be worth while to dwell upon is the amount of the differences between the observed and the calculated densities in connection with the possibility of a slight degree of molecular polymerization. When the mixtures are made up of liquids that are strictly normal, as the hydrocarbons, ethers, etc., the differences are found to be but slight, seldom exceeding more than a ten-thousandth of the density. When one of the compounds is somewhat associated, the differences are greater. Now, Ramsay and Aston[2] have found carbon bisulphide to be slightly associated at low temperatures, and we see, indeed, that in those mixtures which contain carbon bisulphide as a constituent, the differences of density—theoretical and observed—amount to several thousandths or even hundredths. We have here then, a criterion of molecular polymerization in liquids; when a liquid mixed with another which is recognized to be strictly normal, forms mixtures whose specific gravities differ considerably from those calculable by the rule of mixtures, that liquid is composed of more or less associated molecules.

With considerable differences between the values of calculated and observed specific gravities stands in close connection the phenomenon of layer formation. A glance at Table XVIII, p. 446, shows differences in the last column amounting to hundredths of the amount of the quantity measured,

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[1] *Loc. cit.*

[2] Ztschr. phys. Chem., **15**, 89, (1894).

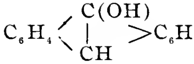
and for certain proportions of the liquids layer formation is observed.

Contributions from the Chemical Laboratory of Cornell University.

DIANTHRANOL—A DIHYDROXYL DERIVATIVE OF DIANTHRACENE.

BY W. R. ORNDORFF AND C. L. BLISS.

In a recent article on dianthracene[1] by Orndorff and Cameron, it was stated that a solution of anthranol in benzene suffered a change in the direct sunlight, similar to that noticed in case of solutions of anthracene itself. To the product formed from anthranol under these conditions, the provisional name dianthranol was given on account of the resemblance in its mode of formation and general physical properties to dianthracene. Since the publication of the article above referred to, a considerable quantity of this substance has been made, and a thorough study of it has shown that the above supposition in regard to it being a dihydroxyl derivative of dianthracene is correct.

Anthranol,  $C_6H_4\langle\overset{C(OH)}{\underset{CH}{|}}\rangle C_6H_4$, was prepared and studied by Liebermann, first in connection with Topf[1] and then with Gimbel.[3] In both cases it was made by the reduction of anthraquinone, according to the equation,

$$C_{14}H_8O_2 + 2H_2 = C_{14}H_{10}O + H_2O.$$

After giving the details of their method of preparation of this substance and describing its properties, Liebermann and Topf state in regard to it that "Vielfaches Umkrystallisiren oder längeres Stehen ihrer Lösungen verträgt sie nicht; die dann erhaltenen Krystalle lösen sich bald nur noch zum geringen Theile in Alkali. In trockenem Zustand hält sie sich länger, selbst in Jahre alten Präparaten lässt sich oft neben veränderter Substanz unverändertes Anthranol nachweisen. Als Erkennungsmittel des Anthranols dient die gelbe Lösung desselben in Alkali.

Durch Kohlensäure wird aus dieser Lösung das Anthranol unter Entfärbung ausgefällt; schüttelt man die

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[1] This JOURNAL, **17**, 517.
[2] Ann. Chem. (Liebig), **212**, 6.
[3] Ber. d. chem. Ges., **20**, 1854. (1887).

Lösung mit Luft so tritt ebenfalls nach einiger Zeit, wenn auch meist nicht ganz vollständige Entfärbung der Flüssigkeit unter Abscheidung eines weissen Niederschlags ein. Es war zu vermuthen, dass derselbe, sowie überhaupt die an der Luft veränderte Substanz, aus Anthrachinon bestehen würde. Letzteres liess sich auch immer leicht in dem Umwandlungsproduct nachweisen und durch Krystallisation abtrennen, doch geht die Oxydation durch ein Zwischenstadium hindurch, welches nicht in reiner Form erhalten wurde."

No other statement occurs in the literature concerning this change in solutions of anthranol, nor has the product formed ever been investigated. As it seemed quite likely that this change was connected with the action of light on solutions of anthranol observed by Orndorff and Cameron, and that the product formed was the same in both cases, the present investigation was undertaken to show whether this supposition was correct or not, and also to determine the relation of this product to anthranol itself.

Experimental.

The anthranol used in this work was made and purified according to the method given by Liebermann and Gimbel by the reduction of pure anthraquinone in acetic acid solution with tin and hydrochloric acid. It melted with decomposition at 163–170° C. (uncor.) and crystallized in lemon-yellow colored needles. A solution of this anthranol in benzene was exposed to the action of the bright sunlight for some weeks during the summer of 1895. The solution at first became colored dark green with a bluish fluorescence, then yellow, and finally, after a few days, reddish-yellow, some white crystals, entirely different in appearance from crystals of anthranol, separating out. These crystals were filtered off, and a second crop having a yellow color was obtained from the filtrate after some of the solvent had been distilled off. In the mother-liquor there remained a small amount of unchanged anthranol and some anthraquinone. The crystals were then purified by recrystallizing several times from benzene, using bone-black to remove the yellow color. It was found exceedingly difficult to get rid of this yellow coloring material, and, though the benzene solution was treated with bone-black a number of times, the crystals finally obtained still had a marked yellow tinge. They melted at 245–255° C. and sometimes as high as 260–263° (depending on the rapidity with which they were heated), and always with decomposition. An analysis of the best product melting at 260–263° C. gave the following results:

I. 0.1584 gram gave 0.0650 gram H_2O and 0.5043 gram CO_2.
II. 0.1325 " " 0.0560 " " " 0.4219 " "

	Found.		Calculated for
	I.	II.	$(C_{14}H_{10}O)_x$.
Carbon	86.83	86.84	86.60
Hydrogen	4.56	4.69	5.15
Oxygen (by difference)	8.61	8.47	8.25

These results show that the substance formed by the action of light on anthranol has the same percentage composition as the anthranol itself. As it seemed probable that the new substance was white when pure, we endeavored to purify our product further. It was almost insoluble in ether and so slightly soluble in alcohol that these solvents could not be used for recrystallizing. In chloroform, on the other hand, it was so very soluble that this solvent was also excluded. When boiled with acetone the yellow material appeared to go into solution more readily and separated out first on cooling, so that by careful management an almost white product was obtained, and by repeating the process pure white crystals resulted. These crystals, which melted at 255–260° C. (uncor.) with decomposition were then analyzed with the following results:

0.2180 gram gave 0.0891 gram H_2O and 0.6956 gram CO_2.

	Found.	Calculated for $(C_{14}H_{10}O)_x$.
Carbon	87.02	86.60
Hydrogen	4.54	5.15
Oxygen (by difference)	8.44	8.25

Some preliminary experiments having shown that the melting-point of anthranol crystallized from high-boiling solvents was raised very markedly, and that the product formed appeared to be identical with that resulting from the action of light on solutions of anthranol, we next endeavored to make the new product by boiling a solution of pure anthranol in xylene for a long time. After heating the solution in a flask connected with an inverted condenser for twelve hours, the change appeared to be complete. On cooling, crystals resembling those obtained by the action of light on solutions of anthranol separated out, and, on concentrating the filtrate from these, a second crop of crystals was obtained. This crude product, melting at 240–250° C. (uncor.), was purified by fractional crystallization from glacial acetic acid and then from benzene, using bone-black to remove the yellow color of the solutions. The crystals made in this way were pure white, and melted with decomposition at 246–251° C. (uncor.), using a standardized thermometer. An analysis gave the following results:

I. 0.1703 gram gave 0.0748 gram H_2O and 0.5434 gram CO_2.
II. 0.2009 " " 0.0858 " " " 0.6402 " "

	Found.		Calculated for
	I.	II.	$(C_{14}H_{10}O)x$.
Carbon	87.01	86.91	86.60
Hydrogen	4.88	4.74	5.15
Oxygen (by difference)	8.11	8.35	8.25

These results show that the product formed on boiling a solution of anthranol in xylene is the same as that obtained by the action of light on a solution of anthranol in benzene, and that the product has the same percentage composition as anthranol itself.

We next investigated the product formed when a solution of anthranol in potassium hydroxide is shaken with air. This substance is regarded by Liebermann as an intermediate product between anthranol and anthraquinone, though he gives no analyses and probably did not have the substance in a pure form. Pure anthranol was dissolved in a hot dilute solution of potassium hydroxide, the solution filtered and a current of air, freed from carbon dioxide, passed through the reddish yellow-colored solution until it was almost decolorized. A white precipitate was formed, which appeared to be totally insoluble in the solution of potassium hydroxide. This was decanted off, washed with a fresh solution of potassium hydroxide, then with hot water, filtered, dried, and recrystallized from acetone. The crystals were yellow-colored at first, but by boiling the solution with bone-black, or by decolorizing it with sulphur dioxide, we finally obtained them in beautiful transparent tablets, melting at 250° C., and showing all the characteristic of the dianthranol prepared by other methods.

From these results it will be seen that the product formed by the oxidation of anthranol in caustic potash solution is the same as that obtained by the action of light on solutions of this substance, as well as by heating a solution of anthranol in xylene. In order to determine the exact relation between anthranol and this new product, both having the same percentage composition, molecular weight estimations were now made by the boiling-point method, using the apparatus[1] recently described by Orndorff and Cameron for this purpose. The following are the results obtained with the new product :

DIANTHRANOL.

$C_{14}H_{10}O = 194$; $C_{28}H_{10}O_2 = 388$.

Solvent : *Chloroform.*

Boiling-point 60°.2 C. at 741.7 mm. barometric pressure.

Molecular elevation for 100 grams 36.6°.

I.

	Grams solvent.	Grams substance.	Concentration in 100 grams.	Observed elevation.	Barometer mm.	Molecular weight.
1	201.23	0.6527	0.3244	0.028°	739.2	424
2	"	1.1834	0.5881	0.049	739.1	439
3	"	1.6134	0.8018	0.069	739.0	425
4	"	1.9671	0.9775	0.086	738.9	416

Barometer 739.3–738.9 mm.

Molecular weight at infinite dilution, **405**

II.

	Grams solvent.	Grams substance.	Concentration in 100 grams.	Observed elevation.	Barometer mm.	Molecular weight.
5	213.90	1.0562	0.4938	0.041°	739.3	441
6	"	2.0545	0.9605	0.084	739.6	418

Solvent : *Benzene.*

Boiling-point 79.6° C. at 744.5 mm. barometric pressure.

Molecular elevation for 100 grams 26.6°.

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[1] This JOURNAL, 17, 517.

	Grams solvent.	Grams substance.	Concentration in 100 grams.	Observed elevation.	Barometer mm.	Molecular weight.
7	113.03	0.7972	0.7053	0.050°	743.5	375
8	"	1.4789	1.3084	0.094	743.6	370

These results show that the formula of the new compound is $C_{28}H_{20}O_2$, but, as the molecular weight of anthranol itself is not known, it is impossible to say whether this product is an isomer or a polymer of anthranol. We therefore next determined the molecular weight of anthranol, using the same method and apparatus as before, and working with the purest material we could prepare. The results follow :

ANTHRANOL.

$$C_{14}H_{10}O = 194\,;\ C_{28}H_{20}O_2 = 388.$$

Solvent: *Benzene.*

Boiling-point 79.6° C. at 744.5 mm. barometric pressure.

Molecular elevation for 100 grams 26.6°.

	Grams solvent.	Grams substance.	Concentration in 100 grams.	Observed elevation.	Barometer mm.	Molecular weight.
1	119.88	0.5742	0.4790	0.064°	743.7	199
2	"	0.9343	0.7794	0.095	"	218
3	"	1.2782	1.0663	0.129	"	220
4	"	1.5100	1.2596	0.150	"	223

Barometer 743.6–743.7 mm.

Molecular weight at infinite dilution 186

We see from these results that the new substance has double the molecular weight of anthranol, and that the relations between it and anthranol is exactly the same as that existing between dianthracene and anthracene. The name dianthranol serves very well to recall this relation, and also to show that it is a derivative of dianthracene.

The dianthranol made by one of the above processes and crystallized first from glacial acetic acid and then from benzene, is a beautiful product crystallizing in colorless tabular or columnar crystals. The pure substance melted with decomposition at about 250° C., sometimes as low as 246° C. and even as high as 255° C., depending on the rapidity with which the material was heated. It is almost insoluble in ether, slightly soluble in alcohol, more soluble in acetone, glacial acetic acid and benzene, and very soluble in chloroform. In solutions of the alkalies dianthranol is insoluble even on long boiling. This serves as an excellent method to separate dianthranol from anthranol. When a solution of dianthranol in benzene is allowed to evaporate slowly to dryness in contact with the air, it is partially oxidized to anthraquinone.

Some dianthranol was heated in a test-tube in a sulphuric-acid bath to its melting-point, and kept at this temperature for about an hour. The material in the tube blackened and seemed to be entirely decomposed. After cooling, however, some yellow needles were found to have sublimed out of the black product. These were completely soluble in a boiling solution of potassium hydroxide with a yellow color, and were again precipitated on the addition of hydrochloric acid. They melted at 160°–180° C. with decomposition, and gave none of the tests for anthraquinone. The substance appeared to be anthranol, but the quantity formed was too small for analysis. It seems, therefore, quite probable that dianthranol undergoes at its melting-point a change into anthranol, similar to that observed when dianthracene is heated to its melting-point, and is converted into anthracene. As anthranol melts with decomposition at 163–170° C., it is not at all surprising that this change is far from quantitative. Anthranol crystallizes in the orthorhombic system, while dianthranol is monoclinic, as will be seen from the following crystallographic measurements, kindly made for us by Professor A. C. Gill, of the Mineralogical Department of this University. The anthranol and dianthranol measured were both recrystallized from benzene.

Anthranol.

"The crystals of anthranol are long six-sided needles of a pale straw-yellow color. Those measured were from 5 to 20 mm. in length, and scarcely ½ mm. in diameter. The parallel extinction, taken together with the fact that four of the six faces are equally inclined to the remaining two, establishes the orthorhombic form of these acicular crystals. No reflecting terminal planes could be found, hence the length of the vertical axis was only approximately determined by measuring the plane angle of the end faces on the brachypinacoid. The average of 11 measurements ranging from 124°40′ to 131° was 127°20′, hence :

$$a : b : c = 0.8124 : 1 : 0.402 \ (?)$$

Faces measured with goniometer ; $\infty P\ (110)$ and $\infty P\breve{\infty}\ (100)$.

$110 : 1\bar{1}0 = 78°11'$; $110 : 010 = 50°56'$ (calculated from other angle, 50°54′30″).

"Anthranol has an *extremely* high double refraction and dispersion.

"The crystals show a good basal cleavage."

Dianthranol.

" The crystals of dianthranol are monoclinic, usually elongated in the direction of the ortho-axis, and often tabular parallel to the orthodome ($\bar{1}01$).

The results of the measurements of eighteen crystals are as follows : $\grave{a} : \bar{b} : \acute{c} = 2.307 : 1 : 1.7701$; $\beta = 87°3'30''$.

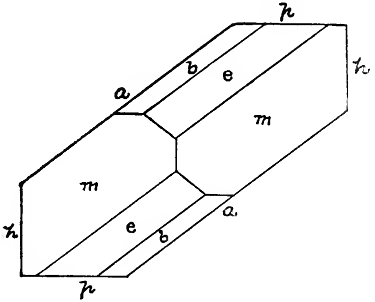
The forms observed, $a = +P\bar{\infty}\ (\bar{1}01)$; $p = oP\ (001)$; $h = \infty P\bar{\infty}\ (100)$; $m = \infty P\ (110)$; $e = P\grave{\infty}\ (011)$; and $b = +\frac{1}{2}P\ (\bar{2}21)$.

A list of the principal angles follows :

	Measured.	No. of measurements.	Calculated.
110 : 100	66°33′30″	32	
100 : 001	89°3′30″	25	
100 : 10$\bar{1}$	53°4′40″	26	
110 : $\bar{1}$10	46°52′40″	14	46°53′
001 : $\bar{1}$01	37°52′11″	24	37°51′50″
001 : 011	60°28′	2	60°32′42″
$\bar{1}$10 : $\bar{1}$01	76°10′10″	16	76°10′26″
001 : $\bar{1}$10	90°23′	2	90°22′28″
011 : $\bar{1}$00	90°34′	1	90°27′44″
$\bar{1}$01 : $\bar{2}$21	42°33′30″	4	42°34′9″
001 : $\bar{2}$21	44°5′	2	44°9′33″

"The accompanying figure shows the projection of the observed faces on the clinopinacoid. There is great variation in the relative development of the end-faces, though the b-faces are usually much smaller than here shown."

"The plane of the optical axes is the clinopinacoid (010), and the inclined dispersion is plainly seen in thin crystals. One optical axis is nearly normal to the orthodome ($\bar{1}01$), which is usually the most extensive face on the crystals. More rarely, however, the base (001) is largely developed, and in such crystals the acute bisectrix may be seen to lie in the acute angle *β*, somewhat inclined from a position perpendicular to the base."



The change of anthranol into dianthranol seems to be generally accompanied by a partial oxidation of some of the anthranol to anthraquinone, as the latter substance can always be detected, (sometimes only in very small quantity) in the crude dianthranol. That heat alone will not cause the change was shown by boiling some of the anthranol in solution in xylene in an atmosphere of dry carbon dioxide. No change was noticed in the melting-point of the crystals obtained from this solution after boiling for an hour and a half, and even after eight hours boiling very little change had occurred, though the melting-point had now risen from 162–170° C. to 172–185° C. A solution in mesitylene, after being boiled for four hours in the same way, desposited on cooling crystals, which appeared for the most part to be anthranol, though they began to melt at 180°, and were not completely fused till the temperature reached 265° C. These crystals gave a slight reaction also for anthraquinone.[1] Even where the change is brought about by the action of sunlight on solutions of anthranol in benzene, anthraquinone was found in the mother-liquors from which the dianthranol crystallized out. When the dianthranol was made by passing a current of air through an alkaline solution of anthranol, anthraquinone was detected in the crude product, as Lieberman also found, though it may have resulted here from the further oxidation of some of the dianthranol.

We next endeavored to determine if the hydroxyl groups underwent any change when anthranol is converted into dianthranol. This appeared probable at first from the fact that the dianthranol was insoluble in solutions of the caustic alkalies even on long continued boiling. To solve this question we tried to make the diacetyl derivative of dianthranol. It was found exceedingly difficult to replace the hydrogen atoms by acetyl groups, but by heating the substance in a sealed tube to 180–190° C. with a considerable excess of acetic anhydride and some fused sodium acetate we finally succeeded. The crystals formed in the sealed tubes, which were of a dark red color, were filtered from the liquid, washed with water, dissolved in hot alcohol, and this solution boiled with bone-black to remove the color. Water was then added to the hot alcoholic solution. On cooling, reddish-yellow leaflets crystallized out. After repeating this process of purification several times a pure product was obtained, consisting of light yellow-colored plates, which melted with decomposition at 276–279°C. An analysis of this product gave the following results, which show that the substance is a diacetyl derivative of dianthranol:

0.0740 gram gave 0.0358 gram H_2O and 0.2210 gram CO_2.

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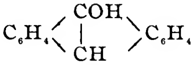
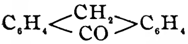
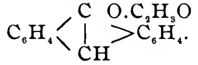
[1] Anthraquinone was detected here by boiling a small amount of the substance with zinc dust and dilute caustic soda solution, when a red color appeared. Pure anthranol and dianthranol will not give this reaction.

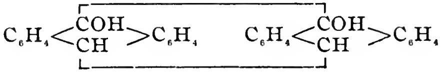
	Found.	Calculated for $\left(C_6H_4<\begin{matrix}CH.\\ CO(C_2H_3O)\end{matrix}>C_6H_4.\right)_2$
Carbon	81.45	81.35
Hydrogen	5.37	5.09
Oxygen (by difference)	13.18	13.56

This diacetyldianthranol was very soluble in chloroform, the solution having a beautiful bluish-violet fluorescence. As this fluorescence was not permanent, however, but gradually disappeared on standing, it is probably due to some impurity. Diacetyldianthranol is difficultly soluble in benzene and alcohol, and differs very markedly in other respects from the acetyl derivative of anthranol which has the same percentage composition. Its melting-point, crystal form, and general physical properties are different, so that there seems to be do doubt that the substance is diacetyldianthranol. Attempts to determine the presence of the acetyl groups qualitatively by heating the substance with alcohol and sulphuric acid gave unsatisfactory results, as the product seemed not to be acted on by these reagents.

Theoretical.

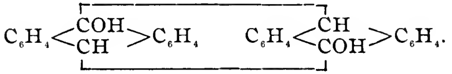
The formula of anthranol is undoubtedly $C_{14}H_{10}O$, as has been proved by the analysis and our determination of its molecular weight. The structural formula has been shown by Liebermann and Topf to be  $C_6H_4<\begin{matrix}COH\\ |\\ CH\end{matrix}>C_6H_4$ and not  $C_6H_4<\begin{matrix}CH_2\\ CO\end{matrix}>C_6H_4$ from the fact that it forms an acetyl derivative  $C_6H_4<\begin{matrix}C\ O.C_2H_3O\\ |\\ CH\end{matrix}>C_6H_4$.

The formula of dianthranol has been shown to be $C_{28}H_{20}O_2$, and it has been proved by the formation of the diacetyl derivative that it contains two hydroxyl groups. It appears, therefore, to be made up of two molecules of anthranol joined in such a way as to leave the two hydroxyl groups intact. This may be conceived as taking place by the breaking of the para bond between the two γ-carbon atoms, and the joining of the two anthranol groups thus formed. This may take place in two ways, as shown by the following formulas:



$$\mathrm{C_6H_4}<\begin{matrix}\mathrm{COH}\\ \mathrm{CH}\end{matrix}>\mathrm{C_6H_4} \qquad \mathrm{C_6H_4}<\begin{matrix}\mathrm{COH}\\ \mathrm{CH}\end{matrix}>\mathrm{C_6H_4}$$

and



$$\mathrm{C_6H_4}<\begin{matrix}\mathrm{COH}\\ \mathrm{CH}\end{matrix}>\mathrm{C_6H_4} \qquad \mathrm{C_6H_4}<\begin{matrix}\mathrm{CH}\\ \mathrm{COH}\end{matrix}>\mathrm{C_6H_4}.$$

Both formulas would represent the dianthranol as a γ-dihydroxyl derivative of dianthracene. The second of these formulas, however, would seem the more probable for dianthranol, for the reason that here like groups are represented as far away from each other as possible, while the unlike groups —CH and —COH are joined together. The crystallographic study of this substance also leads to the same conclusion. Dianthranol is undoubtedly monoclinic, as shown by Dr. Gill's measurements, and it will be seen by a careful study of the stereochemical model of the second formula that it also has a monoclinic symmetry while that of the first formula has an orthorhombic symmetry. The molecule of dianthranol is so large that it is very probable that the symmetry of the crystal is here determined by the symmetry of the molecule. Again it will be noticed from Dr. Gill's report that, while dianthranol is certainly monoclinic, it approaches very closely to the orthorhombic system, the angle β being 87°3'30", which is very nearly 90°. This agrees with the second formula, which possesses a monoclinic symmetry, to be sure, but which is very nearly, though not quite, orthorhombic. The fact that dianthranol has none of the properties characteristic of a pinacone, which it would probably show if it were constituted as the first formula represents it, is also in favor of the second formula for this substance. The insolubility of the compound in potassium hydroxide solution is easily understood, when we consider that it is a tertiary alcohol and not a phenol.

Anthranol itself is not soluble in alkaline solution in the cold, but only on boiling. Liebermann suggests that this solubility of anthranol may be due to the formation of an addition-product like  $C_6H_4<\genfrac{}{}{0pt}{}{CHOK}{CHOH}>C_6H_4$. In the case of dianthranol, the formation of such an addition-product is not possible.

The formation of dianthracene from anthracene by the action of the sunlight was shown to be probably due to the breaking of the para bond between the γ-carbon atoms and the union of the two molecules of anthracene to one of dianthracene. The transformation of anthranol to dianthranol is probably due to the same cause. Here, however, it is worthy of note that this change may be brought about by oxidation as well as by the action of light.

CORNELL UNIVERSITY, ITHACA, N. Y.,
March, 1896.

Contribution from the Chemical Laboratory of Harvard College.

XCIV.—BROMINE DERIVATIVES OF METAPHENYLENE DIAMINE.[1]

BY C. LORING JACKSON AND SIDNEY CALVERT.

INTRODUCTION.

In the course of an extended investigation of the behavior of the tribromdinitrobenzol, melting at 192°, carried on now for some years in this laboratory, we took up the reduction of this substance with tin and hydrochloric acid, since, if the bromine was not removed, new bromine derivatives of metaphenylene diamine must be obtained, or, on the other hand, the replacement of the bromine by hydrogen would be of interest, because cases in which a halogen is removed from the benzol ring under these conditions, are far from common. As, however, two of those already observed had occurred in the work on derivatives of tribromdinitrobenzol done in this laboratory, we had reason to hope that the proposed experiments might furnish us with an additional case, and contribute something toward determining the conditions under which this replacement of bromine by hydrogen takes place. After we had begun our work there appeared a paper[2] by

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[1] Presented to the American Academy of Arts and Sciences, May 9, 1894.

[2] Ber. d. chem. Ges., **25**, 552.

Schlieper on the removal of bromine from aromatic compounds by tin and hydrochloric acid, in which he announced his intention of making an extended research in this field; we accordingly wrote to Victor Meyer, under whose direction Schlieper was working, asking if we might finish our work, and he has with great courtesy given us permission to do so.

We have succeeded in finding only the following cases in which bromine is replaced by hydrogen in aromatic compounds by reduction with tin and hydrochloric acid. Unsymmetrical brommetadinitrobenzol gives metaphenylene diamine.[1] Tribromdinitrobenzol sulphonic acid gives bromdiamidobenzolsulphonic acid.[2] Dibromdinitrophenylmalonic ester gives bromamidoxindol,[3] nitrite of bromdinitrophenylmalonic ester gives amidoxyoxindol.[4] Bromnitrophenol gives amidophenol, and bromnitranisol gives amidoanisol.[5] Metabromorthonitrobenzoic acid and its isomeric form both give anthranilic acid[6] and Hübner also states[7] that he obtained small quantities of orthophenylene diamine from nitroparabromaniline, but that the principal product was the bromphenylene diamine; this, however, seems to be the only case observed, and none are recorded to our knowledge in the para series. We could find no record of the removal of other halogens under these conditions, until Schlieper published a second paper[8] (after our work on tribromdinitrobenzol was finished), in which he describes the reduction of chlor- and iodnitrophenols or anisols, when he found that iodine was removed just as bromine was, but that chlorine was not replaced by hydrogen. On the other hand he found that bromine could not be removed from derivatives of ortho- or paranitrophenols, as was to be expected from the work of previous observers. From his experiments he infers that bromine or iodine is replaced by hydrogen under the influence of tin and hydrochloric acid, when it stands in the ortho position to the two negative groups (OH. Br. NO_2. 1, 2, 3), although he has not yet succeeded

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[1] Zincke and Sintenis: Ber. d. chem. Ges., **5**, 792.

[2] Baessmann: Ann. Chem. (Liebig), **191**, 244.

[3] Jackson and Bancroft: This JOURNAL **12**, 301.

[4] Jackson and Bentley: This JOURNAL **14**, 360.

[5] Schlieper: Ber. d. chem. Ges., **25**, 552.

[6] Hübner and Petermann: Ann. Chem. (Liebig), **149**. 135.

[7] Ann. Chem. (Liebig), **209**, 360. [8] Ber. d. chem. Ges., **26**, 2465.

in bringing an absolute proof that this is the constitution of the substances with which he worked.

Our experiments proved that when tribromdinitrobenzol was treated with a mixture of tin, hydrochloric acid, and a little alcohol,[1] all three of the atoms of bromine were replaced by hydrogen, the product being metaphenylene diamine. Schlieper's inference given in the preceding paragraph, therefore, is not of general application, as, if this were the case, only one atom of bromine would have been removed from the tribromdinitrobenzol, since only one of them is in the ortho position to both of the nitro groups, the constitution of this substance being Br. NO_2. Br. NO_2. Br. H. It is to be observed also that the conversion of unsymmetrical brommetadinitrobenzol into metaphenylene diamine, observed by Zincke and Sintenis, is not in harmony with this inference of Schlieper. Although, therefore, the diortho position is not essential to the removal of bromine by tin and hydrochloric acid, there is no doubt that Schlieper is right in considering it the most favorable position for this purpose, as the replacement by hydrogen of an atom of bromine standing between two nitro groups has been repeatedly observed in this laboratory with comparatively weak reducing agents, such as sodium malonic ester, and probably sodium acetacetic ester, or sodic ethylate.

In trying to find the cause of the replacement of all three atoms of bromine by hydrogen in the reduction of tribromdinitrobenzol, the most obvious theory was that the attachment of the atoms of bromine to the benzol ring was weakened by the presence of the two negative nitro groups, as is so frequently observed in other reactions. If this was the case, the bromine would be removed before the nitro groups were reduced, and tribromphenylene diamine would not lose its bromine on treatment with tin and hydrochloric acid. Upon trying this experiment, however, we found that the whole of the bromine was removed from the tribromdiamine as easily as from tribromdinitrobenzol.[2] It follows, therefore, that the nitro groups

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[1] Schlieper used stannous chloride and hydrochloric acid in his work, and it is possible that this difference may have modified the result.

[2] Other reagents, for instance sodic ethylate or sodic hydrate, do not remove bromine from the diamine.

are not the cause of the easy removal of the three atoms of bromine in the reduction of tribromdinitrobenzol. A parallel experiment with dibromphenylene diamine showed that this substance gave up its bromine with much more difficulty than the corresponding tribrom compound, for, whereas the tribrom derivative was converted into phenylene diamine in a few minutes, it took over twelve hours to bring about the same change in the dibrom compound. It is evident from these unexpected results that the removal of the bromine atoms depends in part upon their position toward each other, and this is not strange, as in other cases it has been observed that three bromine atoms, when in the symmetrical position in a benzol ring, are more loosely attached than two in the meta position; but this is not the only cause of their removal, since symmetrical tribrombenzol is not reduced by tin and hydrochloric acid. It would seem, therefore, that the replacement of these atoms of bromine is caused principally by the fact that there are other radicals attached to the ring, with little regard to the nature of these radicals, as the highly positive amido groups apparently produce the same effect as the highly negative nitro radicals. An additional argument for this conclusion was furnished by experiments on the reduction of tribromaniline which was converted into dibromaniline by the action of tin and hydrochloric acid for a few hours. From the facts at present known we are unable to deduce any rule in regard to the positions which these other radicals must occupy in order to cause the replacement of bromine by hydrogen, when the compound is treated with tin and hydrochloric acid.

After we had found, as just described, that the bromine was removed by the action of tin and hydrochloric acid upon tribromdinitrobenzol, we turned our attention to the study of the bromine derivatives of metaphenylene diamine, as only one of these had been described,— a dibromphenylene diamine, which Hollemann[1] stated he had obtained by the action of bromine water on the chloride of phenylene diamine. He gives, however, neither melting-point nor analysis of his substance. Upon trying to repeat his preparation we found that bromine

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[1] Ztschr. Chem. 1865, 555.

water converted the chloride of phenylene diamine (or the free base suspended in water) into a tribromphenylene diamine melting at 158°. As the product is the same, when an insufficient quantity of bromine is used, a portion of the phenylene diamine remaining unaltered in this case, the statement of Hollemann must have rested on an error of observation. A paper by Vaubel,[1] which appeared after our work on this subject was finished, confirms our result, as he found by a volumetric method that three atoms of bromine are substituted for hydrogen in the molecule of phenylene diamine, when it is treated with a mixture of potassic bromide, sulphuric acid, and potassic bromate. We have made the same tibromphenylene diamine by the action of zinc dust and acetic acid on the tribromdinitrobenzol; this method of preparation proves that its constitution is Br. NH_2. Br. NH_2. Br. H.

A dibromphenylene diamine can be obtained by the action of bromine in excess upon phenylene diacetamide. The dibromphenylene diacetamide melts at 259° to 260°; the free base at 135°. We have not succeeded in determining the constitution of this dibromphenylene diamine. Nor have we obtained the corresponding monobromphenylene diamine. A monobromphenylene diamine belonging to another series was obtained, however, by reducing tetrabromdinitrobenzol (melting-point 227°) with tin and hydrochloric acid, it melts at 93°–94°, and from our experiments on the reduction of tribromdinitrobenzol there can be little doubt that it has the symmetrical constitution Br. H. NH_2. H. NH_2. H. When treated with bromine three atoms are substituted for three of hydrogen in its molecule, and the tetrabromphenylene diamine is formed, which melts at 212°–213°.

The presence of the bromine in the molecule of metaphenylene diamine has a strong effect on its tendency to form salts and on the composition of the salts formed. The tetrabrom and tribrom compounds do not form salts under ordinary conditions, but tribromphenylene diamine can be converted into its chloride by passing hydrochloric acid through a solution of it in benzol; this salt, however, gives up part of its hydrochloric acid at ordinary temperatures, the whole of it at

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[1] J. prakt. Chem. [2], 48, 75.

100°. The dibromphenylene diamine, on the other hand, forms salts more easily, and its chloride is only partially decomposed at 100°, while the bromide of this base seems to be even more stable. All three of these salts contain but one molecule of the acid, the chloride of dibromphenylene diamine, for example, having the following formula $C_6H_2Br_2NH_3ClNH_2$. The monobromphenylene diamine forms salts still more easily, and they are also more stable. The bromide contains two molecules of hydrobromic acid, having the formula $C_6H_3Br(NH_3Br)_2$. We have also prepared the tribromphenylene diacetamide, which does not melt at 330°, and the tribromphenylene diurethane melting at 212°.

EXPERIMENTAL PART.

Tribrommetaphenylene Diamine, $C_6HBr_3(NH_2)_2$.

The most convenient method for preparing this substance consists in passing a stream of air and bromine vapor into a solution containing metaphenylene diamine, for instance, that obtained by adding sodic hydrate or carbonate to the product of the reduction of metadinitrobenzol with tin and hydrochloric acid until all the tin is precipitated and filtering out the hydrate of tin. In adding the bromine an excess must be avoided, as this turns the product black, and we have therefore found it well to filter the precipitate out by means of cheese-cloth as fast as a sufficient quantity of it was formed, continuing the action of the bromine vapor on the successive filtrates as long as a precipitate appeared. The crude product, which was always dark colored, was dried, and then crystallized from alcohol containing a little benzol until it showed the constant melting-point 158°, when it was dried at 100° and analyzed with the following results:—

I. 0.1459 gram of the substance gave by the method of Carius 0.2392 gram of argentic bromide.

II. 0.2022 gram of the substance gave 14.65 cc. of nitrogen at a temperature of 19° and a pressure of 771.9 mm.

	Calculated for $C_6HBr_3(NH_2)_2$.	Found. I.	II.
Bromine	69.56	69.78	...
Nitrogen	8.11	....	8.21

These analyses prove that the substance is tribromphenylene diamine, and therefore our experimental result does not agree with that of Hollemann,[1] who stated that he obtained a dibromphenylene diamine by the action of bromine water on a solution of the chloride of phenylene diamine. As it was possible that this difference in the results of the action might be due to the fact that Hollemann used a salt of phenylene diamine, whereas we used in our first experiments the free base dissolved and suspended in water, we repeated our experiment with a solution of the chloride of phenylene diamine, and obtained precisely the same result as with the free base, that is, the tribromphenylene diamine melting at 158°. We are therefore forced to the conclusion that Hollemann's statement is due to an error in observation.

Properties.—Tribromphenylene diamine crystallized from alcohol appears in long slender needles united longitudinally into ribbons with the ends serrated so strongly that they look like combs. It is white, with marked silky lustre, and melts at 158°. It is not very soluble in cold but freely in hot alcohol; somewhat more soluble in methyl than ethyl alcohol; freely soluble in ether, benzol, chloroform, glacial acetic acid, or carbonic disulphide; very slightly soluble in ligroïn, but good crystals may be obtained from its solution in hot ligroïn; essentially insoluble in water. Strong hydrochloric acid dissolves it easily in the cold, depositing after long standing white transparent crystals which soon turn brown; on heating the solution in hydrochloric acid it turned dark brown, almost black, showing decomposition of the substance; the formation of a similar nearly black decomposition-product was brought about at once by cold strong nitric acid. Cold strong sulphuric acid dissolved the tribromphenylene diamine at once, the solution having a purplish tint, which turned to dark brown if it was allowed to stand for some time, or if it was stirred in a current of air for a short time. Nevertheless on one occasion a white solid was obtained, but before it could be collected a black spot appeared in one part of it which spread rapidly through the whole mass. Dilute sulphuric acid had no apparent effect on it in the cold, but decomposed

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[1] Ztschr. Chem. 1865, 555.

it when hot. These observations show that the presence of the three atoms of bromine has destroyed in great measure the basic properties of the phenylene diamine; but still it is possible to prepare salts of our substance, if proper precautions are observed, and the chloride is described somewhat later in this paper. Potassic hydrate, even when a boiling concentrated solution was used, produced no effect upon it.

When the tribromphenylene diamine is treated with tin and hydrochloric acid, it is converted into phenylene diamine. The details of this work are given later in this paper. The success of this experiment suggested to us that the bromine might be removed also by other reagents; accordingly we heated some tribromphenylene diamine dissolved in benzol and alcohol with sodic ethylate, the action in one trial being continued for four days, but at the end of this time we recovered nearly the whole of the tribromphenylene diamine taken, and although the filtrate after treatment with nitric acid and argentic nitrate gave a slight precipitate, we ascribe this rather to the complete decomposition of a small portion of the substance (indicated by the dark brown color of the product) than to any simple reaction. As therefore sodic ethylate had no action, it did not seem to us worth while to try other experiments with less energetic reagents.

Chloride of Tribromphenylene Diamine, $C_6HBr_3NH_3ClNH_2$.—Although the tribromphenylene diamine forms no salts under ordinary conditions, we hoped that we might obtain its chloride by the method which yielded such excellent results to Gattermann[1] when he applied it to the tribromaniline. Accordingly hydrochloric acid gas was passed into a solution of tribromphenylene diamine in benzol, until it ceased to form a white precipitate, and the liquid fumed strongly. The precipitate was then filtered out, and dried by pressing between filter paper as quickly as possible, after which it was analyzed as follows:

0.3096 gram of the salt lost 0.0272 gram of hydrochloric acid at 100°.

	Calculated for $C_6HBr_3NH_3ClNH_2$.	Found
Hydrochloric Acid	9.56	8.79

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[1] Ber. d. chem. Ges., **16**, 636.

The residue was entirely free from hydrochloric acid. This result is not so near the theoretical percentage as could be wished, but nevertheless proves that the salt is a monochloride of tribromphenylene diamine. The poor result is undoubtedly to be ascribed to the instability of the compound, which lost as much as 3.3 per cent. of its weight by standing four days in a desiccator over sulphuric acid, and therefore might well have lost the 0.77 of one per cent during the drying on filter paper. The chloride as obtained was of a light brown color, although it is probably white when perfectly pure, and as indicated by the description of its analysis is very unstable, decomposing slowly in dry air at ordinary temperatures, quickly and completely when heated to 100°. We should judge that it is somewhat more stable than the chloride of tribromaniline prepared by Gattermann,[1] as might be expected from the presence of the second amido group. It seems to be soluble in strong hydrochloric acid since the tribromphenylene diamine dissolves in this reagent, but it is decomposed by water.

Tribromphenylene Diacetamide, $C_6HBr_3(NHC_2H_3O)_2$.—This substance was made by treating tribromphenylene diamine with acetyl chloride, using anhydrous benzol as a solvent. The action began even in the cold as shown by the deposition of a white precipitate, but to make certain that it was complete the mixture was heated under a return-condenser for one hour. At the end of this time the white sandy precipitate was filtered out, and purified by extraction with glacial acetic acid, followed by recrystallization from the same solvent boiling. It was dried at 100°, and analyzed with the following results:

I. 0.2726 gram of the substance gave 0.3561 gram of argentic bromide by the method of Carius.

II. 0.2548 gram of substance gave 0.3358 gram of argentic bromide.

	Calculated for $C_6HBr_3(NHC_2H_3O)_2$.	Found.	
		I.	II.
Bromine	55.94	55.59	56.08

Properties.—The tribromphenylene diacetamide crystallizes from hot glacial acetic acid in bunches of small white plates

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[1] Loc. cit.

much longer than they are broad, which have square ends and frequently radiate from a centre; from alcohol in radiating groups of compound crystals made up of needles united longitudinally. It does not melt at 330°, and is very slightly soluble in all the common solvents. The best solvent for it is hot glacial acetic acid, but it is far from freely soluble even in this.

Tribromphenylene Diurethane, $C_6HBr_3(NHCOOC_2H_5)_2$.—Five grams of tribromphenylene diamine were boiled with about twice the amount of chlorocarbonic ester required by the theory in a return-condenser for three hours. The crude product (which weighed 6.5 grams), was purified at first by precipitating the substance with ligroïn from its solution in a mixture of benzol and alcohol, afterward by recrystallization from a mixture of alcohol and ligroïn, or alcohol and water, until it showed the constant melting-point 212°, when it was analyzed with the following results:

I. 0.3036 gram of the substance gave by the method of Carius 0.3454 gram of argentic bromide.

II. 0.1945 gram of the substance gave 0.2239 gram of argentic bromide.

	Calculated for $C_6HBr_3(NHCOOC_2H_5)_2$.	Found. I.	II.
Bromine	49.08	48.42	48.99

Properties.—The tribromphenylene diurethane when deposited from alcohol forms very small crystalline masses, which under the microscope are seen to be rosettes made up of what at first sight appear to be short needles, but on closer examination prove to be groups of finer needles united longitudinally, since they betray their complex nature by the frayed or brush-like appearance of their ends, which resemble a partially untwisted cord. Its color is white, and it melts at 212°. It is soluble in cold alcohol, easily soluble in hot; easily soluble in chloroform, or acetone, less so in ether; somewhat soluble in cold benzol, easily soluble in hot, from which it crystallizes in the same form as from alcohol, but not so well; slightly soluble in carbonic disulphide even when hot; essentially insoluble in ligroïn. Water dissolves it to a very slight extent when hot. Hydrochloric acid produced no apparent effect hot or cold; sulphuric acid did not act on it in the cold, but when hot dissolved it; from this solution it seemed to be precipitated unchanged by water, if the heating had not been long continued, but long heating with the strong acid decomposed it. A concentrated solution of potassic hydrate seemed to have no effect on it in the cold, but when heated turned the substance brown, and finally black with apparently complete decomposition. The best solvent for it is alcohol diluted with either water or ligroïn.

Reduction of Tribromdinitrobenzol.

Tribromdinitrobenzol (melting at 192°, made from symmetrical tribrombenzol) was reduced by treatment either with zinc and acetic acid, or with tin and hydrochloric acid, but the products were different in the two cases as described in the following sections.

Reduction with Zinc Dust and Acetic Acid.—This reduction we found it best to carry on in an atmosphere of carbonic dioxide, as the liquid showed a strong tendency to turn black during the process. The zinc dust contained in a flask kept full of carbonic dioxide was covered with acetic acid of 80 per cent., and the tribromdinitrobenzol added in small quantities at a time. If the zinc dust and tribromdinitrobenzol were mixed together before adding the acetic acid the action was far too violent; in fact, once the mixture took fire when the acetic acid was added. Even when the process was carried on as directed, the action was energetic at first, but later it was necessary to warm the flask gently to assist the reaction. The products were in part dissolved in the aqueous liquid, which with all our precautions, was invariably dark colored, and partly appeared as a crystalline powder in the bottom of the flask. The insoluble part was recrystallized from benzol, by which it was separated into a large fraction melting at 158°, a small amount of substance melting at a lower temperature, and a little unaltered tribromdinitrobenzol. The principal product was shown to be tribromphenylene diamine by its melting-point, but to confirm this it was dried at 100° and analyzed, when it gave the following results:

0.2337 gram of the substance gave by the method of Carius 0.3786 gram of argentic bromide.

	Calculated for $C_6HBr_3(NH_2)_2$.	Found.
Bromine	69.56	68.95

This percentage of bromine, although not agreeing with that calculated so closely as could be wished, is yet accurate enough when taken in connection with the melting-point to leave no doubt as to the nature of the substance formed, and therefore we did not attempt to get a number nearer to the theoretical.

The amount of tribromphenylene diamine formed by the reduction was considerable; in one case 10 grams of tribromdinitrobenzol yielded 4.7 grams of it, and 0.9 gram of tribromdinitrobenzol were recovered unaltered, so that the percentage of the theoretical yield was 60.6. The remainder of the product was contained in the aqueous solution (and to a less extent in the small amount of lower-melting material from the benzol mother-liquors); it undoubtedly consisted of phenylene diamine, from which part or all the bromine had been removed, since the aqueous solution gave tribromphenylene diamine when treated with bromine water, a behavior which, as we have already stated, belongs to solutions of phenylene diamine and its salts.

Reduction with Tin and Hydrochloric Acid.—We found it best to proceed as follows: Some granulated tin with a piece of platinum and about 300 cc. of strong hydrochloric acid were gently warmed in a flask closed by a cork provided with a Bunsen valve, until the greater part of the air had been expelled. 10 grams of tribromdinitrobenzol mixed with enough alcohol to make a thick paste were then added, and the reduction was allowed to go on, warming or cooling the mixture as was necessary, until all the organic substance had dissolved. If the solution thus obtained was a strong one, beautiful white needles of a double tin salt were deposited on cooling; if it was more dilute, they usually appeared after standing a day, but in some cases the substance obstinately refused to crystallize. The crystals were filtered out, and decomposed in concentrated solution with sulphuretted hydrogen, when the filtrate from the sulphide of tin left on evaporation a crystalline solid, which after three crystallizations from a mixture of water and hydrochloric acid, was analyzed with the following results:

I. 0.2220 gram of the substance gave 31.8 cc. of nitrogen at a temperature of 26°.5 and a pressure of 756.9 mm.

II. 0.2983 gram of the substance gave by the method of Carius 0.4727 gram of argentic chloride.

	Calculated for $C_6H_4(NH_3Cl)_2$.	Found.	
		I.	II.
Nitrogen	15.47	15.79	....
Chlorine	39.21	....	39.17

The tin and hydrochloric acid had therefore reduced both the nitro groups, and also removed all three of the atoms of bromine from the tribromdinitrobenzol; and that the removal of bromine had taken place from the whole of the substance was made probable by the fact that all the organic matter dissolved, whereas the tribromphenylene diamine, as already stated in this paper, is insoluble in water or dilute hydrochloric acid. An additional confirmation of the presence of phenylene diamine was given by the following experiment. The base set free from the soluble chloride analyzed above was treated with bromine water, when a precipitate was formed, which after recrystallization from alcohol containing a little benzol, melted at 158°, and was therefore the tribromphenylene diamine which is made in this way from metaphenylene diamine.

When we began work on this subject we made many analyses of the double tin salt which crystallized out of the solution after the reduction; but although in two different preparations we obtained numbers agreeing with the salt $C_6H_4(NH_3ClSnCl_2)_2$, discovered by Gudemann,[1] we found that in others its composition varied so much that no certain inference in regard to the composition of the base formed could be drawn from these analyses, and therefore prepared the salt free from tin as described above.

After we had shown by the work just described that the three atoms of bromine are removed from tribromdinitroben-

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[1] Ztschr. Chem., 1865, 51.

zol by tin and hydrochloric acid, it became of interest to determine whether their removal was due to the effect of the two nitro groups upon them. This seemed a probable supposition, because it has been repeatedly observed that atoms of bromine can be easily removed from the benzol ring when they stand in the ortho position to nitro groups, and work done in this laboratory has proved that this tribromdinitrobenzol is a very reactive body, but on the other hand it did not seem likely that the bromine atoms would be removed before the reduction of the nitro groups, as all previous experience seems to show that the latter are much more easily attacked than the former. It was obvious that this point could be decided by trying the action of tin and hydrochloric acid on tribromphenylene diamine, for none of the bromine would be removed from this substance if this action depended on the presence of the nitro groups. Accordingly five grams of tribromphenylene diamine were mixed with tin and hydrochloric acid and a piece of platinum added to increase the action. In the cold no change was observed, and therefore the mixture was warmed on the water-bath, when, after a vigorous reaction had gone on for a short time, all the organic matter dissolved. The brown clear solution deposited crystals as it cooled, but disregarding these the whole was treated with an excess of sodic hydrate and extracted with ether repeatedly. The residue from the ethereal extracts was an oil, which solidified after it had been scratched with a sharp glass rod, and then melted at about 62°. There was little doubt therefore that this substance was metaphenylene diamine, which melts at 63°, and this view was confirmed by the following observations. The substance gave a white salt with hydrochloric acid soluble in water, but nearly insoluble in hydrochloric acid. To a solution of this chloride bromine water was added, taking care to avoid an excess; this produced a white precipitate, which after recrystallization from benzol, melted at 158°, and was therefore tribromphenylene diamine. It follows from this experiment (which was repeated several times) that tribromphenylene diamine gives up all its bromine to tin and hydrochloric acid, and therefore that the removal of the bromine atoms does not depend on the loosening effect of the two nitro groups.

Action of Tin and Hydrochloric Acid on Tribrombenzol and on Tribromaniline.—After we had shown, as just described, that all the bromine can be removed from tribrommetaphenylene diamine by the action of tin and hydrochloric acid, it occurred to us that the comparatively loose attachment of the bromine to the benzol ring might be due to the fact that the three atoms of bromine were in the symmetrical position, since Blau has shown that one of these atoms in tribrombenzol can be replaced by the methoxy radical, and we have confirmed this observation. This hypothesis seemed the more probable because dibrommetaphenylene diamine is reduced under these conditions much more slowly than the tribrom compound. If this view is correct, tin and hydrochloric acid should remove bromine from the symmetrical tribrombenzol, and accordingly we tried the following experiment. Ten grams of tribrombenzol were mixed with granulated tin and strong hydrochloric acid, a piece of platinum added to promote the action, and enough alcohol to dissolve a large part of the tribrombenzol. The reason for adding the alcohol was that we thought the action of the reducing agent on the tribrommetaphenylene diamine might be in part due to its tendency to dissolve in the acid, or still more to the solubility of the products of the reduction in the acid, and we hoped by the addition of the alcohol to establish similar favorable conditions in the case of tribrombenzol. The mixture was heated under a return condenser over the water-bath for a week. At the end of this time enough water was added to precipitate any brombenzols which might be present, and the heavy crystalline precipitate thus obtained was filtered, and washed until it was free from stannous chloride. It was then dried and weighed, when 9.5 grams were obtained, so that the loss was no greater than would be expected from the rough way in which the experiment had been carried on. This substance melted at 120°, and was therefore unaltered tribrombenzol (melting-point 119°.6). It follows from this experiment that tin and hydrochloric acid do not remove bromine from symmetrical tribrombenzol, and, therefore, that the conversion of tribrommetaphenylene diamine into metaphenylene diamine by these reagents is not due to the symmetrical position of the bromine atoms, although it may have a subsidiary effect in assisting this conversion.

An experiment similar to that just described was tried with 10 grams of tribromaniline. The conditions were exactly the same as those used for tribrombenzol, given at length in the preceding paragraph. Upon adding water to precipitate the organic substances, after the reduction was completed, only a very small precipitate was formed, which in time changed to long needles. This precipitate weighed less than 0.5 gram, and as it melted at 118° was undoubtedly unaltered tribromaniline. The filtrate from this precipitate was treated with an excess of sodic hydrate, the precipitate thus formed dissolved in hydrochloric acid, and reprecipitated with sodic hydrate in excess to remove the hydrate of tin as completely as possible, and then extracted with alcohol. The alcoholic extract deposited long white needles, which melted at 78–79°, and were therefore probably dibromaniline. To establish the nature of the substance more fully, we tried the following experiments. The amido group was replaced by bromine, when a product was obtained melting at 44°, the melting-point of the unsymmetrical tribrombenzol, and this when treated with nitric acid, was converted into the mononitrotribrombenzol, melting at 93°. There can be no doubt therefore that the tin and hydrochloric acid have removed one of the atoms of bromine from the ortho position to the amido group, replacing it by hydrogen. A quantitative experiment gave the following results: 10 grams of symmetrical tribromaniline yielded after reduction for six hours, 5 grams of dibromaniline, from which were obtained 5 grams of unsymmetrical tribromaniline, and from this 5.2 grams of tribromnitrobenzol.

Dibrommetaphenylene Diacetamide, $C_6H_2Br_2(NHC_2H_3O)_2$.

Whereas free metaphenylene diamine gives a tribrom derivative when treated with bromine water, we have obtained only the dibrom compound from metaphenylene diacetamide, even when a considerable excess of bromine was used. The samples analyzed were prepared by the method given below, but a better method discovered later is described after the analyses: Metaphenylene diacetamide was dissolved in common acetic acid with the aid of gentle heat, and treated at first with bromine, and afterward with bromine water, until a slight excess had been added. The new substance separated from the solution as it was formed, and after standing a short time it was filtered out, and purified by crystallization from hot glacial acetic acid until it showed the constant melting-point 259°, when it was dried at 100° and analyzed with the following results:

I. 0.2471 gram of the substance gave 19 cc. of nitrogen at a temperature of 29° and a pressure of 754.3 mm.

II. 0.2145 gram of the substance gave by the method of Carius 0.2294 gram of argentic bromide.

III. 0.2033 gram of the substance gave by the method of Carius 0.2198 gram of argentic bromide.

	Calculated for	Found.		
	$C_6H_2Br_2(NHC_2H_3O)_2$.	I.	II.	III.
Nitrogen	8.00	8.33	....	....
Bromine	45.71	....	45.52	46.01

The substance can be obtained more expeditiously in a pure state by avoiding the preparation of solid phenylene diacetamide as follows: A strong ethereal solution of phenylene diamine is treated with acetic anhydride until a portion gives a white or yellow precipitate with bromine (if unaltered phenylene diamine is present the precipitate will be brown). When this is the case an excess of bromine water is added to the solution, and the mixture stirred vigorously until the precipitation is complete. The product is essentially pure without recrystallization.

Properties.—The dibrommetaphenylene diacetamide crystallizes by slow evaporation from an alcoholic solution in very small, rather short prisms. If on the other hand the crystallization takes place by cooling, obscurely crystalline masses are obtained in which it is hard to make out any definite form; they seem to be prisms coated with needles. Its color is white, and it melts at 259° to 260° with decomposition, as is shown by the fact that the melted mass turns black and puffs up to many times its original volume. On account of this decomposition it is necessary to keep the melting-tube in the oil bath as little as possible in determining the melting-point. If the substance is allowed to remain in the bath while its temperature is raised, a melting-point as low as 250° may be obtained. It is very slightly soluble in cold alcohol, and only a little more soluble in hot; very soluble in benzol, chloroform, or carbonic disulphide; somewhat more soluble in acetone or glacial acetic acid; essentially insoluble in ether or ligroïn. The best solvent for it is glacial acetic acid or alcohol, although it is soluble in the latter only sparingly and with great difficulty. It is very slightly soluble in boiling water, insoluble in cold. Strong hydrochloric acid saponifies it quickly when the two are gently heated together; strong sulphuric acid dissolves it in the cold, but without decomposition, as the unaltered substance is obtained by diluting and neutralizing the acid; it decomposes the substance when hot; if dilute it has no apparent effect when cold, but when heated saponifies and afterward decomposes it; strong nitric acid dissolves it quickly when cold, but the substance is recovered unaltered on neutralization; when hot it decomposes it. A strong solution of potassic hydrate saponifies it when hot.

Dibrommetaphenylene diamine. $C_6H_2Br_2(NH_2)_2$.—This substance was obtained by removing the acetyl groups from the preceding compound as follows: 10 grams of the dibromphenylene diacetamide were heated with from 30 to 40 cc. of commercial strong hydrochloric acid for half an hour in a flask with a return-condenser; at the end of this time the solid was completely dissolved, and the liquid had taken on a dark brownish-red color. After it was cold the solution was treated at first with sodic carbonate, and finally with sodic hydrate in excess, which precipitated a brown solid. This was filtered out, washed until free from alkali, and purified by crystallization from boiling water containing a little alcohol, until it showed the constant melting-point 135°. In this recrystallization long heating of the solution should be avoided, as this seems to decompose the substance with precipitation of a black compound. The pure substance was dried at 100° and analyzed with the following result:

0.3872 gram of the substance gave by the method of Carius 0.5473 gram of argentic bromide.

	Calculated for $C_6H_2Br_2(NH_2)_2$.	Found.
Bromine	60.15	60.16

Properties.—The dibromphenylene diamine crystallizes in fine needles which are white if the substance is perfectly pure, but usually show a brownish color, which is due to an impurity so slight that it has no effect upon the analysis. It melts at 135°, and is easily soluble in alcohol whether hot or cold. It is very soluble in acetone; easily soluble in ether, somewhat less soluble in benzol, or chloroform, if cold, easily soluble if hot; slightly soluble in cold carbonic disulphide, soluble when hot; very slightly soluble in cold ligroïn, more soluble when it is hot; nearly insoluble in cold water, slightly soluble in hot, but it is decomposed if boiled for some time with water. The best solvent for it is dilute alcohol. It shows a much stronger tendency to form salts than the tribromdiamine, as it dissolves in either hydrochloric acid or hydrobromic acid, and the solution leaves the salt on spontaneous evaporation; cold strong sulphuric acid turns it purple and then dissolves it, but on standing the sulphate separates from this solution in glistening white or pinkish plates, which seem to belong to the monoclinic system; when hot, sulphuric acid decomposes it; strong nitric acid dissolves it, and then decomposes it even in the cold, forming a brown solution. A cold solution of potassic hydrate has no effect upon it, but, if the mixture is heated, decomposition sets in as is shown by the appearance of a black color. We selected for further study the chloride and the bromide of the base with the results described below.

We have also studied the action of tin and hydrochloric acid on the dibromphenylene diamine. For this purpose 3.75 grams of the dibromphenylene diamine were warmed with tin, hydrochloric acid, and platinum under the conditions already described when speaking of the tribromphenylene diamine. The action in this case was very slow; whereas the tribrom compound dissolved after treatment for a short time, it was necessary to carry on the action for over twelve hours in order to bring the dibromamine into solution. The product yielded an oily free base, smelling like metaphenylene diamine, which, however, we did not succeed in obtaining in a solid state. It gave an easily soluble chloride, so there can be no doubt that bromine was removed. We were unable to determine with certainty the cause of the very slow removal of the bromine from the dibromphenylene diamine; it is possible that it is only mechanical, as it was observed that this substance showed a tendency to form a coating on the surface of the tin, or on the other hand it may be that the symmetrical position of the three atoms of bromine in the tribromphenylene diamine has the effect of loosening their attraction for the benzol ring. The latter explanation seems to us the more probable.

Chloride of Dibromphenylene Diamine, $C_6H_2Br_2NH_3ClNH_2$.—This salt can be made by dissolving the diamine in strong aqueous hydrochloric acid and allowing the solution to evaporate spontaneously, but we did not use this method in preparing the salt for analysis, because we feared it might undergo a partial decomposition, if deposited from a solution containing water. We therefore prepared it by passing hydrochloric acid gas through a solution of the diamine in benzol, until the liquid fumed strongly, and no more solid matter was deposited. The precipitate thus obtained was pressed repeatedly between filter paper, and dried for one hour over sulphuric acid, when it gave the following result on analysis:

0.2173 gram of the salt gave by the method of Carius 0.3713 gram of the mixture of argentic chloride and bromide.

	Calculated for $C_6H_2Br_2NH_3ClNH_2$.	Found.
Chlorine and bromine	64.63	64.28

The chloride of dibromphenylene diamine is much more stable than the corresponding tribrom compound, since, whereas the chloride of tribromphenylene diamine lost all its hydrochloric acid when heated to 100° for a short time, the chloride of dibromphenylene diamine showed a loss under the same conditions of only 5 per cent. instead of the 12.07 per cent., which represents the loss, if the whole of its hydrochloric acid had been given up. Further, the salt of the dibrom compound can be made by the action of a strong aqueous solution of hydrochloric acid upon the free base, while, although the tribrom base dissolves in strong hydrochloric acid, we have not succeeded in obtaining the solid chloride from this solution. It must not be inferred from this comparison, however, that the choride of dibromphenylene diamine is especially stable, for this is not the case, since it loses nearly 4 per cent. of its weight by standing in a desiccator, and is also decomposed by water.

Bromide of Dibromphenylene Diamine, $C_6H_2Br_2NH_3BrNH_2$.—This substance was made by adding dibromphenylene diamine to distilled hydrobromic acid (boiling-point 123°) until it ceased to dissolve easily in the cold. A good deal of trouble was encountered in obtaining the solid salt from this solution, as heating decomposed it, and none of the organic solvents miscible with water gave a precipitate with it; spontaneous evaporation indeed gave the salt, but as we did not know its properties at the time of the preparation we were afraid of decomposition during such long standing, and accordingly proceeded as follows: The aqueous solution was covered with a rather thick layer of ether, and the whole stirred vigorously for about a quarter of an hour; under this treatment the bromide crystallized out in the lower part of the ether, when it was separated, washed with ether, and dried in a desiccator over sulphuric acid. It then gave the following results on analysis:

I. 0.4433 gram of the substance gave by the method of Carius 0.7191 gram of argentic bromide.

II. 0.3014 gram of the substance gave 0.4884 gram of argentic bromide.

	Calculated for $C_6H_2Br_2NH_3BrNH_2$.	Found. I.	II.
Bromine	69.16	69.04	68.96

The sample used for the first analysis had been dried for only three hours, and for the second had stood in a desiccator over sulphuric acid for three days, showing that the salt is stable under these circumstances. The bromide is therefore more stable than the chloride, as that lost nearly 4 per cent.

of its weight in a desiccator, which amounts to one-third of the acid that it contains.

The bromide of dibromphenylene diamine forms white needles, which turn brown quickly, when exposed to the air. It is decomposed by water, but is soluble in ethyl, or methyl alcohol, the solution apparently decomposing on standing; insoluble in ether, benzol, or ligroïn.

Reduction of Tetrabromdinitrobenzol.—The tetrabromdinitrobenzol was prepared essentially by the method given by Bancroft and one of us,[1] but a few improvements in the process should be mentioned here. By using a large amount of glacial acetic acid the yield of tetrabrombenzol was materially raised. The details of this process will be found in our paper, "On the Behavior of Certain Halogen Derivatives of Benzol." In converting the tetrabrombenzol into the dinitro compound we found that the quantities of sulphuric acid and nitric acid used could be reduced to 50 cc. of each for 10 grams of tetrabrombenzol, if the tetrabrombenzol was pure; if this was not the case the best method was to treat the tetrabrombenzol with the acid mixture, which had already been used once with tetrabrombenzol; the product of this action of the residual acid was then treated with one-half the amount of fresh sulphuric acid and nitric acid needed for the complete conversion of the tetrabrombenzol into the dinitro compound, and in this way a nearly pure product was obtained at little expense of fuming nitric acid. With pure tetrabrombenzol the yield was very nearly quantitative, 100 grams giving 121 grams of a product melting at 220°, which, after one recrystallization, melted at 227°, the correct melting-point for tetrabromdinitrobenzol; as 100 grams should give 122.8 grams, this makes the yield of this crude product over 99 per cent.

To reduce the tetrabromdinitrobenzol it was mixed with alcohol, tin, and hydrochloric acid, and the mixture heated on the water-bath in a flask with a return-condenser, more hydrochloric acid being added from time to time. When the volume of liquid became unpleasantly large, it was evaporated in an open dish to a convenient volume, and returned

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[1] This JOURNAL, **12**, 290.

to the flask with fresh alcohol and acid. After the organic matter had gone completely into solution, which usually happened after boiling for about seventy hours, the liquid was again concentrated and rendered strongly alkaline with crude sodic hydrate. The hydrate of tin was filtered out with cheese-cloth, and dried as thoroughly as possible by sucking air through it, after which it was shaken repeatedly with rather large amounts of alcohol. The alcoholic extract thus obtained was freed from alcohol by distillation, followed by evaporation on the water-bath, when an oil and an aqueous solution were left, which were separated, if possible, mechanically; if not, by shaking with ether. The oil obtained directly or from the ether solidified after a short time. The aqueous filtrate from the hydrate of tin with the liquid separated from the oil was shaken with ether repeatedly, and the oil thus obtained added to the main portion. The aqueous solution, after shaking with ether, gave a very slight precipitation on the addition of bromine, but the amount of tetrabromphenylene diamine obtained in this way was so small that this treatment is hardly worth while. The principal product, after it had solidified, was purified by dissolving it in rather dilute alcohol and saturating the solution with sulphuretted hydrogen, when it was warmed gently, and allowed to stand in a corked flask for some time; after filtering off the sulphide of tin it was evaporated to dryness, and the residue recrystallized from pure ligroïn (boiling from 60–70°) until it showed the constant melting-point 93–94°, when it was dried in a desiccator and analyzed with the following result:

0.2117 gram of the base gave by the method of Carius 0.2113 gram of argentic bromide.

	Calculated for $C_6H_3Br(NH_2)_2$.	Found.
Bromine	42.79	42.48

Properties of Monobrommetaphenylene Diamine.—It crystallizes from a mixture of benzol and ligroïn in white spindle-shaped forms often a centimeter long; from benzol alone in bundles of small needles united longitudinally; from alcohol in not very well developed prisms apparently belonging to the monoclinic system and often twinned. It melts at 93–94°, and is readily soluble in acetone, alcohol, ether, or chloroform; in benzol, or carbonic disulphide it is slightly soluble in the cold, more freely when hot; nearly insoluble in cold ligroïn, difficultly soluble in hot; it is moderately soluble in cold water, as shown by the fact that such a solution gives a good precipitate with bromine water, in hot water it is even more soluble, the solution as it cools depositing oil drops, which later change to needles. The best solvent for it is a mixture of benzol and ligroïn, but crystallization from pure ligroïn is necessary to get a perfectly white product. It shows a tendency to separate from its solutions at first as an oil, and also to become decomposed, when in solution, forming a brown product.

The monobromphenylene diamine shows marked basic properties. Hydrochloric acid or hydrobromic acid gives with it a salt soluble in water, a description and analysis of the bromide formed in this way is given below; moderately strong sulphuric acid also gives a soluble salt, which forms white crystals when the solution is allowed to evaporate spontaneously; dilute nitric acid seems to have little action on it in the cold, but when hot converts it into a brown substance. Sodic hydrate seems to have no action even when warmed with it for several minutes on the water-bath. The constitution of the monobromphenylene diamine is probably $NH_2.H.NH_2.H.Br.H$, as the tribromdinitrobenzol made from symmetrical tribrombenzol loses all its bromine when reduced under the conditions used in obtaining the monobromphenylene diamine from tetrabromdinitrobenzol.

Bromide of Monobromphenylene Diamine, $C_6H_3Br(NH_3Br)_2$. —Monobromphenylene diamine was mixed with distilled hydrobromic acid (boiling-point 124–125°), and the liquid heated to boiling. The solid was then brought into solution by the careful addition of just the proper amount of water to the boiling solution, after which more of the hydrobromic acid was added, until crystallization began, when the mixture was allowed to cool. The crystals thus obtained were washed with hydrobromic acid and then with ether, dried by pressure with filter-paper, and washed with ether a second time. After drying over sulphuric acid the salt was analyzed with the following result:

0.2474 gram of the substance gave according to the method of Carius 0.3945 gram of argentic bromide.

	Calculated for $C_6H_3Br(NH_3Br)_2$.	Found.
Bromine	68.77	67.86

This analysis leaves much to be desired, but the result is near enough to show that the formula given above is correct. The salt forms colorless, transparent, glassy crystals, which look like cubes under the microscope; freely soluble in water, slightly in hydrobromic acid.

Tetrabromphenylene Diamine, $C_6Br_4(NH_2)_2$.—This substance was made by dissolving the monobromphenylene diamine, melting at 93–94° in ether, and adding a slight excess of bromine; the product, after recrystallization from a mixture of chloroform and ligroïn, showed the constant melting-point 212–213°, when it was dried and analyzed with the following result:

I. 2357 gram of the substance gave by the method of Carius 0.4166 gram of argentic bromide.

II. 0.2493 gram of the substance gave 0.4432 gram of argentic bromide.

	Calculated for $C_6Br_4(NH_2)_2$.	Found. I.	Found. II.
Bromine	75.47	75.22	75.67

Properties of Tetrabromphenylene Diamine.—It crystallizes in very small white needles, which melt at 212–213°, and are freely soluble in benzol, chloroform, ether, acetone, or carbonic disulphide; slightly soluble in cold alcohol, freely in hot; almost insoluble in cold ligroïn, slightly soluble in hot. The best solvent for it is a mixture of chloroform or benzol with ligroïn. The tetrabromphenylene diamine has nearly, if not quite, lost the basic properties of a diamine, as was to be expected, since it is loaded with so many negative bromine atoms. Hydrobromic acid had but little apparent action on it, even when hot, although the liquid deposited after long standing a few transparent crystals, which may have been the bromide.

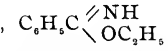
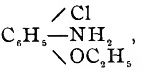
Contribution from the Kent Chemical Laboratory of the University of Chicago.

ON BENZIMIDOETHYL AND BENZIMIDOMETHYL ETHERS.

BY F. W. BUSHONG.

In connection with a study of imidomethyl carbonate, cyanimidomethyl carbonate and other imido ethers,[1] undertaken at the suggestion of Dr. J. U. Nef, it was considered of interest to study the properties of benzimido ethers. Pinner[2] has described a large number of hydrochloric acid addition-products of the imido ethers, but he has in only a few cases briefly mentioned the free ethers as being very unstable products, which he was unable to obtain in a pure state. Thus, for example, he describes benzimidoethyl ether as an oil which on standing, or more quickly on heating to 100°, decomposes into alcohol and cyanphenin.

Wheeler[3] has more fully described benzimidomethyl ether and its behavior, especially towards aromatic ortho compounds, but he makes no attempt to purify or analyze the crude reaction-product.

Benzimidoethyl ether,  $C_6H_5C\begin{cases}{\!/\!/}NH\\ \diagdown OC_2H_5\end{cases}$.—By passing dry hydrochloric acid gas into benzonitril and alcohol, according to the method of Pinner,[4] the crystalline addition-product,  $C_6H_5{-}\begin{cases}/Cl\\ NH_2\\ \diagdown OC_2H_5\end{cases}$, was prepared. This was powdered, washed with absolute ether and dried in a vacuum; 9.25 grams of the dry salt were gradually added to 100 cc. of a 10 per cent. solution of caustic soda, which was cooled by a freezing-mixture. The oil, which separated out, was immediately extracted with ether, and dried with calcium chloride; after distilling off the ether, an oil was obtained which boiled at 106–9° at 15 mm. pressure; redistilled at ordinary pressure, it boiled absolutely constant at 218°, without the slightest decomposition, as shown by the analysis.

I. 0.2081 gram substance gave 0.5504 gram CO_2 and 0.1460 gram H_2O.

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[1] Nef: Ann. Chem. (Liebig), **287**, 265-360.

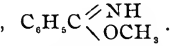
[2] "Die Imidoaether und ihre Derivate."

[3] This JOURNAL, **17**, 397.

[4] Ber. d. chem. Ges., **16**, 1654.

II. 0.3456 gram substance gave 29.6 cm. N_2 at 18°, and 749.3 mm.

	Calculated for $C_9H_{11}NO$.	Found.
C	72.48	72.13
H	7.38	7.78
N	9.40	9.75

Benzimidomethyl ether,  $C_6H_5C\begin{matrix}\nearrow NH \\ \searrow OCH_3\end{matrix}$.—In like manner benzimidomethyl ether was prepared from benzonitril and methyl alcohol. It was found to boil at 96° at 10 mm., and 206° at ordinary pressure.

I. 0.2148 gram substance gave 0.5621 gram CO_2, and 0.1246 gram H_2O.

II. 0.2054 gram substance gave 18.3 cm. N_2 at 17°.5 and 750.5. mm.

	Calculated for C_8H_9NO.	Found.
C	71.11	71.37
H	6.66	6.43
N	10.37	10.18

Both ethers are colorless mobile liquids, quite stable when pure and dry, and have a peculiar pleasant odor; they can be kept for months without change. I have not only verified the statement of Wheeler that the methyl ether does not solidify at —30°, but have been unable to solidify the ethyl ethers at the same temperature.

ON THE HALOGEN DERIVATIVES OF THE SULPHONAMIDES.

By J. H. Kastle, B. C. Keiser, and Ernest Bradley.

Some months ago there appeared[1] a preliminary notice by one of us (Kastle) of the halogen derivatives of the sulphonamides, in which it was proposed to use one of these derivatives, *viz.*, benzenedichlorsulphonamide, $C_6H_5SO_2NCl_2$, as a reagent for bromine and iodine. Attention was therein called to the rather unsatisfactory condition of our knowledge regarding similar derivatives of the amides of the carbonic acids; and consequently to the advisability of making further studies of this class of compounds. For some

[1] This Journal, 17, 704.

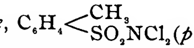
months past investigations along this line have been conducted in this laboratory with the results recorded below.

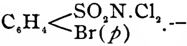
Chlorine Derivatives.

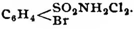
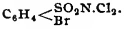
Benzenedichlorsulphonamide, $C_6H_5SO_2N.Cl_2$.—This compound was prepared by leading into the solution of benzenesulphonamide in the smallest possible quantity of caustic soda (1–10) a rapid current of chlorine gas. Under these conditions a copious, white, crystalline precipitate was thrown down. This was filtered off and purified by heating the precipitate with water, when the chlorine derivative melts to a heavy oil, and any unchanged amide dissolves. The hot water was poured off from the heavy oil, and the latter substance poured into cold water, when it solidified to a crystalline mass, closely resembling a solid sulphonchloride. The crystalline mass was then pulverized in a porcelain mortar and dissolved in the smallest quantity of alcohol in which it would dissolve. To this alcoholic solution water was added immediately, drop by drop, as long as any precipitate was produced. Under these conditions the dichlorsulphonamide was obtained in pearly white laminæ, which, in general appearance, greatly resemble the original amide. Looked at in considerable quantity the compound has a distinct greenish-yellow color, due to the presence of free chlorine. It is also exceedingly difficult to obtain the compound so that it does not possess a slight odor of either chlorine or a sulphonchloride, or of both. The reason of this will be discussed in a subsequent part of the paper. The benzenedichlorsulphonamide melts sharply at 70° C. to a clear, slightly yellowish oil. Heated in quantity to 218–220° C. it explodes. At 150° C. and over, it begins to decompose with evolution of chlorine gas and the formation of benzenesulphonchloride. It acts readily as an oxidizing agent yielding the amide among the other products of oxidation. Treated with strong acids such as hydrochloric or hydrobromic acid, it gives off chlorine, and the amide is produced. It gave the following numbers on analysis :

	Found. Per cent.	Calculated for $C_6H_5SO_2N.Cl_2$. Per cent.	Calculated for $C_6H_5SO_2NH_2Cl_2$. Per cent.
Hydrogen	0.26	0.22	0.30
Chlorine[1]	31.02	31.35	31.14

The results of this and the other analyses of the other compounds described in this paper will be discussed in a subsequent portion.

p-Toluenedichlorsulphonamide,  $C_6H_4<^{CH_3}_{SO_2NCl_2(p)}$. — This compound was prepared by the same method as that above described, *i. e.*, by dissolving the *p*-toluenesulphonamide in the smallest possible quantity of caustic soda solution (1–10), and passing a rapid current of chlorine gas into the solution. Like the benzene compound it can be purified by heating with water and recrystallizing from alcohol by the addition of small quantities of water to the alcoholic solution. It resembles the corresponding benzene compound very closely. It tends to crystallize in rather smaller crystals, and it is rather more difficult to dry it and get it in pure condition. In its odor it strongly suggests a sulphonchloride, into which it doubtless decomposes as does the corresponding benzene compound. The toluene compound melts at 80° C. and explodes at high temperatures. Unfortunately the results of the determination of the amount of chlorine in this compound have been misplaced. From its characteristic properties there can be no doubt as to its nature.

p-Brombenzenedichlorsulphonamide,  $C_6H_4<^{SO_2N.Cl_2}_{Br(p)}$.—This compound was prepared like the two compounds already described. When purified by dissolving in alcohol and precipitating with small quantities of water, it was obtained as a white crystalline powder possessing the odor of chlorine. It was found to melt at 106° C. It gave the following number for chlorine on analysis :

	Found.	Calculated for  $C_6H_4<^{SO_2NH_2Cl_2}_{Br}$.	Calculated for  $C_6H_4<^{SO_2N.Cl_2}_{Br}$.
	Per cent.	Per cent.	Per cent.
Cl	23.36	23.1	23.25

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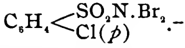
[1] The halogen in all of the compounds herein described was determined by boiling the compound in water with zinc dust, filtering, and titrating with one-tenth normal silver nitrate and ammonium sulphocyanide.

Bromine Derivatives.

Benzenedibromsulphonamide, $C_6H_5SO_2N.Br_2$.—This compound was obtained as a yellow crystalline precipitate by adding bromine or bromine water to a caustic soda solution (1–10) of the amide. On adding the bromine it sometimes happened that a lighter yellow compound was obtained—a substance doubtless of the nature of a double salt of this composition—$C_6H_5SO_2NBr_2NaBr$. By adding an excess of bromine or by simply allowing this double salt to stand under water, the sodium bromide was removed and the dibromsulphonamide obtained. It is possible to precipitate it out of an alkaline solution of the amide in pure state; if not so obtained it may be purified; like the corresponding chlorine compound, by dissolving it in alcohol and precipitating it out with small quantities of water, when it is obtained in dark yellow laminæ, which somewhat resemble lead iodide. The pure bromine compound melts at 110° C. with decomposition and evolution of bromine. Heated suddenly it explodes, bromine being evolved. The compound is almost or quite insoluble in cold water but is slightly soluble in hot water. It dissolves readily in alcohol, ether, chloroform, and carbon bisulphide. Several specimens of the compound gave the following numbers on analysis:

Specimen I, recrystallized from water, gave 50.65 per cent. Br.
" II, " " " " 50.42 " " "
" III, " " benzene and then from chloroform gave 49.07 per cent. Br.

	Calculated for $C_6H_5SO_2NH_2Br_2$. Per cent.	Calculated for $C_6H_5SO_2N.Br_2$. Per cent.
Bromine	50.47	50.79

p-Chlorbenzenedibromsulphonamide,  $C_6H_4<\begin{matrix}SO_2N.Br_2\\Cl(p)\end{matrix}$.–This compound was the first of the halogen derivatives of the sulphonamides obtained. It has already been briefly described in the preliminary notice above referred to. As therein stated, it was prepared by adding bromine water to a caustic soda solution of *p*-chlorbenzenesulphonamide. The substance thus obtained was crystalline, yellow in color, possessed a slight odor of bromine, and gave the following numbers on analysis:

	Found.	Calculated for $C_6H_4<\begin{matrix}SO_2NH_2Br_2.\\Cl(p)\end{matrix}$	Calculated for $C_6H_4<\begin{matrix}SO_2N.Br_2.\\Cl(p)\end{matrix}$
	Per cent.	Per cent.	Per cent.
Bromine	45.53	45.51	45.78
Nitrogen	3.80	3.98	4.00
Sulphur	9.10	9.10	9.15

The attempt was also made to prepare the dibromine derivatives of a few other sulphonamides but without success. With *p*-brombenzenesulphonamide in alkaline solution, bromine and bromine water give a pasty yellow mass, which it was difficult to purify and crystallize, and which rapidly loses bromine on exposure to the air. The compound was not obtained sufficiently pure for analysis. It may be well to note in this connection that no such difficulty was encountered in the preparation of the chlorine compound; in fact the tendency to form such chlorine derivatives might almost be described as characteristic, at least of the sulphonamides of the benzene series.

According to Linebarger,[1] iodine substitution-products of the carbonic amides are impossible. Such would also seem to be the case with the sulphonamides. No such derivative has as yet been prepared, although several attempts have been made in this direction. We might reasonably expect that such a compound could be prepared by bringing the chlorine or bromine compound into a solution of potassium iodide. No such compound, however, is obtained, but in its stead compounds, crystallizing in plates, having a greenish bronze-like luster, which seem to have the nature of periodides of the sulphonamides, somewhat similar, doubtless, in composition and properties to the periodides of the sulphonates described by Kastle and Hill.[2] These compounds are still under investigation. Among other interesting properties they give up by far the greater portion of their iodine when boiled with water, or when dissolved in chloroform or carbon bisulphide, and it is in consequence of this latter property that we can use the dichlor derivatives of the sulphonamides in

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[1] This JOURNAL, **16**, 216.

[2] This JOURNAL, **16**, 116.

testing for iodine, as previously described in the preliminary notice above referred to.

Theoretical.

In the preliminary notice above referred to attention was called to the fact that but little seemed to be known whereas a good deal seemed to be taken for granted regarding the nature of the halogen derivatives of the sulphonamides. From what is known regarding the variable valence of nitrogen, and when it is borne in mind that the amides are very closely related to ammonia, it would not be far-fetched to imagine the existence of both substitution- and addition-products among the halogen derivatives of acid amides. From a theoretical standpoint such compounds as $C_6H_5SO_2N.Cl_2$ and $C_6H_5SO_2NHCl$ might exist, in which the nitrogen remained trivalent; or such compounds as $C_6H_5SO_2NH_2Cl_2$ and $C_6H_5SO_2NH_2.HCl$ in which the nitrogen has become quinquivalent as in the ammonium salts. To the former class of compounds have been relegated all the halogen derivatives of the carbonic amides[1] thus far discovered; whereas, in the latter class have been placed the halogen addition-products of the alkyl amides recently described by Remsen and Norris,[2] and also certain derivatives of the acid anilides which have lately been described by Wheeler and Walden.[3] The question, therefore, naturally suggests itself, to which of these two classes of nitrogen derivatives do the compounds described in the first part of this paper belong? Are these compounds substitution- or addition-products of the sulphonamides? These questions can, of course, only be answered through the study of the composition and chemical conduct of the compounds. Unfortunately, the differences in composition between such addition- and substitution-products are not sufficiently great to warrant a conclusion, as to the nature of these substances, from the analytical data alone. For example, the bromine addition-product of benzenesulphonamide, $C_6H_5SO_2NH_2Br_2$, contains 50.47 per cent. of bromine, whereas, the corresponding substitution-product contains 50.79 per cent. of bromine. Hence, if a compound, on analysis, were found to

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[1] Ber. d. chem. Ges., **15**, 407; and **19**, 2274.

[2] This JOURNAL, **18**, 90.

[3] *Ibid*, **18**, 85.

contain 50.65 per cent. of bromine, as was nearly the case, it would agree within the limits of experimental error with either of the above compounds, and, hence, something more than the quantity of bromine would have to be known before the nature of this compound could be made out. It is true that in most instances the quantities of chlorine or bromine are a little lower than the quantities required by the theory for the substitution-products; and, hence, agree better as a whole with the theoretical numbers for the addition-products. It should be borne in mind, however, in this connection, that these compounds are somewhat unstable, decomposing into acid chlorides and giving off small quantities of chlorine or bromine even at ordinary temperature. The chemical conduct of these derivatives towards a good many of the simple reagents has been studied, and has been found to be such as to suggest that they are substitution- rather than addition-products of the sulphonamides. That such is indeed the case may be seen from the following:

1. It has been observed that, when these substances are rapidly heated, they explode with evolution of the halogen. In this respect, at least, these compounds show an analogy to nitrogen trichloride, NCl_3, which is suggestive. Further, if these substances really be addition-products, such as C_6H_5-$SO_2NH_2Cl_2$, and at the same time explosive, then it is difficult to understand why the chlorine should not come off in combination with hydrogen as hydrochloric acid, instead of in the free state. If, however, we regard the compound, $C_6H_5SO_2N.Cl_2$, as analogous to nitrogen trichloride, then, inasmuch as it contains so much chlorine in direct combination with the nitrogen, it ought to prove explosive and chlorine ought to be given off in the explosion. Again, it has been observed that, when the dichlorine derivative of benzenesulphonamide is slowly heated and kept at 170° C. for several hours, it decomposes with evolution of chlorine, nitrogen, and a little hydrochloric acid gas and benzenesulphonchloride is formed. It is certainly difficult to understand how such a reaction as this is possible with an addition-product such as $C_6H_5SO_2NH_2Cl_2$. Certainly, if the decomposition were sufficiently deep-seated actually to remove the nitrogen

from the compound, then the chlorine ought to come off in combination with the hydrogen as hydrochloric acid gas. Or, in the event that the nitrogen did not escape as a gas, it would not be very far-fetched to suppose the formation of ammonium chloride as one of the products of such a decomposition. No ammonium salt, however, was found in the residue, and only small amounts of hydrochloric acid were formed as compared with the free chlorine. On the other hand, if the decomposition with which we are here dealing be one of the substitution-product, $C_6H_5SO_2N.Cl_2$, then the reaction is not so difficult to understand. It would probably take place in the sense of this equation :

$$C_6H_5SO_2N.Cl_2 = C_6H_5SO_2Cl + N + Cl.$$

The small quantity of hydrochloric acid probably resulting from the action of a part of the nascent chlorine on the phenyl portion of the benzenesulphonchloride.

2. Strong acids act upon the halogen derivatives of the sulphonamides with great ease—setting free the halogen, and forming the corresponding amide. For example, a quantity of the bromine compound of benzenesulphonamide was heated with concentrated hydrochloric acid. Bromine was rapidly evolved and, on evaporating the liquid, and cooling, a white substance was obtained which, upon recrystallization from hot water, was found to possess all of the physical characteristics of benzenesulphonamide. It was found to melt at 152 C., and gave a beautiful yellow precipitate of the original bromine compound on treatment with bromine in alkaline solution. In the same way the chlorine derivative of *p*-brombenzenesulphonamide gave off chlorine abundantly when treated with concentrated hydrochloric acid with the formation of the original amide of *p*-brombenzenesulphonic acid; and, in like manner, bromine was evolved and benzenesulphonamide obtained when the benzenedibromsulphonamide was treated with hydrobromic and with nitric acid. It is difficult to see how acids would act upon addition-products, such as $C_6H_5SO_2NH_2Br_2$. On the other hand, just as nitrogen trichloride reacts with hydrochloric acid to form ammonium chloride and chlorine, so these halogen derivatives, if

analogous to the nitrogen trichloride, ought to react similarly, forming the corresponding amide. And the fact that they do act thus is a strong argument, therefore, in favor of the view that these derivatives are like nitrogen trichloride and hence substitution-products. A comparison of these two equations brings out this analogy:

(1) $NCl_3 + 3HCl = 6Cl + NH_3 + HCl(NH_4Cl)$.

(2) $C_6H_5SO_2N.Cl_2 + 2HCl = 4Cl + C_6H_5SO_2NH_2$.

3. The halogen derivatives of the sulphonamides are good oxidizing agents; and whenever they act thus it is with the production of the corresponding sulphonamide as one of the products of the reaction. Such being the case, a determination of the oxidizing power of these derivatives will also show whether they are addition- or substitution-products. If addition-products, such as $C_6H_5SO_2NH_2Cl_2$, they will have an oxidizing power equivalent to one atom of oxygen, thus:

I. $C_6H_5SO_2NH_2Cl_2 + H_2O = C_6H_5SO_2NH_2 + 2HCl + O$.

Whereas, if these halogen derivatives be really substitution-products, then each molecule of the compound will have an oxidizing power equivalent to 2 atoms of oxygen, thus:

II. $C_6H_5SO_2N.Cl_2 + 2H_2O = C_6H_5SO_2NH_2 + 2HCl + 2O$.

This point has been thoroughly tested with such reducing agents as sulphurous acid, hydriodic acid, and sodium arsenite with the following results:

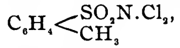
With Sulphurous Acid.

1 cc. H_2SO_3 solution is equivalent to 2.4 cc. 1/10 normal iodine solution.

Experiment 1.—Took 0.1996 gram benzenedichlorsulphonamide with 20 cc. sulphurous acid solution. After standing until the chlorine compound was dissolved the solution required 16 cc. 1/10 normal iodine solution to complete the oxidation of the H_2SO_3. Hence the sulphurous acid oxidized by chlorine compound = 0.1312 grams. Calculated according to equation II, 0.1449 grams.

Experiment 2.—Took 0.4639 gram of benzenedibromsulphonamide with 40 cc. sulphurous acid solution. After solution of the bromine compound the solution took 40 cc. 1/10 normal iodine solution. Hence the sulphurous acid oxidized by bromine compound = 0.2296 gram. Calculated = 0.2415 gram.

Experiment 3.—In experiments 3 and 4, 1 cc. H_2SO_3 used = 1.28 iodine solution; 1 cc. iodine solution = 0.0128 gram iodine. Took 0.1704 gram bromine compound with 50 cc. sulphurous acid. Allowed to stand several hours. It took 42 cc. iodine solution to complete oxidation. Hence the sulphurous acid oxidized by bromine compound = 0.091882 grams; calculated = 0.088716 grams.

Experiment 4.—Dissolved 0.1788 gram of (*p*)-toluenedichlorsulphonamide,  $C_6H_4{<}\substack{SO_2N.Cl_2\\ CH_3}$, in potassium iodide solution. To this solution added 50 cc. sulphurous acid. Titrated with iodine solution. It took 33.1 cc. iodine solution. Hence the sulphurous acid oxidized by this chlorine compound = 0.1276 grams; calculated 0.1221 grams.

With Dilute Hydriodic Acid.

Experiment 1.—Took 0.1855 grams benzenedibromsulphonamide in 50 cc. dilute hydriodic acid. Boiled for a few minutes under an inverted condenser; cooled and added 30 cc. hyposulphite 1/10 normal, and titrated with 1/10 normal iodine solution. It took 6.2 cc. iodine solution. Hence a quantity of iodine was liberated from the hydriodic acid by the bromine compound, equivalent to 23.8 cc. $Na_2S_2O_3$ 1/10 N = 0.3024 gram I; calculated according to equation = 0.3006 gram I.

$$C_6H_5SO_2N.Br_2 + 4HI = C_6H_5SO_2NH_2 + 2HBr + 4I.$$

Experiment 2.—Took 0.1612 gram benzenedichlorsulphonamide with 50 cc. dilute hydriodic acid. Treated as in the preceding experiment. Added 30 cc. $Na_2S_2O_3$ 1/10 normal, and titrated with iodine solution. Took 2.4 cc. normal iodine solution. Hence a quantity of iodine was liberated from the hydriodic acid by the chlorine compound equivalent to 27.6 cc. $Na_2S_2O_3$ 1/10 N; Hence, found = 0.3515 gram I; calculated as above = 0.3623 gram I.

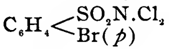
With Arsenious Acid. (Sodium Arsenite 1/10 N.)

Experiment 1.—Boiled 0.1676 gram of benzenedibromsulphonamide with 30 cc. arsenite solution. Cooled and titrated with 1/10 normal iodine solution. Took 7.6 cc. iodine solution. Hence there was formed As_2O_5 equivalent to 22.4 cc. arsenite solution 1/10 normal = 0.1287 gram As_2O_5; calculated according to equation below = 0.1223 gram As_2O_5.

$$C_6H_6SO_2N.Br_2 + 2H_2O + As_2O_3 = C_6H_5SO_2NH_2 + 2HBr + As_2O_5.$$

Experiment 2.—Took 0.1172 gram benzenesulphonamide with 50 cc. As_2O_3 solution 1/10 normal. Boiled, cooled, and titrated with iodine solution, 1 cc. of which contains 0.0128 gram I. Took 14.7 cc. iodine solution. Hence a quantity of As_2O_5 was formed by the bromine compound equivalent to 14.7 cc. of the iodine solution; found = 0.0852 gram As_2O_5; calculated according to equation above = 0.0855 gram As_2O_5.

Experiment 3.—Took 0.1834 gram of *p*-toluenedichlorsulphonamide,  $C_6H_5{<}\genfrac{}{}{0pt}{}{CH_3}{SO_2N.Cl_2(p)}$. Boiled with 40 cc. 1/10 normal As_2O_3 solution. This took 9.3 cc. iodine solution used in experiment 2. Hence a quantity of As_2O_5 formed by the chlorine compound, equivalent to 29.9 cc. of this iodine solution. Hence, found = 0.1732 gram As_2O_5; calculated 0.1764 gram As_2O_5.

Experiment 4.—Took 0.2052 gram of *p*-brombenzenedichlorsulphonamide,  $C_6H_4{<}\genfrac{}{}{0pt}{}{SO_2N.Cl_2}{Br(p)}$ with 40 cc. 1/10 normal As_2O_3. Boiled, cooled, and titrated with same iodine solution as used in experiments 2 and 3 above. Took 12.8 cc. iodine solution. Hence, As_2O_5 found = 0.1530 gram; calculated = 0.1547 gram.

In the light of these results it is readily seen that these compounds have an oxidizing power equivalent to two atoms of oxygen, and that hence they are to be regarded as *substitution-* rather than *addition*-products of the sulphonamides. In view of these results it is proposed to call these two classes of derivatives, dichlorsulphonamides and dibromsulphonamides, respectively. This nomenclature has been employed, we believe, correctly, throughout this paper, using with the name dichlor- or dibromsulphonamide such prefixes as were naturally suggested by the composition of the compounds. While the results above described seem to leave no doubt as to the nature of these derivatives, other methods of proof have already suggested themselves which will be tested in due time, and several interesting syntheses seem possible through the use of these derivatives, which we soon hope to attempt.

STATE COLLEGE OF KENTUCKY,
LEXINGTON, April, 1896.

THE REDUCTION OF COPPER SULPHIDE.

BY DELIA STICKNEY.

J. Uhl in his paper[1] "Ueber Einwirkung von Schwefeldioxyd auf Metalle" speaks of reducing copper sulphide by heating it in a stream of hydrogen. A simpler way to accomplish the reduction is to let the compound come in contact with the flame of the ordinary Bunsen burner until a change in color is seen. Copper sulphide made by heating copper turnings and flowers of sulphur in an ignition-tube was held by forceps in the flame for five or ten minutes. The bluish-black sulphide turned dark red, and the odor of sulphur dioxide was noticed. To determine whether this was metallic copper or cuprous oxide, the experiment was made on a larger scale. Copper sulphide prepared in the usual way was ground, and heated in a porcelain dish with the flame playing directly upon it. During the heating, the mass showed blue, green, and black colors, shades of red and of metallic copper, and under the lens, many threads of bright copper were distinctly seen in the soft, spongy mass. The unreduced part was hard and brittle, but the colored parts were soft and friable. After successive grindings and heatings, very few hard lumps remained, but each time the mass felt softer under the pestle, and looked more like spongy copper.

To see if cuprous oxide was formed in any great amount, equal quantities of this product and of cuprous oxide were treated with concentrated hydrochloric acid, cuprous oxide dissolved entirely, but the other left a bright residue in the bottom of the tube. A test with ammonia showed that but little had dissolved. The residue was taken out, dried upon

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[1] Ber. d. chem. Ges., **23**, 1215.

filter paper, and examined under a lens. The greater part was bright copper but there were also some particles of a dark color, probably a little of the sulphide not reduced. Some of the product obtained by grinding and heating in this way was put into the flame of the blast lamp, and heated gradually until the copper melted. A little matte, tarnished on the outside, was formed in the bottom of the dish, which analysis showed to contain 97—98 per cent. pure copper.

Experiments were now made with copper sulphide heated under different conditions. It was used just as it came from the tube, and heated undisturbed for one to four hours. The hard, black mass gradually fell apart loosely, and formed the most beautiful product that had been obtained. Varying shades of red were seen, mixed with iridescent, bluish-black parts, arranged often in bands, and in the centre, and on the bottom, the little bright sheafs of metallic copper containing threads one-fourth to one-half inch in length were very abundant. To see if greater heat hastened the process, the sulphide was heated in the same way by the blast lamp. It melted a little on the edges, but remained a hard, brittle, gray mass with but little of the red color on it, showing that the gentle reducing action of the Bunsen flame was needed rather than a high degree of heat.

Once the sulphide came from the tube in which it was made, so hot that the free sulphur burned in the air. When the action was over, a few red spots were seen here and there. This suggested that a little free sulphur might hasten the reduction, and when the process was half completed, the addition of this seemed to shorten the time. Cupric oxide and cuprous oxide were intimately mixed with sulphur and heated, and here the reduction to copper was much quicker than in the case of the sulphide.

For the purpose of determining if contact with the flame was essential, some of the sulphide was heated for four to five hours in a porcelain crucible with the flame underneath, free contact with the air being allowed. Hardly any change in color was seen. On the top there was a slight reddish tinge, and a little sulphur was set free, but the mass was still hard and dark, keeping its shape. The form of the sulphide seemed to make no difference, for the results were the same whether it was powdered or in the form of filings or foil.

This easy method of reduction may be of use in general chemistry, as forming the complementary part of the familiar experiment with copper and sulphur, illustrating synthesis. The pupils' questions show always the desire to reverse the process, and get the copper back again.

English High School, Cambridge, Mass.
April, 1896.

REVIEWS AND REPORTS.

A YEAR'S PROGRESS IN THE FIELD OF CARBOHYDRATES.

During the year 1895 the activity devoted to research among the carbohydrates has in no wise abated, and although no results of a striking character have been obtained as compared with those of some recent years, there has been evident progress toward a more definite and scientific knowledge of these bodies. In the following lines an attempt is made to bring together the gist of most of the papers published during this time, although in so broad a field it will not be surprising if a few publications have been overlooked. No attempt has been made to include in this review the strictly technical publications.

General Reactions.

The most important general reactions of sugars brought out during the year is the so-called glucoside synthesis discovered by Fischer and his pupils. Although the reaction was noted in development in 1894, its perfected form has been announced during the last year. Ether-like compounds between the sugars and a considerable number of alcohols are made by mixing the constituents and subjecting them to the action of a very small amount of hydrochloric acid. From the resulting solutions the new glucosides crystallize freely upon concentration.[1] In this way compounds between most of the glucoses or mono-saccharides and methyl and ethyl alcohols and acetone[2] have been prepared. These bodies are of the nature of ethers and are very suggestive of the natural glucosides. It is thought that this use of small amounts of acids to bring about similar reactions will prove of general application.

Another reaction of a general nature is that occurring be-

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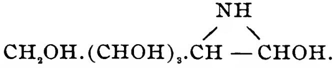
[1] E. Fischer: Ber. d. chem. Ges., **28**, 1145, 1167; also A. Speier: *Ibid.*, **28**, 2531.

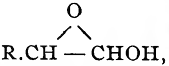
[2] C. Councler: *Ibid.*, **28**, 24.

tween the glucoses and ammonia.[1] The sugars are found to be appreciably soluble in absolute methyl or ethyl alcohols in the presence of ammonia, from which solution there separates on standing a crystalline compound of imide character. The compounds are fairly stable, although, after some time, ammonia is slowly set free. The structure is supposed to be that represented by the formula



$$CH_2OH.(CHOH)_3.CH\overset{NH}{\diagup\;\diagdown}CHOH.$$

Such compounds of ammonia with dextrose, lactose, maltose, galactose, xylose, arabinose, rhamnose, fructose and mannose, have been prepared, for which the discoverers proposed the name "osamines."

Certain sugars (dextrose, levulose and mannose) exhibit a change in their specific rotation when in contact with dilute solutions of the alkalies or alkaline earths. This has been overlooked in the many studies of the action of alkalies on sugars. It now appears that this is due to intramolecular changes by which either of these three sugars may respectively be transformed into the other.[2] This occurs most easily with a small amount of the alkali (about one per cent.). The authors explain the reaction as follows: R.CHOH.CHO becomes  $R.CH\overset{O}{\diagup\diagdown}CHOH$, or $R.CO.CH_2OH$. The possibility of such changes as these may throw light upon the phenomenon of multirotation and upon many other reactions. They are particularly suggestive in connection with Fischer's syntheses, where the reduction of certain acids in alkaline solution led to aldoses or alcohols of a different series.

The possibility of the existence of isomeric acetyl derivatives of the same sugar according to whether sodium acetate or zinc chloride is used in their preparation has been studied.[3] The stable compounds like inosite yield the same product with either reagent. With sodium acetate the di-saccharides yield products which permit the regeneration of the sugar, but not with zinc chloride. The glucoses yield three different bodies if treated with one or the other of these reagents or a mixture of the two.

The actual synthesis of new sugars has naturally not received many contributions. Fischer[4] has given a very inter-

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[1] C. A. Lobry de Bruyn: Ber. d. chem. Ges., **28**, 3082; also Recueil des Travaux des Pays-Bas., **14**, 98 and 135; W. E. Stone: This JOURNAL, **17**, 196.

[2] C. A. Lobry de Bruyn and W. van Ekenstein: Ber. d. chem. Ges., **28**, 3078.

[3] C. Tanret: Compt. Rend., **120**, 194.

[4] Ber. d. chem. Ges., **27**, 3189.

esting review of his work in which he states that no observation in this field conflicts with the theory of the asymmetric carbon atom, and in which he points out that configuration has a marked influence upon the physical, chemical and physiological properties of sugars. In continuation of his synthetical studies,[1] the *d*- and *l*-gulonic acids obtained respectively from *d*-gluconic and xylose-carbonic acids have been transformed by heating with pyridine into *d*-idonic and *l*-idonic acids, and these by reduction into the *d*- and *l*-idoses respectively, and finally into *d*- and *l*-idite, the latter being quite different from mannite. On combining the two active bodies in each case there were obtained the inactive idonic acid, idose and idite. These compounds complete the possible members of the mannite series.

New Carbohydrates.

The subtance volemite, mentioned by Bourquelot as being obtained from the fungus *Lactarius volemus* is identified by Fischer as a heptavalent alcohol or heptite, $C_7H_{16}O_7$, which by mild oxidation is converted into heptose.[2] This differs from the synthetic gluco- and gala-heptites and constitutes the second known natural heptite.

A substance has been obtained from young rye plants which is soluble in water with a specific rotation of $(\alpha)_D = 28°.9$, and easily converted into levulose. The name of β-levulose, or preferably secalose, has been assigned to it.[3]

The sugar agavose, from the *Agave Americana*, has been shown to be sucrose.[4]

By acting on amygdalin with the yeast enzyme which converts maltose into dextrose, it is found that one-half of the theoretical amount of sugar is set free. There remains a new substance, which upon hydrolysis with hydrochloric acid, breaks up into benzaldehyde, prussic acid and a second molecule of dextrose.[5] This would indicate that amygdalin contains a maltose molecule, one-half of which can be split off without affecting the glucoside structure.

Glucoses or Mono-saccharides.

Glycerose is said to be formed on treating glycerin with mercuric chloride. At 160° the reaction becomes violent and calomel is rapidly thrown down. A number of products distil off, among which glycerose was recognized by the reduc-

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[1] E. Fisher and I. Fay: Ber. d. chem. Ges., **28**, 1975 and 1981.

[2] E. Fischer: *Ibid.*, **28**, 1973.

[3] Schulze and Frankfurt: *Ibid.*, **27**, 3525.

[4] Stone and Lotz: This JOURNAL, **17**, 368.

[5] E. Fischer: Ber. d. chem. Ges., **28**, 1508.

tion of Fehling's solution in the cold, and by phenylhydrazine compounds; but it was optically inactive.[1]

Pentoses.—Xylose has been prepared from the cocoanut shell by mild hydrolysis, and, on using more concentrated acids, dextrose was also obtained from the same source.[2]

Arabinose is produced by hydrolysis of the gum of *Acacia decurrens*, in connection with galactose—a result quite similar to that obtained from gum arabic.[3]

From xylan, monobenzoyl and monoacetyl esters have been prepared.[4] Tetra-acetyl xylose and the oxidation of xylose to trioxyglutaric acid, mentioned by the same author, have been previously described by other investigators.

Arabinose and xylose compounds of chloral have been prepared, both products yielding a characteristic blue color with orcin hydrochloride.[5]

A compound of arabinose with benzhydrazide has been made similar to that with dextrose, described below.[6] Ether-like compounds of both arabinose and xylose with alcohols, acetone, and also phloroglucin have already been mentioned.

The preparation and properties of crystallized rhamnose are described in connection with its compounds with alcohols and acetone.[7]

The physiological aspects of the pentoses and pentosans still attract attention. Sixty-five per cent. of the pentosans in fodder was digested by sheep and fifty-three per cent. by rabbits. That portion digested did not seem to be assimilated, since pentoses constantly appeared in the urine of the animals.[8] Pentoses are frequently noted in urine and the phenomenon is the excuse for a new term "pentosurie."[9] This occurrence does not accompany diabetes and is not to be regarded as an alarming condition.[10]

Hexoses.—Dextrose combines with alcohols and acetone to a kind of glucoside, as already described. Two acetone derivatives were thus obtained, dextrose-diacetone, which can be sublimed, and a mono-acetone, soluble and non-sublimable. These compounds are not affected by yeasts or yeast enzymes, and are, therefore, probably of different structural character from the glucosides or di-saccharides.[11]

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[1] Fonces-Diacon: Bull. Soc. chim., Paris, [3], **13**, 862.

[2] B. Tollens and Tromp de Haas: Ann. Chem. (Liebig), **286**, 306.

[3] W. E. Stone: This Journal, **17**, 196.

[4] R. Bader: Chem. Zeit., **19**, 55.

[5] M. Hanriot: Compt. Rend., **120**, 21.

[6] Radenhausen: Zeit. Ver. Rübenzuck, Ind., 1894, 768.

[7] E. Fischer: Ber. d. chem. Ges., **28**, 1162, 1158.

[8] H. Weiske: Ztschr. physiolog. Chem., **20**, 489.

[9] E. Salkowski: Berl. Klin. Woch, schr., **32**, 364.

[10] F. Blumenthal: *Ibid.*, **32**, 567.

[11] E. Fischer: Ber. d. chem. Ges., **28**, 2496

By treating the glucoses (mono-saccharides) with benzhydrazide in alcoholic solution, hydrazides are formed, which are soluble in water. On heating them with benzaldehyde they are decomposed with regeneration of the glucose. In this way dextrose can be separated from the levulose of invert sugar, levulose not entering into the reaction.[1] Attempts have also been made to prepare similar derivatives with semicarbazide, but without definite results, although they all behaved like the hydrazides toward benzaldehyde.[2]

Molecular modifications of dextrose have been noted, each of different rotatory power, and formed under different conditions of crystallization. α-glucose $((\alpha)_{\mathrm{D}} = 106^\circ)$, β-glucose $((\alpha)_{\mathrm{D}} = 52^\circ.5)$, and γ-glucose $((\alpha)_{\mathrm{D}} = 22^\circ.5)$, are described. These have the same molecular weights but different heats of solution. Similar modifications of other sugars could not be prepared.[3]

The transformation of dextrose into mannose or levulose as well as the preparation of dextrosamine with ammonia have already been mentioned.

Dextrose has been obtained by the hydrolysis of cocoanut shells,[4] and from the sumach (*Rhus*).[5] The sugar obtained from indican, either by hydrolysis or ferments is dextrose.[6]

The inversion of starch for the production of crystallized dextrose is advantageously preformed by heating with dilute oxalic acid, eventually under pressure.[7]

Levulose, generally regarded as an unstable sugar, is found to undergo deep-seated changes when heated with water from 100° to 120°. Humus-like substances are formed and a mixture of furfurol, formic acid and formaldehyde distils over.[8]

By the action of oxalic acid on levulose under pressure, β-oxy-γ-methylfurfurol was formed. Sorbinose seems to undergo a similar change, which would indicate a tendency of the ketose sugars to form cyclic compounds,[9] The aldoses undergo no such change.

Levulose has been prepared from orange peel.[10] It shares in the general reactions already referred to under the glucoside syntheses, and the transformation into dextrose and mannose.

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[1] H. Wolff: Ber. d. chem. Ges., **28**, 160; also Th. Curtius: *Ibid.*, 522.

[2] A. and W. Herzfeld: Zeit. Ver. Rübenzuck. Ind.. 1895, 853.

[3] C. Tanret: Compt. Rend., **120**, 1060.

[4] Tollens and Tromp de Haas: Ann. Chem. (Liebig), **286**, 386.

[5] C. Böttinger: Archiv. f. Pharm., **233**, 125.

[6] C. J. van Bookeren: Landw. Versuch. Stat., **45**, 195.

[7] C. J. Lintner and G. Düll: Ber. d. chem. Ges., **28**, 1522.

[8] B. Rayman and O. Sulc: Böem. Zeit. f. Zuck. Ind., **19**, 765.

[9] J. Keiermayer: Chem. Zeit.. **19**, 1003.

[10] R. W. Bauer: Landw. Versuch. Stat., **45**, 293.

Mannose can be prepared from vegetable ivory by hydrolyzing with hydrochloric acid and precipitating the mannose as a hydrazide, which, on treatment with benzaldehyde suffers decomposition, the mannose being liberated in pure form.[1] The transformation of the mannose into dextrose and levulose as well as its share in the glucoside reactions has been noticed.

Galactose has been obtained from the gum of *Acacia decurrens*, which probably contains a galacto-araban complex capable of hydrolysis.[2] Compounds of galactose with alcohols and phloroglucin have been noted.

Disaccharides.

Sucrose.—As the result of rather extended observations by himself and his pupils, Schulze regards sucrose as a form of reserve food in the plant, derived probably from starch of which it is a transport form.[3] Of interest are the recorded occurrences of sucrose in seeds and plants from which it has been separated by the strontian method. Among seeds containing sucrose, are noted oats, rye, wheat, buckwheat, ripe and unripe peas, soja bean, peanut, hemp, sunflower, coffee, and lupine; sucrose is found in etiolated germinating plants of lupine, sunflower, vetch, and potato; in green plants of rye, vetch, potato, elder and hazel; in tubers of potato and roots of the carrot and in the flowering buds of the pear.

From a careful study of the action of acids upon sucrose for purposes of inversion it appears that acetic acid produces complete inversion, but that the optical properties of such a product are different from those of a solution inverted by hydrochloric acid.[4]

It has been claimed that citric acid is produced when sucrose is oxidized by potassium permanganate, but this has been vigorously denied by several experimenters who at least have been unable to obtain the results described.[5]

Sucrose combines with litharge to form a compound with the formula $C_{12}H_{18}O_{11}Pb_2 5H_2O$. This is readily precipitated when litharge is mixed to the consistency of a paste, with molasses. The compound can afterwards be decomposed with carbon dioxide, leaving a pure sugar solution. The method is adapted to the recovery of sugar from molasses.[6]

Lactose.—Molecular modifications of lactose have been announced similar to those of dextrose.[7]

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[1] Duyvene de Witt, Zeit. Ver. Rübenzuck. Ind., 1895, 794.

[2] W. E. Stone, This JOURNAL, **17**, 196.

[3] E. Schulze and S. Frankfurt, Ztschr. physiolog. Chem., **20**, 511.

[4] H. A. Weber and W. McPherson, J. Am. Chem. Soc., **17**, 368.

[5] T. Phipson, Chem. News, **71**, 296; also **72**, 31, 100, 165, 190, 235, 268.

[6] G. Cassner, Dingl. Pol. Jour, **298**, 65.

[7] Compt. Rend., **120**, 1060.

one with the specific rotation of $(\alpha)_D = 55°$ and the other 34°.[1]

Maltose.—The oct-acetyl derivative of maltose has been subjected to repeated study, and its properties described somewhat differently from those given in the original paper by Herzfeld.[2] [3]

Maltose can be regenerated from its hydrazide by the substituting action of benzaldehyde.[4] By the action of fuming hydrochloric acid on dextrose, maltose is said to be formed and by longer action dextrins result. This reaction reminds one of the glucoside synthesis, and it is probable that the synthesis of the complex sugars will eventually be accomplished along this line.[5]

Raffinose has been noted in the germs of wheat, thus adding one more to the rather unusual occurrences of this sugar.[6]

Of the polyvalent alcohols, mannite seems to be of common occurrence in nature, as is also dulcite. The Schrophulariaceæ are particularly productive of these bodies.[7] Mannite forms a tri-acetone compound.[8]

Amorphous Carbohydrates.

An amorphous substance extracted from *Polyporous betulinus* has been named paraisodextran. Its formula is $C_6H_{10}O_5$, and by hydrolysis it yields dextrose.[9]

The pectins are regarded by Tollens as being closely related to the carbohydrates as chiefly indicated by their hydrolytic products. It is pointed out that they are of an acid character, as shown by their solubility in alkalies. It is probable that they contain the carboxyl group, COOH, and that they are oxy-derivatives of the mucous bodies.[10]

Cellulose.—The researches of Cross, Bevan, and their associates, upon cellulose, are among the most interesting of those of recent date on the carbohydrates, especially in view of their technical application.[11]

The general results of these investigations go to show that cellulose, in the general sense, or the fibers of plants are not at all of homogeneous character. The different constituents of cellulose are distinguished by their resistence to or be-

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[1] Tanret: Bull. Soc. Chim., Paris, [3], **13**, 625.

[2] A. Ling and J. Baker: Chem. News, **71**, 71; and Ber. d. chem. Ges., **28**, 440.

[3] A. Herzfeld: Ber. d. chem. Ges., **13**, 267.

[4] A. Herzfeld: *Ibid.*, **28**, 440.

[5] H. Ost: Chem. Zeit., **19**, 1501.

[6] E. Schulze and S. Frankfurt: Ztschr. physiolog. Chem., **20**, 511.

[7] Monteverde: Annales Agronom., **19**, 444.

[8] E. Fischer: Ber. d. chem. Ges., **28**, 1168.

[9] E. Winterstein: *Ibid.*, **28**, 774.

[10] Tollens and Tromp de Haas: Ann. Chem. (Liebig), **286**, 278.

[11] Cellulose: by Cross and Bevan: (Longmans, Green & Co., 1895.)

havior toward certain reagents. Typical cellulose is a polyhydroxylated body, forming a variety of compounds with acids and alkalies, such as alkali-cellulose-xanthate, acetyl, benzoyl and nitrated compounds.

Compound celluloses or ligno-celluloses, found in most plant fibers, are regarded as more or less oxidized derivatives of pure cellulose. These latter are unstable and tend to form cyclic compounds, such as furfurol, lignone, and keto-R-hexene bodies.

Significant among these secondary celluloses are certain bodies which, upon distillation with acids, yield furfurol in considerable quantities. These the authors regard as being distinct from the pentosans, of which bodies this reaction was heretofore supposed to be characteristic. Tollens confirms this view, but points out that these furfurol-yielding bodies (or furfuroids as Cross suggests) are nevertheless of very indefinite and, so far, little understood substances.[1] E. Schulze, whose work in this field entitles his opinion to much respect, intimates that it is still much too early to attempt any definite classification of the forms and varieties of cellulose.[2]

Cellulose is at least of quite a different chemical character from starch, as shown by its greater resistance to hydrolysis. In many respects it behaves like a salt, forming, for instance, with zinc salts, double salt-like compounds, and it acts as an electrolyte to the extent that, when subjected to an electric current, metals are transferred from the anode to the cellulose fiber. Pure cellulose can apparently be transformed to some extent into oxy-cellulose under the action of concentrated sulphuric acid.[3]

Pure anhydrous cellulose shows a distinct rise of temperature when placed in a moist atmosphere, indicating the formation of a definite compound.[4]

By the action of nitric acid on ligno-cellulose, energetic oxidation takes place and reduced oxides of nitrogen are liberated. Unchanged fiber, volatile acids, oxalic acid and soluble derivatives result. The reaction consists in the main of the destructive oxidation of the non-cellulose groups.[5]

Cellulose-di-sulphuric acid results from the solution of cellulose in concentrated sulphuric acid.[6]

[1] Tollens and Tromp de Haas: Ann. Chem. (Liebig), **286**, 296.

[2] E. Schulze: Chem. Zeit., **19**, 1465.

[3] Cross, Bevan and Beadle: Chem. News, **71**, 121.

[4] Clayton Beadle: *Ibid.*, **71**, 1.

[5] E. Baley and J. Chorley: *Ibid.*, **71**, 226.

[6] A. L. Stern: *Ibid.*, **70**, 267.

Cellulose from certain fungi, particularly *Boletus edulis*, when heated with strong hydrochloric acid, yields glucosamine chloride, which would indicate a substance resembling chitin in this material.[1]

In the cell walls of yeast there are thought to be two kinds of cellulose, one stained by iodine and soluble in water, and the other not stained and insoluble. The latter yields some mannose in addition to dextrose when hydrolysed.[2]

Starch.—Discussion goes on unremittingly as to the nature of the many products resulting from the action of acids or ferments upon starch. Different English and German chemists strongly doubt the existence of the so-called isomaltose,[3] while Lintner and E. Fischer still maintain its individuality.[4] The former even distinguishes two forms of isomaltose, differing in their susceptibility to diastatic action and in fermentability by certain yeasts.[5] Brown and Morris point out that the products of the action of diastase on starch behave like a mixture of maltose and dextrin as regards their rotation and reducing power. Apparent exceptions where the action has taken place in the cold, are due to the semi-rotation of maltose under such conditions.[6]

An attempt to determine the molecular weights of the soluble forms of starch by analysis of their baryta compounds, while not leading to exact results, showed that amylo-dextrin, erythro-dextrin and achroo-dextrin possess diminishing molecular weights in the order named.[7]

A study of the comparative action of oxalic acid and diastase upon starch shows that the products are similar, except that maltose is not found as a result of the acid treatment.[8]

Starch is converted into sugar by saliva, pancreas extract and by the blood.[9]

The amount of iodine fixed by potato starch differs with the conditions. The maximum is 18.6 per cent. in the presence of an excess of the reagent; the iodine thus combined reacts with sodium thiosulphite.[10]

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[1] E. Winterstein: Ber. d. chem. Ges., **28**, 167; also E. Gilson, *Ibid.*, 821.

[2] E. Salkowski: *Ibid.*, **27**, 3325.

[3] Ling and Baker: Chem. News, **71**, 71; and **72**, 45; also Brown and Morris: *Ibid.*, **71**, 125, and **72**, 45; H. Mittelmeier: Wchschr. Brau., **12**, 480; H. Ost: Chem. Zeit., **19**, 1501.

[4] E. Fischer: Ber. d. chem. Ges., **28**, 3024.

[5] C. J. Lintner: Zeit. gesamt. Brauw., **17**, 378, and **18**, 173.

[6] Chem. News, **71**, 123.

[7] K. Bülow: Pflüger's Archiv., **62**, 131.

[8] C. Lintner and G. Düll: Ber. d. chem. Ges., **28**, 1522.

[9] C. Hamburger: Dissertation, Physiol. Inst., Breslau, 1895.

[10] Gaston Rouvier: Compt Rend., **120**, 1179.

Analytical.

In the determination of sucrose by inversion, the invert sugar is said to have only 96 per cent. of the reducing power of dextrose. O'Sullivan finds that, if very dilute acid be used in the cold for inversion, the product has from 98.7 to 100.8 per cent. of the reducing power of dextrose, and that practically the same factor may be used.[1]

A method is proposed for the estimation in the same material of sucrose, maltose, dextrose and dextrin by the use of a formula employing density, rotation, and reducing data.[2]

The reducing power of maltose is found to vary according to whether sodium or potassium hydroxide is employed in the Fehling's solution. Dextrose shows no such variation.[3]

In the presence of neutral or basic lead acetate the Fehling's test gives less sugar than otherwise, while the presence of salts giving an alkaline reaction with litmus increases the reduction.[4]

Some time since an alkaline solution of potassium copper sulphate was suggested as a substitute for the ordinary Fehling's solution, and now some modifications are proposed to this in the way of greater dilution which promises to give better results.[5]

If the Fehling's test be made with the surface of the liquid fully exposed to the air, more or less of the sugar becomes oxidized by the alkali and the apparent amount of sugar is diminished. This objection may be overcome by covering the liquid with oil or boiling in flasks.[6]

A new method for determining the amount of cuprous oxide thrown down in the Fehling's test is to dissolve the precipitate in nitric acid, add an excess of potassium iodide and titrate the solution with standardized sodium thiosulphate.[7]

For the determination of starch, various modifications of the use of malt extract are suggested also by comparison of color produced by iodine with the color obtained from a standard solution.[8]

Action of Ferments and Enzymes.

Increased attention has been given to the action of yeasts

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[1] J. O'Sullivan: J. Soc. Chim. Ind., **14**, 555.

[2] Weber and McPherson: J. Am. Chem. Soc., **17**, 312.

[3] T. A. Glendenning: Chem. News, **72**, 254.

[4] A. Borntrager: Stazione speriment. agric. Ital., **28**, 449.

[5] H. Ost: Chem. Zeit., **19**, 1784.

[6] J. Kjeldahl: Chem. Zeit., **19**, 218.

[7] E. Riegler: Wein. Med. Blatt, **22**, 344.

[8] P. Hibbard: J. Am. Chem. Soc., **17**, 64; M. Dermstedt and F. Voigtländer: Hamburg Staats Chem. lab. J. Krieger: Amerik. Bierbrauer, **27**, 580.

and enzymes upon sugars. It appears that many of these agents act selectively, inverting certain sugars and not affecting others.[1] Ordinary beer yeast yields a soluble substance, which inverts both sucrose and maltose. A similar extract from the "kefir" yeast inverts lactose. An extract from *Schizo-saccharomyces octosporus* completely inverts maltose, but is without effect on sucrose. From *S. maximus* was obtained an enzyme with exactly the opposite property of inverting sucrose, and not maltose. These enzymes receive the names of invertin and maltase. *Monilia candida* contains maltase, but no invertin. It is well known that different species of yeast are of quite different fermenting powers, and this is doubtless due to their specific enzymes.

Melibiose, resulting from the partial decomposition of raffinose, is not affected by invertin from ordinary yeast.[2] This is proposed as a means of estimating raffinose, solutions containing the same to be inverted by invertin, leaving the melibiose unchanged.[3] Maltose behaves differently towards the invertin or glycase of yeast and the glycase of grains.[4]

Fischer shows in an interesting way that the action of enzymes on sugars is modified by the configuration of the latter.[5] For instance, only those glucosides which contain the dextrose molecule are susceptible to the yeast enzyme. Emulsin, however, acts upon glucosides containing either the dextrose or galactose molecule. Only the so-called β-galactosides were so decomposed and, since lactose shows the same relation, it is regarded as having a similar constitution. The methyl derivatives of gluco-heptose, rhamnose, arabinose and xylose are not so affected, and it is noticeable that they all belong to the "*d*-dextrose" series. These data will also throw light upon the constitution of the di-saccharides. For the three best known of this group, sucrose, lactose and maltose, exist specific enzymes, invertin, maltase and lactase. The behavior of the less definitely studied di-saccharides toward these enzymes will establish their relationship to one or the other of those whose structure is to some extent known.

W. E. STONE.

April 15, 1896.

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[1] E. Fischer and P. Lindner: Ber. d. chem. Ges., **28**, 984.

[2] *Ibid.*, 3034.

[3] A. Bau: Chem. Zeit., **18**, 1794.

[4] C. Lintner and E. Kröber: Ber. d. chem. Ges., **28**, 1050.

[5] *Ibid.*, **28**, 1429.

A PHYSICAL-CHEMICAL STUDY OF THE GAS BATTERY.

The van't Hoff theory of osmotic pressure and the Arrhenius theory of the dissociation of electrolytes have led in the hands of Nernst[1] to a more or less satisfactory expression for the electromotive force of concentration elements, liquid elements, etc. This has been developed very clearly by Ostwald in his Lehrbuch[2] which, together with the original paper by Nernst, must be consulted for details.

The theory of the gas battery being but an extension of the theory of the liquid element furnishes another means of testing experimentally these well known and very important developments.

Take a simple example of the gas battery, hydrogen over one electrode, and chlorine over the other, using platinum electrodes, and hydrochloric acid as the electrolyte. Hydrogen and chlorine will pass into solution at the two poles until there is an equilibrium between the force driving these substances into solution and the osmotic pressure of the hydrochloric acid solution which acts against the above-mentioned force. The hydrogen pole is negative, since the solution-tension of the hydrogen is greater than the osmotic pressure of the solution, the hydrogen atoms becoming ions by taking positive electricity from the platinum electrode, which thus becomes negative. Exactly the reverse takes place at the other electrode, chlorine atoms becoming ions by taking negative electricity from the electrode, which therefore becomes positive.

The electromotive force, in terms of the Nernst theory, is deduced thus by Smale:[3]

Let P_1 be the solution-tension of hydrogen.
" P_2 " " " " " chlorine.
" T " " absolute temperature.
" p_1 and p_2 be the osmotic pressures of the electrolytes used, and π_1 and π_2 the E. M. F. at the hydrogen and chlorine poles, respectively.

The electromotive force at the hydrogen electrode is expressed thus :

$$\pi_1 = 0.0002\ T \log. \frac{P_1}{p_1} \text{ volts.}$$

But since the solution-tension of chlorine, oxygen, etc., is negative, the electromotive force at this pole is,

$$\pi_2 = 0.0002\ T \log. \frac{p_2}{P_2} \text{ volts.}$$

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[1] Ztschr. phys. Chem., **4**, 129.

[2] Lehrb. Bd., **2**, 825–845.

[3] Ztschr. phys. Chem., **16**, 562.

The electromotive force of such a system would be,

$$\pi_1 - \pi_2 = \pi_0 = 0.0002\ T \log.\left(\frac{P_1}{p_1} - \frac{p_2}{P_2}\right).$$

$$= 0.0002\ T \log.\left(\frac{P_1}{p_1} + \frac{P_2}{p_2}\right).$$

The theoretical consequences of this equation are very interesting. P_1 and P_2, the solution-tensions, are independent of the nature and concentration of the electrolyte. p_1 and p_2, the osmotic pressures, change with the concentrations, but for approximately equally dissociated solutions, are practically constant. Smale has shown[1] then, that in terms of the theory, the electromotive force of a hydrogen-oxygen battery should be *independent* of the *nature* and *concentration* of the electrolyte, provided the electrolytes are equally dissociated. For a hydrogen-chlorine battery, the electromotive force *depends on the concentration of the electrolyte*, and increases with increase in dilution.

These points can all be tested rigidly by experiment, and this has been done by Smale,[2] working in the laboratory of Ostwald. The apparatus which he employed is shown in Figs. 1 and 2.

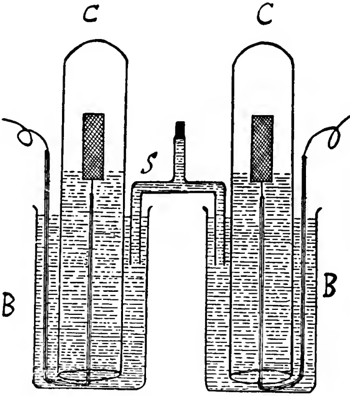

Fig. 1.

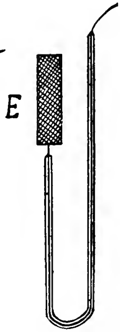

Fig. 2.

C C are two glass cylinders dipping into beakers *B B*, which contain a solution of the electrolyte used. The beakers

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[1] Ztschr. phys. Chem., **16**, 563.

[2] *Ibid.*, **14**, 577.

are connected by the tube *S*, also filled with the electrolyte. The electrode *E*, say of platinum, consists of a strip of this metal, attached to a platinum wire, which is fused into the glass tube, as shown in Fig. 2. Electrical connection with the exterior is made by means of a copper wire, introduced into the glass tube, as shown in Fig. 2. The cylinders are at first filled with a solution of the electrolyte, and the gases introduced by displacement, until the electrode is partly surrounded by the gas and partly by the electrolyte. Strips of platinum, such as are cut from ordinary foil, could not be used directly, since such would not give constant results. It was necessary to cover these with a layer of platinum black, deposited electrolytically upon them, from a dilute solution of platinum chloride.

The electromotive force of a given combination was measured by balancing the battery in question against a Leclanché element, on a specially constructed resistance box, using a Lippmann capillary electrometer, which permitted measurements to 0.0001 volt. The Leclanché element was frequently calibrated by means of a one-volt element, indeed, before and after each measurement. The volt element was compared with a standard Clark element.

The first point tested is whether the electromotive force is independent of the nature and concentration of the electrolyte used, when hydrogen was employed at the one pole and oxygen at the other. The electrolytes comprised seven acids, three bases and seven salts. The concentrations for the same electrolyte vary in most cases from 0.1 to 0.001 normal. The electromotive force of the cell as a whole was measured, and also the tension at each pole, by means of a calomel electrode.[1]

A few results for acid, base and salt are given :

Electrolyte.	Concentration. Normal.	E. M. F. Direct measurement.	Value of the H-Electrode.	Value of the O-Electrode.
Hydrochloric acid	0.1	0.998	0.332	0.665
" "	0.01	1.036	0.391	0.642
" "	0.001	1.055	0.438	0.616
Potassium hydroxide	0.1	1.098	1.027	0.072
" "	0.01	1.095	0.991	0.103
" "	0.001	1.093	0.954	0.137
Sodium sulphate	0.1	1.074	0.547	0.527
" "	0.01	1.069	9.563	0.506
" "	0.001	1.069	0.572	0.497

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[1] Ostwald : Hand und Hilfsbuch zur Ausführung physiko-chemischer Messungen, S. 257.

The results substantiate very strikingly the deductions from the theory. Certain discrepancies, however, manifest themselves, but these seem to admit of a satisfactory explanation through the secondary reactions at the oxygen pole.

The second point, that the electromotive force of a hydrogen-chlorine battery, depends on the *concentration* of the electrolyte, increasing with increase in dilution, was then tested. The following results,

Electrolyte.	Concentration. Normal.	Entire E. M. F.	E. M. F. H-Electrode.	E. M. F. Cl-Electrode.
Hydrochloric acid	1.0	1.360	0.288	1.071
" "	0.1	1.472	0.343	1.129
" "	0.01	1.547	0.403	1.144
" "	0.001	1.621	0.456	1.175

bear out the theory on this point. But the theory admits of still further experimental test.

If the electrodes are of two metals, *e. g.*, platinum and palladium, surrounded by the same gases, which do not attack them, and immersed in the same electrolyte, the electromotive force, at each electrode is, in terms of the theory, formulated thus:

$$\pi_1 = 0.0002\ T \log. \frac{P_1}{p_1} \text{ volt};$$

$$\pi_2 = 0.0002\ T \log. \frac{P_2}{p_2} \text{ volt}.$$

P_1 and P_2 are the solution-tensions of the gas in platinum and palladium, respectively; p_1 and p_2 the osmotic pressures at the electrodes, which are equal in this case, since the same electrolyte is used on both sides. Therefore we have

$$\pi_1 - \pi_2 = 0.0002\ T \log. \frac{P_1}{P_2} \text{ volt}.$$

The metal electrodes play then only this rôle, that they offer a large surface to the gas, facilitating its solution. The *electromotive force* of such an element should therefore be *independent* of the *nature* of the electrode used, since the solution-tension is a constant according to the theory. It should, further, be *independent* of the *size* of the electrode.

The first point was tested by means of the oxygen-hydrogen battery, using sulphuric acid as the electrolyte. The metals employed were platinum, palladium and gold.

Electrode.	Entire E. M. F.	Value of the H-Electrode.	Value of the O-Electrode.
Platinum	0.693	0.277	0.417
Palladium	0.684	0.270	0.412
Gold	0.655	0.258	0.415

Again the agreement of fact with theory is fairly satisfactory.

The same combination as that just employed, was used in determining the effect of the *size* of the electrode on the electromotive force of the cell. Platinum electrodes, 3 cm. long, were used, varying in breadth from a wire 0.2 mm. in diameter, to foil 10 mm. across. These results were obtained:

Breadth of electrode. mm.	Entire E. M. F.	Value of H-Electrode.	Value of O-Electrode.
0.2	0.733	0.323	0.410
2.0	1.017	0.317	0.699
7.0	1.073	0.317	0.745
10.0	1.070	0.317	0.744

The size of the electrode, beyond a certain value, has little or no effect upon the electromotive force. Within this value the decrease in the tension is to be sought for at the oxygen electrode, as is seen above. A certain amount of surface is therefore necessary, that the oxygen electrode should reach its full tension, an amount which is not realized in the first two sizes employed. Beyond this point the theory again finds strong support in the facts.

Another point of considerable interest brought out by this work of Smale deals with the temperature-coëfficient of solution-tension. Nernst,[1] the author of the conception of the solution-tension of metals, in referring to thermo-elements, regarded the solution-tension of mercury electrodes as having a *positive* temperature-coëfficient. Smale has tested this experimentally, by determining the electromotive force of an element with hydrogen over both electrodes, which were of platinum, the gas being kept at different known temperatures on the two sides of the cell. The same electrolyte, 0.01, normal sulphuric acid, was used at both poles. The electromotive force of such an element must depend upon two variables, the change in osmotic pressure and the change in the solution-tension of the hydrogen. The results led to the conclusion that the solution-tension *decreases* with increase in temperature. Other work has shown[2] that the solution-tension of metals, which was originally assumed to be a constant independent of the solution, is directly dependent on the na-

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[1] Ztschr. phys. Chem., **4**, 172. [2] Jones: Ztschr. phys. Chem., **14**, 346.

ture of the solvent. The idea of solution-tension has thus already undergone serious modifications, and will probably be regarded with some suspicion, especially if it leads us to such conclusions, as that this pressure is to be represented in such a case as magnesium, by 10^{44} atmospheres.

Smale has pointed out further, another line, along which a physical-chemical study of the gas battery might be extended. That in which the *same gas*, say hydrogen, is used over the two poles, but under *different pressures*. The tension of the individual electrodes would be expressed in this case by

$$\pi_1 = \frac{0.0002\ T}{2} \log. \frac{P_1}{p_1} \text{ volt.}$$

$$\pi_2 = \frac{0.0002\ T}{2} \log. \frac{P_2}{p_2} \text{ volt.}$$

Since P_1 and P_2, the solution-tension of the gas is constant, and p_1 and p_2 are the pressures of the gas at the two electrodes, we have

$$\pi_1 - \pi_2 = \pi = \frac{0.0002\ T}{2} \log. \frac{p_2}{p_1} \text{ volt.}$$

The constant 0.0002 T in the above equation, is divided by 2, since the hydrogen molecule, which passes over into ions, consists of two atoms. This is closely analogous to the concentration element, where the same gas, under the same pressure on both sides, comes in contact with two different concentrations of the same electrolyte. In this case the electromotive force is expressed by the equation,

$$\pi = 0.0002\ T \log. \frac{p_2}{p_1} \text{ volt,}$$

in which p_2 and p_1 are the osmotic pressures of the two solutions of the electrolyte.

To summarize, the work as a whole furnishes another beautiful experimental confirmation of that theory, which has enabled us to calculate the electromotive force of concentration elements, liquid elements, etc., and, for the first time, has furnished us with a satisfactory explanation of the action in the Voltaic cell, although the cell itself has been known for a century.

HARRY C. JONES.

ELEKTRO-METALLURGIE, DIE GEWINNUNG DER METALLE UNTER VERMITTLUNG DES ELEKTRISCHEN STROMES. VON DR. W. BORSCHERS. Second, enlarged, and revised edition. First and second parts, with 188 cuts. Harold Bruhn, Braunschweig, 1895 and 1896. pp. 393.

The rapid strides which electro-metallurgy has made in the last few years, and the renewed practical interest in the electrolytic deposition of the metals, have created a demand for a new edition of Dr. Borschers' work. The electro-metallurgist will find in this greatly enlarged edition, a clear account of the processes which he may wish to employ, as far as such are ascertainable up to the present. The first division of the book discusses the methods available for obtaining magnesium, lithium, beryllium, sodium, potassium, calcium, strontium, barium, aluminium, cerium, lanthanum, and didymium. The second part has to do with the electro-metallurgy of copper, silver, gold, zinc, cadmium, mercury, tin, lead, bismuth, antimony, chromium, molybdenum, tungsten, uranium, manganese, iron, nickel, and cobalt, and the platinum metals.

The methods employed in obtaining sodium, aluminium, copper, silver, gold, zinc, and lead are discussed at considerable length. The work is introduced by a chapter on electrolysis, so that the scientific electro-chemist, as well as the more practical metallurgist, will find here material of interest. The illustrations are very carefully drawn and are printed with unusual clearness. A translation of this admirable work into English would supply a deficiency in America and England. H. C. J.

LEHRBUCH DER ELEKTROCHEMIE. VON DR. MAX LEBLANC, Privatdozent an der Universität, Leipzig. With 32 figures in the text. Leipzig: Oskar Leiner, 1896. pp. 226.

An introductory chapter, dealing with the principles and laws underlying the study of electricity, is followed by a brief historical sketch of the development of electrochemistry up to the present. Chapter 3 has to do with Arrhenius' theory of electrolytic dissociation, tracing the rise of this theory also historically. Under wandering velocities of ions, the classic work of Hittorf is brought very prominently to the front; a table of Hittorf's values for the velocities of a number of anions, concluding this subject. Chapter 5 is devoted to the conductivity of electrolytes, treating of the law of Kohlrausch, the determination of dissociation-constants by means of measurements of conductivity, the relation between dissociation-constants and chemical constitution, dielectric constants of solvents and their dissociating power, etc., and is characterized by clearness throughout. Chapter 6 forms nearly half of the book. It treats of electromotive force, including a discussion of the relation between chemical and electrical energy; an account of what is meant by electrolytic solution-pressure, and of its application in the calculation of potential differences; the concentration element, the liquid element, the thermal element, and the chemical element. The author is in an especially favorable position to deal with polarization, which is the subject of Chapter 7, since much of the work there described is his own. He may, however, find readers who will not entirely agree with him as to the primary decomposition of water in electrolysis. The book concludes with an account of the constant and inconstant primary batteries in common use, and with a brief statement with respect to accumulators.

This work is less complete, in parts, than that of Jahn, (Grundriss der Elektrochemie), but this is somewhat offset by its admirable system, which is, in the main, that adopted by Ostwald, in that part of his Lehrbuch which deals with electrochemistry. Le Blanc expresses his indebtedness to this source, and to Ostwald in person, for invaluable assistance. While there are some omissions to which it is difficult to become reconciled, one is inclined to avoid any unfavorable comment on a piece of work, which, as a whole, has been done so well.

H. C. J.

LABORATORY EXPERIMENTS IN GENERAL CHEMISTRY. By CHARLES R. SANGER, A.M., Ph.D., Eliot Professor of Chemistry in Washington University. St. Louis: Published by the Author. 1896. 60 pp.

The experiments here described do not differ markedly from those included in several other compilations. In fact, Professor Sanger says "they are compiled from various sources." The author has, of course, endeavored to select the best from a number of manuals and, no doubt, for the object he has in view, he has succeeded in making a better guide than any of those from which he has drawn. It is intended for students of the Engineering School, and for students of the College who may elect the course.

A SHORT COURSE OF EXPERIMENTS IN GENERAL CHEMISTRY WITH NOTES ON QUALITATIVE ANALYSIS. By CHARLES R. SANGER, A.M., Ph.D., Eliot Professor of Chemistry in Washington University. St. Louis: Published by the Author. 1896. 50 pp.

The author has been worried, as many others have been, by the question "What ought to be done in Chemistry for the medical student?" His state of mind is revealed by the following passage taken from the preface of this little book: "The aim of the course is to teach as much of the theory of Chemistry and to impart as much practical knowledge of qualitative methods as is possible in the limited time (seven months) which can be devoted to it. For this reason no special attempt is made to teach the subject from the purely medical stand-point, for the author believes that a good theoretical and practical foundation is necessary before taking up the special subject of medical chemistry. In other words this course takes the place, so far as it can, of the more extended collegiate courses in General Chemistry and Qualitative Analysis, which the author hopes to see at some time made a condition of entrance to all medical schools. So long, however, as a medical school is obliged to provide for elementary instruction in chemistry, this should be of such a nature as to impart essential facts through the student's own work and deduction in the laboratory, with as little as possible of book work.''

This is sound doctrine. The experiments appear to be well chosen, and the descriptions clear.

THE SCIENTIFIC FOUNDATIONS OF ANALYTICAL CHEMISTRY, TREATED IN AN ELEMENTARY MANNER. By WILHELM OSTWALD, Ph.D. Professor of Chemistry in the University of Leipzig. Translated with the Author's sanction by GEORGE M'GOWAN, Ph.D. Macmillan and Co.: New York and London. pp. 207. Price, $1.60.

Since the original German edition of this work has already received notice in this Journal,[1] it remains but to call attention to the appearance of the English translation. It is stated in the Translator's preface, that ''Professor Ostwald has made here and there an emendation upon the original German edition, and has added a section of a chapter upon electro-analysis.'' In some eight pages the electrolytic deposition of the metals is thus placed with other analytical processes, on a scientific basis.

The work of Dr. M'Gowan deserves high commendation. He has not added to the unfortunate attempts to translate German literally into English, but, without sacrificing the meaning of the original, has prepared, not only a readable, but an attractive book. Indeed, from the point of view of clearness, the English in many places, does not suffer by comparison with the original. The accuracy of the translation is assured by the fact that Professor Ostwald has examined the revised proof-sheets. H. C. J.

A TEXT-BOOK OF GAS MANUFACTURE FOR STUDENTS. By JOHN HORNBY, F. R. C. London: John Bell & Sons. New York: Macmillan & Co., 1896. $1.50. 225 pp.

This book in intended for young men studying gas engineering, and as a text-book for those preparing for the examinations of the City and Guilds of London Institute. It is an excellent book. The chemistry of gas manufacture is clearly and sufficiently treated, yet in a way intelligible to those whose knowledge of chemistry is but slight. The thorough

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[1] Vol. 16. 564.

explanation of different methods of manufacture and of mechanical detail make it interesting and valuable to any reader. E. R.

THE ELEMENTS OF CHEMISTRY. By PAUL C. FREER, M.D., Ph.D., University of Michigan. Boston: Allyn and Bacon, 1895. pp. 284.

Prof. Freer's book differs from any of the chemical textbooks in use. It treats of the elements hydrogen, oxygen, nitrogen, chlorine and carbon, of water and air, of the oxides of carbon and sulphur, of the oxides and hydroxides of sodium and potassium, of hydrochloric, carbonic, and sulphuric acids, of chlorides of primary and secondary carbonates and sulphates, of ammonia and ammonium salts, of methane and its chlorine substitution-products. This is all. A careful and lucid study of the above with eighty-one laboratory experiments, many of which are quantitative, serves as a basis for an admirably clear and simple treatment of chemical theory.

A student intending from the outset to follow chemistry as a profession would profit greatly by beginning with the study of this book with a good teacher.

The limited amount of time given to chemistry in school or college will, however, prevent the general introduction of a book treating of so few elements and compounds, and demanding so large a proportion of the time allotted. E. R.

RÉPERTOIRE DES RÉACTIFS SPÉCIAUX, GÉNÉRALEMENT DÉSIGNÉS SOUS LEURS NOMS D' AUTEURS. FERDINAND JEAN: 17, Faubourg-St-Denis, et G. MERCIER, 158, rue Saint-Jacques. Paris, 1896. 12 mo.

The large number of reactions and tests which have come into use, and are generally referred to, in the literature, by name only, warrants and renders valuable any attempt at such a compilation; but as the authors have, within the space of one hundred pages, collected (in alphabetical order) some four hundred such reactions, principally relating to physiological and pharmaceutical chemistry, it has been scarcely possible to give them in all cases in sufficient detail to be useful. It would have considerably enhanced the value of the book had references been given to the original articles or more extended works. Many common tests have been overlooked. Numerous typographical errors occur, and the quality of the paper is not what is to be desired in a book intended to be handled. M. D. S.

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OXIDATION OF SODIUM SULPHIDE AND HYDROSULPHIDE TO THE SULPHATE BY ELECTROLYSIS.

BY FRANK W. DURKEE.

It is very well known that potassium and sodium chlorates can be made from the chlorides in solution by electrolysis, and various other substances oxidized by the same means. Sodium sulphate mixed with acid sodium hydrosulphite, $NaHS_2O_4$, has been produced from acid sodium sulphite,[1] but I am not aware that any one before has attempted to make sulphates from the alkaline sulphides and hydrosulphides by electrolysis. At the request of Mr. F. S. Pearson, Engineer of the Metropolitan Traction Co., of New York City, experiments were begun to show whether or not it would be possible to transform the ammonium compounds in gas liquors directly into sulphate of ammonium by use of the electric current. In the preliminary experiments, gas carbon electrodes were used, and ammoniacal sulphide and hydrosulphide solutions, but with this arrangement the three-ampere current, which passed through the solution for several hours, failed to produce any sulphate. The sulphide solution was blackened, however, by the finely divided particles of carbon which separated from the electrodes. Copper electrodes,

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[1] E. H. Ekker: Rec. Trav. Chim., 14, 57-64, (1895).

when used in place of the carbon, were soon covered with copper sulphide and the ammonium sulphur compounds were not oxidized. The oxidation went on very well when platinum electrodes were used, and ammonium sulphate in considerable quantity was produced. Solutions of sodium hydrosulphide and sodium sulphide were then subjected to electrolysis, and sulphate of sodium obtained. These experiments, however, were not conducted in a way to show that all of the alkaline metals in the compounds present could be changed to sulphate by electrolysis. This point seemed of so much importance that an attempt was made to settle it, first of all, at the beginning of the investigation and in the following way:

Fifty cc. of a solution of sodium hydroxide, prepared from sodium and distilled water, were measured out into a small flask, and supersaturated with hydrogen sulphide. An equal volume of the same solution of sodium hydroxide was then added, and the resulting solution, approximating a sulphide, was poured into a tall beaker of about one liter capacity. 300 cc. of water were added. To prevent loss by spattering during the process of electrolysis, the beaker was covered with a watch-glass, notched to admit the wires which extended to the electrodes. The electrodes themselves, of thick platinum foil, were cylindrical in form, three inches long and one inch in diameter. Heavy platinum wires connected the electrodes to the battery circuit. When in use, the electrodes were thrust nearly to the bottom of the beaker, were parallel, and one and a half inches apart. After proper connections had been made with a storage battery, a current of about 3.1 amperes flowed through the liquid for about eleven hours and thirty-five minutes. Then the circuit was broken and the solid matter, mostly sulphur, filtered out. Afterwards enough water was added to the filtrate to make 1000 cc. A second solution was then prepared in exactly the same way as the first and made up to 1000 cc.

It followed, therefore, that 1 cc. of the new solution contained as much sodium as 0.1 cc. of the original solution of sodium hydroxide, and 25 cc. as much as 2.5 cc. of the solution of hydroxide. If, then, pains be taken to determine accurately the weight of sodium combined as sulphate in 25 cc. of the solution after electrolysis, it should exactly equal the weight of the sodium in 2.5 cc. of the solution of hydroxide, if the oxidation to sulphate by electrolysis is complete and quantitative. Tested qualitatively, the solutions were neutral and gave the reactions only of sodium sulphate. Consequently, to get the weight of sodium sulphate, it is only necessary to evaporate to dryness in a weighed platinum crucible, on a water-bath, 25 cc. of the solutions after electrolysis, heat and weigh. The weight of the sodium could then be calculated from the weight of sodium sulphate found. Duplicate determinations of sodium sulphate were made in each solution and the results are below.

Solution No. I.

a. Weight of Na_2SO_4 in 25 cc., 0.2641 gram.

b. Weight of Na_2SO_4 in 25 cc., 0.2653 gram.

Weight of Na calculated from an average of weights of Na_2SO_4 obtained in the above determination 0.0857 gram.

Solution No. II.

a. Weight of Na_2SO_4 in 25 cc., 0.2636 gram.

b. Weight of Na_2SO_4 in 25 cc., 0.2638 gram.

Weight of Na calculated from an average of the weights of Na_2SO_4 obtained in the above determinations 0.0854 gram.

To determine the effects of the electric current upon solutions of hydrosulphide of sodium, 100 cc. of the solution of sodium hydroxide were supersaturated with hydrogen sulphide, diluted to 400 cc. by addition of water, and treated for about eleven hours with a three-ampere current. Considerable sulphur separated. This was filtered off and enough water added to make 1000 cc. During the electrolysis some of the sulphur was oxidized to sulphuric acid, as was shown, both by the use of blue litmus paper and by a quantitative determination with barium chloride in hydrochloric acid solution. In all, two solutions, like the one just described, were prepared and analyzed as before, with the following results :

Solution No. I.

a. Weight of Na_2SO_4 in 25 cc., 0.2648 gram.

b. Weight of Na_2SO_4 in 25 cc., 0.2638 gram.

Weight of sodium calculated from an average of the weights Na_2SO_4 obtained in the above determinations 0.08545 gram.

Solution No. II.

a. Weight of Na_2SO_4 in 25 cc., 0.2636 gram.

b. Weight of Na_2SO_4 in 25 cc., 0.2640 gram.

Weight of sodium calculated from an average of the weights of Na_2SO_4 obtained in the above determinations 0.08545 gram.

Determined by standard acid, the sodium in 2.5 cc. solution of sodium hydroxide was 0.0860 gram. The sulphate method gave, as an average of duplicate determinations, 0.0858 gram, and the average of 0.0860 gram and 0.0858 gram is 0.0859 gram, the weight of sodium in 2.5 cc. of the solution of sodium hydroxide.

This weight, 0.0859 gram, should correspond to the weight of sodium in 25 cc. of the solution after electrolysis, if the oxidation of the sulphur compounds to sulphate is complete. For the sake of a better opportunity for comparison, the figures already obtained by analysis have been inserted below in a group.

Sodium in 2.5 cc. NaOH solution, 0.0859 gram.

Solution of Na_2S after Electrolysis.

Sodium in 25 cc. of No. I,	0.0857 gram.
Sodium in 25 cc. of No. II,	0.0854 gram.

Solution of NaSH after Electrolysis.

Sodium in 22 cc. of No. I,	0.08545 gram.
Sodium in 25 cc. of No. II,	0.08545 gram.

While the weights of sodium found in 25 cc. of the solutions after electrolysis do not exactly agree with the weight found in 2.5 cc. of the solution of sodium hydroxide, the agreement is so close that the complete change of sulphide and hydrosulphide to sulphate by electrolysis seems certain.

By what chemical change or changes is sulphate of sodium produced from sodium sulphide electrolytically? During the electrolysis of sulphide solutions, in the apparatus before described, some information on this point has been obtained by inspection. As soon as the current began its work electrolytic hydrogen escaped rapidly from the solution about the negative electrode. On the other hand, very little oxygen escaped at the positive. After the current had passed for a short time, the solutions, nearly colorless at first, grew yellow about the negative electrode, and the yellow color rapidly diffused throughout the electrolyte. Later light yellow sulphur made its appearance on the positive electrode. It scaled off, however, as the electrolytic process proceeded, and the greater part dissolved in the surrounding liquid. Next, in order, fine, white sulphur separated in little clouds about the positive electrode, near the surface of the liquid, but dissolved completely as it sank toward the bottom of the beaker cell. With the continuation of the electrolytic process, the clouds of fine, white sulphur became larger and denser, so that immediately before the yellow color disappeared from the electrolyte altogether, they did not dissolve, but gradually diffused throughout the liquid and finally settled down upon the bottom of the beaker. At this stage of the electrolysis, and a little later, much more oxygen escaped from the solution than at any previous time during the passage of the electric current. The solutions were gradually warmed by the electrolytic action.

Taken up in reverse order, the phenomena above described are to be interpreted as follows: The fine white sulphur separating in little clouds about the positive electrode, shows that sodium thiosulphate, $Na_2S_2O_3$, is present and being oxidized to sulphate in the electrolyte, while the light yellow sulphur, which adheres at first to the positive electrode, indicates the presence of polysulphides. These assertions rest upon the data collected during the electrolysis of sodium polysulphide and thiosulphate solutions in the apparatus already described. By such experiments, it has been found, that the sulphur from a thiosulphate solution always comes down finely divided and white, and does not adhere closely to the positive electrode. In a polysulphide solution, on the other hand, it clings tightly to the positive electrode at first, later scales off, and is light yellow in color. The yellow color of the electrolyte also indicates the presence of polysulphides. Again after filtering off the precipitate formed by adding excess of ammoniacal zinc solution, the filtrate always gives the reactions of thiosulphate, on addition of an acid, provided the electrolysis is broken off after the little clouds of white sulphur begin to separate. The oxidation of sodium sulphide and hydrosulphide to sulphate is complete when the white sulphur separates no longer at the positive electrode. As for the electrolytic hydrogen, since it escapes from the electrolyte, it could not have acted chemically upon any substance therein. Moreover, if it had acted chemically, it must have acted as a reducing agent, in which event, from the nature of the substances in the liquid, sulphur would probably have separated at the negative electrode instead of the positive, just as it does in the electrolysis of aqueous solutions of sulphur dioxide, or would have combined with the liberated hydrogen to form hydrogen sulphide. But nothing of the sort happens. On the other hand, since electrolytic oxygen does not escape from the electrolyte, at least not during the first stages of the electrolysis, it must combine chemically to oxidize some substance or substances in the solution. It would seem very probable, therefore, that the oxidation of sodium sulphide and hydrosulphide to the sulphate is not retarded to any extent, at least, by the presence of electrolytic hydrogen, in which event the oxidation might be expected to go on, except so far as rate is concerned, is very much the same way that it does when air is drawn through solutions of sodium sulphide.

Drawing air through solutions of sodium sulphide, according to Lunge,[1] first produces sodium hydroxide and sodium thiosulphate: $2Na_2S + 4O + H_2O = 2NaOH + Na_2S_2O_3$. The thiosulphate then takes oxygen from the air and forms sodium sulphate, and sulphur separates: $Na_2S_2O_3 + O = Na_2SO_4 + S$. Afterwards yellow polysulphides result from the solution of the free sulphur in sodium sulphide and hydroxide, come in contact with more oxygen, sulphur separates again, and an additional amount of thiosulphate is pro-

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[1] Soda Industry, p. 531.

duced: $Na_2S_5 + 3O = Na_2S_2O_3 + 3S$.[1] Very likely other polysulphides are produced, but are all changed to the thiosulphate by the free oxygen, according to similar reactions.

If, therefore, the electrolytic oxidation of sodium sulphide to the sulphate takes place as above described, at any instance after the electric current has acted on the solution for some time, and indeed, until very near the end of the electrolytic oxidation, the sum of the weights of sodium in the sulphide, hydroxide, sulphate, thiosulphate, and polysulphide, must equal the weight of sodium in the solution of sodium sulphide before electrolysis. Moreover, if these weights do equal each other, it follows that the oxidation takes place through the formation of these compounds and no others. So, to settle the point under consideration, it is only necessary to subject solutions of sodium sulphide to electrolytic action for different periods of time, and then to rigorous quantitative analysis, in order to determine whether the oxidation takes place according to the above reactions or not.

For convenience, the sulphide solutions, intended for analysis and described below, have been numbered.

Number I. was prepared by supersaturating with hydrogen sulphide 50 cc. of the solution of sodium hydroxide, already described and analyzed, and adding 50 cc. more of the same solution of sodium hydroxide. After diluting with 300 cc. of water, the solution was subjected to electrolysis, in the apparatus before used. A 3.1 ampere current passed for one hour and thirty minutes, after which the solution was filtered and made up to 1000 cc. by addition of water. Numbers II., III., IV. and V. were prepared by the method used in the preparation of No. I., but the electric current and time of electrolysis varied in each case. No. II. was subjected to the action of a 3.1 ampere current for two hours; No. III. to a 3.2 ampere current for two hours and thirty minutes; No. IV. to a 3.0 ampere current for two hours and thirty minutes; No V. to a 3.1 ampere current for six hours and forty minutes. As a high reading ampere meter was used a part of the time, in some cases, the above figures representing amperes, may not be entirely reliable.

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[1] Dopping: Ann. Chem. (Liebig), 46, 172.

In 50 cc. of the electrolytes, which, theoretically, contain as much sodium as 5 cc. of the solution of sodium hydroxide, the determination of sodium in the different compounds has been made by the following analytical methods: To get the weight of sodium in the sulphate, hydrochloric acid and barium chloride have been added to 50 cc. of the electrolytes, and the resulting barium sulphate determined in the usual way. The weight of sodium in sodium sulphate has then been calculated from the weight of barium sulphate obtained.

The weight of sodium in sulphides has been obtained by use of standard zinc solution, prepared by dissolving 3.253 grams of pure zinc in hydrochloric acid and adding ammonia to supersaturate the liquid. Enough water was then added to make 1000 cc. Nickel nitrate upon a white plate has been used as indicator in these titrations.

The first step in the method used for the determination of sodium in the form of the thiosulphate has been to add to the solution a slight excess of the zinc solution described above. The resulting sulphide of zinc and free sulphur have then been filtered off, excluding the air as much as possible meanwhile, and excess of bromine has been added to the filtrate to oxidize the thiosulphate to acid sulphate. After acidifying with hydrochloric acid, an excess of barium chloride has been added, the weight of the barium sulphate afterward determined in the usual way, and from it the corresponding weight of sodium calculated. By subtracting from this the weight of sodium found in sodium sulphate, twice the weight of the sodium combined in the thiosulphate has been obtained.

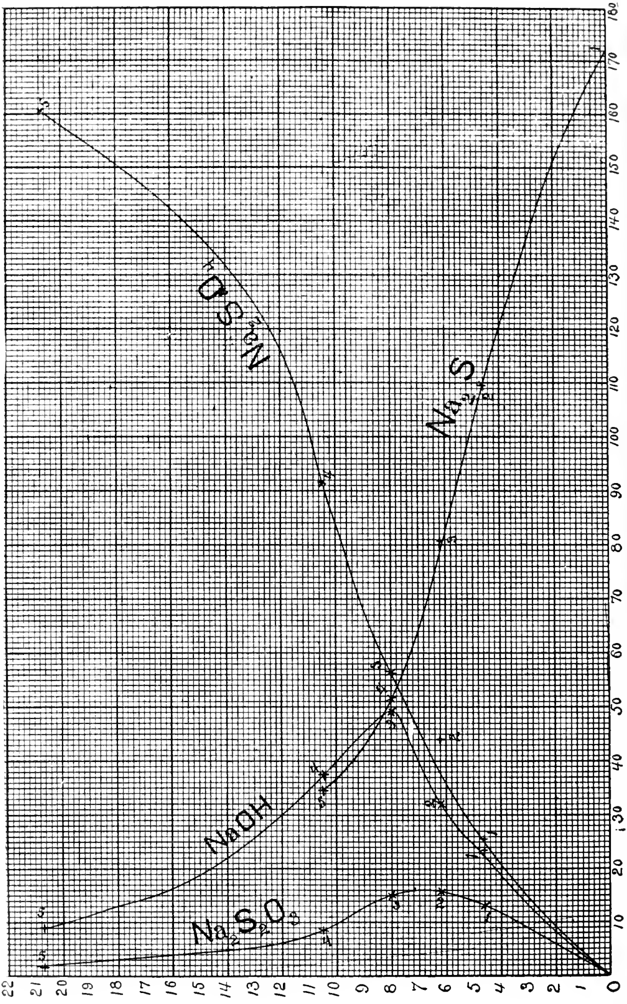
In the determination of sodium in the form of hydroxide, a large excess of standard sulphuric acid has been added to 50 cc. of the electrolyte solutions. Afterwards they have been rapidly boiled to expel sulphur dioxide and hydrogen sulphide, filtered and titrated back with standard sodium hydroxide, using methyl orange in cold solution as indicator. By subtracting the weight of the sodium in the standard solution of sodium hydroxide used, from the weight of sodium that the standard sulphuric acid would neutralize, the weight of sodium acted upon by the standard sulphuric acid in the electrolyte solution under examination has been obtained. The difference between this weight of sodium and the sum of the weights of sodium in sulphides and thiosulphate equals the weight of sodium in the hydroxide.

For the sake of comparison, the analytical results have been arranged in tabular form. The results themselves are averages obtained in duplicate determinations. The weights are given in grams:

Solutions.	No. I.	No. II.	No. III.	No. IV.	No. V.
Time,	1 h. 30 m.	2 h.	2 h. 30 m.	3 h. 30 m.	6 h. 40 m.
Amperes,	3.1	3.1	3.2	3	3.1
Ampere-hours,	4.6	6.2	8	10.5	20.7
Na in Na_2SO_4,	0.0251	0.0441	0.0563	0.0915	0.1604
Na in Na_2S,	0.1096	0.0806	0.0515	0.0354	....
Na in $Na_2S_2O_3$,	0.0131	0.0158	0.0145	0.0086	0.0019
Na in NaOH,	0.0236	0.0320	0.0492	0.0367	0.0090
	0.1714	0.1725	0.1715	0.1722	0.1713

Barring experimental errors in the preparation of the standard solution subjected to electrolysis and analysis, each should contain 0.1718 gram of sodium per 50 cc. It will be seen that the weight of sodium in sodium thiosulphate plus sodium in the hydroxide, sulphate and sulphides corresponds so closely to the theoretical weight of sodium in 50 cc. of the solution that it seems impossible to have the oxidation take place through the formation of any compound or compounds of sodium besides those above mentioned. Sulphides disappear first, the hydroxide next, and the thiosulphate last of all. By using ampere-hours and milligrams of sodium in the sulphide, thiosulphate, sulphate and hydroxide, the oxidation curves below have been plotted. One square to the right of the zero mark represents 1 mg. of sodium, while five squares upward represent an ampere-hour.

The method used for the estimation of the polysulphides of sodium is based upon the fact that, when an alkaline solution of zinc chloride is added to a solution of polysulphides, the sulphur above one atom separates out, and zinc sulphide is produced. The free and combined sulphur can then be filtered off, oxidized to sulphuric acid and zinc sulphate by


Na_2SO_4
Na_2S
NaOH
$Na_2S_2O_3$
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180

bromine, and calculated from the weight of the barium sulphate which results on addition of hydrochloric acid and barium chloride. The resulting weight of sulphur is that of all the sulphur in sulphides and polysulphides. By subtracting the weight of sulphur that would combine with the weight of sodium, found by means of the standard solution of zinc chloride, to form sodium sulphide, the weight of sulphur in the polysulphides of sodium above one atom has been obtained.

Solutions I., II., III. and IV. gave the following weights (in grams) of sulphur above one atom in the polysulphides:

I.	II.	III.	IV.
0.0208	0.0256	0.0415	0.0199

These determinations are valuable inasmuch as they show the amount of polysulphide present at different stages of the electrolysis and correspond, as nearly as could be judged, to the varying intensity of the yellow color in the solutions.

The effect of a three ampere current at 50 volts, alternating 130 times per second, was next tried upon three sulphide solutions.

Platinum wire, either double or single, was used for the electrodes. After the electrolysis, the solutions were filtered and diluted with water to 1000 cc. Theoretically, therefore, 50 cc. of No. I. contain 0.1716 gram of sodium; No. II., 0.1802 gram; and No. III., 0.1802 gram. The methods used in the analyses of the solutions obtained by use of the direct current and already described have been used over again in the analyses of I., II. and III., and the results are below. The weights are given in grams.

Solutions.	No. I.	No. II.	No. III.
Approximate time of electrolysis,	2 h.	3 h. 30 m.	5 h.
Approximate number of amperes,	3	3	3
Na in Na_2SO_4,	0.0033	0.0107	0.0218
Na in Na_2S,	0.1596	0.1152	0.0857
Na in $Na_2S_2O_3$,	0.0022	0.0249	0.0368
Na in NaOH,	0.0058	0.0299	0.0361
	0.1709	0.1807	0.1804

It would appear from these results, therefore, that the oxidation of sodium sulphide to sulphate by means of the alternating current is the same, so far as chemical changes are cerned, as oxidation by the direct current. The rate of oxidation, using platinum wire electrodes, is, of course, much slower with the alternating current than with the direct when large electrodes were used. However, if the electrolysis were continued long enough, there is no reason to suppose that all the sulphide in the electrolyte could not be oxidized to sulphate. In these experiments it was not considered advisable to carry an electrolysis beyond five hours, inasmuch as the platinum electrodes dissolved under the combined influence of the alternating current and electrolyte, which never happened when the direct current was employed. Some idea of the rapidity with which platinum dissolves under the above conditions can be obtained from a platinum determination made in Solution No. II. 100 cc. gave 0.0216 gram platinum. At the end of the electrolysis, therefore, the platinum electrodes weighed 0.216 gram less than at the beginning. Judging from the red color in the electrolytes and the precipitation of platinum sulphide when acids were added, sodium thioplatinate was produced. This part of the subject, however, needs further investigation.

TUFTS COLLEGE, MASS.,
MAY 11, 1896.

A METHOD FOR OBTAINING CRYSTALLINE SILICON.

BY G. DE CHALMOT.

In a recent number of this JOURNAL[1] I mentioned that a mixture of calcium silicide and crystalline silicon can be obtained in an electric furnace from a mixture of silica, calcium oxide, and carbon. The silicide in this mixture can be destroyed by heating with hydrochloric acid, after which the calcium chloride can be washed out, and the silicic acid dissolved in sodium carbonate solution. The crystalline silicon which remains contains some silicide of iron. I found it more convenient to remove the silicic acid with hydrofluoric acid. It is then also possible to dissolve most of the iron sili-

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[1] Page 320.

cide, and I have reduced the amount of iron in the remaining silicon to 1 per cent.

The mixture of calcium silicide and silicon is lighter than the slag from which it is derived, which is seen from the following data:

Specific gravity of alloy.	Specific gravity of slag.
2.31	2.83
2.22	3.12

The metal has a tendency to move to the cathode, hence the yield in an upright furnace can be considerably increased by having the cathode for the upper pole. In this case gravity and electrolysis both tend to move the metal in the same direction, *viz.*, upward. It is necessary that the upper pole should be kept covered with the mixture in order to prevent the burning of the metal.

I have found that with purer materials it becomes harder to obtain calcium silicide, and that it is almost impossible to obtain any, if very little iron is present. For the formation of this silicide the presence of some iron seems to be essential.

The yield of calcium silicide and silicon is not large, and I have substituted other oxides of metals for calcium oxide, thereby considerably increasing not only the yield of silicide, but also of free silicon.

I again heated a mixture of oxide of metal, silica, and carbon with a direct current of low voltage and high amperage.

I thus obtained a mixture of silicide of iron and silicon with 69 per cent. of silicon. The copper silicide with 51.5 per cent. silicon and the silver silicide mentioned on page 96 of this volume are other products of the same method.

I have given more special attention to manganese because its silicide can easily be separated from the free silicon. I obtained from mixtures containing powdered quartz 40 parts, Mn_3O_4[1] 5 parts, charcoal 15 parts, calcium oxide 15 parts, two alloys, of which the following are partial analyses:

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[1] Which contained some iron.

	I.	II.
Si	73.77	68.85
Mn	23.86	26.11
Fe	0.92	1.49
Ca	trace	1.82

I obtained from a mixture containing quartz 40 parts, Mn_3O_4 15 parts, charcoal 15 parts, calcium oxide 7.5 parts, an alloy which contained:

	III.
Si	57.23
Mn	40.31
Fe	2.81
Ca	trace

These alloys are crystalline and contain some well developed crystals which, however, can not be separated.

These alloys contain mainly silicide of manganese and crystalline silicon. They are slightly attacked by boiling dilute hydrochloric acid, more by strong hydrochloric acid, and energetically by cold hydrofluoric acid, which dissolves all the manganese silicide, leaving the silicon.

I treated a part of II with hydrofluoric acid for four days, renewing the acid four times after pouring off the old acid. I washed out the residue and boiled it with diluted hydrochloric acid in order to dissolve all the manganese salt, and I thus obtained a crystalline powder, which was free of manganese and contained 97.77 per cent. of silicon. The silicon was determined by melting it with a mixture of alkali carbonate and nitrate, and weighing the silica. The yield of silicon was 33 per cent., some having been lost with the acid that was poured off.

In order to obtain an idea of the composition of the manganese silicide which is present besides the free silicon, I treated 0.3933 gram of II with cold hydrofluoric acid in a platinum dish and extracted it three times, each time for twelve hours. Instead of pouring off the acid each time, I diluted it with water and filtered through a small ash-free filter and, after unfolding this, washed off into the platinum dish the silicon adhering to the filter, with a few drops of water. After boiling the residue with hydrochloric acid it was collected on a weighed filter. It weighed 0.1610 gram = 40.94 per cent. of free silicon.

If we assume that the calcium and iron were present as the silicides, $CaSi_2$ and $FeSi_2$, we can calculate the amount of silicon united with the manganese.

Total silicon, 68.85 per cent.

	Per cent.
Silicon for 1.49 per cent. Fe	1.51
" " 1.82 " " Ca	2.57
Free silicon	40.94
	45.02

Silicon united with manganese, 23.83 per cent.

26.11 per cent. of manganese in the form of $MnSi_2$ would require 26.97 per cent., of MnSi 13.48 per cent., and of Mn_2Si 6.74 per cent. of silicon.

0.4558 gram of III was treated as stated above. The residue was 0.0575 gram = 12.62 per cent. free silicon.

The calculation for III is:

	Per cent.
Silicon for 2.81 per cent. Fe	2.84
Free silicon	12.62
	15.46

Total silicon 57.23 per cent.

Silicon united with manganese 41.77 per cent.

40.31 per cent. of manganese in the form of $MnSi_2$ requires 41.63 per cent., of MnSi 20.81 per cent., and of Mn_2Si 10.41 per cent. of silicon.

These calculations are subject to the following errors, which, however, partially neutralize each other:

1. The residue of silicon contains impurities, for example, some of the iron silicide.

2. In II there is probably some carborundum.

3. It may be that cold hydrofluoric acid does somewhat attack crystalline silicon if it acts for thirty-six hours. But these errors have hardly influenced the result to such an extent as to leave doubt as to the formula of the manganese silicide, which is in both samples $MnSi_2$.

This silicide differs from the silicide, Mn_2Si, of Vigoureux,[1] as it is not easily attacked by dilute acids. This result corresponds with that obtained with iron silicides where the silicide is attacked less readily if it contains more silicon.

WILLSON ALUMINUM CO.,
SPRAY, N. C.

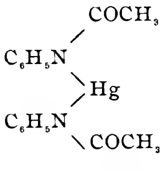
Contributions from the Sheffield Laboratory of Yale University.

I.—ON SOME MERCURY SALTS OF THE ANILIDES.

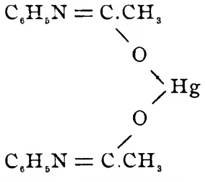
BY H. L. WHEELER AND B. W. MCFARLAND.

Numerous investigators have had occasion to work with the sodium and silver salts of the anilides and have used these compounds in syntheses, while little attention has been given to the mercury salts. Mercury acetanilide first prepared by Oppenheim and Pfaff[2] seems to be the sole representative of the mercury salts of the anilides that has been prepared. This compound has recently been examined by Piccinini,[3] and he concludes that it is a mercurammonium derivative, since the mercury can be removed from it at ordinary temperature by means of sodium thiosulphate, potassium iodide, or ammonium bromide, thus differing from Pesci's[4] paramercurioacetanilide, which is not effected by these reagents.

The experiments of Piccinini, however, do not decide whether mercury acetanilide has the structure



or



The former structure corresponds to that generally accepted for the sodium salts of the anilides, the latter to that of the silver salts.

We are now prepared to show that formanilide and paraformtoluide give mercury salts, and, that these salts—as well

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[1] Compt. rend., **121**, 771.

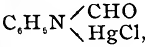
[2] Ber. d. chem. Ges., **7**, 624.

[3] Ber. d. chem. Ges., **28**, R. 113.

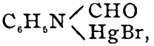
[4] Ber. d. chem. Ges., **28**, R. 112.

as mercury acetanilide—react with benzoyl chloride as if they had the metal joined to nitrogen. We have also found that the action of bromine and iodine on mercury formanilide is similar to that of benzoyl chloride.

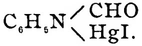
In the course of the above-mentioned reaction such mercuric halogen compounds as the following are directly obtained:



$C_6H_5N\begin{array}{l}\diagup CHO\\ \diagdown HgCl,\end{array}$

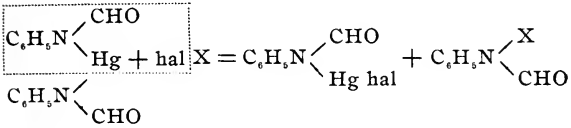


$C_6H_5N\begin{array}{l}\diagup CHO\\ \diagdown HgBr,\end{array}$



$C_6H_5N\begin{array}{l}\diagup CHO\\ \diagdown HgI.\end{array}$

The reactions may be represented by the following equation in which hal represents halogen and X either C_6H_5CO—, Br, or I.



$$\begin{array}{l} C_6H_5N\begin{array}{l}\diagup CHO\\ \diagdown Hg\end{array} \\ C_6H_5N\begin{array}{l}\diagup \\ \diagdown CHO\end{array}\end{array} + \text{hal}\,X = C_6H_5N\begin{array}{l}\diagup CHO\\ \diagdown Hg\ \text{hal}\end{array} + C_6H_5N\begin{array}{l}\diagup X\\ \diagdown CHO\end{array}$$

These halogen mercuric compounds represent a part of the mercuric salt united to halogen. They are undoubtedly nitrogen derivatives, being analogous to the well-known ammonia compound H_2N—HgCl, the so-called white precipitate, and to the aniline salts, $C_6H_5N<^{H}_{HgCl(Br)(or\ I)}$, $C_6H_5N<^{H}_{HgOCOCH_3}$, etc., described by Pesci.[1]

It is also to be noticed that in the above-mentioned reactions of the mercury salts, besides the halogen mercury compounds, nitrogen-substituted anilides are also formed. For example: Benzoyl chloride and mercury formanilide give formylbenzanilide, $C_6H_5N<^{CHO}_{COC_6H_5}$, in addition to chlormercury formanilide, $C_6H_5N<^{HgCl}_{CHO}$; and the diacid anilide when treated with alkali or dilute acid is decomposed into benzanilide, $C_6H_5N<^{H}_{COC_6H_5}$, and formic acid. The diacid anilide, therefore, has both acid groups attached to nitrogen, since such a decomposition could only result from a nitrogen

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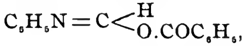
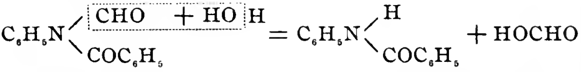
[1] Gazz. chim., **22**, [1], 378.

derivative, *i. e.*, $C_6H_6N<\genfrac{}{}{0pt}{}{CHO}{COC_6H_5}$. On the other hand, if the diacid anilide were an oxygen derivative, *i. e.*,



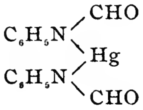
$$C_6H_5N=C<\genfrac{}{}{0pt}{}{H}{O.COC_6H_6},$$

it is evident that the formyl group could not be removed without also removing the benzoyl radical, and we should get aniline, formic and benzoic acids instead of benzanilide. The decomposition of the diacid anilide, therefore, is to be represented as follows:

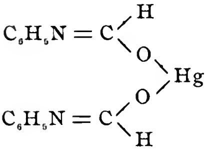


The above facts show that the mercury salts of the anilides have the mercury undoubtedly united to nitrogen, for were it joined to oxygen, it would be impossible to explain the formation of the halogen mercury compounds and the diacid anilides by the usual theory, in tautomeric reactions, of addition and separation, since in this case an assumption of an elaborate rearrangement would also be necessary.

The mercury salts are therefore to be represented by the following structure:



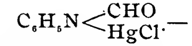
and not



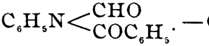
Experimental Part.

Mercury Formanilide, $(C_6H_5NCHO)_2Hg$, is most conveniently prepared by dissolving formanilide and mercuric bromide in alcohol, then adding the calculated quantity of sodium ethylate, and diluting with water. The resulting precipitate [Analysis I] can be crystallized from water [Analysis II]. It then separates in colorless needles which melt at about 194°. Mercury formanilide can also be obtained by use of mercuric nitrate and sodium ethylate, or by boiling an alcoholic solution of formanilide with mercuric oxide [Analysis III] or mercurous oxide [Analysis IV]. It also results when sodium formanilide is boiled with mercurous nitrate.

	Found. I.	II.	III.	IV.	Calculated for $C_{14}H_{12}N_2O_2Hg$.
Hg	45.0	45.2	46.1	45.4	45.4
N		6.2			6.3

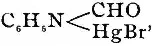
Chlormercury formanilide,  $C_6H_5N<^{CHO}_{HgCl}$. — When mercury formanilide is suspended in benzene, and one molecule of benzoyl chloride is added the reaction takes place, slowly in the cold, rapidly when warmed. On filtering and washing the residue with benzene, pure chlormercury formanilide remains [Analysis I]. This compound is also obtained when equal molecules of formanilide, mercuric chloride, and sodium ethylate are mixed in alcoholic solutions [Analysis II]. It crystallizes from water in shining colorless plates melting at 191° [Analysis III].

	Found. I.	II.	III.	Calculated for $C_7H_6NOHgCl$.
Hg		56.4	56.5	56.3
Cl	9.6	9.9		9.9

Formylbenzanilide,  $C_6H_5N<^{CHO}_{COC_6H_5}$. —On concentrating the above-mentioned benzene solution, this diacid anilide is obtained in colorless, brittle prisms, which on recrystallizing from benzene melt at 112°. It crystallizes from water in needles, and when recrystallized from this solvent or from alcohol the melting-point does not change. Analysis gave :

	Found.	Calculated for $C_{14}H_{11}NO_2$.
C	75.27	74.67
H	4.93	4.88
N	6.1	6.22

When formylbenzanilide is treated with acids or alkalies, the formyl group is removed and benzanilide is formed. This was identified by its melting-point and general properties. It is to be noticed that this diacid anilide from mercury formanilide is identical in all its properties with formyl benzanilide obtained from silver formanilide and benzoyl chloride.[1]

Brommercury formanilide,  $C_6H_6N<^{CHO}_{HgBr}$, was obtained

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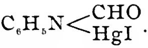
[1] This Journal, 18, 381.

when mercury formanilide was suspended in carbon disulphide and 1 molecular proportion of bromine added. During this operation the whole was cooled with ice. The residue was washed with carbon disulphide until colorless, dried in the air, and then analyzed [Analysis I]. Another portion was crystallized from dilute alcohol from which it separated in bunches of radiating, yellow-white plates. The trace of color and the analysis indicate that in this operation a slight decomposition had taken place [Analysis II].

	Found.		Calculated for
	I.	II.	$C_7H_6NOHgBr$.
Hg		50.2	50.0
Br	19.9	19.4	20.0

The above-mentioned carbon disulphide solution was evaporated over sulphuric acid by means of a pump. This left a brown or black mass. The color was not removed from the solution in carbon disulphide or ether by boiling with animal charcoal. Attempts to isolate the unstable formylbromaminobenzene[1],  $C_6H_5N<\begin{smallmatrix}Br\\CHO\end{smallmatrix}$, were therefore abandoned. We then boiled the residue with water. This extracted a colorless substance containing bromine, crystallizing in needles from hot water and melting at 119°. It was, therefore, the expected parabromformanilide, resulting probably from the molecular rearrangement of formylbromaminobenzene.

Iodmercury formanilide,  $C_6H_5N<\begin{smallmatrix}CHO\\HgI\end{smallmatrix}$.—Molecular proportions of mercury formanilide and iodine were mixed in carbon disulphide, and the whole was allowed to stand for twenty-four hours. The residue which remained was filtered, washed with carbon disulphide, dried, and analyzed. It decomposed on boiling with water.

	Found.	Calculated for C_7H_6NOHgI.
I	28.5	28.4

The carbon disulphide filtrate from iodmercury formanilide was evaporated to dryness at ordinary temperature. A black residue resulted as in the case of the bromine reaction. From

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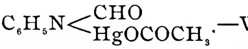
[1] Slosson: Ber. d. chem. Ges., **28**, 3268.

this residue we succeeded in extracting a small amount of paraiodformanilide by boiling with water. On crystallizing from water it gave the correct melting-point, 108°.

In another experiment chloroform was used instead of carbon disulphide, and an excess of mercury formanilide was present. We succeeded in this experiment in showing the presence of a substance which easily liberated iodine, but which was not obtained in pure condition. This unstable compound was probably iodisoformanilide or formyliodaminobenzene which Comstock and Kleeburg[1] obtained from the silver salt of formanilide. On warming this with formic acid, then crystalling from water as they describe, we obtained paraiodformanilide, crystallizing from water in colorless needles, and melting at 108°.

Mercury formanilide acetate, 
$C_6H_5N<\begin{matrix}CHO\\HgOCOCH_3\end{matrix}$.—When mercuric acetate is mixed with formanilide in alcoholic solution, acetic acid is liberated. On concentrating the solution bunches of colorless slender prisms of the above compound separate. Again, on dissolving dry mercuric acetate in a very strong alcoholic solution of formanilide and then warming, the whole suddenly solidifies. When this mass is crystallized from strong alcohol the same colorless prisms result :

	Found.	Calculated for $C_9H_9NO_3Hg$.
Hg	53.1	52.8

Mercury formparatoluide, $(CH_3C_6H_4NCHO)_2Hg$. — Ten grams of formparatoluide and 14 grams of mercuric bromide were dissolved in 40 cc. of 95 per cent. alcohol, then 1.7 gram of sodium also in 40 cc. of alcohol were added. This, on shaking, gave a clear solution, to which an equal volume of water was added. The mercury salt then separated in a thick mass of crystals. These were washed with alcohol [Analysis I]. A portion crystallized from water gave colorless needles [Analysis II]. Another specimen was prepared by using mercuric chloride instead of the bromide, and this was crystallized from 50 per cent. alcohol and analyzed [Analysis III].

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[1] This JOURNAL, **12**, 493.

	Found. I.	Found. II.	Found. III.	Calculated for $C_{16}H_{16}N.O_2Hg$.
Hg	43.48	43.25	43.00	42.73

Chlormercury formparatoluide,  $CH_3C_6H_4N<\genfrac{}{}{0pt}{}{CHO}{HgCl}$. — This was obtained as a residue when the above mercury salt, suspended in benzene, was treated with benzoyl chloride [Analysis I]. It crystallizes from water in colorless needles, and the analysis indicates that in this treatment a slight decomposition takes place [Analysis II].

	Found. I.	Found. II.	Calculated for $C_8H_8NOHgCl$.
Hg	54.19	52.53	54.20

Formylbenzparatoluide,  $CH_3C_6H_4N<\genfrac{}{}{0pt}{}{CHO}{COC_6H_5}$.—The benzene solution from chlormercury formparatoluide was evaporated, and the residue taken up in ether. This operation was repeated. The material was then crystallized from a mixture of ligroïn and ether, when colorless prisms were obtained melting at 101°.

	Found.	Calculated for $C_{15}H_{13}NO_2$.
N	5.36	5.85

On warming this product with dilute sodium hydroxide, the formyl group was removed and benzparatoluide was obtained.

Acetbenzanilide,  $C_6H_5N<\genfrac{}{}{0pt}{}{COCH_3}{COC_6H_5}$.—The preparation of this compound was perfectly analogous to that of formylbenzanilide and formylbenzparatoluide. Mercury acetanilide, best prepared according to the directions of Piccinini,[1] and benzoyl chloride were mixed in molecular proportions in benzene. On filtering, evaporating the benzene solution, and crystallizing the residue from dilute alcohol, an oil separated which changed to long needles, melting at 68°. When this material was crystallized three times from dilute alcohol the melting-point remained constant.

	Found.	Calculated for $C_{15}H_{13}NO_2$.
N	5.81	5.85

On warming with dilute sodium hydroxide and then crystallizing from alcohol, pure benzanilide was obtained, melting

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[1] *Loc. cit.*

from 162° to 163°. Here, also, as in the case of formylbenzanilide and formylbenzparatoluide, alkali removes the lower acid group.

Mercury symmetrical tribromacetanilide, $(C_6H_2Br_3NCOCH_3)_2Hg$.—This was prepared like mercury acetanilide, except that dilute alcoholic solutions were used. The precipitate, washed with water and then with alcohol, gave on analysis 22.4 per cent. of mercury instead of 21.4 per cent. It crystallizes from 50 per cent. alcohol in bunches of needles.

Mercury formyl-α-naphthylamine, $(C_{10}H_7NCHO)_2Hg$.—This was prepared like mercury formparatoluide. It gave colorless needles, which were washed with water, and then with hot alcohol. A mercury determination gave 36.4 per cent. mercury instead of 37.6 per cent.

It will be noticed that, as the solubility of the anilide in water or dilute alcohol decreases, pure mercury salts are to be obtained only with difficulty. For this reason acetparatoluide and benzanilide did not give mercury salts of even approximate purity by the above methods.

New Haven, May, 1896.

II.—ON THE USE OF ANTIMONY TRICHLORIDE IN THE SYNTHESIS OF AROMATIC KETONES.

By William J. Comstock.

Among the reagents which may be used in special cases instead of aluminium chloride in syntheses involving the separation of hydrochloric acid, there is no record, as far as I have found, of the use of antimony trichloride. Indeed the applicability of aluminium chloride is so general that one would hardly search deliberately for a condensing-agent to replace it, although its use does involve certain objectionable features on account of its extremely hygroscopic properties. It is certainly more agreeable to handle antimony trichloride, which has moreover comparative cheapness in its favor, as well as the advantage that in case it has absorbed moisture by long standing or exposure, the anhydrous chloride can be readily recovered. Should it be a question of working on a large scale where the expense is the important, perhaps the one essential, consideration, the use of antimony trichloride would undoubtedly be preferred, as it can be recovered from the product of the reaction by evaporation of the hydrochloric acid solution used to free the ketone from antimony, and subsequent distillation of the residue. I have found that a mixture of an acid chloride with an aromatic hydrocarbon and antimony trichloride, evolves hydrochloric acid when heated, and that for the synthesis of benzophenone and its homologues the method can be used with excellent results. The yields compare favorably with those obtained by Elbs[1] who made a careful study of the Friedel and Crafts reaction for the synthesis of the same ketones. The reaction does not take place at ordinary temperature and cannot be successfully applied with low-boiling chlorides, as, for instance, to the synthesis of acetophenone. It is not my intention to work through the list of ketones to whose synthesis the method might be applied; but I give experiments in three typical cases, leading to well known compounds, to show the yields, advantageous proportions, etc. Without doubt the method can be used to condense any acid chloride having a moderately high boiling-point, with an aromatic hydrocarbon. For the preparation of ketones from the phenol ethers the method can be used, but its advantages are rather doubtful on account of the saponifying action of the antimony trichloride.

Gattermann, Ehrhardt and Maisch[2] have made many ketone syntheses with the phenol ethers according to the method of Friedel and Crafts but as the yields are not given, I have no means of comparing the two condensing-agents.

Hartmann and Gattermann[3] have shown that the phenol ethers are saponified by aluminium chloride, and state that this causes a loss in the preparation of the ketones. The saponifying action of antimony trichloride on the phenol ethers reduces the yield of ketone far below that found in the experiments with hydrocarbons given below, although the reaction takes place more readily. I have obtained about 40 per cent. of the theoretical yield of pure *p*-methoxybenzophenone, and doubtless the yield could be improved by a careful

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[1] J. prakt. Chem., **35**, 465.

[2] Ber. d. chem. Ges., **23**, 1199.

[3] *Ibid.*, **25**, 3531.

study of the conditions. Indeed, by diluting with carbon bisulphide the amount of bye-products is reduced, but the time required is much longer. As to the use of antimony trichloride for the synthesis of compounds other than ketones, I have made no careful study, but will mention a few observations that seem of interest in this connection. It is not possible to prepare triphenylmethane from chloroform by this method; there is no evolution of hydrochloric acid when chloroform, benzene and antimony trichloride are heated, even when large quantities of chloride are used. The reaction between benzal chloride and benzene seems to take place very readily, but the product contains a large amount of dark resinous matter, and so much that is not triphenylmethane that I have not studied the case further.

Syntheses with benzyl chloride in presence of antimony trichloride are not to be recommended. To be sure, diphenylmethane can be prepared with a yield of about 12 per cent., but the greater part of the benzyl chloride is converted into more complicated, high-boiling compounds, apparently the same anthracene derivatives that are formed when benzyl chloride is treated with aluminium chloride. In consideration of the possibility, though a remote one, of a direct synthesis of the ethereal salts from ethyl chlorcarbonate, I have made one experiment, with paraxylene. But the result showed that the reaction takes place in the same way as with aluminium chloride, *i. e.*, carbonic acid is given off together with the hydrochloric acid, and the product of the reaction is a mixture of unaltered paraxylene with higher-boiling hydrocarbons, but no ethereal salt.

Smith and Davis[1] have described addition-products of antimony trichloride with benzene and napththalene, compounds having the composition of two molecules of hydrocarbon to three molecules of antimony trichloride, and it is worth mentioning that aluminium chloride and antimony trichloride are the two metallic chlorides with which "molecular" compounds of the aromatic hydrocarbons have been obtained. Whether this has any connection with the syntheses which can be carried out in presence of these chlorides is doubtful.

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[1] J. Chem. Soc., 41, 411.

Experimental.

In conducting the operation, the mixture is heated in a flask with reflux-condenser, either by a direct flame, or better by means of a paraffin or other bath. The only precautions to be taken are to use substances free from water, to protect the mixture from the moisture of the air during the operation by means of a calcium-chloride tube, and to avoid raising the temperature too rapidly during the early part of the operation. The evolution of hydrochloric acid is rapid at 140°. This is true in the cases given below, as well as in other cases where the reaction was tried as a test-tube experiment only, without working up the product. The temperature of the bath is gradually raised as high as 200°. When the evolution of gas stops, and the odor of the acid chloride has disappeared, the mixture is washed with strong hydrochloric acid in a separatory funnel until the antimony is entirely removed. The ketone is then taken up in ether, dried over potassium carbonate, and finally distilled. Should there be difficulty in getting the ketone to separate from the acid solution, it can be taken up in ether at once, but in this case it requires repeated shaking of the ethereal solution with hydrochloric acid to remove the antimony trichloride. In carrying out the reaction with small quantities it is, however, desirable to take up in ether at once. For removing the antimony trichloride from the ketones it is also possible to use a strong solution of potassium or calcium chloride, acidified with hydrochloric acid.

Benzophenone.

Benzoyl chloride reacts more slowly with benzene than it does with the higher hydrocarbons. It is impossible to carry out the reaction with a small proportion of antimony trichloride, as the temperature of the mixture cannot be raised sufficiently high. With 56 grams of benzoyl chloride, 32 grams of benzene, and 75 grams of the trichloride, the reaction required forty hours for its completion. The yield of pure benzophenone, boiling at 306–308°, was 51 grams or 70 per cent. of the theoretical. The proportions given in the following experiment are to be recommended, as they enable one to carry out the reaction within reasonable time limits:

112 grams C_6H_5COCl.
70 grams C_6H_6.
300 grams $SbCl_3$.

The reaction was completed in about twelve hours. The yield was 108 grams of benzophenone boiling at 306–308°, *i. e.*, 74 per cent. of the theoretical.

The yield of crystallized, but not carefully rectified, ketone is of course larger. Elbs gives the yield of "pure crystallized ketone," obtained by the Friedel and Crafts reaction, as 70 to 75 per cent. of the theoretical.

Benzoyl Chloride and Toluene.

Experiment 1.—The mixtnre used was made up thus:

56 grams C_6H_5COCl.
40 grams C_7H_8.
15 grams $SbCl_3$.

The time required to complete the reaction was forty-two hours. The yield of mixed ortho- and paratolylphenyl ketones, 56 grams or 72 per cent. of the theoretical, boiling between 177° and 182°, at a pressure of 16 mm.

Experiment 2.—The mixture used in this case was:

56 grams C_6H_5COCl.
40 grams C_7H_8.
60 grams $SbCl_3$.

The reaction was completed in five hours; yield of mixed ortho- and para-ketones, 62 grams, or 80 per cent. of the theoretical. According to Elbs, the yield of mixed ortho- and paraketones runs up as high as 95 per cent. of the theoretical, when aluminium chloride is used. As to the porportion of ortho and para in the mixture, there is apparently a higher percentage of ortho-ketone formed when antimony trichloride is used. Elbs states that from his mixture of the two ketones he could obtain 80 to 95 per cent. of pure paratolylphenyl ketone, and that the mixture "caked" at ordinary temperature. I obtained 64 per cent. of pure para-ketone from the mixture. The separation is of course incomplete, but the mixture of ketone, which I obtained, did not "cake" till it was cooled with ice.

Paraxylylphenylketone.

The following mixture was used:

28 grams C_6H_5COCl.
22 grams paraxylene.
20 grams $SbCl_3$.

The reaction was completed in about six hours. The yield of pure ketone, boiling between 317–319°, was 34 grams, or 80 per cent of the theoretical.

In another experiment the same amounts of benzoyl chloride and paraxylene were used with 30 grams of the trichloride. The reaction was completed in $4\frac{1}{2}$ hours; yield 31 grams, or 74 per cent. of the theoretical. Elbs obtained 60 to 70 per cent.

New Haven, May, 1896.

Contributions from the Laboratory of General Chemistry, University of Michigan.

I.—THE ACTION OF SODIUM ON ALDEHYDE.

By Paul C. Freer.

Some years ago I demonstrated that acetone gives a well defined sodium derivative from which both *o* and *c* acyl bodies can be obtained by the action of benzoyl chloride[1], and the proof that sodium acetone is a substance of the structure

$$CH_3.CONa : CH_2$$

was furnished by this means, as well as by the action of ethyl chlorcarbonate.[2] This work showed the previously accepted theory that only those ketones could form sodium derivatives in which the grouping—$CO.CH_2$—or—CO.CHR—is in proximity to negative radicles, to be without foundation. It seemed interesting, therefore, to discover if aldehyde would behave in a similar manner and form sodium aldehyde when brought in contact with metallic sodium. The problem, however, offered greater difficulties because of the well known ease with which aldehyde enters into the formation of condensation-products in the presence of dehydrating agents. The result proved that my expectation was correct: pure

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[1] This Journal, **15**, 582.

[2] *Ibid*, **13**, 22: **17**, 1.

aldehyde[1] reacts violently with sodium so that dilution with absolute ether and cooling is imperative ; a white crystalline sodium derivative is formed and a gas is evolved, which careful analysis proved to be pure hydrogen.[2]

During this reaction air must be rigidly excluded, for the products are easily attacked thereby. The sodium compound, under any circumstances, begins to turn yellow after a few minutes, and soon changes to a brown, sticky mass, which it is impossible to filter. An analysis is of course out of the question. Owing to this rapid polymerization it was impossible to obtain well-defined products by the action of benzoyl chloride as was the case with acetone, a thick resin resulting which did not invite further investigation. This means of advance, however, was not necessary, as a slight experimental *detour* gave most satisfactory results, and afforded an insight into the constitution of the sodium derivative, which left nothing to be desired. This method—which I intend to investigate as to its general applicability—consisted in the action of sodium upon a mixture of benzoyl chloride and aldehyde.

The Action of Sodium on Benzoyl Chloride and Aldehyde.

Aldehydoaldol Benzoate.—1.5 grams of sodium in a flask with inverted condenser are covered with 150 cc. of absolute ether, the air is expelled by means of dry hydrogen and then a mixture of 9.1 grams of benzoyl chloride with an excess of aldehyde, is slowly run in, the flask being kept cool throughout.[3] An immediate reaction sets in, hydrogen is evolved, and sodium chloride separates. After the action is complete, and the odor of benzoyl chloride has disappeared, the ethereal solution is washed with water and small quantities of a dilute solution of caustic potash, until all benzoic acid is removed.

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[1] All of the aldehyde used in this and subsequent experiments was carefully fractioned ; its boiling-point was 19–20°. In the preliminary experiments this product was further shaken with phosphorus pentoxide, poured off, and refractioned so that no moisture was present. Subsequently this precaution was abandoned as unnecessary.

[2] Beckmann and Paul [Ann. Chem. (Liebig) **266**, 281] have tried the action of benzaldehyde on sodium. The brief mention of their results shows that they obtained sodium hydrobenzoin thereby. This action is entirely different from that of sodium in acetaldehyde, as the following work will show.

[3] I convinced myself that pure benzoyl chloride has no action on sodium.

It is then dried over sodium sulphate and the ether evaporated in a vacuum. There results a thick, slightly yellow syrup, which soon becomes permeated with a mass of prismatic crystals. When the quantity of the latter no longer increases, they are filtered out—an operation which takes a long time, even with the best of vacuum pumps—spread on a porous plate and then recrystallized from as small a quantity of alcohol as possible. The product is a white, crystalline solid, separating from ligroïn in large shiny prisms, tolerably soluble in alcohol, soluble in benzene and chloroform, insoluble in water; melting-point 86–87°. The results of the analyses were as follows:

	Calculated for $C_{13}H_{16}O_4$. Per cent.	Found. I.	II.
C	66.1	65.9	65.36
H	6.71	6.9	7.04

A molecular-weight determination according to the cryoscopic method, in benzene solution, gave the following results:

Solvent.	Substance.	*D.*	*M.*
20.2617	0.0477	0.05	256.9
"	0.0974	0.10	236.0
"	0.1515	0.16	229.5
"	0.2333	0.24	235.5

The calculated molecular weight is 236. It will be observed that there is no increase in the molecular weight with increasing concentration, which renders it probable that no hydroxyl group is present, for Auwers has shown[1] that many hydroxylated bodies give an increase in the molecular weight as the amount of substance in unit weight of solvent is increased. The formula obtained is that which would result from one molecule of benzoate of aldol and one of aldehyde. The constitution of the body is proved by the following results:

Decomposition of the Compound, $C_{13}H_{16}O_4$, by Water at 100°.

7 grams of the pure body and 10 grams of water were sealed in a tube and heated for one and one-half hours at 100°. On

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[1] Ztschr. phys. Chem., **12**, 689; **15**, 33.

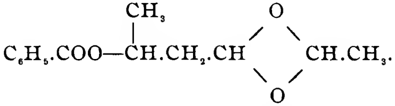
cooling no pressure was observed and the liquid was permeated with crystals of benzoic acid (3.5 grams). The latter was filtered out, dissolved in sodium carbonate, reprecipitated, and a melting-point of 121° obtained. There remained 0.7 gram of a thick syrup insoluble in sodium carbonate and probably identical with the oil originally formed by the action of benzoyl chloride and aldehyde on sodium, and from which the crystals of aldehydoaldol benzoate had been filtered. The clear aqueous solution, which had a strong odor of aldehyde and from which the benzoic acid had been separated, was repeatedly extracted with pure ether, dried over sodium sulphate, and the ether distilled. There remained a thick syrup (1.5 grams) which was fractioned *in vacuo*. It had a boiling-point of 87° at 28 mm., was perfectly soluble in water, reduced an ammoniacal solution of silver nitrate, gave a strong odor of crotonic aldehyde when heated at ordinary pressures —in short it was aldol. The ether which had been distilled from the original solution, on saturation with dry ammonia, produced aldehyde ammonia in small quantity. The decomposition-products of the compound, $C_{13}H_{16}O_4$, with water are therefore benzoic acid, aldol, and aldehyde.

Distillation of the Compound, $C_{13}H_{16}O_4$.

All attempts to distill the solid unchanged, even in a vacuum, failed, because decomposition set in long before the boiling-point was reached. As the products of destructive distillation are of the greatest importance in determining the constitution of the body, 11.2 grams of the pure solid were placed in a distilling-flask connected with a condenser and jacketed receiver, filled respectively with ice-water and a freezing-mixture, and the decomposition was carried on over a free flame. A colorless liquid passed over between 80° and 120°, and when all of this had distilled the thermometer rapidly rose to 240°, and the distillate then solidified in the condenser. This solid was benzoic acid. The liquid was carefully fractioned, first on a water-bath, then on an oil-bath. A low-boiling, colorless fluid passed over below 38°, and this, on refractioning, boiled at 21–22°; it had the odor of aldehyde, reduced silver nitrate, and promptly formed aldehyde-resin with a solution of caustic potash, and was therefore pure acetaldehyde. After all the latter had been driven over, the remainder distilled between 85° and 106°. A small portion passed over below 90°. This consisted of crotonic aldehyde and a little of a lower-boiling body which on oxidation yielded in part isocrotonic acid and which therefore contained isocrotonic aldehyde. The major portion boiled between 104° and 105° (2.2 grams). This liquid had the well-known odor of crotonic aldehyde and, on oxidation with moist silver oxide, and recrystallization from ligroïn, produced pure solid crotonic acid with a melting-point of 71°. The products of destructive distillation are, therefore, benzoic acid, crotonic aldehyde, and acetaldehyde. The same result is observed if the solid body is heated with dilute hydrochloric acid for one hour at 100°; benzoic acid, crotonic aldehyde and acetaldehyde being formed. When heated in a pure state in a sealed tube the body breaks down into the same products at 150°. Boiling with alcohol very slowly produces benzoic ether.

The solid of the formula, $C_{13}H_{16}O_4$, is insoluble in cold dilute caustic potash or in alkaline carbonates; on warming it dissolves, the solution turns yellow, and aldehyde resin is produced, a portion of the solid separating on cooling, if the heating process has not been carried too far. It does not react with bromine in chloroform solution, is not attacked by cold potassium permanganate solution, and does not react with phenylhydrazine. In preparing the body, care must be taken to have exactly enough sodium and benzoyl chloride in the reacting mixture so that both are completely altered: an excess of ether prevents the formation of the solid and produces only the thick syrup mentioned above; an excess of aldehyde is also necessary. The absence of the solid, when the conditions of the reaction are not accurately adhered to, is of course due to the extreme ease with which it is decomposed by acids and alkalies. Even on standing in moist air, crystals of benzoic acid gradually form, extending out from the original body in sharp, shiny needles, which are easily distinguished.

The above results demonstrate clearly that the solid body is a benzoic ester of aldol, in which, however, the aldehyde grouping has disappeared, and at the same time the analyses and decomposition-products show that there also is acetaldehyde in the substance. In order to account for these facts it is necessary to assume that the latter substance is joined to the molecule in some such manner as it is in paraldehyde, *i. e.*, by means of oxygen. The only structural formula which fulfills the conditions is therefore



This acetal-like linking of acetaldehyde is similar to that observed by Schultz and Tollens[1] in their work on the action of formaldehyde on polybasic alcohols. This formula accounts for all of the reactions—the easy decomposition into benzoic acid, aldol, and aldehyde by water; the breaking down into benzoic acid, crotonic aldehyde, and aldehyde on destructive distillation; the formation of aldehyde resin on heating with potash; the indifference toward bromine, etc. The solid body, $C_{13}H_{16}O_4$, is therefore aldehydoaldol benzoate.

Constitution of Sodium Aldehyde and Formation of Benzoyl-Aldol Derivatives.

As has been mentioned, sodium acts on aldehyde, liberating hydrogen and producing a white crystalline body, which, however, in a very few minutes breaks down, giving a thick resin. On the other hand, the action of sodium on a mixture of aldehyde and benzoyl chloride produces bodies which contain the benzoyl group attached to oxygen. This demonstrates that in the sodium derivative which is at first formed the sodium is also attached to oxygen. Two possibilities present themselves: one, that the metal condenses aldehyde to aldol, and that the sodium derivative of the latter body is the first product; the other, that sodium aldehyde is first formed, the latter body then generating the higher condensation-products,

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[1] Ann. Chem. (Liebig), 289, 20.

which stop at aldol if benzoyl chloride is present to form stable derivatives, but which go farther if no such medium is present.

The latter view is the correct one, because sodium, in contact with aldol, acts in a manner entirely different from the way it does on aldehyde. No solid separates for some time after bringing sodium in contact with aldol, the reaction going on to form a soluble sodium aldol, which finally precipitates in part as a white crystalline solid. The latter rapidly turns yellow but even after twenty-four hours it remains as a powder, entirely different from the sticky mass obtained from aldehyde. Sodium aldehyde is therefore produced by the action of sodium on aldehydes and the reactions given above demonstrate that the sodium is attached to oxygen, so that sodium aldehyde is really *sodium vinyl alcohol*—$CH_2 : CHONa$.

This substance is only capable of a brief existence, for it soon decomposes, forming high molecular condensation-products (such as aldehyde-resin). In the presence of benzoyl chloride the condensation, owing to the production of a stable body, stops with aldol, the latter being produced either by addition of aldehyde to sodium aldehyde,

$$CH_2 : CHONa + HCH_2.CHO = CH_3.CHONa.CH_2.CHO, \text{ and}$$
$$CH_3.CHONa.CH_2CHO + ClCO.C_6H_5 = CH_3.CHO.CO.C_6H_5.CH_2CHO + NaCl;$$

or by the addition of aldehyde to vinyl benzoate,

$$C_6H_5.COO.CH : CH_2 + HCH_2.CHO = CH_3.CHO.CO.C_6H_5.CH_2.CHO.$$

The first view is the more likely, and this demonstrates that the first step toward the formation of aldehyde-resin consists in the production of aldol in the presence of alkaline condensation-agents. This is also shown by the fact that aldehyde-resin is readily produced from aldol by warming with a solution of caustic potash. If an excess of aldehyde is present, the aldol benzoate which is at first formed by the action of sodium is further in part condensed to produce the solid $C_{13}H_{16}O_4$:

$$CH_3.CHO.CO.C_6H_5.CH_2.CHO + CH_3.CHO = CH_3.CHO.CO.C_6H_5.CH_2.CHO_2.CH.CH_3.$$

These views are further borne out by a study of the thick syrup which is produced simultaneously with the solid.

The Liquid Product of the Action of Sodium on a Mixture of Benzoyl Chloride and Aldehyde : Action of Phenylhydrazine.

The fluid portions of the reaction-products which, as was mentioned above, constitute a thick syrup with a disagreeable odor resembling that of aldehyde, on standing, gradually deposit crystals of benzoic acid, although the ethereal solution from which they came was thoroughly shaken with sodium carbonate before evaporating. This decomposition goes on continuously so that the oily product must be used promptly in order to obtain the best results. This oil instantly takes up bromine in chloroform solution, with the separation of benzoic acid and the formation of a brominated thick oil which remains after filtering and which was not further investigated. Phenylhydrazine acts most readily. If the thick syrup is dissolved in absolute ether and an excess of phenylhydrazine is slowly added, a crystalline precipitate separates in fine silky needles. This is filtered, washed with ether and recrystallized, first from benzene and finally from hot alcohol, from which it separates in large shiny concentric plates, melting at 166–167°. The analyses gave the following results:

	Calculated for $C_{13}H_{12}N_2O$.	Found. I.	II.	III.
C	73.57	73.81	....	....
H	5.66	5.92	....	....
N	13.2	....	13.7	13.5

The properties and combustion, therefore, agreed with monobenzoyl phenylhydrazine, so that decomposition had taken place. No other solid body could be separated from the mother-liquors, which, however, finally changed to a nearly solid mass of monobenzoyl phenylhydrazine, permeated by a thick resinous hydrazone. I at first thought that the monobenzoyl phenylhydrazine owed its origin to free benzoic acid, which might have separated by decomposition even after all dissolved acid had been removed by sodium carbonate, but I soon convinced myself that benzoate of phenylhydrazine (melting-point 80–82°) does not change into benzoyl phenylhydrazine even by those means which are generally employed to obtain the hydrazides of the acids of the fatty series. Thus, when distilled *in vacuo* it gives off aniline, benzoic acid, and ammonia, and it does not change when heated in a sealed tube at 130° for six hours; at a higher temperature decomposition sets in. It is certain, therefore, that the oily product of the action of sodium on benzoyl chloride and aldehyde is decomposed by phenylhydrazine, separarating the benzoyl group to form monobenzoyl phenylhydrazine, and the oily hydrazones of the aldehyde with which the benzoic acid was united. This easy decomposition demonstrates beyond a doubt that the benzoyl group was attached to oxygen in the liquid, just as was proved to be the case with the solid product of the reaction. A similar splitting off of the benzoyl group as benzoyl phenylhydrazine was observed by Nef in the case of his β-benzoylisocrotonic ester.[1] From this result it seemed highly probable that the oil was aldol benzoate, and in order to prove this point the destructive distillation of the syrup was resorted to.

Distillation of the Liquid Product of the Action of Sodium on Benzoyl Chloride and Aldehyde.

This operation resulted as did the decomposition of the solid, with the exception that only a very small quantity of aldehyde, no more than is generally observed on boiling aldol itself, was recovered. All attempts to fraction the syrup without decomposition, even at a pressure of 2 mm., failed. As a consequence, about 20 grams of the thick syrup were distilled at ordinary pressures, while every precaution was taken to retain all of the low-boiling products. Decomposition readily sets in, and a colorless liquid passes over between 90° and 130°, the thermometer then rapidly rises, and finally

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[1] Ann. Chem. (Liebig), **276**, 203.

there is left benzoic acid, mixed with some aldehyde-resin. The low-boiling product was refractioned, a very little acetaldehyde passed off, then a considerable quantity of a mixture between 75° and 90° which could be further separated into a little acetaldehyde and much crotonic aldehyde, with some substance boiling at 83° to 87°. The latter kept getting less, however, at each redistillation, yielding more crotonic aldehyde, so that finally the attempt to isolate a pure product was abandoned and the part boiling between 75° and 100° was oxidized with silver oxide. I obtained in this way, after acidifying and repeated extraction with pure ether, mostly solid crotonic acid, but there was also present a liquid acid which had the pronounced odor of isocrotonic acid, and which, on conversion into the potassium salts, showed the characteristic needles of potassium crotonate along with the imperfectly crystalline knobs of the isocrotonate. The lower-boiling liquid therefore contained some of the long-sought isocrotonic aldehyde, although the quantity was too small to isolate and analyze, and it probably also suffered change on each distillation. It is likely that a careful preparation of crotonic aldehyde according to the usual method (from aldol) will also show some isocrotonic aldehyde, and I intend to look for this body when the return of cold weather renders successful work in this direction possible. The liquid boiling between 100° and 106° gave pure, solid crotonic acid on oxidation. It seemed almost certain from these results that the thick syrup which I had distilled was aldol benzoate, and in order to prove this point I prepared the latter body from aldol, sodium, and benzoyl chloride.

The Action of Benzoyl Chloride on Aldol and Sodium.

10.7 grams of freshly distilled, pure aldol (b. p., 87° at 28 mm.) were mixed with 17 grams of benzoyl chloride and diluted with two volumes of absolute ether and this solution was added to 2.8 grams of sodium, covered with 100 cc. of the same medium. Reaction set in at once, hydrogen was evolved, and sodium chloride separated. After the action was complete the ethereal solution was shaken out with water and then with sodium carbonate, dried over fused sodium sulphate, and the ether evaporated. There remained a thick syrup, which gradually deposited benzoic acid on standing *in vacuo*. The acid was filtered and the remaining liquid distilled under ordinary pressure. The result was identical with that observed with the thick oil obtained from sodium, aldehyde, and benzoyl chloride—*i. e.*, crotonic aldehyde, a liquid boiling between 75° and 90°, and some acetaldehyde[1] were obtained; benzoic acid, with a little aldehyde-resin, remained behind. There seems to be no doubt, therefore, that the second product of the reaction between benzoyl chloride, aldehyde, and sodium benzoate is aldol.

The reactions which have been given demonstrate that we have here, in all probability, a general method for preparing derivatives of substances, the sodium compounds of which are too easily decomposed to admit of isolation (as is the case with sodium aldehyde), for in this event the action of sodium on a mixture of benzoyl chloride and the body in question can be resorted to. It is strange that very little reduction of the aldehyde takes place during the action of sodium on the mixture; that this is the case, however, is shown by the fact that only a trace of benzoic ester was observed at any time during the progress of the work.

In conclusion, I wish to thank Mr. J. E. Whitsit for his ever willing assistance in this research.

ANN ARBOR, May, 1896.

II.—ON THE CONSTITUTION OF SOME DERIVATIVES OF FORMIC ACID.

BY PAUL C. FREER AND P. L. SHERMAN, JR.

FIRST PAPER.

Formic acid occupies a unique position in the series of homologous acids, of which it is the first member. It contains but one carbon atom in each molecule, and neither methyl nor methylene groups. Nevertheless, it has been customary to class it with the other members and to assume in it the existence of the carboxyl group$-\mathrm{C}\begin{smallmatrix}\nearrow\!\!\!\!\nearrow \mathrm{O}\\ \searrow \mathrm{O}-\mathrm{H}\end{smallmatrix}$. This struc-

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[1] Acetaldehyde is always formed in small quantity from aldol on fractioning.

ture should give to the acid a dual character, and therefore the statement that formic acid is both an acid and an aldehyde is given in many of the text-books on organic chemistry.[1] Nevertheless, the aldehyde character is only expressed by the ease with which the acid is oxidized, for formates, either of the metals or of organic radicles, do not unite with bisulphites, nor does formic acid give the characteristic aldehyde reaction with fuchsine solution. Furthermore, formic acid acts upon phenylhydrazine to produce only the formate of the base, and finally by the separation of water, the hydrazide, but no compound which is analogous to the hydrazones, which can be produced from aldehydes, can be obtained directly from it. With ammonia the acid produces ammonium formate, and finally formamide, but here also the characteristic aldehyde ammonia reaction is lacking. The nearest homologue of formic acid which undoubtedly contains both an aldehyde and carboxyl group is glyoxylic acid, $CH(OH)_2—COOH$, and although the aldehyde group is hydrated, this substance most certainly conforms with other aldehydes in its entire behavior. In short it must be acknowledged that, if formic acid really does contain an aldehyde grouping, the latter most certainly lacks all of the characteristics, save one, of those bodies which we ordinarily regard as aldehydes.

Formic acid as a member of the homologous series of fatty acids should exhibit physical properties in conformity with those of its fellows, but nevertheless some of these are certainly at variance. So, for example, the difference between the boiling-points of formic and acetic acids is 17°; between acetic and propionic 23°; and this latter difference is pretty constantly observed in the case of the remaining members of the series. The transition of formic acid to acetic acid represents a replacement of hydrogen by methyl, so that for a more legitimate comparison it might be advisable to consider the difference between the boiling-points of propionic and isobutyric acids, and this is only 13°, as against 17° for that between formic and acetic acids. This abnormity in the boiling-points does not, however, show much as regards the

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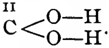
[1] Meyer and Jacobson: Lehrbuch der org. Chemie, 1, 318; Beilstein, 1, 394,

nature of formic acid, as methyl alcohol displays a similar variance from ethyl alcohol, while the halogen derivatives and amines show a decreasing difference for increasing atomic weights. The following table will show this relationship more clearly ·

Name.	B. P. Degrees.	Diff. Degrees.	Name.	B. P. Degree.	Diff. Degree.	Name.	B. P. Degree.	Diff. Degree.
Hydroxylmethane	64.8		Chlormethane	—23.7		Brommethane	4.7	
Hydroxylethane	78.4	13.6	Chlorethane	12.5	36.2	Bromethane	38.4	33.7
Hydroxylpropane	97.4	19.0	Chlorpropane	46.4	33.9	Brompropane	70.8	32.4
Hydroxylbutane	116.8	19.4	Chlorbutane	77.9	31.5	Brombutane	100.4	29.[illegible]
Iodomethane	42.8		Aminomethane	—6.0		Methane acid	100.6	
Iodoethane	72.5	29.7	Aminoethane	18.7	24.7	Ethane acid	118.1	27.5
Iodopropane	102.2	29.7	Aminopropane	49.5	30.8	Propane acid	139.4	[illegible]
Iodobutane	131.4	29.2	Aminobutane	76.5	27.0	Butane acid	161.5	22.1

In some other physical properties also formic acid shows a variation from other members of the series. Thus its avidity is 1.68, as compared with 0.424 for acetic, 0.325 for propionic and 0.316 for butyric acid.[1] The difference between its magnetic molecular rotation and that for acetic acid is 0.854,[2] while the constant for the series is 1.010; although it must be remembered in this connection that the interval between acetic and propionic acids is also smaller than the normal (0.937). The difference in the heat of combustion between formic and acetic acids is 1401[3], while the corresponding difference between acetic and propionic acid is slightly higher, being 1566. Finally in its molecular refraction formic acid is entirely normal and conforms with its homologues. The above shows that, although a difference between formic acid and the others does exist in some respects, yet the study of the physical properties has thrown no light upon its construction.

If, however, formic acid is not both acid and aldehyde, as is generally understood to be the case, it then according to our present views of structural chemistry must be an unsaturated compound and be derived from a bivalent carbon atom



$\overset{\text{II}}{\text{C}}<^{\text{O—H}}_{\text{O—H}}$. Such a formula at first glance seems extremely improbable, but a little consideration will show that

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[1] Ostwald: Lehrbuch d. allg. chemie, **2**, 651.

[2] Ztschr. pkys. Chem., **32**, 523.

[3] Ostwald: Lehrbuch d. allg. chemie, **2**, [1], 400–405.

it is not impossible. The acid would, if this structure were the correct one, be derived from carbon monoxide as an anhydride, and the ready formation of formates from carbon monoxide and alkaline hydroxides would favor this view. Furthermore, there is the marked tendency of formic acid to break down into carbon monoxide and water. Formic acid is monobasic, however, so that, even if it contains the two hydroxyl groups, only one of these is capable of forming salts, but this fact does not exclude the possibility of the hydroxyl formula, for just as tertiary sodium phosphate is so unstable as to be decomposed by water, and the tertiary phosphite does not exist at all, so might the secondary formate be an impossibility. It has been shown by Hell and Mühlhäuser[1] that formic acid can take up bromine in the presence of carbon bisulphide to form an unstable addition-product, which breaks down into carbon dioxide and hydrobromic acid, but, beyond this attempt to show the unsaturated nature of formic acid, nothing has been done. Hell and Mühlhäuser worked with a formic acid of 97 per cent. and claim that bromine and the acid do not unite except when carbon bisulphide is present, but this inactivity may easily have been caused by the impurities of the acid used.

A study of the literature of formic acid fails also to show any proofs of its ascribed aldehyde structure, except as has been mentioned, its well known reducing power.

The purpose of the present research is to throw some light on the constitution of the "formyl" group—CHO, both in the free acid and in combination. And with this object in view, we have first taken up the study of formylphenylhydrazine, formamide, and formic ether.

In the basic formyl derivatives[2] the formyl group is not reactive as an aldehyde. Formamide does not form the phenylhydrazone with phenylhydrazine, but, on the other hand, ammonia is separated and formylphenylhydrazine produced.[3]

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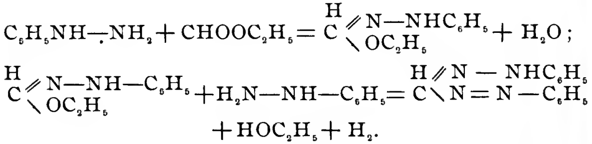
[1] Ber. d. chem. Ges., **11**, 245.

[2] The formates of both fatty and aromatic bases show a marked tendency to split off water and thus form the amides and hydrazides; in the case of phenylhydrazine, for example, this tendency is so marked that on pouring an excess of formic acid into phenylhydrazine, heat enough is generated to transform the formate into the hydrazide, $C_6H_5NH—NH—CHO$.

[3] Gazz. Chim., **16**, 200.

The formation of formazyl hydrogen from formic ether, according to von Pechman,[1] if it were to be produced as that author thinks probable, by the action of a second molecule of phenylhydrazine on formylphenylhydrazine, $C_6H_5NH-NH-CHO + C_6H_5NH-NH_2 = C_6H_5NH-NH-CH = N-NH-C_6H_5 + H_2O$, and the further oxidation of the hydrazo- to the azo-group, would seem to contradict this statement, as this reaction indicates that the formyl group has an undoubted aldehyde character. On heating formylphenylhydrazine and phenylhydrazine together for several hours, even in the presence of zinc chloride, we found, however, that no reaction whatever had taken place, so that we were forced to conclude that this explanation is not correct. In regard to the formation of formazyl hydrogen, the conditions seem to be as follows: Formic ether when mixed with phenylhydrazine and kept cold and free from air, turns deep red and gradually deposits formylphenylhydrazine, while, at the same time, appreciable quantities of formazyl hydrogen are produced. The yield of the latter body is much increased if the temperature is raised, and of course that of formylphenylhydrazine is correspondingly diminished. On the other hand, if the free acid is brought into contact with phenylhydrazine, no formazyl hydrogen, or at least too small a quantity to be isolated, is produced in the cold, and this quantity is not increased perceptibly by heating. This would seem to indicate a difference between formic acid and formic ether, so that in the latter case the reaction would in part take place as follows:



$$C_6H_5NH-NH_2 + CHOOC_2H_5 = \overset{H}{C}\left\langle\begin{array}{l}N-NHC_6H_5\\ OC_2H_5\end{array}\right. + H_2O;$$

$$\overset{H}{C}\left\langle\begin{array}{l}N-NH-C_6H_5\\ OC_2H_5\end{array}\right. + H_2N-NH-C_6H_5 = \overset{H}{C}\left\langle\begin{array}{l}N-NHC_6H_5\\ N=N-C_6H_5\end{array}\right. + HOC_2H_5 + H_2.$$

This does not, however, indicate an aldehyde grouping in formic ether, for under the best conditions only a small part of the ether reacts in this way. It simply shows that the difficulty of saponifying formic ether gives an opportunity for a secondary reaction, which does not take place with the free

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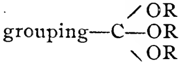
[1] Ber. d. chem. Ges., **25**, 3179.

acid. There is no proof therefore of the aldehyde structure of formic ether. The latter body readily reacts with sodium, as will be shown below, while orthoformic ether, which of course can have but one structure, does not react at all in the cold. The hydrogen attached to carbon, therefore, is not of an acid character, even where the strongly negative grouping

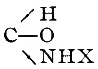


$$-\mathrm{C}\begin{cases}\mathrm{OR}\\ \mathrm{OR}\\ \mathrm{OR}\end{cases}$$

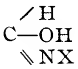
exists in close proximity.

The following structural formulas are, according to our present views, possible for the *basic* derivatives of formic acid :

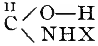
I.



II.



III.



The only work which might have thrown light on this subject has been done with the metallic derivatives of these compounds. Hofmann,[1] whose work dates back to 1865, found that formanilide displayed the hitherto unknown property of forming a sodium salt, which although unstable, could nevertheless be isolated and analyzed. Tobias[2] extended Hofmann's results to ortho- and paraformtoluide, and prepared the sodium salts of these substances, and characterized them as easily crystallizing, colorless bodies, which, on standing, decompose into the corresponding bases and sodium formate. Norton and Livermore[3] found that sodium formanilide reacted with methyl iodide to form monomethyl formanilide and thus the synthetical value of the sodium salts of basic derivatives of formic acid was made apparent. To prepare the alkyl derivatives of aniline, Pictet and Crepieux[4] made use of the above outlined method for preparing the alkyl formanilides, and separated the formyl group by saponification with alkalies ; while Harries[5] carried out the same reactions with phenylhydrazine, preparing in this way the di- and trialkyl derivatives. It will be observed that none of the above experimentation throws any light upon the constitution or behavior of

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[1] Monatshefte d. Berl. Akad., 1865, 659.

[2] Ber. d. chem. Ges., **15**, 2450.

[3] *Ibid.*, **20**, 2273.

[4] Ber. d. chem. Ges., **21**, 1106.

[5] Ber. d. chem. Ges., **27**, 696.

the formyl group. Having in mind the well known property of silver salts to form oxyderivatives, Comstock and Kleeberg[1] treated sodium formanilide in alcoholic solution with silver nitrate. A silver salt was formed, which in its subsequent behavior with alkyl iodides differed materially from the sodium salt. For, when brought in contact with methyl iodide, silver iodide separated, and the resulting methyl derivative proved to be methyl isoformanilide, $C_6H_5N{=}CHOCH_3$. From this reaction Comstock and Kleeberg give to the silver salt the undoubtedly correct formula $C_6H_5N = CHOAg$. The free isoformanilide would, therefore, be represented by Formula II given above, and the methyl derivative an imidoether. In order that this supposition in regard to the constitution of the silver salt may be true, as well as that made in regard to the sodium salts, it must be taken for granted *a priori* that the alkyl group in every case assumes the place vacated by the metal. To see if this rule holds good in every case the study of formylphenylhydrazine was taken up, for with this compound exceptional conditions are offered.

When formylphenylhydrazine (1 mol.) is dissolved in a concentrated alcoholic solution of sodium ethylate (1 mol.), and the solution diluted with ether, a mono-sodium salt slowly crystallizes out on standing, which on exposure to the air turns red and breaks down into sodium bicarbonate and various basic compounds. To determine the position which the sodium holds in the molecule, the substance, both suspended in dry ether and in alcoholic solution, was subjected to the action of ethyl iodide. A reaction took place in both cases, but the resulting bodies showed marked differences, both in appearance and chemical behavior. In the first place a monoethylformylphenylhydrazine was obtained which melted at 106°, and crystallized in rhombohedrons. A study of its reduction-products proved it to have the following structure: $C_6H_5NH{-}N(C_2H_5)CHO$. The reaction product in the second case where the sodium salt of formyl-phenylhydrazine was dissolved in absolute alcohol, and an excess of ethyl iodide allowed to act upon it in the cold, was a monoethyl derivative having a melting-point of 78–79°, and crystallizing in

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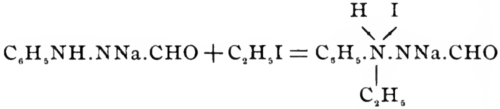
[1] This JOURNAL, **12**, 492: **13**, 255.

long needle-shaped crystals. Its constitution, as obtained through its reduction-products is, $C_6H_5N(C_2H_5)—NH—CHO$. We found that no traces of the other ethyl derivative were obtained until the reacting solution was heated at 100° under pressure for several hours, and even then the amount produced constituted but a small percentage of the entire ethyl compound formed. Under similar conditions free formylphenylhydrazine gave no ethyl derivatives whatever.

The above experiments would seem to show that one and the same sodium salt of formylphenylhydrazine is capable of forming two different, well-defined monoethyl derivatives, according to the conditions under which the reaction takes place. An explanation of this fact calls for something more than the theory of direct substitution of ethyl for sodium. Were that the only reaction possible between sodium formylphenylhydrazine and ethyl iodide, we should obtain but one ethyl derivative so long as there was but one sodium salt present. The fact that pure products were obtained under different conditions shows conclusively that the sodium salt could not have been a mixture, and its entire appearance and crystallographical properties support this view. This being the case the reaction must have taken place as follows: The possibility that the sodium atom is attached to oxygen is excluded, because were addition of ethyl iodide to take place at the unsaturated nitrogen-linking, with a subsequent splitting off of sodium iodide or hydriodic acid, we should obtain exclusively an ethyl derivative of the structure, $C_6H_5—NH—(C_2H_5)—CHO$. But the fact that under certain conditions the body melting at 79° is the sole product of the reaction, shows that such an addition could not have taken place. For the same reason the structure, $C_6H_5NHNH.\overset{\text{II}}{C}.ONa$, is excluded. It follows from this that the sodium must be attached to one of the nitrogen atoms. One of these ethyl derivatives is then formed by direct replacement, the other by the addition of ethyl iodide to the neighboring nitrogen atom, this addition being then followed by separation of sodium iodide:

$$C_6H_5NH.NH.CHO + Na = C_6H_5.NH.NNa.CHO + H;$$

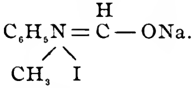


$$C_6H_5NH.NNa.CHO + C_2H_5I = C_6H_5.\overset{H\ \ I}{\underset{C_2H_5}{N}}.NNa.CHO$$

$$= C_6H_5N(C_2H_5)NH.CHO + NaI.$$

The reason for such an addition to the sodium salt, where none takes place with the free body, is due to the increased positiveness of the nitrogen atom through the proximity of the sodium.

From the preceding experiments it will be seen that the position of the sodium atom cannot be stated with any degree of certainty, for the same reasoning would apply no matter to which nitrogen atom the sodium were attached. But it is to be presumed that addition takes place more readily in the cold than in the heat. Consequently the formula $C_6H_5NH.NNa.CHO$ is the more probable. The fact, however, that the ethyl derivative of the formula $C_6H_5NH—N(C_2H_5)CHO$, does not react with sodium ethylate nor sodium, shows that the sodium atom is attached to the nitrogen atom next to the formyl group.

The above results show that the position of a sodium atom cannot be determined from a study of the derived ethyl bodies. The result of Comstock and Kleeberg must therefore be interpreted as follows: In formanilide the proximity of the phenyl group renders the formyl group capable of reacting in its tautomeric or hydroxyl form, and, as a consequence, both the sodium and silver salts contain the metal attached to oxygen. The sodium, however, has a sufficient influence upon the nitrogen atom to render it capable of taking up methyl iodide so as to form the compound,  $C_6H_5\underset{CH_3\ \ I}{N} = \overset{H}{C} — ONa.$ Subsequently there is a separation of sodium iodide and the formation of the methyl formanilide $C_6H_5N(CH_3)—CHO$ or $C_6H_5\underline{NCH_3 = CHO}$. In the silver salt, on the other hand, the silver being much less positive, no addition to the nitrogen atom takes place, but methyl is substituted directly for silver and the imido ether, $C_6H_5N = CHOCH_3$, is formed. With suitable alkyl or acyl halides and alteration of conditions, it will probably be possible to procure both oxy and nitrogen derivatives from the silver salt.[1]

In continuing the work on formyl derivatives we have performed a few introductory experiments with formamide. Auwers[2] has shown that bodies for which a hydroxyl grouping may be assumed in most cases display a peculiar cryoscopic behavior, in that the molecular weight rapidly increases with increasing concentration of the solution. This is notably the case with formamide. In order to see if the same results hold good for derivatives of formanilide, we repeated the work with the mono- and diethyl derivatives. Formanilide is insoluble in benzene, and ethylene bromide. Monoethyl formamide gave rapidly increasing molecular weights, while diethyl formamide remained constant. Thus, if Auwers' conclusions are correct, the monoethyl derivative contains a hydroxyl group. We prepared sodium formamide and found it to be a substance of exceptional stability when dry. It does not react with ethyl iodide even on heating to 130° under pressure. When moist it breaks down into ammonia and sodium bicarbonate.[3]

An unstable silver salt can be precipitated from aqueous solutions of sodium salt. Both the sodium and silver salts give back free formamide on decomposition with dilute acids. The action of sodium on monoethyl formamide is slow, accompanied by an evolution of hydrogen ; with diethyl formamide no reaction takes place under twenty-four hours, and then decomposition, with the evolution of diethylamine, sets in.

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[1] Since the above was written, Wheeler and Boltwood (This JOURNAL, **18**, 381,) have shown that the silver salt of formanilide gives *n*-acyl derivatives with benzoyl chloride.

[2] Ztschr. phys. Chem., **15**, 33.

[3] On treatment with bromine it apparently decomposes completely into sodium bromide, nitrogen and carbon dioxide, at least at present we have not been able to isolate anything else, and no addition-product could be identified. We intend to investigate this curious reaction further. The action of acetyl chloride on sodium formamide has given an oil which with alkalies readily breaks down into ammonia, acetic and formic acids. The results will be published in detail in a subsequent paper.

EXPERIMENTAL PART.

Formylphenvlhydrazine, $C_6H_5NHNHCHO$.—To 200 grams of phenylhydrazine 200 grams of concentrated formic acid are added in one portion. Through the spontaneous generation of heat, the formate of the base which is at first formed, dissolves quickly, and after some hours standing, more quickly on cooling, the hydrazide crystallizes completely. After filtering and washing with ether and drying, the preparation is pure.

The very slight formation of formazyl hydrogen which accompanies the reaction is made apparent through the coloring of the liquid red, but not sufficient quantities of this substance were formed to be isolated.

Sodium Formylphenylhydrazine, $C_6H_5NHNNaCHO$.—In a glass-stoppered flask of some 250 cc. capacity, 10 grams of metallic sodium were dissolved in just enough absolute alcohol to form a clear solution. To this, when cold, were added 59 grams of powdered formylphenylhydrazine, and the flask tightly stoppered. The formylphenylhydrazine dissolved in sodium ethylate upon hard shaking, and a clear, slightly pinkish solution was formed. This solution was at once poured into a liter of ether, and allowed to stand in a cool place. Under these conditions no precipitation of sodium ethylate took place, while after a short time sodium formylphenylhydrazine began to crystallize in small bunches of felt-like needles. After twenty-four hours the crystallization was complete, and the salt was filtered, washed with ether and dried, care being taken that the entire process should be carried out in an atmosphere of dry hydrogen.

Sodium Determinations.

I. Some of the well washed sodium salt was dried quickly on a porous plate, transferred at once to a platinum crucible and weighed. The sodium was estimated as the sulphate.

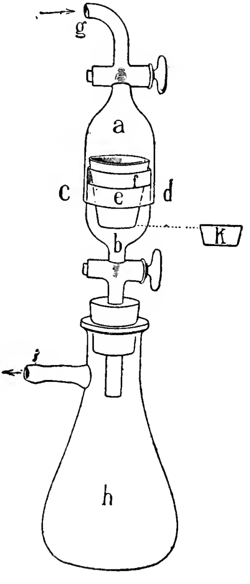
II. A small amount of the salt was filtered into a Gooch platinum crucible, which was so fixed in a glass tube that the salt could be filtered and dried to constant weight in an atmosphere of hydrogen.[1]

	Calculated for $C_7H_7N_2ONa$.	Found. I.	Found. II.
Na	14.55	14.40	14.23

The decomposition of the dry sodium formylphenylhydrazine in the air is very rapid. Aniline and phenylhydrazine are given off and sodium bicarbonate forms the principal part of the residue. When dissolved quickly in cold dilute hydrochloric acid, almost the theoretical amount of free formylphenylhydrazine may be recovered. A dry distillation of the body in an atmosphere of hydrogen gave aniline in large quantity.

Action of Ethyl Iodide on Formylphenylhydrazine.

To 2 grams of formylphenylhydrazine in a sealing-tube were added 2 grams of ethyl iodide and a small amount of absolute alcohol. The tube was sealed and allowed to stand over night. As no reaction took place, the tube was then heated for three hours at 100°. The solution on opening the tube was colored dark red. Both unchanged ethyl iodide and formylphenylhydrazine were recovered, also a small amount of dark colored decomposition-product. It is obvious, therefore,



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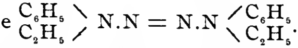
[1] The accompanying cut will illustrate the apparatus used. *a* and *b* are tubes with a ground joint at *c d*, their other ends being closed by well-fitting, glass stop-cocks. The crucible *e* is held in place by the rubber band *f*. A small piece of filter paper is placed in the bottom of the crucible, the crucible put in place, and the entire apparatus, except the wash-bottle and cork, filled with hydrogen and weighed. The tube *a* is then removed, the substance quickly washed into the crucible with ether and the tube replaced. Dry hydrogen is allowed to enter at *g*, and is sucked out at *i*. After the substance has been dried to constant weight, the crucible is taken out, the cap *k* placed over the perforated bottom, and the sodium estimated in the usual manner.

that ethyl iodide does not react upon free formylphenylhydrazine under these conditions.

Action of Ethyl Iodide on Sodium Formylphenylhydrazine in Solution.

The reaction may be carried out by dissolving the freshly crystallized and dried sodium salt in absolute alcohol, and then subjecting it to the action of ethyl iodide. A quicker method, and one which gives exactly the same results, is the following: To the alcoholic solution of sodium formylphenylhydrazine, prepared as directed on page 572, care being taken to have the formylphenylhydrazine present in slight excess, somewhat more than the calculated amount of ethyl iodide was added, and the tightly-stoppered bottle allowed to stand 48 hours with occasional shaking. The reaction was finished when the mixture was neutral. The contents of the bottle were then poured into a distilling-flask, the alcohol and small amount of unchanged ethyl iodide boiled off under diminished pressure and at a low temperature and the oily remainder, together with the precipitated sodium iodide was poured into water. A heavy, colorless oil separated and solidified on standing. After drying on a porous plate and recrystallizing from ether, long, needle-shaped crystals were obtained, which melted without decomposition at 78–79°. These were easily soluble in all the organic solvents except petroleum ether. The following results were obtained on analysis:

	Calculated for $C_9H_{12}N_2O$.	Found.
C	65.85	65.69
H	7.31	7.43
N	17.07	17.31

The analyses give results agreeing with those of a monoethylformylphenylhydrazine. To determine the position of the ethyl group, 9 grams of the body were reduced in a boiling mixture of 8 grams of metallic sodium and 75 grams of amyl alcohol. The flask in which the reduction was carried out was so connected with an inverted condenser containing warm water, and with wash-bottles, that all gases and low-boiling products of reduction were carried over and absorbed by dilute hydrochloric acid. After the reduction was completed, and the metallic sodium entirely dissolved, the contents of the flask were poured into a separating-funnel, and shaken out with dilute hydrochloric acid, and the acid solution evaporated to dryness. A dark-colored, solid hydrochloride remained. This was decomposed with alkali, extracted with ether and distilled, boiling between 215–232°. The composition of one of the constituents of this oil, which was evidently a mixture, was easily determined by oxidation in ethereal solution with yellow mercuric oxide. Colorless prismatic crystals were precipitated from the solution. They melted at 108° and in other ways proved identical with Fischer's[1] phenylethyltetrazone  $\genfrac{}{}{0pt}{}{C_6H_5}{C_2H_5}\rangle N.N = N.N \langle \genfrac{}{}{0pt}{}{C_6H_5}{C_2H_5}$. The oil must therefore be composed in part of *u*-ethylphenylhydrazine $C_6H_5N(C_2H_5).NH_2$. To determine the substance which was not acted on by the oxide, the etherial solution, from which the tetrazone had been filtered, was concentrated and the residue distilled with steam. A basic oil distilled over, and was easily identified as ethylaniline by means of its hydrochloride.

The contents of the wash-bottles, in which the gaseous reduction-products had been absorbed, were studied and found to contain nothing but ammonium chloride in small quantities. The products of the reduction were, therefore, unsymmetrical ethylphenylhydrazine, ethylaniline and ammonia. To have yielded these products, the constitution of the original body must have been $C_6H_5N(C_2H_5)NH—CHO$.

An attempt to ethylate α-ethylformylphenylhydrazine farther, by heating it for three hours at 100° under pressure with an excess of ethyl iodide, was without result, the body remaining unchanged.

Action of Ethyl Iodide and Sodium Ethylate on α-Ethylformylphenylhydrazine.

To a concentrated alcoholic solution of sodium ethylate containing 1 gram of metallic sodium, 7 grams of α-ethylformylphenylhydrazine and somewhat more than the calculated amount of ethyl iodide were added. The resulting clear

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[1] Ann. Chem. (Liebig), 199, 327.

solution was heated under pressure at 100° for 30 minutes, when a large amount of sodium iodide had separated. After evaporating off the alcohol and unchanged ethyl iodide, the residue was thrown into water, and the heavy oil which separated, after washing with dilute acids and alkalies, was taken up with ether, the ether evaporated and the residue fractioned. On the second fractioning a pale yellow and rather light oil was obtained, which boiled regularly at 139–140° under a pressure of 5 mm. The analysis gave the following results :

	Calculated for $C_{11}H_{16}N_2O$.	Found.
N	14.58	14.93

The nitrogen determination gives figures corresponding to those of diethylformylphenylhydrazine. To determine the position of the ethyl groups, the body was reduced with sodium and amyl alcohol, following the method used in the reduction of the monoethyl body. The products of reduction were found to be ethylamine and ethylaniline. The former body was found as the hydrochloride in the hydrochloric acid wash-bottles, and was identified as such and also by means of the isonitrile reaction.

The further fact that alcoholic potash was incapable of breaking off an ethyl group even when warmed with it showed that no imido ether could be present. Diethylformylphenylhydrazine does not react with phenylhydrazine either at ordinary temperatures or when heated several hours under pressure. Further, the body does not react with sodium.

Action of Ethyl Iodide on Dry Sodium Formylphenylhydrazine.

Dry sodium formylphenylhydrazine, suspended in dry ether, was enclosed in a glass-stoppered bottle with an amount of ethyl iodide, slightly in excess of that required by theory, and heated for three hours at 100° in an autoclave. By this time the liquid was light red in color, and sodium iodide had been formed. The contents of the flask were treated with water, the ethereal solution separated, dried with calcium chloride, and distilled. The remaining solid product crystallized out of ether or alcohol in large rhombohedrons having a melting-point of 106°, and soluble in all the ordinary solvents except petroleum ether and water. The yield is almost quantitative if sufficient care has been taken to free the sodium salt from alcohol. Otherwise varying amounts of the α-ethyl derivative will be formed, which will both decrease the yield and greatly increase the work of purification. The analyses gave the following results :

	Calculated for $C_9H_{12}N_2O$.	Found.
C	65.85	65.52
H	7.31	7.41
N	17.07	17.50

The results of the analyses show the body to be a mono-ethyl derivative of formylphenylhydrazine. As its melting-point and other physical properties easily distinguish it from the α-ethyl derivative, its constitution must be either (I) $C_6H_5NH—N(C_2H_5)—CHO$, or (II) $C_6H_5NH—N{=}CHOC_2H_5$. Its stability against saponification by either aqueous soda or alcoholic potash is evidence against the imido ether formula. A further proof of its constitution (I) is given by its reduction-products formed according to the previously described method. The bodies isolated were aniline and ethylamine. Several experiments were made to determine whether with ethyl iodide and an alcoholic solution of sodium formylphenylhydrazine any appreciable amount of the β-ethyl body was formed. Twenty-five per cent. of the entire quantity of the ethyl derivative formed was the largest yield, and this was obtained but once on heating the solution four hours at 100° under pressure. The average yield with varying temperature and duration of heating, as well as with different proportions of the reacting substances was only 5 to 7 per cent.

Action of Ethyl Iodide and Sodium Ethylate on β-Ethylformylphenylhydrazine.

The reaction was carried out in the same manner as described in the treatment of the α-ethyl body and afterwards also with a large excess of both ethyl iodide and sodium ethylate. The body remained entirely unchanged. Metallic sodium also did not react upon a xylene solution of the body when heated.

Action of Acetic Anhydride on Formylphenylhydrazine.

Formylphenylhydrazine (8 grams) were mixed with a slight excess of acetic anhydride. There was no reaction in the cold. Upon warming to 130°, there results a clear, thick syrup which does not crystallize. This syrup is perfectly soluble in water, soluble with great difficulty in moist ether, and insoluble in dry. On heating a mixture of formylphenylhydrazine and acetic anhydride in a distilling-flask, the reaction begins at 90° when acetic, but no formic, acid passes off. At 200° carbon monoxide is evolved, and when the pressure has been reduced to 35 mm. a thick oil distils, which partly solidifies on standing. The oily part is phenylisonitrile C_6H_5NC. The solid part was dried on a porous plate and recrystallized from benzene. Its melting-point, 126°, showed it to be symmetrical acetylphenylhydrazine. On treating the previously mentioned syrup with stannous chloride and tin, phenylhydrazine is formed. The body is, therefore, acetylformylphenylhydrazine, in which both the acid groups are attached to the same nitrogen atom. The acetyl group is, therefore, not attached to oxygen, and were formylphenylhydrazine a hydroxyl body, the result could only have been brought about by addition of acetic anhydride, and the subsequent splitting off of acetic acid. This supposition is not probable, however, in view of the fact that in sodium formylphenylhydrazine the sodium is attached to nitrogen. That the acetyl group is not attached to oxygen is also shown by the extreme difficulty with which acetylformylphenylhydrazine is decomposed by dilute cold caustic potash, months being necessary for its decomposition. The non-existence of oxyacetyl derivatives, however, does not absolutely prove the non-existence of a hydroxyl group.

Action of Benzoyl Chloride and Sodium Ethylate on Formylphenylhydrazine.

Metallic sodium (1.3 grams) was dissolved in absolute alcohol, and to the solution formylphenylhydrazine (8 grams) was added and mixed. On the addition of benzoyl chloride (8 grams) a reaction at once begins and is finished after two or three hours standing, when the odor of benzoyl chloride has disappeared. A white solid slowly separates. After adding a small amount of soda and shaking well, the solid is filtered off and macerated with dilute caustic soda. After washing and drying, it may be recrystallized from alcohol. A small amount of the body can be recovered from the soda by acidifying. Its melting-point, 174–175°, and appearance characterize it as dibenzoylphenylhydrazine. From the alcoholic solution, containing the more soluble material, crystals separate. These melt at 134–141°, and when slowly recrystallized, they can be shown to consist of a mixture of mono- and dibenzoylphenylhydrazine, the mono-benzoyl body melting at 169°.

The only possible explanation of the above reaction is that hydrochloric acid was split off, and this in turn saponified the formyl group. This action of benzoyl chloride on sodium formylphenylhydrazine is exactly a counterpart of the reaction of ethyl iodide on the same body, only in the latter case as no free formylphenylhydrazine is formed, the separation of sodium iodide and not of hydriodic acid took place.

Sodium Dibenzoylphenylhydrazine.

Dibenzoylphenylhydrazine, when dissolved in concentrated sodium ethylate, gives upon standing and dilution with ether, a white, felt-like, crystalline sodium salt, from which an acetyl derivative can be prepared by boiling with acetyl chloride. The analysis gave the following result:

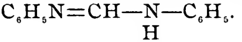
	Calculated for $C_{20}H_{15}N_2O_2Na$.	Found.
Na	6.81	7.01

Action of Chlorcarbonic Ether on Formanilide.

Wheeler having just published a paper[1] describing the action of chlorcarbonic ether on silver formanilide by which he obtained ethylisoformanilide and diphenylformamidine, it was of interest to discover if free formanilide would give the same results. The following experiment was therefore tried: To 10 grams of formanilide 9 grams of chlorcarbonic ether were added and warmed on the water-bath until solution took place and a slight evolution of carbon dioxide began. The liquid was then placed in a vacuum over lime until the odor

[1] This JOURNAL, **18**, 381.

of chlorcarbonic ether had disappeared, and the evolution of carbon dioxide ceased. The oil was then washed with water until the aqueous solution upon neutralizing with alkali gave no precipitation. It was then free from halogen and could not be made to solidify upon cooling with a freezing-mixture. After standing a day, it was then transferred to a distilling-flask and placed in a vacuum, but after slight warming it broke down, giving off a gas and changing to diphenylformamidine, thus showing conclusively, according to Wheeler,[1] thai it was ethylisoformanilide, $C_6H_5N{=}CHOC_2H_5$.

On neutralizing with alkali, the water with which the oil was washed gave a white crystalline precipitate, which melted at 134–135°, and thus showed itself to be diphenylformamidine,  $C_6H_5N{=}CH{-}\underset{H}{N}{-}C_6H_5$. The free formanilide therefore conforms to the silver salt in behavior.

Cryoscopic Molecular-Weight Determinations of Mono- and Diethylformamide.

Monoethylformamide.

Grams solvent (Benzene).	Grams substance.	Depression of freezing-point.	Concentration of solution. per cent.	Molecular weight found.
23.4823	0.0661	0.18°	0.28	76.6
"	0.1345	0.375	0.57	74.0
"	0.2807	0.635	1.2	93.0
"	0.4975	0.86	2.1	121.0

Diethylformamide.

Grams solvent (Benzene).	Grams substance.	Depression of freezing-point.	Concentration of solution. per cent.	Molecular weight found.
23.2	0.0622	0.14°	0.27	96.0
"	0.2318	0.57	0.98	86.0
"	0.5098	1.01	2.20	97.0
14.6	0.7471	2.45	5.10	106.0

Sodium Formamide.

Five grams of sodium were dissolved in a slight excess of absolute alcohol, and the solution diluted with dry ether almost to precipitation of the sodium ethylate. To this solution 10 grams of pure formamide were added and well shaken. A crystalline precipitate forms at once. After a few hours' standing the precipitation is complete and the solution may be filtered, washed with alcohol and ether, and dried in a

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[1] This JOURNAL, 18, 381.

vacuum over sulphuric acid. The analyses gave the following results:

	Calculated for H_2CONNa.	Found.
Na	34.32	33.42
N	20.89	20.91

Sodium formamide is stable when dry. On exposure to moist air, however, decomposition takes place, and ammonia is formed, together with sodium bicarbonate, and therefore these two decomposition-products in small amounts are always found in sodium formamide. When dissolved in cold, dilute hydrochloric acid, free formamide is regenerated. Investigations on the action of acyl chlorides and chlorcarbonic-ether on sodium formamide are in progress.

Silver Formamide.

Sodium formamide was dissolved in the smallest possible amount of ice-water, and to it was added the calculated amount of silver nitrate in concentrated aqueous solution. A silver-white, voluminous precipitate forms at once, which is very sensitive to light. When washed with alcohol and dried, it is a grayish powder, extremely soluble in water, and on decomposition with dilute acids, forms free formamide.

Action of Sodium on Formic Ether.

Pure formic ether was dissolved in absolute ether and subjected to the action of sodium in molecular proportions. The action was instantaneous, both hydrogen and carbon monoxide being given off, and in the proportion of one to two. An analysis of the remaining sodium compound proved it to be sodium ethylate. The reaction taking place may be represented as follows:

$$2HCOOC_2H_5 + 2Na = 2NaOCOC_2H_5 + H_2.$$

The sodium formic ether, which has but a momentary existence, then breaks down into sodium ethylate and carbon monoxide.

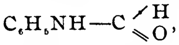
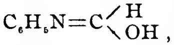
When amyl formate is substituted for the ethyl ether, the reaction is slower, and shows plainly the two phases mentioned above. The gas at first given off in the reaction proved to contain 74 per cent. of hydrogen, while, towards the end of the reaction, only carbon monoxide was evolved. This would show that the sodium compound of amyl formate is capable of a short existence. When ethyl iodide is allowed to take part in the reaction, some traces of a body which colors ferric chloride may be obtained.

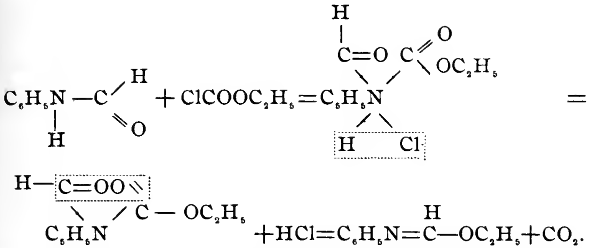
Sodium acting upon a mixture of ethyl formate and benzoyl chloride gave a brown sodium compound, apparently an addition-product, with a peculiar disagreeable odor. On standing, the body decomposed, giving off carbon monoxide, and leaving nothing but ethyl benzoate. Further investigations along this line will be undertaken.

Sodium in the presence of orthoformic ether was entirely indifferent.

Summary.

The experiments show that in sodium formylphenylhydrazine the sodium is attached to nitrogen, and that, therefore, no hydroxyl group is present. They do not furnish any evidence of the presence of the aldehyde group, so that, at the present state of our knowledge, we must conclude that it has neither, and a structural formula according to our present theories is not possible.

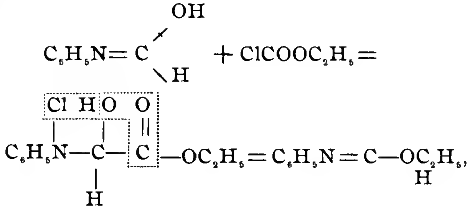
In the salts, at least, of formanilide, there is strong evidence of a hydroxyl grouping. Regarding the free body, we can say nothing, for acetic anhydride reacts only to give an N-acetyl body, and chlorcarbonic ether, in forming ethylisoformanilide, may do so quite as well from the body  $C_6H_5NH{-}C{\diagup H \atop \diagdown O}$, as from the body  $C_6H_5N{=}C{\diagup H \atop \diagdown OH}$, for the ethoxy grouping may have its derivation from the chlorcarbonic ether as well as from the formyl group. The following equations will make this clear :



$$\underset{\mathrm{H}}{\mathrm{C_6H_5N}}-\mathrm{C}\begin{smallmatrix}\mathrm{H}\\ \mathrm{O}\end{smallmatrix}+\mathrm{ClCOOC_2H_5}=\underset{\boxed{\mathrm{H}\quad\mathrm{Cl}}}{\overset{\overset{\mathrm{H}}{|}}{\mathrm{C{=}O}}\ \ \mathrm{C}\begin{smallmatrix}\mathrm{O}\\ \mathrm{OC_2H_5}\end{smallmatrix}\atop \mathrm{C_6H_5N}}=$$

$$\mathrm{H}-\boxed{\mathrm{C{=}OO}}\ {\atop \mathrm{C_6H_5N}}\ \mathrm{C-OC_2H_5}+\mathrm{HCl}=\mathrm{C_6H_5N}=\overset{\mathrm{H}}{\mathrm{C}}-\mathrm{OC_2H_5}+\mathrm{CO_2}.$$

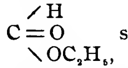
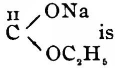
This splitting off of carbon dioxide and change of the hydrogen atom is parallel to that observed with dibasic acids on heating. It is certainly more readily comprehended than the other reaction :



$$\mathrm{C_6H_5N}=\mathrm{C}\begin{smallmatrix}\mathrm{OH}\\ \mathrm{H}\end{smallmatrix}+\mathrm{ClCOOC_2H_5}=$$

$$\mathrm{C_6H_5N}-\underset{\mathrm{H}}{\overset{\boxed{\mathrm{Cl\ H}}\,\mathrm{O}}{\mathrm{C}}}-\boxed{\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}}-\mathrm{OC_2H_5}=\mathrm{C_6H_5N}=\mathrm{C}\underset{\mathrm{H}}{-}\mathrm{OC_2H_5},$$

in which the transference of ethoxyl must be assumed. In formanilide, therefore, it seems as if the free body were differently constituted from its salts.

The same may be said of free formic ethers, for they react with sodium, and in the case of amyl ether at least, there is a sodium compound produced which is capable of a brief existence. However, the reaction with zinc ethyl and zinc methyl to form secondary alcohols seems to point towards the grouping  $\mathrm{C}\begin{smallmatrix}/\mathrm{H}\\ =\mathrm{O}\\ \backslash\mathrm{OC_2H_5}\end{smallmatrix}$, so that the free ether is probably constituted according to that formula, while the sodium salt probably contains natroxyl. The decomposition of the sodium salt into sodium ethylate and carbon monoxide is much more readily understood if the latter formula,  $\overset{\mathrm{II}}{\mathrm{C}}\begin{smallmatrix}\mathrm{ONa}\\ \mathrm{OC_2H_5}\end{smallmatrix}$ is accepted.

It seems, therefore, that in order to react with sodium the hydrogen atom must be next to a carbonyl group or present as hydroxyl. However, it must be remembered in this connection that diethylformylphenylhydrazine, in which there is a grouping similar to that in formic ether, does not react with sodium, even on heating, so that these results are apparently contradictory, unless we believe that only in the case of the ethyl ether is tautomerism possible. It may be that in the action of sodium on formic ether, alcohol is separated and the reaction take place as it is supposed to do with acetic ether, but then there seems to be no reason why the ortho-ether should not act in the same way. The result shows, therefore, that different bodies, such as phenylhydrazine, aniline, or hydrogen, when attached to formyl have a different influence on the possibility of producing the natroxyl group. Why such a difference exists we cannot at present state.

III.—NOTES ON NEW APPARATUS.

I. THE ELECTROLYSIS OF HYDROCHLORIC ACID.

By Geo. O. Higley and B. J. Howard.

The electrolysis of hydrochloric acid in the lecture room, so as to show equal volumes of the two gases, has long been a vexatious subject for experimenters. The latest modification of the old Hofmann apparatus, suggested by Lothar Meyer,[1] is complicated and difficult to operate, while its results, at least in our hands, have not been accurate.

The simple apparatus which we have constructed, gives most satisfactory results. The accuracy of its operation depends upon the fact that the gases traverse but a small layer of liquid, while they are collected and measured in separate tubes, distinct from the ones which contain the eletrodes. They can also be measured under diminished pressure by the use of a leveling-bulb attached to the stop-cock *c* (Figs. 1 and 2.).

In order to operate the apparatus the small cups holding the electrodes are filled with a solution consisting of equal parts of concentrated hydrochloric acid and water, which has

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[1] Ber. d. chem. Ges., **27**, 850.

been saturated with chlorine, and to which an excess of sodium chloride has been added just previous to the experiment, the stop-cock *d* being kept open. The remainder of the apparatus is then filled with chlorine water, and all stop-cocks being closed, the current is turned on for five or ten minutes. The apparatus is then opened, the leveling-bulb adjusted so that the liquid rises to *d*, then *d* is closed, and electrolysis carried on under increased or diminished pressure. The results in the former case are less satisfactory than in the latter. With increased pressure from 8.5 to 9.3 cc. of chlorine are collected for every 10 cc. of hydrogen, while with diminished pressure the results are very nearly in absolute accord with theory. The gases are finally measured under atmospheric pressure.

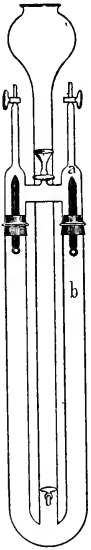

Fig. 1.
Front view.

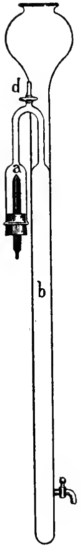

Fig. 2.
Side view.

2. DISTILLATION IN A VACUUM.

By P. C. Freer.

Distillation in a nearly absolute vacuum is now possible in every laboratory by the use of the Kahlbaum automatic mercury air-pump. One difficulty presents itself, where very low pressures are used, in the impossibility of obtaining tightly ground joints, so that more or less leakage has heretofore been unavoidable unless the expensive and complicated apparatus of Kahlbaum[1] is used. A simple receiver which answers the purpose admirably is shown in Fig. 3. *C* is a gutta-percha plug which is surrounded by a rubber ring, fitting tightly into a bell-mouthed cylinder, which is tubulated at the bottom of the widest part, and provided with a pinch-cock. The connection with the air-pump is made by *d*, and with the distilling-flask by *c*; *b* is a glass rod ground into a

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[1] Ber. d. chem. Ges., **28**, 392.

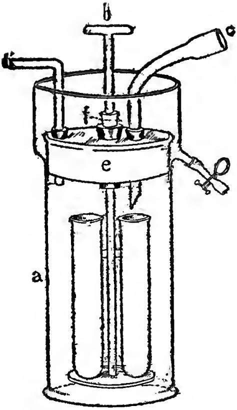

Fig. 3.

tube at *f* and carrying the receivers, the latter being fastened by rubber straps and a flat cork support below. The upper bell-mouth is filled with mercury after the apparatus is adjusted and before evacuating, so that a mercury valve is obtained for the entire receiver. The remaining joints for the thermometer and for the side tube in the distilling-flask can also be made into mercury valves by means of Kahlbaum's device. If desired, the tubulus of the distilling-flask can be bent so as to pass into the cap directly without an adapter and thus another joint be avoided. When distillation is over, the mercury is run off through the side tube in the cylinder. By the use of this apparatus and a Kahlbaum pump, vacua, which are practically perfect, can always be obtained without trouble.

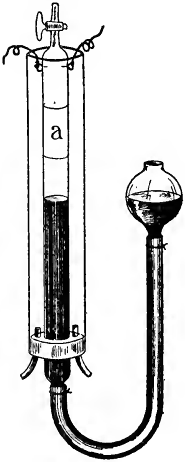

Fig. 4.

3. THE DEMONSTRATION THAT TWO VOLUMES OF HYDROGEN AND ONE VOLUME OF OXYGEN FORM TWO VOLUMES WATER VAPOR.

The apparatus of Hofmann is expensive and complicated, the explosion takes place under no very diminished pressure, and the eudiometer is often shattered. Besides, there is always an adjustment necessary after explosion so as to bring the mercury column back to its former height. The following modification is in my opinion a great improvement. It consists of a tube *a* (Fig. 4) with a stop-cock and platinum explosion-wires. The tube is jacketed and arranged so that it can be heated to 100°. The explosive mixture is admitted by means of the stop-cock without any trouble, and measured under atmospheric pressure. The explosion is carried on under diminished pressure, so that any possible shattering of the tube is avoided, and finally by adjusting the leveling-bulb, the original conditions can quickly be reestablished.

ANN ARBOR, MAY, 1896.

IV.—THE ACTION OF METALS ON NITRIC ACID.

3. THE REDUCTION OF NITRIC ACID BY SILVER.

BY GEO. O. HIGLEY AND W. E. DAVIS.

In a former paper[1] it was shown that while the products of reduction of nitric acid by copper and lead are identical, *viz.*, —nitrogen dioxide, trioxide, nitric oxide and nitrous oxide—there is a striking difference in the respective proportions of these gases produced by the action of these two metals under the same conditions of temperature and excess and concentration of acid. Not only does lead produce nitrous oxide from a much greater variety of concentrations of acid, but also the metal-equivalent of this gas is about ten times greater than is obtained with copper under the same conditions. A similar difference appears throughout the whole work. It seemed, therefore, as far as the work had been carried, that each metal had a specific effect on the acid, and therefore that the action is probably one of direct deoxidation rather than of reduction through the medium of nascent hydrogen. In order to throw further light upon this point, a series of determinations have been made with silver, according to the method described in the previous papers upon this subject.

The metal employed was in the form of foil and was chemically pure. The quantity used in each experiment was 500 mg. In order to minimize the effect of reduction-products, the volume of acid was so chosen that there was present in every determination at least ten times the quantity of acid necessary for solution of the metal.

The results obtained are given in a table which shows: 1, temperature during solution; 2, volume and specific gravity of acids; 3, weight of nitrogen trioxide obtained from titration of nitrosyl-sulphuric acid contained in the Winkler tube;

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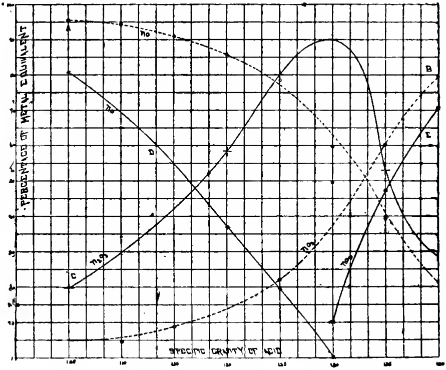
[1] This JOURNAL, **17**, 18.

No. of experiment.	Temperature.	Acid.		Winkler tube. Mgs. N_2O_3.	Nitrometer. Mgs. N_2O_3	Nitric dioxide. Mgs.	Equivalent in Mgs. Ag.	Nitric trioxide. Mgs.	Equivalent in Mgs Ag.	Nitric oxide, cc.	Equivalent in Mgs. Ag.	Percentage Ag. found.
		Volume.	Specific Gravity.									
1	80°	50.0	1.05	17.44	....	....	....	17.44	98.88	27.75	401.65	100.1
2	80°	18.0	1.10	10.35	....	....	....	10.35	58.68	30.33	439.8	99.6
3	70°	18.0	1.10	30.2	....	....	....	30.2	171.2	22.36	325.0	99.25
4	60°	15.0	1.15	31.82	....	....	....	31.82	180.4	20.94	303.63	97.0
5	60°	15.0	1.15	21.97	....	....	....	21.97	124.79	24.68	357.86	97.0
6	20°	13.0	1.20	51.04	52.81	....	....	51.04	289.6	12.8	185.7	97.0
7	30°	12.0	1.25	69.75	68.18	....	....	69.75	392.4	6.5	94.3	97.6
8	30°	12.0	1.25	87.85	104.93	41.38	97.41	70.77	401.3	....	....	99.62
9	60°	11.5	1.30	88.66	115.67	65.34	149.12	61.65	349.55	....	....	99.7
10	60°	11.5	1.30	88.67	97.96	22.00	48.6	79.38	450.4	....	....	99.8
11	65°	11.0	1.35	87.85	129.75	101.13	232.19	45.8	267.0	....	....	99.1
12	65°	11.0	1.35	88.66	130.48	101.13	232.19	46.84	265.68	....	....	99.7
13	70°	10.0	1.40	88.67	147.82	134.57	332.00	29.6	167.0	....	....	99.7
14	70°	10.0	1.40	88.67	152.37	154.19	357.09	24.97	141.6	....	....	99.7

4, weight of trioxide obtained from nitrometer analysis; 5, weights of dioxide and trioxide of nitrogen with equivalent weight of metal; 6, volume of nitric oxide with weight of equivalent metal; 7, percentage of metal accounted for. The results are also given in the form of curves with specific gravity of acid as abscissæ and percentage of metal-equivalent as ordinates.

An examination of the table reveals the fact that the most concordant results are obtained with the stronger acids. In determinations made with acids having a specific gravity less than 1.30, the decomposition of nitrogen dioxide by water into nitric acid and nitric oxide seems to be, to some extent, independent of conditions.

Neither nitrogen nor nitrous oxide is produced by the action of silver on nitric acid of any concentration with which work was done. This is in harmony with the results of Acworth and Armstrong,[1] who in three determinations made with silver and 1 : 2 acid, obtained only nitric oxide, the small amount of nitrogen collected being attributed to leakage of the apparatus. Montemartini[2] also states that as a result of the action of silver on 27.6 per cent. acid, only nitric oxide and nitrous acid are produced.



It now being definitely settled that nitrogen trioxide does

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[1] J. Chem. Soc., **32**, 71.

[2] Gaz. chim. ital., **22**, 405.

not exist in the gaseous condition,[1] curves *C*, *D*, and *E* are given principally for purposes of comparison with those previously published.

Curves *A* and *B* are obtained by adding to the metal equivalents of nitric oxide and nitrogen dioxide respectively, the amounts obtained by calculating nitrogen trioxide into nitric oxide and dioxide and then into metal.

Nitrogen dioxide is the principal reduction-product with concentrated acid, accounting for over 70 per cent. of the metal dissolved. In experiments with acids of greater degrees of dilution there is a rapid and somewhat regular decrease of this gas due to a greater tendency to decomposition with water into nitric oxide and nitric acid.

Curve *A*, that of nitric oxide, is the complement of that of the dioxide since it represents the decomposition-product of the latter.

Silver is less reactive than copper, since the latter, when dissolved in dilute nitric acid (sp. gr. 1.05–1.15), yields nitrous oxide, accounting for from five to fifteen per cent. of the metal employed, while the former produces no nitrous oxide under the same conditions.

V.—ON THE ESTERIFICATION OF HALOGEN-SUBSTITUTED ACETIC ACIDS.

SECOND PAPER.

BY D. M. LICHTY.

A preliminary investigation of the esterification of the chloracetic acids by ethyl alcohol, reported by me to this JOURNAL,[2] showed the desirability of conducting research in this direction, at a lower temperature than 154° (adopted at that time for the sake of making the results comparable with those of Menschutkin), and of making the initial period, for which the amount of etherification is determined, as short as possible.[3] The reasons for this alteration were two-fold: First, decomposition, to a greater or lesser extent, takes place with halogen-substituted acetic acids at the higher temperature (154°), while I have convinced myself that at 80° none is

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[1] Lunge and Porschnew: Ztschr. anorg. Chem., **7**, 209

[2] Vol. **17**, 27.

[3] *Ibid.*, 31.

observed, unless the period during which the heating continues is long.[1] Since, as will be shown by the data recorded in this paper, the influence of the halogens is very pronounced during the initial stages of esterification and comparatively small in the final, and since therefore, this decomposition toward the end of long periods is of no great moment, the latter temperature was selected for the thermostat. Secondly, short intervals for the determinations would enable me to construct a velocity-curve for the reactions which would give me a complete insight into the results, a thing not to be obtained if the first determination is made after one hour, after the method of Menschutkin. The alterations in the conditions have given most satisfactory results, and the curves demonstrate that the rate of esterification depends on two factors, one the mass-action of water *versus* alcohol, and the other the specific nature of the acid. The experimental part contains the results obtained with mono-, di- and trichloracetic acids.

Chloracetic Acids and Ethyl Alcohol.

The method used in these determinations is essentially identical with that reported in the previous paper, the only departures being those mentioned in the introduction. These consisted

(1) In selecting 80° as more suitable than 154°, secondary reactions being wholly absent at the former temperature, while at 100° and above there is more or less decomposition, as is shown by the development of gas or by carbonization.[2]

(2) In beginning the estimations at the end of one minute instead of one hour.

(3) In sealing into the tube with the alcohol and acid a piece of glass rod which served to break the alcohol bulb

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[1] This was observed with tribromacetic acid.

[2] A mixture of equivalent quantities of monochloracetic acid and alcohol, heated for several days in a sealed tube at 154°, yields chloracetic ester, glycolic ester, ethyl chloride in large quantities, glycolic acid and glycolides. The reaction is such as to make the degree of esterification finally reached, much less than it is at the end of an hour. This falling off is obviously due to the decomposition of the ester, and the formation of these secondary products. In the case of trichloracetic acid, the action of the water formed by the esterification probably changes the acid to chloroform and carbon dioxide, a reaction which is well known, and which would soon decrease the amount of free acid present, just as experiment shows to be the case.

after the tube and its contents had reached the temperature of the glycerin-bath, thus making it possible to have the temperature the same during the entire period of reaction, an important condition for the attainment of accurate results for the short interval determinations. The esterification was stopped by immersing the tubes in water at about 15° C., and the free acid remaining was determined by means of ammonia, approximately decinormal, with rosolic acid as indicator.

Monochloracetic Acid and Ethyl Alcohol.[1]

Time (Minutes).	Percentage of acid converted.					Mean.
1	1.6	1.67	1.72	1.83	2.07	1.78
3	5.10	5.15	5.08	5.06		5.09
5	8.34	7.50	6.77	6.99		7.65
10	12.34	12.87	13.19	14.24	14.27	13.38
15	18.25	19.62	18.18	16.57		18.15
20	22.82	23.51	22.09	20.91		22.23
25	25.09	27.54	25.07	26.05	25.83	25.91
30	28.35	28.85	28.66	28.67		28.63
45	35.59	35.75	36.16	36.36		35.96

Time (Hours).	Percentages.			Mean.
1	41.63	42.10	41.95	41.89
2	57.55		57.11	57.33
3	61.80		60.98	61.39
5	62.15		63.15	62.65
10	66.97		67.29	67.13
14½	67.48		67.42	67.45
24	67.48			67.48
42	66.41		69.23	67.82
48	68.03		68.02	68.12
157	68.68		68.62	68.65

Discussion of Data.—The initial rate of esterification is 1.78 per cent. During the first three minutes 5.09 per cent. of the acid is esterified, or 1.69 per cent. per minute; during the first five minutes 7.65 per cent., or 1.53 per cent. per minute. The rate continues to decrease as the time increases, and somewhere between 20 and 25 minutes it is numerically equal to the time in minutes. From this point the mean increment in percentage of acid esterified is less than one unit for each increment of one minute in time, becoming about two-thirds of a unit for a period of one hour; less than half a unit for a period of two hours, and but little more than one-third of a unit for

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[1] One molecule of each.

three hours. After this the esterification proceeds very slowly, reaching at the end of 24 hours a value about one unit below that obtained at the end of 157 hours, when the amount esterified is 68.65 per cent. The decrease in the rapidity of esterification is thus seen to be gradual, but quite regular. This is shown very clearly by means of the curve plotted by taking the time (in minutes) as abscissæ, and the percentages as ordinates. (See accompanying plates.) In general, the lack of concordance in the results obtained in several cases at the end of the same interval in different trials, during which the conditions were apparently the same, shows clearly that the course of the process is influenced by conditions which are not readily detected, and which are therefore very difficult to control.

Since the limit to which the esterification of a given acid and a given alcohol, mixed always in the same proportions, may be carried, is independent of the temperature[1] and of small differences in the sizes of the tubes,[2] its value for one acid and a given alcohol, at one temperature, may properly be compared with that for another acid and the same alcohol at another temperature, provided that the tubes in which the reactions take place do not differ much in size. Since the latter condition was fulfilled, we shall compare the limits obtained with acetic and monochloracetic acids respectively, and we find that they differ by about two units, being 66.57 per cent. for the former and 68.65 per cent. for the latter. The substitution of one atom of chlorine for hydrogen in acetic acid has then only a slight influence upon the limit of esterification.

The rate of esterification depending upon the temperature, it is not legitimate to compare the rate for the acid under consideration, obtained at 80°, with that for acetic acid, until the esterification of the latter is also investigated at the same temperature. The amount of each acid which is esterified in one hour at 154°, has been determined, the hour rate for acetic acid being 46.95 per cent. (Menschutkin[3]), and for monochloracetic acid 67.01 per cent.[4] The rate for the latter acid exceeds that of the former by 20 units, or about 43 per cent.

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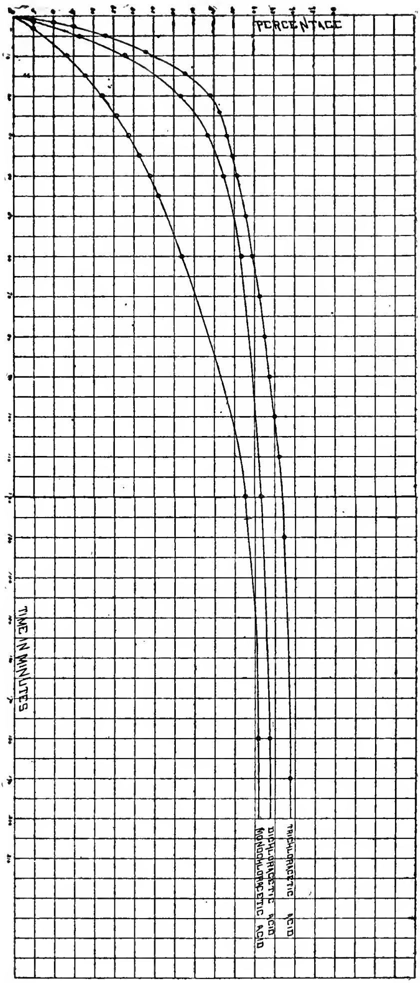
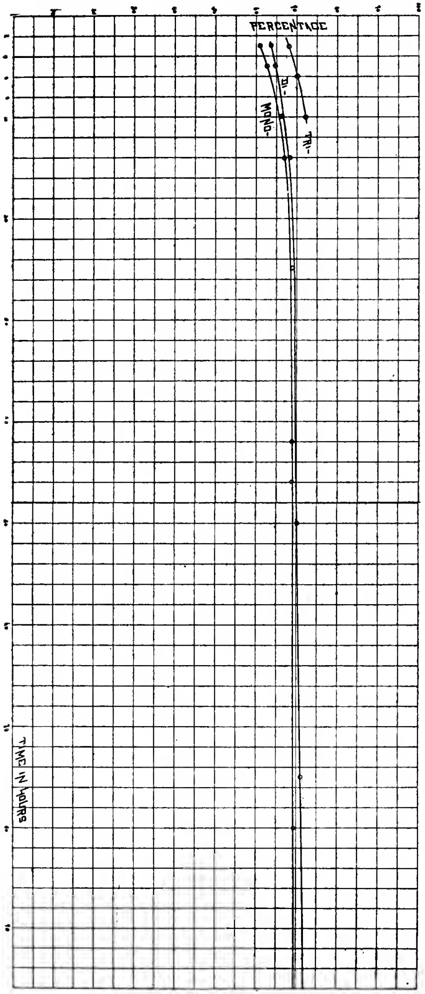
[1] Berthelot and Péan de Saint Gilles: Ann. chim. phys. [3], **68**, 234–238, (1863).

[2] *Ibid.*, **68**, 239–245.

[3] Ber. d. chem. Ges., **11**, 1507; Ann. chim. phys. [5], **20**, 305.

[4] This JOURNAL, **17**, 29.


PERCENTAGE
TIME IN MINUTES
TRICHLORACETIC ACID
DICHLORACETIC ACID
MONOCHLORACETIC ACID


PERCENTAGE
MONO-
DI-
TRI-
TIME IN HOURS

Esterification of Dichloracetic Acid and Alcohol.[1]

Time.	1m.	3.	5.	10.	15.	20.	30.	40.	1h.	2.	3.	5.	10.	20.	25.	50.	75.	100.	
Percentage.	5.83	10.09	19.87	30.60	37.17	43.73	47.62	51.79	56.87	60.94	60.08	65.28	66.19	67.73	67.94	70.34	69.10	71.42	74.07
	3.48	11.00	19.57	26.17	34.35	44.96	47.76		58.50	58.79	59.88	64.46	66.53		68.92	67.08	69.30	71.02	67.86
	5.61	11.70	17.16	32.71	34.27	46.62	49.64		57.34	58.60	68.34	63.43	67.87			67.36	69.20	70.51	69.07
	4.27	13.54	12.36	32.85	40.49	40.96	46.74		57.31	65.10	67.26	66.00					74.10	70.84	74.89
	4.08	10.31	12.57	29.30	35.46	40.08			57.07	65.80									
	4.10		17.36	28.31		39.75			55.75	64.84									
			16.52	25.12					54.55										
			16.35	24.70					54.43										
				23.95					56.55										
Mean.	4.56	11.33	16.48	28.08	35.53	42.68	47.94	51.79	56.49	62.34	63.88	64.95	66.84	67.73	68.43	68.29	70.42	70.95	71.22

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[1] One molecule of each.

Could a comparison be made between minute rates the percentage increase in the rate due to the substitution of one atom of chlorine would without doubt be much higher than the above.

Discussion of Data.—An inspection of the mean values in the foregoing table shows that the initial rate of esterification of dichloractic acid and ordinary alcohol is 4.56 per cent., which is 2.56 times the initial rate for monochloacetic acid; that the mean amount of acid esterified during the first three minutes is 11.33 per cent., or 3.77 per cent. per minute, and that the amount esterified during the first five minutes reaches 16.48 per cent., or 3.3 per cent. per minute. The reaction at first subsides a little more gradually than in the case of monochloracetic acid, but from the end of the twenty-minute period more rapidly. (See curve.) The mean increment becomes at the end of the first hour nearly one unit per minute, numerical equality between the time in minutes and the per cent. esterified being reached some minutes before the end of the first hour. For the first two hours the mean increment is about one-half of a unit per minute; for the first three hours a little over one-third of a unit per minute. The mean of four determinations of the limit of esterification is 71.22 per cent., which is less than three units above the limit for monochloracetic acid.

Trichloracetic Acid and Ethyl Alcohol.[1]

Time.	1m.	2.	3.	4.	5.	7.	9.
Percentages.	10.29	15.78	18.49	22.17	23.32	28.41	32.68
	9.70	15.02	19.36	22.89	23.28	27.67	31.91
				22.91	23.15		
				22.43	23.21		
Mean	9.99	15.40	18.92	22.60	23.24	28.04	32.30
Time.	11.	13.	15.	17.	20.	23.	26.
Percentages.	36.83	39.84	43.16	45.84	49.15	50.18	52.16
	36.08	39.57	42.81	45.98	48.91	50.74	51.51
Mean	36.45	39.70	42.98	45.91	49.03	50.46	51.83
Time.	30.	35.	40.	50.	60.	70.	80.
Percentages.	53.19	54.44	55.79	57.49	59.42	61.35	62.26
	52.86	54.32	55.23	57.23	59.23	60.82	62.34
Mean	53.02	54.38	55.51	57.36	59.39	61.08	62.30

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[1] One molecule of each.

Time.	90.	100.	110.	120.	130.	160.	190.
Percentages.	63.71	64.29	65.32	66.24	67.17	67.42	68.36
	63.39	64.37	65.56	66.13	66.64	67.66	68.15
Mean	63.55	64.33	65.44	66.18	66.90	67.54	68.25

Time.	4h.	6.	10.
Percentages.	68.41	70.15	72.26
	68.52	70.02	72.41
Mean	68.46	70.08	72.23

Discussion of Data.—For this acid the initial rate is 9.99 per cent., which is 5.61 times the rate for monochloracetic acid, and 2.19 times that for dichloracetic acid. During the first three minutes the amount of acid esterified reaches 18.92 per cent., a mean rate of 6.31 per cent. per minute, while at the end of the first five minutes the amount esterified is 23.24 per cent., a mean rate of 4.65 per cent. per minute. Numerical equality between the time in minutes and the percentage esterified is reached between one hour and one hour and ten minutes. The mean increment becomes about half a unit per minute at the end of two hours and ten minutes, and about one third of a unit at the end of three hours. There is therefore great similarity between the courses taken by the esterification of di- and trichloracetic acids respectively. This fact is still more plainly shown by the graphic representation of the reactions.

The amount esterified at the end of ten hours was found to be 72.33 per cent., and since this value is but two units above that for a period of six hours, it cannot be far from the limit, which therefore is only a few units higher than that of dichloracetic acid.

Summary.	Mono-.	Di-.	Tri-.
Initial rate,	1.78	4.56	9.99
Mean rate duting first 3 minutes,	1.69	3.77	6.31
" " " " 5 "	1.53	3.30	4.65
Time at end of which there is numerical equality between number of minutes and percentage,	Between 20 & 25	Between 50 & 60	Between 60 & 70

Summary.	Mono-.	Di-.	Tri-.
Time elapsed when the mean increment in percentage per minute is one-half of a unit,	About 110 m	About 130	About 130
Time elapsed when the mean increment in percentage per minute is one-third of a unit,	A little over 3 h	Between 3 and 4h	About 3h 10m
Limit,	68.65	71.22	About 74.00

The limit of esterification of acetic acid is 66.57 per cent. The substitution of chlorine for hydrogen in acetic acid increases the limit of esterification by 2.08 units, or 3.1 per cent. over 66.57 for one atom of chlorine; by 4.65 units, or nearly 7 per cent. for two atoms, and possibly by 7.5 units, or nearly 11.5 per cent. for three atoms. On the other hand, the initial rate of dichloracetic acid is 2.56 times that of monochloracetic acid, an increase of 156 per cent.; while the initial rate of trichloracetic acid is 5.61 times that of monochloracetic, an increase of 461 per cent. The influence of chlorine is therefore very much greater upon the rate of esterification than upon the limit.

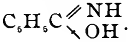
An examination of the curves plotted by taking the time in minutes as abscissæ and the percentages as ordinates shows that those for tri- and dichloracetic acids, respectively, have nearly the same slope, being very steep for the first 20 minutes, and then rapidly turning away from the axis of ordinates toward parallelism with the axis of abscissæ. The curve for monochloracetic acid has at first a slope which is entirely different from that for the other two, lying about midway between the two axes between ten and fifteen minutes; *i. e.*, making with each an angle of 45°. At twenty minutes the angle with the axis of abscissæ is perceptibly smaller than that with the other axis, and the curve continues from this point to turn gradually towards parallelism to the axis of abscissæ. Beyond three hours the three curves are nearly parallel to each other. It seems probable that the mathematical equations for these are very different, but I shall not attempt to derive any mathematical expressions until more data have been obtained by investigating other halogen-substituted acids in the same manner.

This research will be next extended to acetic acid, the bromacetic acids and the halogen propionic acids; to the first to enable us to determine more completely the influence of the halogens upon the initial rate of esterification; to the second to learn whether the courses of the esterification of these acids are similar to those of the corresponding chlorine compounds and what relation exists between the influence of the two halogens; to the third to discover the influence of the position of the halogen.

The author wishes to take this opportunity to thank Mr. S. R. Cook and Mr. Firman Thompson for valuable assistance in this work.

VI.—THE CONSTITUTION OF THE ACID AMIDES.

By Arthur Lachman.

It is only during the last few years that doubts have arisen as to the correctness of the commonly accepted acid amide formula. In 1890 Tafel and Enoch[1] showed that when ethyl iodide acted on benzamide silver, benzimidoethyl ether was obtained; and as they could not isolate any other compound excepting benzamide from the silver salt, they concluded that possibly benzamide was constituted according to the tautomeric hydroxy formula  $C_6H_5C\begin{smallmatrix}/\!\!/NH\\ \backslash OH\end{smallmatrix}$. Two years later, Pinner[2] found that benzimido acetate,  $C_6H_5C\begin{smallmatrix}/\!\!/NH\\ \backslash O.COCH_3\end{smallmatrix}$, is identical with acetyl benzamide, $C_6H_5CONH.COCH_3$; he did not attempt to show which of the structures in question really characterized the substance. Auwers,[3] during a series of molecular-weight determinations in benzene solution, discovered that a number of amides behaved cryoscopically as if they contained hydroxyl groups. And lastly, Cohen[4] has attempted to prove the hydroxy formula by showing, on the one hand, that some amides add sodium ethylate, and, on the other, that the fact that certain amides do not form silver salts may be explained upon a *stereochemical* basis, if we adopt the formula he advocates.

None of this work, however, can be said to have in any way

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[1] Ber. d. chem. Ges., **23**, 103.

[2] *Ibid.*, **25**, 1435.

[3] Ztschr. phys. Chem., **12**, 644; **15**, 33.

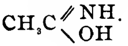
[4] Brit. Assoc. Reports, 1894, 625; J. Chem. Soc., **69**, 19.

contributed to a definite solution of the problem of the amide configuration. We now know that salts may have a different structure from their mother substances—*e. g.*, acetoacetic ether and its salts,—and that an entering alkyl group does not take the place of the metal atom which leaves the molecule. Pinner's result has no special significance until it is shown that benzimido acetate does or does not suffer a rearrangement of its atoms during the process of formation. The results of the cryoscopic investigation are by no means binding, as Auwers himself takes care to emphasize. And as to Cohen's work, the addition of sodium ethylate has as little to do with the hydroxy formula as the absence or presence of silver salts suffices to establish a geometric isomerism. The evidence for the hydroxy formula is rather weak, therefore, as far as the work is concerned that is supposed to establish it.

Previous to a more detailed study of the literature of the subject, however, I am totally unprepared to find that there was scarcely better reason for clinging to the ordinary formula; in fact, the newer had somewhat the advantage.

This assertion is easily substantiated. First of all, it will be best to discuss methods of formation. Manifestly, methods of formation cannot be drawn into the argument, because we judge the steps of a reaction by the resulting products; the *reaction itself* escapes our ken, and is merely an *ex post facto* deduction. Therefore the analogy of formation of, *e. g.*, acetamide and dimethylacetamide is valueless, for with acetamide the reaction may possibly have gone a step farther:

$$\mathrm{CH_3COCl} \rightarrow \mathrm{CH_3CON(CH_3)_2}\,;\ \mathrm{CH_3COCl} \rightarrow \mathrm{CH_3CONH_2} \rightarrow$$

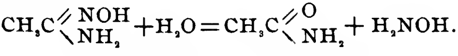


$$\mathrm{CH_3C}\begin{matrix} /\!\!/\,\mathrm{NH} \\ \diagdown\,\mathrm{OH} \end{matrix}.$$

The *chemical* analogy of acetamide and dimethyl acetamide is at present an unproved assumption.

And so we may rule out the following cases:

1. Amidoximes,[1] on warming with water, give amines and hydroxylamine:



$$\mathrm{CH_3C}\begin{matrix} /\!\!/\,\mathrm{NOH} \\ \diagdown\,\mathrm{NH_2} \end{matrix} + \mathrm{H_2O} = \mathrm{CH_3C}\begin{matrix} /\!\!/\,\mathrm{O} \\ \diagdown\,\mathrm{NH_2} \end{matrix} + \mathrm{H_2NOH}.$$

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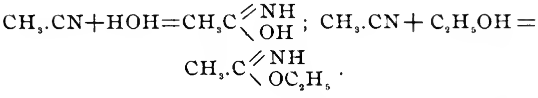
[1] C. F. Nordmann: Ber. d. chem. Ges., **17**, 2746.

2. Imidoether hydrochlorates[1] when heated, yield amides and alkyl chlorides :

$$CH_3CCl\begin{matrix}\diagup\!\!\diagup NH_2\\ \diagdown OC_4H_9\end{matrix} = CH_3C\begin{matrix}\diagup\!\!\diagup NH_2\\ \diagdown O\end{matrix} + C_4H_9Cl.$$

3. Nitriles and water yield amides[2] in exactly the manner in which nitriles and alcohols yield imidoethers :



$$CH_3.CN + HOH = CH_3C\begin{matrix}\diagup\!\!\diagup NH\\ \diagdown OH\end{matrix} ;\ CH_3.CN + C_2H_5OH = CH_3.C\begin{matrix}\diagup\!\!\diagup NH\\ \diagdown OC_2H_5\end{matrix} .$$

It will be noticed that a rigid interpretation of these reactions would lead to contradictory results, as *two* point to the old, and *one* to the new formula.

On examining the *reactions* of the amides, one fact stands out prominently, *viz. : that the amides differ widely in behavior and that they cannot be considered as one group of compounds.* On the contrary they seem to fall into *two* classes, and the behavior of these two classes *is on the whole what would be expected of compounds having the normal amide structure on the one hand, and the imido hydroxy structure on the other.*

Behavior of the Amides Towards Reagents.

All the amides seem to form condensation-products with aldehydes. In these condensations the amides all react like *secondary* bases ; one molecule of aldehyde unites with two of amide. But as some of the amides which condense as secondary bases behave in every other respect as normal amides, this reaction cannot be used in favor of the imide formula. The structure of these condensation-products has been deduced from that of the amides, and as heretofore the latter have all been formulated alike, the condensation-products have been uniformly represented as follows :

$$R.CH<\begin{matrix}NH.CO.R.\\ NH.CO.R.\end{matrix}$$

The action of hydroxylamine on amides has been examined only in a fragmentary manner. According to Janny,[3]

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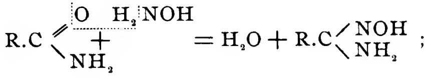
[1] Pinner and Klein : *Ibid.*, **10**, 1892 : Lengfeld and Stieglitz : This JOURNAL, **17**, 105.

[2] Pinner and Klein : Ber. d. chem. Ges., **10**, 1896.

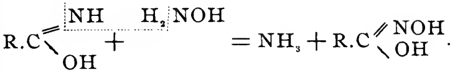
[3] Ber. d. chem. Ges., **15**, 2783.

urea does not react. C. Hoffman[1] has shown that both acetamide and benzamide are acted upon, yielding, however, not amidoximes, as would be expected of normal amides,



$$R.C\genfrac{}{}{0pt}{}{\diagup\!\!\diagup O}{\diagdown NH_2} + H_2NOH = H_2O + R.C\genfrac{}{}{0pt}{}{\diagup NOH}{\diagdown NH_2}\ ;$$

but hydroxamic acids, as might be expected of imido acids:



$$R.C\genfrac{}{}{0pt}{}{\diagup\!\!\diagup NH}{\diagdown OH} + H_2NOH = NH_3 + R.C\genfrac{}{}{0pt}{}{\diagup\!\!\diagup NOH}{\diagdown OH}.$$

The indifference of the amides toward nitrous acid does not rest upon any detailed investigation. As far as it goes, it is best interpreted by the imido formula; the absence of nitroso derivatives might be brought under Baeyer's[2] rule, that imides are the more indifferent to nitrous acid, the less basic the molecule.

Nitric acid, under proper conditions, converts some amides into nitramides (benzene sulfonamide,[3] urea,[4] urethane, guanidine,[5] dicyandiamide[6] and biuret); whereas acetamide[7] and benzamide are decomposed. The formation of primary nitramides would require the amide formula

$$R.CONH_2 + HONO_2 = R.CONH.NO_2 + H_2O,$$

and the amides which are decomposed by nitric acid probably have some other structure.

The action of phosphorus pentachloride on amines was made the subject of a very extensive investigation by Wallach.[8] Wallach concluded that in *all cases* the oxygen atom is first substituted by two chlorine atoms, thus:

$$R.CONH_2 + PCl_5 = R.CCl_2NH_2 + POCl_3,$$

forming amide chlorides, and that these amide chlorides then lose hydrochloric acid, forming imide chlorides, nitriles, or certain complicated bases. The fact that amide chlorides, even under the most favorable conditions, were extremely un-

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[1] *Ibid.*, **22**, 1854.

[2] *Ibid.*, **21**, 682.

[3] Hinsberg: *Ibid.*, **25**, 1195.

[4] Ann. Chem. (Liebig), **288**, 266.

[5] *Ibid.*, **270**, 1.

[6] Ber. d. chem. Gss., **27**, 1520.

[7] Rec. trav. chim., **2**, 95.

[8] Ann. Chem. (Liebig), **184**, 1; **214**, 193.

stable substances, lent color to the general applicability of this interpretation. But a closer examination of Wallach's results leads to a somewhat different interpretation. Only in *one case*—oxamethane—was Wallach able to isolate the amide chloride of an unsubstituted amide. Actamide, mono-, di-, trichloracetamide and benzamide, on treatment with pentachloride gives off hydrochloric acid *immediately*. The unbiassed consideration of these results led to the conclusion that oxamethane *really has the amide formula*, whereas acetamide, benzamide, etc., react *as if they contain hydroxyl groups*.

The action of acid anhydrides and chlorides has been investigated on many sides. Acetic anhydride, for instance, seems to react with all amides alike; acetamide[1] yields diacetamide, benzamide,[2] acetyl benzamide, urethane,[3] acetyl urethane, etc. Acetyl chloride, however, is selective in its action. Acetamide and benzamide[4] do not form acetyl derivatives with it, but suffer the loss of water in part; the same is true of the action of benzoyl chloride[5] on these amides. On the other hand, urea, urethane, oxamethane, are more or less readily converted into acetyl or benzoyl bodies by the corresponding chlorides. Thus we find here the same *difference* in behavior between certain groups of amides referred to above; those amides whose other properties render it probable that they contain the normal $CONH_2$ group giving the normal amine reaction with acid chlorides; the other amides behaving abnormally, though for no evident reason. This difference between the amides is not due to the greater basicity of those which form derivatives with acid residues; for urethane is much less basic than benzamide, and oxamethane has no basic properties whatsoever.

An exception to this grouping of the amides seems to occur when carbonyl chloride is employed. E. Schmidt[6] obtained from this reagent and acetamide a substance which has the composition of diacetylurea, and from benzamide the corresponding compound. But these substances are not the main products of the reaction at any time, being in fact formed only

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[1] Heutschel: Ber. d. chem. Ges., **23**, 2395.

[2] Pinner: *Ibid.*, **25**, 1435.

[3] M'Creath: *Ibid.*, **8**, 1182.

[4] Pinner: *Loc. cit.*

[5] Pictet: Ber. d. chem. Ges., **23**, 3015.

[6] J. prakt. chem. [2], **5**, 63.

at high temperatures; in the cold not a trace of these compounds is formed; and the conclusion is evident that these diacylureas result from the interaction of the primary products. In addition, Schmidt's compounds have properties decidedly at variance with those of other acylated ureas. Thus, they are insoluble in alkalies; on warming the mixture, they break down into amides and carbonic acid, and not into urea and the corresponding acid. For the present, then, we cannot take this reaction into consideration.

The above brief summary of what work has been done on the constitution of the amides, shows clearly, 1st, that the question is in a very unsettled state; and 2nd, that what little evidence there is, points to a division of the amides into two groups, one containing oxamethane, the various carbamides, benzenesulfonamide; the other embracing acetamide, benzamide, and some of their substitution-products. The first group possessing the customary amide formula; the second having the imido hydroxy structure, and being the long-sought, ever-at-hand imido acids.

The present investigation unfortunately can bring almost nothing to the solution of the problem. The amides are characterized by a hopeless indifference to all the reactions that suggest themselves for study. But this very incapacity for reaction is in itself of interest, and in the importance attaching to the question, a brief outline of the work as planned and a short summary of the large number of experiments carried out, may find their excuse for publication.

The object in view was to find out if the classification arrived at above would stand closer scrutiny. For this purpose I subjected first the oxygen atom of the amides to a comparative examination, then the nitrogen atom, and finally the double linking that exists in the second group. In the first series the reagents employed were phosphorus trichloride, hydroxylamine, and alcoholic hydrochloric acid; in the second, nitrous acid and ethyl iodide; in the third, hydrocyanic acid and ethyl hypochlorite.

Summary of Experimental Work.

1. *Phosphorus Trichloride.*—Acetamide gives only a red,

sticky mass, containing chlorine, phosphorous acid, ammonia and acetamide. Hydrochloric acid is given off, but no acetonitrile or acetyl chloride whatsoever is formed.

Benzamide, warmed with the trichloride, gives 75 per cent. of benzonitrile. Ten grams of each were warmed on the water-bath for fifteen minutes, the mixture poured into water, extracted with ether, the ether-extract dried and fractioned. 6.1 grams benzonitrile were obtained, boiling between 187° and 189°; a trace of benzamide remained in the distilling flask.

Urethane is destroyed by excess of the trichloride; if less than one molecular equivalent be used, a portion of the urethane remains unchanged.

Oxamethane was boiled on the water-bath with excess of the trichloride for three hours, and suffered no change.

2. *Hydroxylamine.*—Urea and urethane have stood both with free hydroxylamine and its hydrochlorate for over two months, without showing any sign of reaction.

Methyl acetamide gives a color reaction with ferric chloride after standing several days with the hydrochlorate; but even after seven weeks the solution reduced Fehling's solution very strongly.

With diethylacetamide the same results were obtained, though in this case the experiments were varied by employing free hydroxylamine, and also a large excess of alkali. On boiling a solution of diethylacetamide and the hydrochlorate a constant evolution of gas takes place; after about about thirty hours the solution no longer reduces, but decomposition has gone on to such an extent that I have been unable to isolate the compound formed in sufficient quantity to determine whether it is ethenyl diethylamidoxime or ethenyl hydroxamic acid. However, diethylamine is to be found in the solution, and the reaction has therefore probably resulted in the formation of the latter substance.

Oxamethane has been shown to be attacked at the carbethoxyl group by free hydroxylamine.[1] On prolonged boiling with hydrochlorate the same result would appear to take

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[1] Schiff and Monschli: Ann. Chem. (Liebig), 288, 314.

place, for ammonium oxalate was obtained in considerable quantity.

3. *Alcoholic Hydrochloric Acid.*—This was an attempt to introduce ethyl into the possible hydroxyl group in acetamide and benzamide. After standing in the ice-chest for a month, a large amount of acetic and benzoic esters were obtained. There was no trace of the imido ethers.

4. *Nitrous Acid.*—This was employed in aqueous and in benzene solution, in the presence or absence of mineral acids. Scarcely any difference could be noticed in the behavior of benzamide, urethane, urea, and oxamethane, acetamide reacted markedly slower, but began to be attacked after ten minutes.

5. *Ethyl Iodide.*—The amides were heated with excess of this substance to 100°, for periods ranging from a day to a week. Formamide, acetamide and urea were decomposed after several days heating; urethane and oxamethane were decomposed much more slowly; in none of these cases was an addition-product obtained. Methylacetamide combines with ethyl iodide rapidly; the compound is very deliquescent and forms colorless needles. (Found, 55.3 per cent. iodine; calculated, 55.2 per cent.) Methylurethane was decomposed.

6. *Hydrocyanic Acid.*—Acetamide, acetanilide, benzaldiacetamide and benzamide were dissolved in anhydrous hydrocyanic acid, if necessary, with addition of ether or alcohol. After standing six days no sign of action could be perceived.

7. *Ethyl Hypochlorite.*—This reagent dissolves in an aqueous solution of acetamide, but the commencement of warm weather prevented any detailed investigation.

Conclusion.

There is only one result to be discussed, *viz.*, that obtained with phosphorus trichloride. It is quite impossible that in the above experiment benzamide passed into benzonitrile through the amide-chloride stage. If any intermediate product whatever was formed, it must have been the imide chloride. But the reaction may have simply been a splitting off of water. The proof that the latter explanation will not hold is furnished by the indifference of oxamethane to the same reagent. Oxamethane loses water and passes into a nitrile just as readily as benzamide; and if the action of phosphorus trichloride is merely dehydrating, the reactions in both cases would have been identical. Now oxamethane has been shown to form an amide chloride, and this amide formula explains its indifference to the trichloride. Benzamide, on the other hand, reacts in the same manner with both chlorides, forms as first product not an amide, but an imide chloride, and therefore contains a hydroxyl group.

Wallach's theory of the action of phosphorus pentachloride on the amides is thus no longer universally applicable; though unfortunately there are at present no means of determining where its limits lie.

Further discussion at this point would be profitless. I would merely emphasize that the conclusions arrived at during the consideration of the literature are by no means final. Thus the action of hydroxylamine, be it as it may, is certainly not to be regarded as a direct metathesis, as is shown, *e. g.*, by the fact that with esters[1] it yields hydroxamic acid, and not alkylhydroxamic acids; the phenomena of addition play an important part in its reactions. The same may be true of the action of acetyl chloride, as has been suggested by Pictet.[2]

Mr. F. M. Tschirner carried out a large number of the experiments mentioned, and I should like to avail myself of this opportunity of thanking him for his earnest and valuable assistance.

CHROMIC HYDROXIDE IN PRECIPITATION.

By Harrison E. Patten.

The action of a number of metallic hydroxides in carrying down other substances in precipitation is well established. This "adhesion," as Ostwald calls it, is not limited to gelatinous precipitates, but is noted in the case of some crystalline precipitates, especially barium sulphate, which carries down iron, aluminum, etc., and is very hard to purify when once combined with them.

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[1] Jeanrenand: Ber. d. chem. Ges., **22**, 1272.

[2] Ber. d. chem. Ges., **23**, 3011.

A. V. E. Young[1] has shown that the reaction between alum and potassium hydroxide is not to be represented by the usually accepted equation, but that the distribution of the constituents of the system about the line of solubility is a function of the temperature, volume and total mass of constituents. V. J. Hall has also shown in "A Study of Ferric Hydroxide in Precipitation," that ferric hydroxide under certain conditions decomposes potassium sulphate, carrying the sulphur trioxide into precipitation, leaving the potassium and thus manifesting true chemical action. A. Recoura[2] has shown that chromium forms complex acids, bases and salts, in which chromium, in combination with varying amounts of the radicle SO_4, acts as a complex radicle. The radicle SO_4 in these complex acids, bases and salts, gives no precipitate with barium chloride, and their existence is also proved by their heat of neutralization.

Working along the lines suggested above, I have investigated chromic hydroxide to ascertain the amount of disturbance under definite conditions; further, to answer, if possible, the question whether the chromium or the sulphuric acid, or the combined action of the two, causes this disturbance, and whether there is a recombination of the elements to form a new compound, or merely a mechanical action.

Solutions as described below were used in the work:

1. For the chromium solution 29.4815 grams pure potassium dichromate was reduced with strong hydrochloric acid, excess of acid driven off, and made up to one liter at 22°. This solution contained 0.02819 gram chlorine, and 0.01607 gram chromium sesquioxide per cc. It was unnecessary to determine the potassium.

2. A dilute solution of potassium hydroxide, standardized by titration against oxalic acid and gravimetrically. It contained 0.0350 gram potassium hydroxide per cc.

3. A dilute solution of sulphuric acid, standardized against the potassium hydroxide solution. It contained 0.04206 gram sulphuric acid per cc.

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[1] A Thermochemical Analysis of the Reaction Between Alum and Potassium Hydrate. This JOURNAL, 8, 23.

[2] Recherches sur le Sulfate chromique, ses Transformations et les Acides complexes qui en derivent. Ann. chim. phys. [7], 4, (1895).

As a preliminary step, I determined the amount of potassium hydroxide required for exact precipitation of chromium in Solution 1. 24.86 cc. Solution 1 required 23.68 cc. potassium hydroxide for exact precipitation.

General Method.

The filtrates were analyzed and the percentage of each constituent found deducted from the percentage of the total introduced. The difference gives the percentage of the constituent in the precipitate, which may not be analyzed directly since washing, or diluting the solution in which the precipitate is formed, changes its composition.

The first point to determine is whether or not sulphur trioxide, chlorine, or potassium oxide is carried down by chromium when precipitated by six molecules of potassium hydroxide in the presence of four molecules of potassium sulphate, according to the equation:

$$Cr_2Cl_6 + 6KOH + 4K_2SO_4 = Cr_2(OH)_6 + 6KCl + 4K_2SO_4.$$

Blank Experiment.—First, a blank determination of the sulphur trioxide was made, the system being made up according to the above equation, leaving out the chromium chloride. 112.4 cc. potassium hydroxide and 46.5 cc. sulphuric acid, sufficient to form six molecules of potassium hydroxide and form four molecules of potassium sulphate were made up to 500 cc. at 22°, four portions were drawn off with a 50 cc. pipette and the sulphur trioxide determined as barium sulphate:

$$\left.\begin{array}{l}\text{A. } 0.1596 \text{ gram} \\ \text{B. } 0.1602 \text{ gram}\end{array}\right\} SO_3 \text{ blank for ``total.''}$$

$$\left.\begin{array}{l}\text{C. } 0.1610 \text{ gram} \\ \text{D. } 0.1604 \text{ gram}\end{array}\right\} SO_3 \text{ blank for ``filtrate.''}$$

Series I—Experiment F.

I took 112.4 cc. potassium hydroxide and 46.5 cc. sulphuric acid—sufficient to form six molecules of potassium hydroxide and four molecules of potassium sulphate—added 50 cc. chromium solution from the pipette and made up to 500 cc. at 22°. This I let stand about twenty minutes, shook well, and drew off four 50 cc. portions of precipitate and filtrate mixed, de-

Table—Series I.

Exp.	KOH.	Total Cr_2O_3.	Filtrate Cr_2O_3.	Precipitate Cr_2O_3.	Total SO_3.	Filtrate SO_3.	Precipitate SO_3.	Total K_2O.	Filtrate K_2O.	Precipitate K_2O.	Total Cl.	Filtrate Cl.	Precipitate Cl.	Percentage total.		Percent'ge composition of precipitate.	
														Cr_2O_3 in precipitate.	SO_3 in prec.	Cr_2O_3	SO_3.
A	50 cc. Cr_2Cl_6 3	.0804	.0732	.0072	.1596	.1610 .1603 } *.1606*	.0000	.3031 .3025 } *.3028*	.3047 .3034 } *.3040*	.0000	.1447 .1443 } *.1445*	.1437 .1454 } *.1445*	.0000	8.99	0.00	100.00	0.00
B	3½	.0785	.0575	.0210	.1596	.1606 .1595 } *.1600*	.0000	....	....	....	....	. . .	....	26.75	0.00	100.00	0.00
C	4	.0808	.0507	.0301	.1593	.1594 .1595 } *.1594*	.0000	.3266	.3270	.0000	.1425 .1435 } *.1430*	.1432 .1429 } *.1430*	.0000	37.59	0.00	100.00	0.00
D	4½	.0808	.0432	.0366	.1590 .1593	.1592 .1595 } *.1593*	.0000	....	....	....	....	....	...	45.70	0.00	100.00	0.00
E	5	.0803	.0255	.0548	.1592	.1531 .1543 } *.1537*	**.0055**	.3543	.3553	.0000	.1423 .1422 } *.1422*	.1427 .1426 } *.1426*	.0000	68.47	3.45	90.84	9.16
F	6	.0800	.0000	.0800	.1565 .1563	.1591 .1602 } *.1596*	.0000	.3678 .3675 } *.3676*	.3703 .3700 } *.3701*	.0000	.1436 .1418 } *.1424*	.1427 .1426 } *.1426*	.0000	100.00	0.00	100.00	0.00
G	8	.0803	.0000	.0803	.1594	.1605	.0000	.4732	.4738	.0000	.1422 .1420 } *.1421*	.1448 .1448 } *.1448*	.0000	100.00	0.00	100.00	0.00
Blank	No Cr_2Cl_6 6	....	....	....	.1599 .1602 } *.1601*	.1610 .1604 } *.1607*	....	...	....	....	....	....	....	. .	....	....	....
Blank	50 cc. Cr_2Cl_6 No KOH	.0800 .0800	....	....	....	....	....	....	....	....	.1416 .1418 } *.1417*	....	....	....	....	...	....

livered each portion in a clean, dry beaker and set aside to be analyzed as "totals" for potassium oxide, chlorine, sulphur trioxide and chromium sesquioxide. The remainder of the precipitate and solution were thrown upon a dry filter, the filtrate brought back to 22° and five 50 cc. portions drawn off with the pipette and analyzed as "filtrates" for potassium oxide, chlorine, sulphur trioxide and chromium sesquioxide. Not a trace of chromium was found in the filtrate.

The "totals" were redissolved by hydrochloric acid, reprecipitated by ammonium hydroxide, boiled, and the precipitate washed till no trace of sulphur trioxide could be detected by the barium chloride test. The filtrate and washings were then evaporated to convenient bulk and the sulphur trioxide determined as barium sulphate.

In determining potassium oxide the method is the same as for sulphur trioxide, save that the precipitate of chromium hydroxide is washed till no residue is obtained by evaporating the washings on platinum foil. The washings are then evaporated to dryness, the ammonium salts volatilized, the residue extracted with water, filtered and evaporated, and ignited in a platinum dish as potassium sulphate. The chlorine is determined in the presence of chromium, the totals being redissolved by nitric acid and the chlorine precipitated and weighed as silver chloride. A wash-water containing 25 cc. strong nitric acid and 0.1 gram silver nitrate per liter is found adequate to remove all chromium from the silver chloride.

The "filtrates" were analyzed in the same manner as the "totals." It was assumed that re-solution with hydrochloric acid and reprecipitation by ammonium hydroxide liberates any constituents carried down in the precipitation with potassium hydroxide. This assumption was shown to be correct by comparison of the blank experiment with the totals, and by the constancy of the totals in different experiments.

If, now, the same quantities of sulphur trioxide, chlorine and potassium oxide are found in "totals" and "filtrates," the equation

$$Cr_2Cl_6 + 6KOH + 4K_2SO_4 = Cr_2(OH)_6 + 6KCl + 4K_2SO_4$$

completely represents the reaction. In Series I, Section F, the results confirm this equation.

Experiments E, D, C, B, A, and G were made, using, respectively five, four and one-half, four, three and one-half, three, and eight molecules of potassium hydroxide to precipitate the chromium. Each experiment was made with the same quantity of chromium chloride and potassium sulphate present as in Experiment F, the method of analysis being the same throughout. Throughout this series adhesion is only noted once, in Experiment E, where five molecules of potassium hydroxide were used, 3.4 per cent. of the total sulphur trioxide introduced is carried into precipitation, the potassium oxide and chlorine remaining undisturbed. (See Section E, Series I.)

Series II.

A series of experiments under the same conditions as Series I, but with no sulphate present, was attempted; the object being to ascertain if chlorine or potassium oxide was disturbed in absence of sulphate.

A system containing three molecules of potassium hydroxide to one of chromium chloride was made up, and on standing three hours the precipitate first formed completely redissolved, showing that time is a factor in the action.

Another system identical with the above was then made up, "totals" drawn off as quickly as possible, and the remaining solution and precipitate thrown upon a dry filter. But the precipitate could not be filtered out by the closest quantitative filter-paper. Further, the "totals" did not settle clear, but redissolved on standing.

A system containing four molecules of potassium hydroxide to one of chromium chloride was made up. The precipitate first formed would not settle, could not be filtered and redissolved completely in four hours. This clear solution was then brought to $-1\frac{1}{2}°$, but no precipitate separated.

A system containing five molecules of potassium hydroxide to one of chromium chloride was made up. The precipitate formed would not settle, could not be filtered and redissolved completely in twelve hours. This clear solution was boiled, but gave no precipitate ; it was cooled to —1°, but no precipitate separated.

A system containing six molecules of potassium hydroxide to one of chromium chloride was made up. It gave a definite precipitate ; the results are :

Cl in "total"	0.1432	Cr_2O_3 in "total"	0.0802
Cl in "filtrate"	0.1430	Cr_2O_3 in "filtrate"	0.0000
Cl in "precipitate"	0.0002	Cr_2O_3 in "precipitate"	0.0802

showing no chlorine carried down.

Throughout Series I, with potassium sulphate present, the fractional precipitations gave definite precipitates, filtering clear and settling clear. In contrast to this, note the resolution and failure to filter and settle of the precipitates formed in absence of sulphate in Series II. Further, the "totals" and "filtrates" of all the experiments of Series I had to stand from three to six days before they were examined. In no case did the "totals" redissolve, but on the contrary, in one or two instances, the "filtrates" gave more precipitate.

To make sure that this precipitation in presence of sulphate was due to the sulphate, I added magnesium sulphate to a redissolved system containing five molecules of potassium hydroxide to one of chromium chloride. The precipitation was immediate and almost complete ; the precipitate was then redissolved on the filter with dilute hydrochloric acid and tested for magnesium with the aid of sodium phosphate. Not the slightest trace was shown. Calcium, sodium, and ammonium sulphates were respectively added to the redissolved system, and in every case precipitation was instantaneous and nearly complete. Chlorides and nitrates do not precipitate chromium from this solution.[1]

Series III.

To investigate this action further, the amount of chromium chloride and potassium hydroxide was tripled, but the sulphate left the same as in Series I. Experiments were made with three, four, five, and six molecules of potassium

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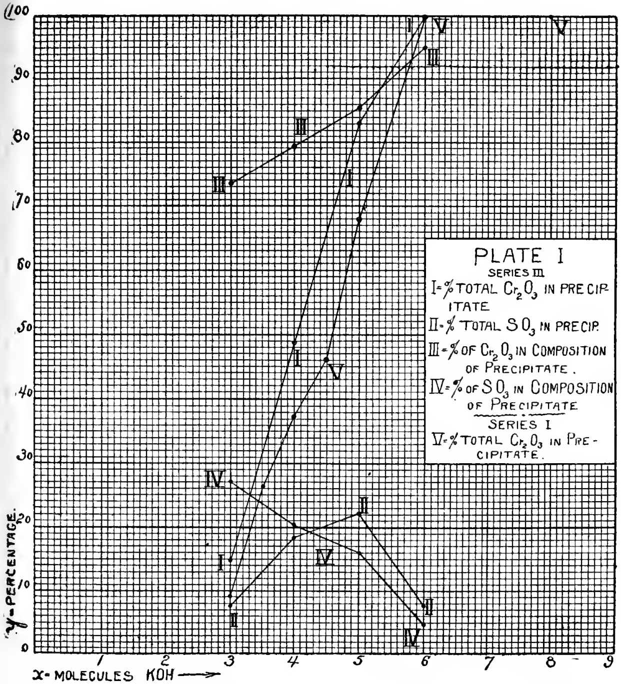
[1] Potassium chloride, magnesium chloride, potassium nitrate and barium nitrate were used.

hydroxide present, the method of analysis being the same as in Series I. (For results see Sections N, O, P, Q, Series III, in table, also Plate I.)

Reliabitity of Results.—The differences upon which my conclusions are based are not great, varying from 3.4 to 22.1 per cent. of the total quantity of sulphur trioxide introduced. But since the difference between duplicate "totals" and "filtrates" in no case exceeds 1 per cent. of the total quantity measured, and in most cases is below 0.5 per cent., their significance cannot be questioned.



Discussion.—Series I shows sulphur trioxide carried down only at five molecules, and then only 3.45 per cent. of the

Table—Series III.

Exp.	KOH.	Total Cr_2O_3.	Filtrate Cr_2O_3.	Precipitate Cr_2O_3.	Total SO_3.	Filtrate SO_3.	Precipitate SO_3.	Total K_2O.	Filtrate K_2O.	Precipitate K_2O.	Total Cl.	Filtrate Cl.	Precipitate Cl.	Percentage total.		Percentage composition of precipitate.	
														Cr_2O_3 in precipitate.	SO_3 in precipitate.	Cr_2O_3.	SO_3.
N	3(50 cc. Cr_2Cl_6) $(3)_3$	.2349	.2016	.0333	.1616	.1495 .1490 } .1493	.0123	....	....	....	.4276	.4279 .4293 } .4286	.0000	14.18	7.61	73.01	26.99
O	$(4)_3$	.2357	.1202	.1155	.1617	.1320 .1321 } .1321	.0 29	....	....	....	....	....	....	49.00	18.30	79.60	20.40
P	$(5)_3$	.2350	.0396	.1954	.1619	.1262 .1258 } .1260	.0359	.6730	.6743	.0000	.4302	.4281	.0021	83.15	22.17	84.48	15.52
Q	$(6)_3$	.2353	.0000	.2353	.1615	.1494 .1502 } .1498	.0117	.7466	.7455	.0011	....	....	....	100.00	7.24	95.27	4.73
R	Blank	....	....	....	.1601	....	....	....	...	....	....	....	....	....	....	...	....
S	50 cc. Cr_2Cl_6 Blank	....	....	....	....	....	....	....	....	....	{ .1426 .1433 } .1430	× 3 } =.4290	....	...	....	....	....

total quantity. It was considered doubtful if much reliance should be placed on such slight evidence. But the results of Series II showed conclusively that the sulphate entered into the reaction, since no precipitation takes place at two, three, four or five molecules of potassium hydroxide in absence of potassium sulphate. The qualitative work, varying the base in combination as 'sulphate, shows that this effect is due to the sulphur trioxide and not to the base.

These facts may be taken as an answer to the first question, "Whether the chromium, or sulphuric acid, or the combined action of the two, causes this disturbance." They show conclusively that the action between the chromium sesquioxide and sulphur trioxide is mutual.

The results of Series III show still more conclusively that there is a recombination of the elements to form a new compound. If this "adhesion" were indeed mechanical in its nature, we should find the action proportional to the amount of precipitate present. But Plate I, Curve II, shows practically the same quantity of sulphur trioxide carried down at three molecules as at six, while there is approximately seven times as much precipitate present at six as at three. Also, at five molecules there is over three times as much sulphur trioxide carried down as at six molecules, and at four molecules a trifle less than at five molecules. The action then is truly chemical in its nature.

Considering Series I, II and III, we see that this disturbance affects only the sulphur trioxide, the chlorine and potassium remaining in solution. The sulphur trioxide then must be united directly to the chromium, or possibly a complex compound is formed.

From these considerations it is beyond question that the sulphur trioxide enters into the reaction at three, three and one-half, four, four and one-half, and possibly at six molecules of potassium hydroxide, as well as at five molecules in Series I. (See table.) But the analyses do not show sulphur trioxide carried down at these points. In explanation of this, I conceive that there is a primary and a secondary action here. First the formation of the new combination of sulphur trioxide and chromium sesquioxide, then a splitting up of the compound by water. The power of water to break up these compounds composed of aluminum sesquioxide and sulphur trioxide, iron sesquioxide and sulphur trioxide, and chromium sesquioxide and sulphur trioxide is well recognized, and it was to overcome the obstacle which this fact presents, that the method of differences has been used throughout this work. The chromium sesquioxide having been thus precipitated by agency of the sulphur trioxide, it appears to remain in precipitation.

Having thus considered the disturbance at complete and fractional precipitation, I purpose at a later date to investigate the action at fractional re-solution of chromium hydroxide by excess of potassium hydroxide.

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AN EMPIRICAL RELATION BETWEEN MELTING-POINT AND CRITICAL TEMPERATURE.

BY F. W. CLARKE.

Although many papers have been written upon relations between boiling-point and critical temperature, the melting-points of substances, at least in this connection, seem to have been little considered. And yet a glance at the subject will indicate its importance. For any substance the limits of the solid state are the absolute zero and the melting-point; while the extreme limits of the liquid condition are the melting-point and the critical temperature. A comparison of these values, therefore, will give for each substance the relative thermometric lengths of the two states of matter, and the results obtained, although empirical, have very decided interest. Unfortunately many of the compounds of which the critical temperature is known, have never had their melting-points determined, and hence the available data are very meagre.

Representing the ordinary melting-points by t and the critical temperatures by T, the relation between them, on the absolute scale, is best represented by the formula

$$\frac{T+273}{t+273}.$$

For the following substances this ratio is very nearly = 2, the data, except when otherwise stated, being taken from Landolt and Börnstein's tables. Fractions of degrees less than 0.5 are neglected.

	t. Degrees.	*T.* Degrees.	*Ratio.*
Nitrogen,	—214.0	—146.0	2.18
Carbonic oxide,	—207.0	—139.5	2.02
Argon,[1]	—190.0	—121.0	1.83
Methane,[1]	—186.0	— 82.0	2.19
Hydrochloric acid,	—112.5	+ 52.0	2.02
Hydrogen sulphide,	— 86.0	+100.0	2.00
Ammonia,	— 75.0	+130.0	2.03
Benzene,	+ 3.0	+288.5	2.04
Acetic acid,	+ 17.5	+322.0	2.05

In other words, for these nine substances the absolute melting-point is very nearly, if not exactly, one half the absolute critical temperature, and the thermometric lengths of the solid and liquid states are approximately equal. Assuming the errors of observation to be evenly distributed in each case between the two temperature factors, we may average the latter and so compare the mean values with those actually recorded. The results are as follows:

	FOUND.		AVERAGE.	
	t. Degrees.	*T.* Degrees.	*t.* Degrees.	*T.* Degrees.
N_2,	—214.0	—146.0	—211.0	—149.0
CO,	—207.0	—139.5	—206.5	—140.0
A,	—190.0	—221.0	—195.0	—117.0
CH_4,	—186.0	— 82.0	—180.0	— 87.0
HCl,	—112.5	+ 52.0	—111.0	+ 51.0
H_2S,	— 86.0	+100.0	— 85.5	+100.5
NH_3,	— 75.0	+130.0	— 73.0	+128.0
C_6H_6,	+ 3.0	+288.5	+ 4.0	+287.0
$C_2H_4O_2$,	+ 17.5	+322.0	+ 22.0	+317.9

When we consider the uncertainty of some of the measurements, the agreement is certainly very close.

This simple relation, however, is not general. In all I have examined the data for about thirty substances, and no universal rule appears. There are, nevertheless, other regularities apparent which connect certain allied substances with one another, and two such groups I subjoin:

[1] Olszewski.

	t. Degrees.	*T.* Degrees.	Ratio.
C_2N_2,	− 34.5	+124.0	1.67
N_2O_4,	− 10.0	+171.0	1.64
NO,	−167.0	− 93.5	1.70
N_2O,	− 99.0	+ 35.5	1.77

These compounds run closely together and are alike in being gaseous compounds of nitrogen. The next group contains five aromatic bodies.

	t. Degrees.	*T.* Degrees.	Ratio.
o-Xylene,	−45.0[1]	+358.0[2]	2.77
m-Xylene,	−53.0	+346.0[2]	2.81
C_6H_5Cl,	−40.0	+361.0	2.78
C_6H_5Br,	−30.5[1]	+397.0[3]	2.75
C_6H_5I,	−28.5[1]	+448.0[3]	2.94

Here again there is an essential identity of ratio with related constitution, a fact which suggests that the method of discussion applied to larger masses of data, is likely to give information of considerable theoretical value.

For most of the other substances which I have considered, the ratio ranges between 2.2 and 3.0. For carbon dioxide its value is only 1.41, for ether it is 3.06. In the latter case the thermometric lengths of the solid and liquid states, therefore, are as one to two. A few bodies only give ratios higher than three. These are—besides ether—

CS_2,	3.36
PCl_3,	3.47
Alcohol,	3.59

Other values are :

Br_2,	2.17	H_2O,	2.34
Cl_2	2.44	$SnCl_4$,	2.47
SO_2,	2.22	$CHCl_3$,	2.62
CCl_4,	2.25	C_2H_4,	2.75

Paraxylene gives the ratio 2.14, varying widely from its isomers.

Concerning the quantity of heat necessary to raise a body from absolute zero to the melting-point, and then from the

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[1] v. Schneider. [2] Altschul.

[3] Young : Theoretically determined.

melting-point to the critical temperature, the data are altogether wanting; but the ratio between those two quantities would certainly be significant. For the regularities which I have here pointed out I have no theoretical explanation to offer. If, however, they serve to stimulate the determination of other low temperature melting-points for compounds of which the critical temperatures are known, this paper will have served a useful purpose. The relations which are already apparent cannot be meaningless, and others must be discoverable.

ALUMINUM ALCOHOLATES.

By H. W. Hillyer.

In work preparatory to using the method of Wislicenus and Kaufmann[1] for reduction in neutral solutions by use of amalgamated aluminum, observations were made which have led to the work of which this is a preliminary notice.

According to these authors amalgamated aluminum does not act on absolute alcohol, but can be preserved for use covered by absolute alcohol. By following their directions, we obtained an amalgam having properties like those described, but in order to avoid all contact with the air and the degeneration of the amalgam, caused by its coating over with hydroxide, instead of an aqueous solution of mercuric chloride, a solution of mercuric chloride in absolute alcohol was used. When this was brought in contact with chipped aluminum an evolution of gas soon commenced, and instead of ceasing, as might have been expected, when the little water in the alcohol had been decomposed, it increased in rapidity and the alcohol became heated nearly or quite to the boiling-point.

The action gradually became more moderate, but continued so long that on cooling the whole gelatinized. The most probable reaction is $Al + 3C_2H_6O = Al(OC_2H_5)_3 + 3H$.

Knowing from the work of Gladstone and Tribe that aluminum alcoholates, in contrast to all other known alcoholates, can be distilled under diminished pressure, an attempt was made to distill the product obtained. After the

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[1] Ber. d. chem. Ges., 28, 1323.

alcohol, a gray distillate of mercury came over under 20 mm. pressure, and then white fumes and an oily liquid solidifying in the receiver. The distillate contains much aluminum, but is greatly contaminated with mercury.

In the attempt to avoid the presence of mercury, which made the purification difficult, other salts soluble in alcohol were tried, but with no special result until, on using fuming stannic chloride, a reaction took place similar to that with the mercuric chloride. In this case spongy tin separated, a gas was rapidly evolved, and the liquid became quite hot. In both cases an application of external heat starts a new evolution of gas. When no more gas was evolved the alcohol was distilled off and the residue in the retort subjected to distillation under diminished pressure. A distillate was obtained rich in aluminum and containing no tin. Determinations of the amount of aluminum seemed to indicate that the substance might be aluminum hydroxydiethylate, $Al(OC_2H_5)_2OH$, but work on the action of ethyl alcohol was temporarily interrupted at this point. Two experiments with methyl alcohol gave good evolution of gas, but no substance could be distilled under a diminished pressure. The retort after distilling off the alcohol contained apparently nothing but aluminum oxide or hydroxide. Work with normal propyl alcohol has resulted in showing definitely that aluminum tripropylate is formed under similar conditions. An account of this work will soon be published in detail.

Isopropyl and amyl alcohol also react on aluminum in the presence of aluminum chloride and the spongy tin formed by its action on stannic chloride in solution in these alcohols. The aluminum is dissolved to give a solution from which it is precipitated, probably as hydroxide, on addition of water or by mere action of the moisture of the air.

The writer desires to reserve for the present the privilege of investigating the action of aluminum on alcohols to which mercuric chloride and stannic chloride have been added, and to investigate the action of sulphur dioxide and of hydrogen sulphide on the alcoholates thus formed.

ORGANIC CHEMICAL LABORATORY,
UNIVERSITY OF WISCONSIN.
May 29, 1896.

THE CONDUCTIVITY OF SOLUTIONS OF ACETYLENE IN WATER.

BY HARRY C. JONES.

The comparatively high conductivity of water solutions of acetylene, found by Mr. Allen and myself,[1] has always been more or less unintelligible to us, and has led me, in the absence of Mr. Allen, to repeat the work. The results obtained showed acetylene to be very considerably dissociated in water, yet these solutions did not show an acid reaction with litmus. The gas used in the first work was prepared from cuprous acetylide furnished us by Prof. Keiser, being liberated from the compound by warming with a solution of potassium cyanide, as he directed. The acetylene solutions were tested for all the impurities which we thought could possibly be formed in the reaction, and found to be free from them all, as far as could be determined by chemical methods.

It occurred to me later that in the reaction between potassium cyanide and cuprous acetylide, a small quantity of ammonia might be generated by the action of the potassium hydroxide formed during the reaction on the excess of potassium cyanide. To test this point, it was decided to prepare cuprous acetylide perfectly free from ammonia, to liberate the acetylene by means of hydrochloric acid, and then to determine whether the acetylene thus prepared had the same conductivity as that obtained by the method suggested by Keiser. The results of this work showed that the acetylene prepared as described above and carefully washed to remove all traces of hodrochloric acid, had very slight, if any conducting power. As we stated in our first paper, the error in standardizing the solutions is necessarily large, but taking this into account, I was never able to obtain a solution of acetylene prepared by the action of hydrochloric acid on the acetylide, which had a molecular conductivity greater than unity.

Some very carefully washed cuprous acetylide was then treated with a solution of potassium cyanide, exactly as in the earlier work, to determine whether ammonia was liberated in the reaction in quantities sufficient to be detected by chemical

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[1] This JOURNAL, 18, 375.

means. The reagents, which were applicable under the conditions, failed to show the presence of ammonia. To my surprise, the acetylene solutions thus obtained, conducted to about the same extent as those prepared from the acetylide by means of hydrochloric acid.

This fact, together with the results first obtained, can, so far as I can see, be explained in only one way; that the acetylide from which the acetylene first studied was obtained, must have contained a small amount of some volatile impurity, probably ammonia, whose presence was not suspected by us, and which therefore escaped detection.

CHEMICAL LABORATORY, JOHNS HOPKINS UNIVERSITY.
May, 1896.

REVIEWS AND REPORTS.

WATER SUPPLY. (CONSIDERED PRINCIPALLY FROM A SANITARY STANDPOINT). BY WILLIAM P. MASON, Professor of Chemistry, Rensselaer Polytechnic Institute. John Wiley & Sons: New York. Chapman & Hall: London. 1896.

Within a moderate compass Professor Mason has brought together for readers of English a large amount of valuable information in regard to water as used by man for drinking and other domestic purposes.

The form in which this information is presented is likely to make the book useful to the general public, as well as to those whose duties more particularly call for knowledge in regard to the important question of water supply for large or considerable populations.

So extensive and important is this question, however, that perhaps no two writers would agree exactly as to the scope to be given a work of the kind under review, or the precise division and order of presentation of the subject.

The chapter devoted to a discussion of the relation of polluted drinking water to disease is calculated to impress the reader with the strength of the evidence in regard to this relation. One point perhaps it would have been well to explain a little more fully. It is said, on p. 96: "No weight should be attached to the argument, so often advanced by the individual householder, that he and his family 'have used the water without evil result for fifty years.' A single family is too small a collection of units upon which to base any estimate touching the question at issue." It ought to be made clear to any one using such an argument, the force of which not unnaturally appears to the average mind very great, that a well so situated as to admit of organic polluting material reaching it may *actually* yield water which produces no disease for fifty years, and yet suddenly become most dangerous from the presence in its immediate neighborhood of a single case of typhoid fever, imported perhaps from a distance.

The purification of water by filtration on the large scale, whether in filter beds of great area through which the water passes by gravity only, or in filtering cylinders under pressure and with previous addition of alum, seems likely to prove a matter of increasing importance in the future in this country, and is treated of in a separate chapter, with illustrative engravings. In connection with the question of natural purification of water the dangerous error is pointed out of the common impression that in frozen form polluted water may be trusted to be wholesome.

In regard to the *avoidance* of pollution in water to be collected for human use, the remarks as to the proper care of a water-shed after it has been selected deserve to be carefully considered and acted upon. They might probably have been exhibited with advantage somewhat more in detail.

The chapter on stored water gives useful facts bearing on the construction and maintainance of reservoirs, but questions of this kind are usually complicated in the most serious way with engineering and financial considerations, so that nearly every case needs practically to be dealt with as a special one.

There are some very judicious cautions as to the limitations within which water supply can be counted on from driven wells or from deep bored, so-called artesian wells, for the advantages of which, real to a certain extent, extravagant claims are not unfrequently made.

The methods for the chemical examination of natural waters are treated in a fairly balanced and impartial way, and the all important question of the interpretation to be put upon the results of such an examination is dealt with in a like spirit of undogmatic common sense. The same remark may be made in respect to the discussion of the bacteriological examination of water, the attempt being made to show in what special directions this mode of investigation is most likely to be of real use, without giving it undue and exaggerated importance.

In regard to the quantity of water needed *per capita* by a given population, one might wish for fuller discussion of the possible means of preventing such enormous waste as occurs in almost all cities and towns, and the special topics of "hardness," with its relations to health, soap consumption, interference with steam boiler use, &c., of the action of water upon lead and other metals, and of the particular relations of the foreign substances in natural waters to industrial use by brewers, dyers, paper makers, etc., are treated only in a very condensed way.

On the whole the book must be pronounced a useful and valuable addition to technological literature. J. W. M.

A DICTIONARY OF CHEMICAL SOLUBILITIES, INORGANIC. BY ARTHUR MESSINGER COMEY, PH.D., formerly Professor of Chemistry, Tufts College. Macmillan & Co.: London and New York. 1896.

This book is likely to be looked upon with mixed feelings by those who most need the information it compiles. It certainly represents much labor, and labor which cannot be said to have been altogether thrown away. Professor Storer's book on the same general plan, published in 1864, has long been out of print, and in this new volume it has been proposed to include much new matter which has accumulated within the last thirty years, and to omit some of the older statements which have undergone correction and are not worth reproduction on merely historical grounds. Yet the result of the compiler's work is not altogether satisfactory.

As a matter of practical convenience the carrying into a work of this kind the distinction between organic and inorganic substances is not desirable, only the latter being included. The preface does not hold out the expectation of another volume, to include organic substances. Storer's book contained both. For an analytical chemist it is awkward to find no mention of such familiar salts as sodium acetate and ammonium oxalate. For practical purposes it is perhaps well to include, as did Storer, not only cases of simple solution, in the ordinary sense of the term, but also those of solutions resulting from evident chemical change. Yet the statement in regard to mercuric oxide—"Sol. in $KI+Aq$."—does not read well; the same remark applies to the assertion that sulphur trioxide is "miscible with water"; one does not see why silver should be recorded as—"Sol. in hot conc. H_2SO_4 with evolution of SO_2"—while no similar statement is made as to mercury; and if such cases are to be included at all it would seem to be quite proper to give the "solubility" of chlorine in carbon disulphide, since the products of interaction, carbon tetrachloride and sulphur monochloride, are both liquid at ordinary temperature and pressure.

Accuracy is of course the feature most of all to be desired in a work of this kind. The author expresses in the preface his doubt that errors have been entirely avoided. Without any very extensive collation with original authorities, the comparison of a considerable number of individual statements gives a very good general impression of the care with which the work has been prepared. Here and there some small errors are noticeable. On p. 204 the name Carnelley is given as Cornelley, and on p. 161 the writer of this notice happened to notice his own name given as authority for the solubility in dilute $NH_4Cl + Aq$. of *potassium* fluosilicate instead of *barium* fluosilicate (as correctly quoted on p. 160).

Some of the older ways of looking at chemical facts are reflected in statements like that on p. 3, quoted from Frémy, as to potassium aluminate—"Decomp. by dissolving in pure H_2O with separation of Al_2O_3." Objection may well be made to some of the forms of expression, such as on p. 148—"Didymium, Di, slowly decomp. by H_2O,"—or, on p. 316—"Phosphorus, P_4. (a) Ordinary phosphorus. Insol. in H_2O, but slowly decomp. thereby,"—or, on p. 196—"Iron carbonyl. Slowly decomp. on air,"—or on p. 269—"Nitrogen sulphochloride. Unstable on air." And it is not easy to see the advantage of including the names of a number of substances in regard to which no statement whatever is made, or only some statement without bearing on solubility. Examples are afforded by such entries as the following—"Ammonium nickel cyanide, $2NH_4CN, Ni(CN)_2$. Easily decomposed." "Barium dithionate chloride, BaS_2O_6, $BaCl_2 + 4H_2O$. (Fock and Krüss, B. **23**, 3001.)" "Potassium fluoxypercolumbate, $2KF, CbO_2F_3 + H_2O$. (Piccini, Z. anorg. **1**, 51.)" "Platinum antimonide, $PtSb_2$. (Christofle, 1863.)" "Terbium, Tr. Metal has not been isolated. Has been decomp. into two or more elements by Krüss (Z. anorg. 4–27.)"

Some of the collections of modern data on particular points are valuable, as for instance those in regard to the attackability of various kinds of glass by water and watery solutions, and those on the relations of the saline and other constituents of natural waters to their action upon metallic lead. The book is neatly printed, and there is at the end a useful table of the principal scientific periodicals referred to, enabling the date of a reference to be found from the series and volume or *vice versâ*. J. W. M.

MILK, ITS NATURE AND COMPOSITION. A HAND-BOOK ON THE CHEMISTRY AND BACTERIOLOGY OF MILK, BUTTER AND CHEESE. BY C. M. AIKMAN, M.A., D.SC. Adam and Charles Black. London.

The aim of the book is to present in a brief and popular way the more important facts of the chemistry and bacteriology of milk and its products. The work is admirably adapted to the needs of intelligent dairymen, and will be found instructive by all non-professionals who wish to understand in a general way the important matters of which it treats.

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AMERICAN

CHEMICAL JOURNAL.

ON TRIMETAPHOSPHIMIC ACID AND ITS DECOMPOSITION-PRODUCTS.[1]

BY H. N. STOKES.

In a paper on the chloronitrides of phosphorus,[2] I mentioned, by way of preliminary notice, that Liebig's chloronitride, $P_3N_3Cl_6$, by appropriate treatment gives an acid, $P_3N_3O_6H_6$, to which I gave the name *trimetaphosphimic acid*. The object of the present paper is to describe in detail the properties and decomposition-products of this, the third member of the metaphosphimic acid series.

In the preliminary notice a metaphosphimic acid was defined as a metaphosphoric acid, $(PO_3H)_n$, in which one-third of the oxygen is replaced by an equivalent number of imide groups, NH, *i. e.*, $(PNO_2H_2)_n$. It was further pointed out that for each acid of this formula, with the exception of the simplest, at least four forms are theoretically possible, two of which are direct substitution-products of the corresponding metaphosphoric acid, containing a nucleus consisting of phosphorus atoms united by oxygen, the other two belonging to a different type, in which the phosphorus atoms are united by nitrogen. This was illustrated by the acid, $P_2N_2O_6H_6$, none of the

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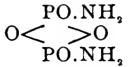
[1] The work described in this paper and the following one on tetrametaphosphimic acid was done in the chemical laboratory of the United States Geological Survey, and I wish to acknowledge my indebtedness to the Director, Hon. C. D. Walcott, and to Prof. F. W. Clarke, for the facilities placed at my disposal.

[2] THIS JOURNAL, **17**, 275, (1895): also Ber. d. chem. Ges., **28**, 437.

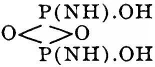
forms of which, it is true, are as yet known with certainty:



$$O<\begin{array}{c}PO.NH_2\\ \\ PO.NH_2\end{array}>O$$

(*a*)

Dimetaphosphoryl amide.



$$O<\begin{array}{c}P(NH).OH\\ \\ P(NH).OH\end{array}>O$$

(*b*)

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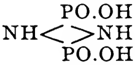
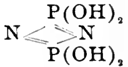


$$NH<\begin{array}{c}PO.OH\\ \\ PO.OH\end{array}>NH$$

(*c*)

Dimetaphosphimic acid.

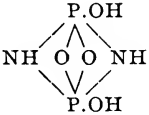


$$N\leqslant\begin{array}{c}P(OH)_2\\ \\ P(OH)_2\end{array}\geqslant N$$

(*d*)

Diphosphonitrilic acid.

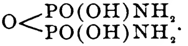
A fifth form might be added:



containing at the same time both the metaphosphoric and the metaphosphimic nucleus.

Schiff[1] described a body to which he gave the name *Phosphaminsaeure*, formed by acting on phosphorus pentoxide with dry ammonia, and which, according to his analyses, has the formula PNO_2H_2.[2] According to Gladstone and Holmes,[3] Schiff's acid is probably a mixture of pyrophosphodiamic and metaphosphoric acids. As Schiff failed to publish nitrogen determinations for his salts, it still remains a question whether a metaphosphimic acid can be produced in this way.

Gladstone, who was the first to devote much attention to phosphorus chloronitride, obtained from it by the action of aqueous ether and of alcoholic alkalies,[4] an acid which he first called deutazophosphoric acid and later pyrophosphodiamic acid, and to which he gave the formula $P_2N_2O_5H_6$, regarding it as the diamide of pyrophosphoric acid[5]



$$O<\begin{array}{l}PO(OH)NH_2\\ PO(OH)NH_2\end{array}.$$

While I am not prepared to deny positively the correctness

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[1] Ann. Chem. (Liebig), **103**, 168, (1857).

[2] I have elsewhere pointed out (This JOURNAL, **15**, 198,) that Schiff's acid has been erroneously described in some of the reference books as amidophosphoric acid, a body which I was the first to obtain.

[3] J. Chem. Soc., [2], **2**, 229, 233, 235.

[4] Q. J. Chem. Soc., **3**, 135, 354; Ann. Chem. (Liebig), **76**, 79; **77**, 315: J. Chem. Soc. [2], **2**, 231.

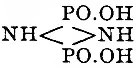
[5] J. Chem. Soc., [2], **6**, 69.

of the formula deduced by Gladstone, and to assert that no such acid can be obtained in this way from phosphorus chloronitride, yet the facts as stated by him are capable of another interpretation, namely, that his acid is not the diamide of pyrophosphoric acid, but trimetaphosphimic acid.

It will be seen that

$$\underset{\text{Pyrophosphodiamate.}}{P_2N_2O_5H_4M'_2} = P_2N_2O_4H_2M'_2 + H_2O,$$

the latter being identical in empirical composition with $P_3N_3O_6H_3M'_3 + 1\frac{1}{2}H_2O$, *i. e.*, a trimetaphosphimate with $1\frac{1}{2}H_2O$. Hence the latter, if containing this amount of water, might be mistaken for a pyrophosphodiamate. The only salts made by Gladstone directly from the chloride, $P_3N_3Cl_6$, were the silver and barium salts; the others were made from a supposed pyrophosphodiamate obtained from phosphorus oxychloride and ammonia, and there is no proof in Gladstone's papers of the identity of the acids from both sources. His figures for the barium salt were, as he admits, not satisfactory, while the analyses of the silver salt were made with a crude preparation, for the purity of which there is no guarantee. I have myself found that barium trimetaphosphimate varies considerably in composition, contains water, and is hygroscopic. Sodium trimetaphosphimate is the only well-defined substance I have been able to obtain by decomposing the chloronitride by alcoholic soda, and the salt is so characteristic as hardly to be mistaken. It seems quite possible, therefore, that Gladstone actually had crude trimetaphosphimic acid in hand and failed to recognize its true nature only because of the unfortunate selection of salts which are amorphous, hydrated, and difficult to obtain pure.

In a paper of much later date Mente[1] described several acids obtained by the successive action of ammonium carbamate and water on phosphorus oxychloride. Among them is one to which he gave the name diimidodiphosphoric acid and the formula,  $NH\left<\begin{matrix}PO.OH\\PO.OH\end{matrix}\right>NH$, and which he regards as identical with Gladstone's pyrophosphodiamic acid. If Mente's formula

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[1] Ann. Chem. (Liebig), **247**, 239, 244, (1888).

is correct, it is the second, or *dimetaphosphimic* acid. I have been unable to repeat Mente's work, and his data are too meagre to admit of a positive conclusion, either as to its molecular weight or even its empirical composition, but it appears not to be identical with trimetaphosphimic acid.

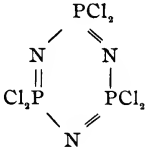
Constitution of Trimetaphosphimic Acid.

Although trimetaphosphimic acid is an uncrystallizable and unstable body, it forms stable salts, several of which crystallize in characteristic forms. Three atoms of hydrogen are replacable by alkali metals, while silver is able to replace either three or six. The following are the most noteworthy :

$P_3N_3O_6H_3Na_3 + 4H_2O$—Rhombic prisms.
$P_3N_3O_6H_3Na_3 + H_2O$—Slender prisms.
$P_3N_3O_6H_3(NH_4)_3 + H_2O$—Scales.
$P_3N_3O_6H_3NaBa + 1\frac{1}{2}H_2O$—Rhombohedra.
$P_3N_3O_6H_3Ag_3$—Monoclinic prisms.
$PN_3O_6Ag_6$—Two forms, white and red.

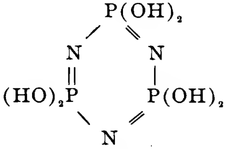
The first, third and fifth serve to identify the acid. The tertiary silver salt, being anhydrous and easily obtained pure, establishes its empirical formula. Those salts which contain water of crystallization do not lose it completely at any temperature short of decomposition, leaving open the question whether the acid may not have the formula $P_3N_3O_7H_8$.

The constitution of trimetaphosphimic acid depends on that of the chloronitride $P_3N_3Cl_6$. The structural formula of the latter has not yet been definitely established, but the following data are available. It is reasonably certain that in the chloronitride phosphorus atoms are united by nitrogen atoms. Its formation from phosphorus pentachloride and ammonia is best explained on this assumption, as is its decomposition into orthophosphoric acid and ammonia. If phosphorus were united to phosphorus and nitrogen to nitrogen, the formation of reducing phosphoric acids or of hydrazine might be expected. Neither is it likely that chlorine is united to nitrogen, for in this case hydroxylamine might be expected to result. Several structural formulas are possible, which meet this requirement, the simplest being that in which the nucleus consists of a symmetrical ring of three phosphorus and three nitrogen atoms.



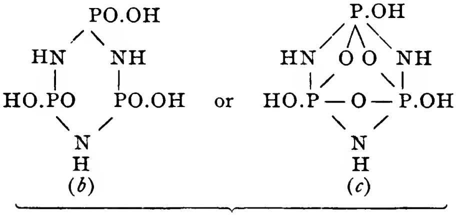
or a similar one with diagonal or "centric" union.

Direct replacement of chlorine by hydroxyl would then give


(*a*)

Triphosphonitrilic acid.

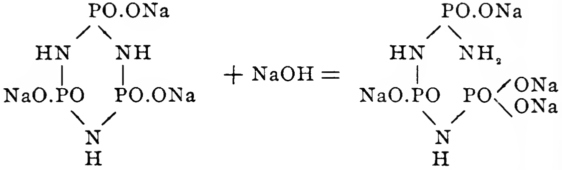
The labile nature of the hydrogen atoms in nitrogenous bodies, as observed in many organic compounds, makes it by no means improbable that an acid of this form may of itself, or under the influence of reagents, undergo transformation into the tautomeric form:



(*b*) (*c*)

Trimetaphosphimic acid.

An acid of the form (*a*) may be expected to give two sodium salts in which respectively three and six atoms of hydrogen are replaced. A salt with six atoms of sodium cannot be produced, however, by any method which I have tried. The only salt besides the ordinary one with three atoms of sodium is one with *four* atoms, and this is formed in the presence of a large excess of caustic soda; it is very unstable and is reconverted into the three-atom salt by repeated precipitation from aqueous solution by alcohol. It is not obvious why an acid of the form (*a*) should give such a salt. If we assume that (*b*) represents the correct formula, and that the acid is the symmetrical inner anhydride or lactam of an open chain acid, we may regard this salt as being formed by addition, thus:



the latter being a salt of *amido-diimidotriphosphoric acid.*[1] Unfortunately I have been unable to prove this with certainty. A silver salt of the composition $P_3N_3O_7H_4Ag_4$ would render it extremely probable, as all silver salts of phosphorus nitrogen acids hitherto observed are free from crystal water. A salt with four atoms of silver can be obtained from the above four-atom sodium salt, but it is very unstable and its composition does not agree with sufficient sharpness with that of the cyclic or open chain form to establish either formula definitely.

I am therefore inclined to give preference to formula (*b*). It seems likely, however, that salts of triphosphonitrilic acid may also exist. The hexa-silver salt has been observed in two well defined forms, as well as a third, possibly intermediate one. One of these is white, amorphous and soluble in ammonium nitrate; it is easily converted into the other of identical composition, which is red, crystalline and insoluble in the same reagent. The colorless salt probably contains silver united to oxygen only, while in the other one-half is united to nitrogen.

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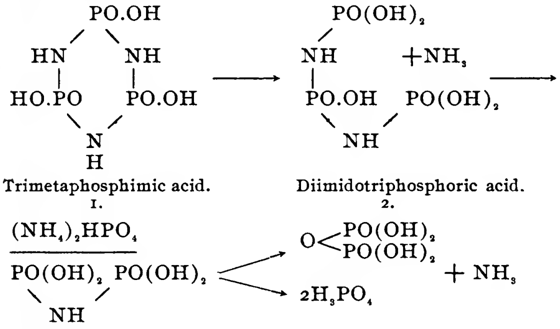
[1] The acids $PO(OH)_2.O.PO(OH)_2$ and $PO(OH)_2.O.PO(OH).O.PO(OH)_2$ being frequently designated as di- and triphosphoric acid, I call those in which the linking oxygen is replaced by imide, NH, *imido*-di- and triphosphoric acid.

Decomposition-Products of Trimetaphosphimic Acid.

An aqueous solution of trimetaphosphimic acid or of one of its salts acidified with one of the stronger mineral acids, decomposes slowly in the cold, rapidly on heating, the ultimate products being orthophosphoric acid and ammonia. If, however, the action be limited, there results a mixture of intermediate acids. The analysis of this mixture, which involved many experimental difficulties, proved the presence of the following:

1. Unchanged trimetaphosphimic acid,	$P_3N_3O_6H_6$.
2. Diimidotriphosphoric acid,	$P_3N_2O_8H_7$.
3. Imidodiphosphoric acid,[1]	$P_2NO_6H_5$.
4. Pyrophosphoric acid,	$P_2O_7H_4$.
5. Orthophosphoric acid,	PO_4H_3.

Assuming formula (*b*) for trimetaphosphimic acid, its decomposition would be thus represented:



Trimetaphosphimic acid.
1.

Diimidotriphosphoric acid.
2.

Imidodiphosphoric acid.
3.

4 and 5.

The second acid is important as a connecting link, proving that trimetaphosphimic acid actually has the triple formula $(PNO_2H_2)_3$. Most remarkable is the formation of pyrophosphoric acid, which occurs directly from imidodiphosphoric acid. The facts are these: If sodium imidodiphosphate be weakly acidified with acetic acid and boiled from five to ten

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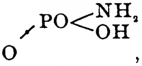
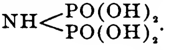
[1] This acid has the same composition and is probably identical with Gladstone's azophosphoric or pyrophosphamic acid. J. Chem. Soc., [2], 6, 66, etc.

minutes, not more than fifteen per cent. is converted into pyrophosphoric acid and the remainder into orthophosphoric acid. Control experiments with sodium pyrophosphate showed that under the same conditions but a small portion is converted into orthophosphoric acid, ninety per cent. of the pyrophosphate being recovered. The pyrophosphoric acid is therefore not an intermediate product, but the imidodiphosphate is converted for the greater part directly into orthophosphoric acid, and in a much less degree into pyrophosphoric acid.

The above formula of imidodiphosphoric acid containing the group P—NH—P, follows directly from that of trimetaphosphimic acid. In view of the ease with which the condensed phosphoric acids split up in aqueous solution into orthophosphoric acid, while the reverse never occurs, it is difficult to see how the action of water or acids on a body of the assumed formula could give pyrophosphoric acid. If we adopt Gladstone's formula[1]  $\mathrm{O}\begin{array}{l}\diagup \mathrm{PO}{<}\begin{array}{l}\mathrm{NH_2}\\ \mathrm{OH}\end{array}\\ \diagdown \mathrm{PO(OH)_2}\end{array}$, we can explain the formation of pyrophosphoric acid, but must at the same time assume that somewhere in the series the group P—N—P has been converted into P—O—P, for in the chloronitride, $P_3N_3Cl_6$, phosphorus can be united only by nitrogen. If the acid were really the amide of pyrophosphoric acid, boiling with acetic acid would first convert it into pyrophosphoric acid which, as above shown, is fairly stable under the observed conditions, and should be found present to the extent of at least ninety per cent. instead of only fifteen per cent. On this ground, it seems to me, we must reject the amidopyrophosphoric formula, and regard the body as imidodiphosphoric acid,



$$\mathrm{NH}{<}\begin{array}{l}\mathrm{PO(OH)_2}\\ \mathrm{PO(OH)_2}\end{array}.$$

This formula does not account for the pyrophosphoric acid. We may, perhaps, conceive that owing to the greater affinity of phosphorus for oxygen than for nitrogen, a group,

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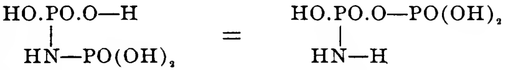
[1] J. Chem. Soc., [2], 6, 70.

$PO.(OH)_2$, is able to change places with a hydroxylic hydrogen atom.



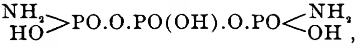
$$\begin{array}{l} HO.PO.O\text{—}H \\ \quad\ \ | \\ HN\text{—}PO(OH)_2 \end{array} \quad = \quad \begin{array}{l} HO.PO.O\text{—}PO(OH)_2 \\ \quad\ \ | \\ HN\text{—}H \end{array}$$

the latter, in common with other amido phosphoric acids, being unstable, and passing easily into pyrophosphoric acid. It may be noted that this transformation seems to be promoted by heat, apparently more pyrophosphoric acid being formed by decomposing trimetaphosphimic acid in hot than in cold solution.

The second acid of the series, diimidotriphosphoric acid, seems really to have the constitution,

$$PO(OH)_2.NH.PO(OH).NH.PO(OH)_2,$$

implied by the name. It forms an acid salt with three, and a neutral salt with five atoms of silver, both of which are colorless. If it were a diamide of triphosphoric acid,



$$\begin{matrix} NH_2 \\ HO \end{matrix}\!\!>PO.O.PO(OH).O.PO<\!\!\begin{matrix} NH_2 \\ OH \end{matrix},$$

the penta-silver salt would have two atoms united to nitrogen, and such a salt, to judge from all phosphorus-nitrogen salts, where this is known to be the case, would be distinctly colored.

Still another intermediate acid is possible, preceding imidodiphosphoric acid, *viz.*, *amidoimidodiphosphoric acid*,

$$\begin{matrix} NH_2 \\ HO \end{matrix}\!\!>PO.NH.PO(OH)_2.$$

I have been unable to detect this acid thus far, but the too high percentage of nitrogen invariably found in imperfectly purified imidodiphosphoric acid, may be due to the presence of small amounts of this body.

In giving formulas to these bodies, I wish to be understood as using them with full appreciation of their uncertainty. A much more exhaustive study is necessary before they can be regarded as established as firmly as those of many organic compounds. There are several directions in which such a study might be of value. Besides the question of tautomerism, the stereochemistry of nitrogen might be attacked with profit from this side. The analogy of nitrogen and phosphorus suggests the possibility of steric phenomena being shown by the latter also. The formula (*b*) suggested for trimetaphosphimic acid, for example, may imply a cis- and cis-trans-form depending on the position of the hydroxyls as well as of the imide hydrogen atoms, in short, quite a number of stereo-isomers may be conceived. I have thus far sought in vain for indications of the existence of such forms.

Finally, I would add that I have no desire to reserve for myself the study of these bodies, either from the above or from any other point of view.

Experimental Part.

Analytical Methods.—Salts of trimetaphosphimic acid and derived bodies are easily decomposed by fusion with sodium carbonate. As the process involves oxidation it is essential to keep the mass in a state of fusion for some time with access of air. Salts of silver of other easily reducible metals and those in which it is desired to determine alkali or nitrogen, must be decomposed by strong sulphuric acid. The substance, contained in a platinum crucible, is first moistened with dilute, and then covered with 4 or 5 cc. strong sulphuric acid, and the covered crucible heated to fuming for an hour in a radiator, care being taken that the fumes do not escape. In determining alkali metal, the resulting phosphoric acid may be conveniently removed by the ferric chloride—acetate method. As the water of crystallization cannot be completely expelled by heat without partial decomposition, it is best determined, together with the hydrogen of the salt proper, by combustion. This is conveniently carried out in a short combustion tube with a 10 cm. spiral of oxidized copper gauze, the substance, contained in a boat, being covered with fused potassium bichromate. As nitrous fumes are formed in abundance, the usual precautions must be taken. In the following, where more than one determination is given, the numbers always refer to different preparations.

Preparation of Trimetaphosphimic Acid.—The sodium salt affords the starting material for all preparations of trimetaphosphimic acid. It may be obtained by saponifying triphosphonitrilic chloride by alcoholic soda, but with much loss, owing to the formation of ethers and other substances of unknown nature. The chloride, as observed by Liebig and by Gladstone, is practically unacted on either by water or anhydrous ether, but as I have pointed out elsewhere[1] its decomposition may readily be effected by shaking its ethereal solution protractedly with water, whereby intimate contact is secured. Decomposition by ether and water alone, however, results in much loss, as the liberated hydrochloric acid rapidly decomposes trimetaphosphimic acid. The following method is perfectly satisfactory and gives practically the theoretical yield.

30 grams of the chloride are dissolved in 150 cc. ether free of alcohol, and the solution gently agitated with a solution of 110 grams crystallized sodium acetate in 200 cc. water, the agitation being conveniently effected by slowly rotating with a small turbine. After about fifteen hours, well formed crystals of the sodium salt begin to appear, and about seventy or eighty hours are required for complete decomposition. This point is best observed by evaporating a few drops of the ether and taking up the residue with water, any undecomposed chloride remaining undissolved. It is best to continue the agitation for a short time longer in order to decompose the chlorhydrines,[2] which are always formed as intermediate products. At the end of the operation nearly all the sodium salt has crystallized out, being almost insoluble in the strong salt solution; a further small amount can be recovered by mixing the solution with alcohol. After washing with 50 per cent. alcohol, the salt is pure enough for most purposes, but may be redissolved in water and precipitated by gradual addition of alcohol.

The same salt also results by decomposing triphosphonitrilic tetrachlorhydrine[3] with soda. It exists in two forms, apparently differing only in the amount of crystal water, the α-salt being formed at ordinary temperatures, the β-salt only above 80°.

α-Sodium Trimetaphosphimate, $P_3N_3O_6H_3Na_3 + 4H_2O$.—

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[1] This JOURNAL, 17, 284.

[2] *Ibid.*, 17, 285.

[3] *Ibid.*, 17, 285.

The air-dried salt, prepared as above, gave the following figures:

	Calculated for $P_3N_3O_6H_3Na_3 + 4H_2O$.	Found. (1)	(2)
P	24.79	24.74	24.82
N	11.22	11.26	
Na	18.41	18.45	18.43
H	2.94	3.05	2.97

(1) P : N : Na : H = 3 : 3.02 : 3.01 : 11.47.
(2) P : Na : H = 3 : 2.97 : 11.

It loses weight slowly *in vacuo*, and 3 molecules of water are given off on long heating at 100°. After 5 hours at 100° the loss was:

	Calculated for $3H_2O$.	Fonnd.
Loss	14.38	14.05

This is one of the most characteristic salts of trimetaphosphimic acid. It forms brittle orthorhombic prisms, usually about 1–2 mm. across, of which Fig. 1 represents the most common form.

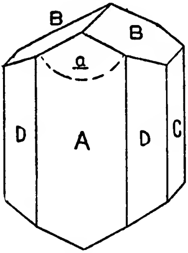


Fig. 1.

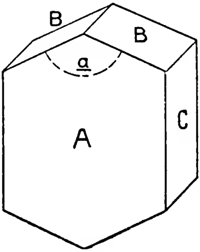


Fig. 2.

$A = \infty P \bar{\infty}$.
$B = P \breve{\infty}$.
$C = \infty P \breve{\infty}$.
$D = \infty P$.

The angle *a*, measured roughly under the microscope, is about 130°. No other faces are ever observed, and D is frequently lacking, giving the form shown in Fig. 2, which is often seen to be elongated in the direction of any one of the axes. They are especially well developed when slowly thrown down by acetic acid and alcohol from alkaline solution; when formed by rapid addition of alcohol in large excess they tend to elongation in the direction of the principal axis, being often acicular, often long flat prisms with imperfectly developed ends.

At 20°, 100 parts water dissolve 18.3 parts; in hot water it is much more soluble, and from its hot solution it crystallizes but slowly ; the larger crystals dissolve in hot water with a decrepitating sound. The reaction towards litmus is neutral. On rapidly heating the dry salt it gives off water and later ammonia, and fuses to a clear glass. It is but slowly decomposed by boiling with water; after three hours heating traces of phosphoric and imidodiphosphoric acid were shown by magnesia mixture. Alkalies do not cause the evolution of any appreciable quantity of ammonia, even when hot; apparently, however, their very long continued action is attended with decomposition.

β-Sodium Trimetaphosphimate, $P_3N_3O_6H_3Na_3 + H_2O$.—This form is deposited when the solution has a temperature of 80° or higher. It was obtained

(1) By boiling the solid α-salt under a strong solution of sodium nitrite (Anal. 1).

(2) By slowly adding boiling alcohol to a boiling solution of the α-salt (Anal. 2).

(3) By pouring a boiling solution of the α-salt into a boiling 25 per cent. solution of sodium acetate.

Doubtless other sodium salts would serve equally well, provided their hot solutions are sufficiently strong to throw it out.

The salt lost nothing at 100° and gave:

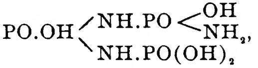
	Calculated for $P_3N_3O_6H_3Na_3 + H_2O$.	Found. (1)	(2)
P	28.97	28.31	28.97
N	13.11		13.08
Na	21.51	21.86	21.19

(1) P : Na = 3 : 3.12.

(2) P : N : Na = 3 : 2.99 : 2.90.

This modification of the sodium salt forms needles, which, under the microscope, are seen to consist of flat prisms terminating in points ; the terminal angles are of two kinds, one rather more, the other rather less than 90°; frequently both of these may be observed at opposite ends of the same crystal. Often, too, the crystals are cut off obliquely, owing to the development of but one terminal plane, in which case the terminal angles are respectively rather more and rather less than 45°. In general properties it resembles the α-salt, which it gives when reprecipitated from cold solution; whether the difference consists merely in the amount of crystal water, or whether it is a chemically distinct body cannot be decided at present.

Tetra-Sodium Salt, (*Sodium Amido-diimidotriphosphate*), $P_3N_3O_7H_4Na_4 + H_2O$.—As pointed out in the introduction, this is best regarded as the neutral salt of an open chain acid,



$$\text{PO.OH}\begin{cases}\text{NH.PO}<\begin{matrix}\text{OH}\\\text{NH}_2,\end{matrix}\\\text{NH.PO(OH)}_2\end{cases}$$

of which trimetaphosphimic acid is the inner anhydride. As positive proof of this cannot be adduced at present, I have preferred to place it among the trimetaphosphimates.

On dissolving sodium trimetaphosphimate in an excess of caustic soda, concentrating and allowing to cool, the salt crystallizes in long brittle needles (Anal. 1). On adding alcohol to a caustic soda solution of sodium trimetaphosphimate (which need not have been heated), it is thrown out as a syrup which crystallizes, slowly if left to itself, at once on adding a fragment of previously prepared salt, to a mass of delicate colorless needles (Anal. 2). These must be washed with alcohol containing a little caustic soda in solution, strongly pressed out and dried out of contact with the air. It contains a large amount of crystal water, which it loses, with the exception of the last molecule, on drying *in vacuo*; the exact amount could not be determined.

The substance dried *in vacuo* lost nothing at 100° and gave:

	Calculated for $P_3N_3O_7H_4Na_4 + H_2O$.	Found. (1)	(2)
P	25.76	25.34	25.60
N	11.66		11.96
Na	25.51	25.60	25.76

(1) P : Na = 3 : 4.08.
(2) P : N : Na = 3 : 3.09 : 4.06.

This salt is very unstable, being decomposed even in the solid state by carbon dioxide. From its cold aqueous solution alcohol precipitates a mixture of unchanged salt and α-sodium trimetaphosphimate, a few reprecipitations converting it completely into the latter and free alkali. Its behavior towards silver nitrate is described under the silver trimetaphosphimates.

Salts with less than three or more than four atoms of sodium could not be obtained.

Potassium Trimetaphosphimate, $P_3N_3O_6H_3K_3$.—A solution of this salt was obtained by decomposing the barium salt with potassium sulphate; on evaporation a transparent, glassy mass resulted. Alcohol precipitated it as a syrup, which, on repeated treatment with absolute alcohol, was converted into indistinct crystals. It was not further examined.

Ammonium Trimetaphosphimate, $P_3N_3O_6H_3(NH_4)_3 + H_2O$.—A solution of this salt was obtained by double decomposition from the barium and silver salts, and by neutralizing the free acid with ammonia. It loses ammonia on evaporation, and leaves a transparent amorphous residue. Its solution, treated with alcohol, gives a deposit of large and beautiful pearly scales, which are characteristic. As these form even in the presence of a large excess of ammonia, it appears that a body analogous to the tetra-sodium salt cannot be thus formed.

The-air dried substance gave:

	Calculated for $P_3N_3O_6H_3(NH_4)_3 + H_2O$.	Found.
P	30.38	30.19
N	27.50	27.03

Magnesium Trimetaphosphimate, $(P_3N_3O_6H_3)_2Mg_3$(?).—Strong solutions of sodium trimetaphosphimate and magnesium chloride give no precipitate, even on boiling. A solution of the magnesium salt may be obtained by double decomposition. From this alcohol throws down an amorphous flocculent precipitate, and it leaves a soluble transparent residue on evaporating. On boiling the solution is slowly decomposed.

A mixture of a not too dilute solution of sodium salt with an excess of a strong solution of magnesium acetate remains clear, but is precipitated by acetic acid ; on adding a little water this precipitate redissolves, reappears on heating and redissolves on cooling; the nature of these precipitates has not been investigated. With more water the solution remains clear on short boiling, but on continued heating a crystalline precipitate forms, which examination shows to consist of magnesium pyrophosphate and imidodiphosphate, orthophosphoric acid remaining in solution.

The fact that trimetaphosphimic acid is not precipitated in the cold by ammoniacal magnesia mixture affords a valuble means of separating it from some of its decomposition-products.

Barium Trimetaphosphimates.—Much time was spent in studying these salts, until it was found that they are devoid of characteristic properties, and that they are of very varying composition. Both neutral and basic salts exist, and there is a strong tendency to form double salts. The tendency to form complex salts is so strong that when barium nitrate, chloride or acetate is used as the precipitant, the product is invariably contaminated with these. It has proved impossible to obtain a single satisfactory analysis, but the following data may be mentioned :

A salt obtained by decomposing an ethereal solution of phosphorus chloronitride with excess of baryta water consisted of a pulverulent, indistinctly crystalline substance for which the rotio P : Ba = 6 : 4.48 was found, while the calculated ratio for neutral salt is 6 : 3.

The potassium salt, precipitated by ammoniacal barium chloride, gave a preparation in which P : Ba = 6 : 3.68.

Triphosphonitrilic tetrachlorhydrine gave a clear solution with ammonia and barium chloride; on boiling a granular precipitate resulted (Anal. 1).

Ethereal chloronitride and barium acetate solution gave a preparation from which the figures under Anal. 2 were obtained.

A precipitate from the potassium salt and neutral barium chloride gave the results recorded under Anal. (3).

	Calculated for $(P_3N_3O_6H_3)_2Ba_3+4H_2O$.	Calculated for $(P_3N_3O_6H_3)_2Ba_3+6H_2O$.	Found. (1)	(2)	(3)
B	19.89	19.16	19.91	20.86	20.46
Ba	43.96	42.35	41.75	41.91	43.79

(1) P : Ba = 6 : 2.85 ; dried at 100°.

(2) P : Ba = 6 : 2.73 ; dried *in vacuo*.

(3) P : Ba = 6 : 2.91 ; dried at 100°.

The neutral salt is slightly soluble in water and easily in a solution of ammonium chloride ; on boiling the latter it is partially reprecipitated. It also dissolves readily in a strong solution of sodium chloride, and, on warming, the barium sodium salt is precipitated.

Barium Sodium Trimetaphosphimate, $P_3N_3O_6H_3NaBa + 1\frac{1}{2}(?)H_2O$.—This salt is almost insoluble in water, and forms a heavy, crystalline powder, which is seen under the microscope to consist of spherical aggregates with many rhombic facets, or occasionally of single minute crystals, apparently rhombohedra. The ordinary amorphous barium salt is invariably formed by precipitating any soluble trimetaphosphimate with a barium salt *in the cold*, but if the chloride or other salts of sodium be present in sufficient quantity, this passes into the crystalline barium sodium salt, at once on heating, or in the cold after a period varying from a few minutes to several hours. The latter also forms at once on precipitating in hot solutions. It was also obtained by decomposing an etherial solution of chloronitride (1 mol. wt.) with a solution of barium acetate (1 mol. wt.) and sodium acetate (9 mol. wts.). As is so common with salts of barium this tends to "carry down" a considerable amount of the precipitant. A preparation made by the last method mentioned contained 0.49 per cent. chlorine, corresponding to a contamination of 1.44 per cent. barium chloride. After making correction for this the figures under Analysis (3) were obtained, which approximate closely to the theoretical.[1] The excess of barium in Analyses (1) and (2) is accounted for in the same manner. Possibly the difficulty is due to the presence of half dissociated barium ions (*e. g.*,—BaCl) in the solution.

The substance lost but little at 100° and gave :

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[1] Richards has pointed out the necessity of making a similar correction in determining sulphuric acid as barium sulphate. Ztschr. anorg. Chem., 8, 413,

	Calculated for $P_3N_3O_6H_3NaBa+1\frac{1}{2}H_2O$.	Found. (1)	(2)	(3)
P	22.09	21.50	21.86	21.99
N	9.99	9.91		
Na	5.47		5.56	5.53
Ba	32.56	35.67	34.22	32.86
H	1.43			1.32

(1) P : N : Ba = 3 : 3.05 : 1.12.

(2) P : Na : Ba = 3 : 1.03 : 1.06.

(3) P : Na : Na : H = 3 : 1.02 : 1.01 : 5.58.

Similar salts containing potassium or ammonium could not be obtained. A barium silver salt consisting of microscopic spherules was obtained by adding silver nitrate to a solution of the neutral barium salt in ammonium nitrate; a qualitative examination showed the presence of barium and silver.

Silver Salts.

Tri-Silver Trimetaphosphimate, $P_3N_3O_6H_3Ag_3$.—This is the most important salt obtained on account of its highly characteristic crystalline form and because it is anhydrous and easily prepared pure, thereby establishing the empirical composition of trimetaphosphimic acid. As those salts which contain crystal water do not lose it completely at a temperature short of decomposition, we should otherwise be unable to decide between the formulas $P_3N_3O_6H_6$ and $P_3N_3O_7H_8$. For comparison the theoretical figures for a silver salt of both of these are given.

The salt may be prepared by precipitating a cold dilute solution (1–50) of the sodium salt by silver nitrate, when it is thrown down at once in the form of colorless elongated microscopic plates, terminated by an angle of 78°. (Analyses 1–4). Much better crystals are obtained if the solution of the sodium salt be acidified with several equivalents of nitric acid and the silver nitrate added slowly, finally in large excess. In this way the crystallization is made to extend over a considerable time, but the precipitation is never complete. (Analysis 5). Thus formed the crystals are usually very well developed, though seldom over 2 mm. long, and consist of thick, monoclinic plates of the forms represented in Figs. 3 and 4, the latter resulting when the crystallization extends over several hours. No other faces are ever observed and the angle *a* (between the edges) measured under the microscope, is very nearly 78°.

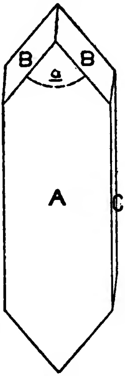

Fig. 3.

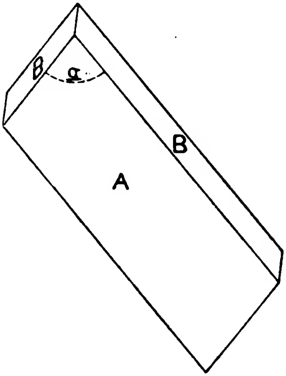

Fig. 4.

$A = \infty P \bar{\infty}$. $B = P \grave{\infty}$. $C = \infty P \grave{\infty}$.

The air-dried salt lost nothing at 100° and gave:

	Calculated for $P_3N_3O_6H_3Ag_3$.	Calculated for $P_3N_3O_7H_5Ag_3$.	Found.					
			(1)	(2)	(3)	(4)	(5)	(6)
P	16.68	16.16	16.50	16.70	16.74	16.64		15.71
N	7.55	7.31		7.53	7.67		7.72	
Ag	58.04	56.20	57.75	57.90	57.77	57.93	57.80	60.08
H	0.54	0.87		0.62				

(1) P : Ag = 3 : 3.02.
(2) P : N : Ag : H = 3 : 2.99 : 2.99 : 3.47.
(3) P : N : Ag = 3 : 2.98 : 3.04.
(4) P : Ag = 3 : 3.
(5) N : Ag = 3 : 3.
(6) P : Ag = 3 : 3.30.

The salt is insoluble in water, easily soluble in ammonia, and somewhat difficultly in dilute nitric acid. It is not affected by light, but on boiling under water it becomes somewhat yellow, owing to the formation of a superficial coating of the six-atom salt and the liberation of free acid, the decomposition-products of which can be detected in the liquid. If free from silver nitrate, caustic soda does not discolor it, even on boiling. On heating it swells up, gives off ammonia and fuses to a mass which contains metallic silver. In order to ascertain if it is actually precipitated in the anhydrous form, or if it contains water which is given off on standing, a freshly precipitated sample was washed with alcohol and ether, pressed out and at once weighed; it lost nothing at 100°, indicating that even at the moment of formation it is anhydrous. Precipitation from boiling solution seems to have no influence on its composition; if, however, the solution of the sodium salt be added to a large excess of a solution of silver nitrate, the resulting precipitate, though white, is amorphous and contains a much too high percentage of silver (Analysis 6), probably indicating an admixture of a more basic salt.

If tri-silver trimetaphosphimate be heated in a current of dry air at a temperature rising gradually from 200° to 260°, very nearly one-third of the nitrogen is given off as ammonia:

	Calculated for NH_3.	Found.
Loss	3.05	2.86

The product is no longer completely soluble in dilute acid. Alternate treatment with sodium chloride and ammonia extracts the silver and an acid which gives an amorphous precipitate with magnesium nitrate mixture. A considerable white residue remains in the form of pseudomorphs of the original substance, which is insoluble in ammonia, and soluble in hydrochloric acid only on boiling.

Salt with 4 Atoms of Silver, $P_3N_3O_6H_2Ag_4$ or $P_3N_3O_7H_4Ag_4$. —If silver nitrate be added slowly to a solution of the 4-atom sodium salt (sodium amidodiimidotriphosphate) each drop produces a white precipitate, which, on stirring, turns yellowish, in presence of an excess of sodium salt; when the latter is used up and an excess of silver nitrate has been added, it again becomes white. If, on the contrary, the sodium salt be added to the silver nitrate, each drop gives a yellow precipitate, turning white on stirring, and remaining so as long as an excess of silver is present. This white amorphous salt is decomposed by washing with pure water, turning yellow, while trimetaphosphimic acid goes into solution. The change may be represented thus:

$$3P_3N_3O_7H_4Ag_4 = 2P_3N_3O_7H_2Ag_6 + P_3N_3O_6H_6 + H_2O.$$

Silver nitrate prevents this change; the precipitate must therefore be washed with 1 per cent. aqueous solution of silver nitrate, then with 1 per cent. alcoholic solution of the same, and finally with ether. On pressing out and drying, it then remains colorless. Preparations made in this manner gave the following results after drying at 100°, at which temperature the salt remains white.

	Calculated for $P_3N_3O_6H_2Ag_4$.	Calculated for $P_3N_3O_7H_4Ag_4$.	Found. (1).	(2).	(3).
P	14.01	13.63	13.32	13.70	13.29
Ag	64.92	63.22	65.79	64.71	65.89

(1) P : Ag = 3 : 4.26; (2) P : Ag = 3 : 4.07; P : Ag = 3 : 4.28.

Unfortunately, the figures do not admit of a positive decision as to the formula, but the extreme instability of the salt as compared with the others, may indicate an acid of different nature from trimetaphosphimic acid.

If this salt be allowed to stand for a day or two under pure water, it is converted into a mixture of tertiary silver trimetaphosphimate and a yellow crystalline salt with 6 atoms silver.

$$3P_3N_3O_7H_4Ag_4 = P_3N_3O_7H_2Ag_6 + 2P_3N_3O_6H_3Ag_3 + 2H_2O.$$

The same change occurs rapidly on boiling. Whatever may be the nature of the salt, this change is doubtless due to the tendency of the silver to wander to the nitrogen; silver nitrate, by opposing dissociation, prevents alteration.

✓ *Salts with 6 Atoms of Silver,* $P_3N_3O_6Ag_6$ and perhaps also $P_3N_3O_7H_2Ag_6$.—Equally unsatisfactory analytical results are given by the salts with 6 atoms of silver. The figures indicate the tendency to formation of salts with the ratio P : Ag = 3 : 6, but the actual ratio only approximates to this, and it is impossible on the basis of the analyses alone to decide which of the formulas $P_3N_3O_6Ag_6$ and $P_3N_3O_7H_2Ag_6$ should be adopted in most cases. After many experiments I have been compelled to abandon for the present the attempt to obtain these substances in entirely satisfactory condition, and give the figures as actually obtained.

If sodium trimetaphosphimate be added to an excess of an ammoniacal solution of silver nitrate[1] or of a solution of silver oxide in ammonium nitrate,[2] a portion of the trimetaphosphimic acid is precipitated as a pure white voluminous and amorphous body, which, as analysis shows, contains approximately 6 atoms of silver. The precipitation is very incomplete, especially when ammoniacal silver nitrate is used, but in this case the substance contains very nearly 6 atoms of silver, while if the silver oxide solution be employed, the percentage of silver is considerably too low.[3] Heated under the mother-liquor it becomes yellowish, and becomes white again on cooling. After washing out (whereby it becomes yellowish) it dissolves quite readily in strong ammonium nitrate solution, but if boiled with less of the same, or less rapidly if heated with water alone, it is quickly converted into a heavy pulverulent substance. This, if highly magnified, is seen to consist of spherules or indistinct prisms, and has a color varying from orange to deep orange-red, usually the latter. This salt likewise contains 6 atoms of silver. The transformation is prevented by any silver nitrate in the solution, unless the effect of this is neutralized by a large quantity of ammonium nitrate.

If a solution of sodium trimetaphosphimate, to which exactly 3 mol. weights caustic soda, or an excess of ammonia have been added, be dropped into an excess of dilute silver nitrate, a light sulphur-yellow, voluminous and amorphous precipitate is formed, which may be washed with cold water without change, and does not change color on drying. This, likewise, contains 6 atoms of silver, and is *insoluble* in ammonium nitrate. If boiled with a trace of silver nitrate it remains unchanged; but, if boiled with pure water it changes slowly, or if sodium trimetaphosphimate or ammonium nitrate

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[1] Prepared by adding ammonia to silver nitrate solution till the brown precipitate just redissolves.

[2] 3 grams silver oxide, 10 grams ammonium nitrate, and 50 cc. water.

[3] The filtrate, on evaporation over sulphuric acid, deposits an imperfectly crystalline substance, at first white, then yellow, which is probably identical with the yellow salt referred to below.

be present, in a few moments, into the same orange-red, crystalline powder above mentioned.[1] On one occasion a deep red crystalline powder was obtained, but the conditions for its formation could not be determined. The following figures resulted from the analyses of these salts, in every case dried at 100°:

	Calculated for $P_3N_3O_7H_2Ag_6$.	Calculated for $P_3N_3O_6Ag_6$.
P	10.39	10.59
Ag	72.21	73.69

		Found.		
	Lowest.	Highest.	Mean.	
White Salt (Amorphous).				
P	10.54	11.28	10.92	4 preparations.
Ag	71.04	71.93	71.58	mean ratio P : Ag = 3 : 5.66
Yellow Salt (Amorphous and Crystalline).				
P	10.23	10.65	10.44	7 preparations.
Ag	71.55	73.13	72.53	mean ratio P : Ag = 3 : 5.99
Orange-red Salt (Crystalline).				
P	10.69	10.91	10.81	5 preparations.
Ag	72.38	72.91	72.61	mean ratio P : Ag = 3 : 5.79
Red Salt (Crystalline).				
P	....	....	10.65	1 preparation.
Ag	....	....	73.18	P : Ag = 3 : 5.93

Unsatisfactory as these figures are, they appear to indicate the existence of

(1) A yellow salt, usually amorphous, occasionally crystalline, approximating in composition to $P_3N_3O_7H_2Ag_6$. As this is only formed in the cold from a trimetaphosphimate to which alkali has been added, it may be a salt of the supposed open-chain acid.

(2) A red crystalline salt of the formula $P_3N_3O_6Ag_6$.

(3) A white amorphous salt of nearly the same composition.

The orange-red salt, invariably containing too little silver, and varying in depth of color, may be a mixture or an intermediate form.

As the white salt is formed only in the presence of silver ammonia compounds, and is quite soluble in ammonium

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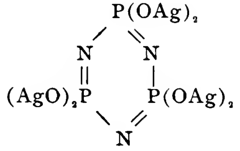
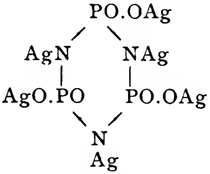
[1] This is seen to crystallize from the liquid, so that temporary solution must take place.

nitrate, it is clearly different in nature from the others. Probably it contains silver united to oxygen only, while in the red salt one-half the metal is associated with nitrogen. We may regard them as salts of the two forms of trimetaphosphimic acid :



Hexa-silver triphosphonitrilate.



Hexa-silver trimetaphosphimate.

The action of silver nitrate in preventing the transformation may be ascribed to its opposing dissociation. No deep decomposition occurs during the transformation, as the ammoniacal solution is not precipitated by magnesia mixture, and sodium trimetaphosphimate is regenerated by treatment with sodium chloride and acetic acid.

Ferric Trimetaphosphimates.—Gladstone[1] states that when pyrophosphodiamic acid is added to ferric sulphate, acidified with sulphuric acid, a clear solution results, which, on boiling, deposits white ferric pyrophosphamate, which is insoluble in acids but soluble in ammonia. The ferric trimetaphosphimates seem to vary considerably in composition and properties and present no characteristic features. The following points were noted : On adding ferric chloride to a moderately strong solution of sodium trimetaphosphimate an amorphous white precipitate forms which redissolves in an excess of the sodium salt, probably with formation of a ferric-sodium salt, but which becomes permanent on adding more ferric chloride. This is scarcely soluble in dilute hydrochloric acid, but readily soluble in ammonia with faint red color. Sodium hydroxide regenerates sodium salt. If, however, the solution of the sodium salt be dilute, no precipitate forms in the cold, even with an excess of ferric chloride, but on boiling, after acidifying, a white amorphous precipitate is produced, which, like the above, is nearly insoluble in dilute acid and easily

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[1] Q. J. Chem. Soc., **3**, 135 ; J. Chem. Soc. [2], **2**, 229 ; [2], **4**, 290 ; [2], **6**, 67.

soluble in ammonia and consists of trimetaphosphimate mixed with decomposition products.

The solubility of these salts in ammonia, which they show in common with other ferric amidophosphates and pyrophosphates may be ascribed to the formation of complex ions containing iron, in other words, of *ferri-trimetaphosphimic acids*, analogous to ferri-oxalic acid[1] and similar bodies.

Free Trimetaphosphimic Acid.—Silver trimetaphosphimate, decomposed under cold water by hydrogen sulphide, gives a solution from which, when fresh, the characteristic salts may be prepared, and from which much alcohol gradually throws out an amorphous sticky mass. The solution, on evaporation *in vacuo*, leaves a transparent, gummy residue from which alkalies evolve much ammonia, and which after redissolving, gives a precipitate with magnesium mixture, indicating partial decomposition. The acid seems therefore to be incapable of crystallization.

In marked distinction from metaphosphoric acid, trimetaphosphimic acid does not coagulate albumen.

Decomposition-Products of Trimetaphosphimic Acid.

Orthophosphoric acid and ammonia are the ultimate products of the action of acids on trimetaphosphimic acid, as well as of the decomposition of the free acid alone in aqueous solution when heated or kept for a long time. I have, however, been able to isolate three well marked intermediate bodies, *viz.*,

Diimidotriphosphoric acid, $P_3N_2O_8H_7$;
Imidodiphosphoric acid, $P_2NO_6H_5$;
Pyrophosphoric acid, $P_2O_7H_4$.

If sodium trimetaphosphimate solution (1—15) be boiled with 2–3 mol. weights nitric acid, the transformation into ammonia and orthophosphoric acid is complete in about 10 minutes, but on interrupting the boiling after 3–4 minutes and cooling, the presence of these products can be detected; the same change occurs slowly in the cold, many days being required for complete decomposition. From this solution silver nitrate throws down first the silver salt of unchanged trimetaphosphimic acid, then the others in the order named and finally

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[1] See Rosenheim, Ztschr. anorg. Chem., **11**, 214, etc.

silver phosphate, which is most easily soluble in nitric acid.

Although these products were first detected in this way, many experiments have convinced me that it is not a practical method of separation. The separation by fractional precipitation is not sharp, the properties of trimetaphosphimic and diimidotriphosphoric acids are so similar and the stability of the latter so slight, that the results are very unsatisfactory. In the absence of trimetaphosphimic acid, however, diimidotriphosphoric acid is readily separated from the later decomposition-products. If, therefore, we have ascertained the time required for all the trimetaphosphimic acid to be decomposed under given conditions, while diimidotriphosphoric acid still remains, we can isolate the latter in a condition of purity. Since the latter is merely a transition-product, the amount present at any time is small, and the actual yield is only about 10 per cent. of the theoretical.

The following method leads to the desired result. 1 mol. weight α-sodium trimetaphosphimate is dissolved in 15 pts. cold water, 3 mol. weights nitric acid (strength about 15 per cent.) added, and the solution allowed to stand for 7 days at the ordinary temperature. Enough ammonia is then added to give a faint odor and an excess of magnesium nitrate mixture[1] added, which throws down imidodiphosphoric, pyrophosphoric and orthophosphoric acids, while diimidotriphosphoric acid remains wholly in solution. The liquid is removed as far as possible from the semi-gelatinous precipitate by suction and pressing out in the filter,[2] without washing. The filtrate is approximately neutralized with nitric acid and precipitated by silver nitrate, a considerable excess of which should be used, as penta-silver diimidotriphosphate is much less soluble in dilute silver nitrate than in water. The slightly washed silver salt still contains some imidodiphosphate, as the magnesium salt of this acid is not wholly insoluble. To remove this it is dissolved in the smallest possible volume and amount of ammonia and a little magnesium nitrate mixture

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[1] Made by dissolving 100 grams crystallized magnesium nitrate and 35 grams ammonium nitrate in water, adding enough ammonia to give a faint odor, and diluting to 1 liter.

[2] Schleicher and Schüll's hardened filters, No. 575, have proved indispensable in this operation.

added, which throws out the remaining imido-diphosphoric acid. The liquid is again filtered by suction, with but little washing, and the silver salt again precipitated by neutralizing with nitric acid, with addition of a little silver nitrate. The moist silver salt is treated with an excess of moderately strong solution of sodium chloride, acidified with acetic acid, the silver chloride filtered off with but little washing and an equal volume of alcohol added to the filtrate, which precipitates *tri-sodium diimidotriphosphate*. This is purified by dissolving in a little water and reprecipitating by alcohol.

The magnesium precipitate, containing imidodiphosphoric and a little pyrophosphoric acids, is pressed out strongly under a screw press, pulverized and dissolved in the least possible amount of dilute nitric acid.[1] Ammonia is added drop by drop till a slight *permanent* precipitate forms, and after filtering, silver nitrate added as long as the precipitate is white. Nearly all the orthophosphoric acid remains in solution, even after adding much silver nitrate, but, if too much be added, or if the amount of orthophosphoric acid be relatively great, the latter portions of the precipitate are yellow. Exact quantitative data cannot be given, but in general it is necessary to use an amount of silver nitrate at least ten times the weight of the mixed magnesium salts. Silver pyrophosphate is partly precipitated towards the end, and partly remains in solution. To get rid of it entirely, as well as of traces of orthophosphoric acid and of a substance of relatively high percentage of nitrogen, the tri-silver imidodiphosphate must be dissolved in ammonia, reprecipitated as magnesium salt, pressed out and reconverted into the silver salt in the same manner. The mother-liquor of the second silver precipitation, if neutralized with ammonia, gives a mixture of silver imidodiphosphate and pyrophosphate; this, after conversion into the sodium salt by sodium chloride, addition of a little caustic soda and precipitating by alcohol gives a syrup which is converted by vigorous rubbing into a pasty mass. This, by repeated solution and reprecipitation by alcohol, gives the characteristic flat prisms of sodium

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[1] This is best done by rubbing up with water in a glass mortar, adding the acid gradually.

pyrophosphate. After conversion into the silver salt this proved to be free from nitrogen and an analysis gave:

	Calculated for $Ag_4P_2O_7$.	Found.
Ag	71.27	70.23

Tedious as the above method is, many experiments have failed to lead to the discovery of a better one, and have convinced me that it cannot be abbreviated in the least without injuriously affecting the quality of the products.

Diimidotriphosphoric Acid, $P_3N_2O_8H_7$.

This acid forms two series of salts, in which three and five atoms of hydrogen are replaced. The alkali salts with three atoms of metal are of neutral, those with five atoms of alkaline reaction. It seems impossible to replace the two remaining atoms, as is pointed out under the silver salts.

Tri-Sodium Diimidotriphosphate, $P_3N_2O_8H_4Na_3$.—The preparation of this salt is described above. It is easily soluble in water, this solution leaving on evaporation a mass of indistinct prisms. Precipitated from its aqueous solution by alcohol it usually forms granules without evidence of crystalline form, but when very slowly precipitated it may be obtained as flat, very obtusely pointed prisms or rhombic plates, visible only when magnified 400 diameters. It contains no crystal water. The substance dried at 100° gave:

	Calculated for $P_3N_2O_8H_4Na_3$.	Found.
P	28.89	28.73
N	8.72	8.77
Na	21.45	20.69

P : N : Na = 3 : 2.02 : 2.92.

A penta-sodium salt probably exists, being obtained by decomposing the penta-silver salt with sodium chloride. It has alkaline reaction and is precipitated by alcohol as an uncrystallizable syrup.

The tri-sodium salt is not precipitated even in strong solution by magnesium chloride or magnesia mixture unless the latter contains much ammonia; in this case the resulting precipitate is easily soluble in ammonium salts, and hence is probably merely magnesium hydroxide. Barium chloride precipitates from a not too dilute solution microscopic spherules, which dissolve readily in a cold, strong solution of sodium chloride ; on boiling this solution a crystalline precipitate is at once formed, consisting of microscopic rhombohedra (?) resembling sodium barium trimetaphosphimate and probably a double salt.

Silver Salts.—Two of these were obtained, one having the formula $P_3N_2O_8H_4Ag_3$, and the other $P_3O_2O_8H_2Ag_5$. The tendency to formation of the latter is so strong that a solution of the tertiary sodium salt gives with silver nitrate a white amorphous precipitate, which, however, is mixed with some crystals of the former.

Tri-Silver Diimidotriphosphate, $P_3N_2O_8H_4Ag_3$.—This salt is very characteristic. It can be obtained pure only by precipitating an acidified solution of the tertiary sodium salt by an excess of silver nitrate. To a solution of the sodium salt in 30 parts water, 1 to 2 molecular weights nitric acid are added and then silver nitrate gradually ; as soon as a milkiness, due to the formation of the penta-salt, is observed, more acid is added, and then more silver nitrate, acid being added as often as necessary; the crystallization soon starts, but several times the theoretical amount of nitrate is required, and under no circumstances is the precipitation complete. Generally spherules with many rhombic facets are obtained, but with slow crystallization (from more dilute solutions) the forms shown in Figs. 5 and 6 result.

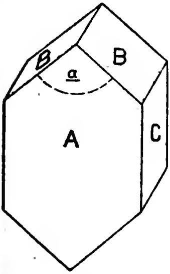

Fig. 5.

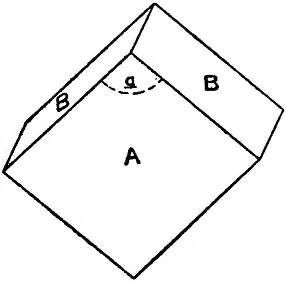

Fig. 6.

$A = \infty P \bar{\infty}$. $B = P \grave{\infty}$. $C = \infty P \grave{\infty}$.

The colorless crystals are monoclinic, and suggest those of tertiary silver trimetaphosphimate, but are shorter and thicker and approach more nearly to the orthorhombic form. No other faces are ever seen. The angle *a* (between the edges), measured under the microscope is very nearly 98°; the acute angle between the edges of B is, roughly speaking, 80°, so that when the form Fig. 6 occurs, and this face is uppermost, it is apt to be mistaken under superficial observation for trimetaphosphimate (angle *a*, 78°).

The salt is practically insoluble in water, easily in ammonia, and rather difficultly in dilute nitric acid. When pure it is not discolored by light or by caustic soda. It contains no crystal water. Analysis gave:

	Calculated for $P_3N_2O_8H_4Ag_3$.	Found. (1)	(2)
P	16.14	16.39	16.29
N	4.87	4.76	
Ag	56.10	55.94	56.36

(1) P : N : Ag = 3 : 2.01 : 2.94. Direct from decomposed solution of trimetaphosphimic acid.

(2) P : Ag = 3 : 2.99. From sodium salt.

Penta-Silver Diimidotriphosphate, $P_3N_2O_8H_2Ag_5$.—One molecular weight tertiary sodium salt is dissolved with addition of not less than 1½ nor more than 4 molecular weights ammonia, and added to an excess of a solution of silver nitrate; the pure white amorphous voluminous precipitate is washed, sucked out and dried *in vacuo*. When fresh it is colorless, but on drying it assumes a yellowish tint, and after standing for some time it is partially converted into crystals, the nature of which was not determined. On boiling with water it also becomes yellowish, and in each case the change of color is accompanied by decomposition, as its ammoniacal solution is partially precipitated in amorphous form by magnesia mixture, an effect which is not observed in the perfectly fresh white salt. Warming with ammonium nitrate destroys the yellow color, which is consequently not due to silver phosphate. The fact that it remains white on boiling with ammonium nitrate serves to distinguish it from the trimetaphosphimates, the more basic silver salts of which, as pointed out, become orange-red under these conditions. The salt is very difficultly, yet perceptibly soluble in water, and is reprecipitated by adding considerable silver nitrate; it is easily soluble in ammonia, and nitric acid converts it partly into the tertiary salt before dissolving it.

Dried at 100° it gave :

	Calculated for $P_3N_2O_8H_2Ag_5$.	Found. (1)	(2)	(3)
P	11.77	12.05	11.96	11.75
N	3.55	3.66	3.65	
Ag	68.23	68.96	68.92	69.24

(1) P : N : Ag = 3 : 2.02 : 4.94.
(2) P : N : Ag = 3 : 2.02 : 4.97.
(3) P : Ag = 3 : 5.08.

Attempts to replace one or both of the remaining hydrogen atoms by silver proved unsuccessful. If the tertiary sodium salt be dissolved with 1–2 molecular weights caustic soda, or even with 5–6 molecular weights ammonia, and added to silver nitrate, the resulting precipitate is discolored by free silver oxide. On standing several days it becomes yellow, but its ammoniacal solution is now precipitated by magnesia mixture, indicating decomposition. The magnesia precipitate gave a silver salt resembling tertiary imidodiphosphate, but the exact nature of the decomposition was not investigated.

Imidodiphosphoric Acid, $P_2NO_6H_5$.

This is probably the substance described by Gladstone under the name *pyrophosphamic acid*. It is moderately stable in cold, not too acid, solution, and hence occurs in large amount among the decomposition products of trimetaphosphimic acid.

Trisodium imidodiphosphate, obtained by decomposing the tertiary silver salt by sodium chloride, has alkaline reaction. Its solution, as well as that of the tetra sodium salt, is precipitated by alcohol as a syrup which cannot be made to crystrllize, and the aqueous solution of which dries to a transparent gummy mass. It is more soluble in dilute alcohol than sodium pyrophosphate.

The *magnesium* salt above described is amorphous, voluminous, and nearly, but not quite, insoluble in water, and somewhat more soluble in solutions of ammonium salts.

Tri-Silver Imidodiphosphate, $P_2NO_6H_2Ag_3$.—This is obtained as an amorphous, white precipitate, when the free acid, or a solution of a tertiary salt is precipitated by silver nitrate. Thus formed, it tends to collect in small lumps, a property which distinguishes it from any of the other silver salts referred to in this paper. When precipitated by acid from its ammoniacal solution it forms a powder that settles slowly. When slowly separating, or when precipitated from hot solutions, it forms semi-crystalline granules, often united to crusts or dendritic forms. When formed in a moderately acid solution it usually shows a slight deficiency of silver (Anal. 1–2), probably due to a trace of a more acid salt, but such a salt cannot be obtained in pure form. Pure tertiary salt can be obtained by decomposing the crude salt with somewhat less than the required amount of sodium chloride, and reprecipitating. It is insoluble in water and is not affected by light.

Dried at 100° it gave :

	Calculated for $P_2NO_6H_2Ag_3$.	Found. (1).	(2).	(3).	(4).	(5).
P	12.47	13.19	12.75	12.34	12.60	12.19
N	2.82	3.13	3.14	2.86	2.96	2.92
Ag	65.03	63.70	63.87	65.21	65.06	66.46

$$P : N : Ag \left\{ \begin{array}{l} (1) = 2 : 1.05 : 2.78 ; \\ (2) = 2 : 1.09 : 2.78 ; \\ (3) = 2 : 1.02 : 3.04 ; \\ (4) = 2 : 1.04 : 2.97 ; \\ (5) = 2 : 1.06 : 3.14 ; \end{array} \right.$$

Tetra-Silver Imidodiphosphate, $P_2NO_6HAg_4$.—This salt exists in a white and in a yellow form. The former is obtained by precipitating a solution of silver oxide in ammonium nitrate by the sodium salt. It forms a voluminous, flocculent precipitate, which remains white only in presence of its mother-liquor ; on washing out it undergoes partial transformation into the yellow form, the same change occurring temporarily on boiling under the mother-liquor. It shows a slight deficiency of silver (Anal. 4).

The *yellow* form is obtained as an amorphous, flocculent precipitate by adding an ammoniacal solution of an imidodiphosphate to an excess of silver nitrate (Anal. 1–2), or as an imperfectly crystalline powder, by evaporating such an ammoniacal solution, containing an excess of silver, over sulphuric acid (Anal. 3). From this it appears that the remaining hydrogen atom is not replaceable by metal. The difference between the white and yellow forms is perhaps due to tautomerism.

Dried at 100°, it gave:

	Calculated for $P_2NO_6HAg_4$.	Found. (1.)	(2.)	(3.)	(4.)
P	10.27	10.17	10.07	....	10.80
N	2.32	2.28	2.45	....	....
Ag	71.39	72.19	72.35	71.01	69.72

(1). P : N : Ag = 2 : 0.99 : 4.01.

(2). P : N : Ag = 2 : 1.07 : 4.13.

(3). P : Ag = 2 : 3.71.

Imidodiphosphoric acid is easily distinguished from diimidotriphosphoric acid by the insolubility of its magnesium salt, by the peculiar granular or lumpy appearance of its tertiary silver salt, by its syrupy tertiary sodium salt, and by its ammoniacal solution giving a yellow salt with silver nitrate, while the silver salt of the latter, found under the same conditions, is either white, or, when too much ammonia has been used, discolored by silver oxide.

Ferric Imidodiphosphate.—No analysis of this was made. It is thrown down on boiling an acidified solution with a ferric salt as a white, amorphous precipitate, difficultly soluble in acids and easily soluble in ammonia.

Cupric Imidodiphosphates.—Several of these appear to exist. The amorphous, light-blue precipitate formed by cupric sulphate in a solution of the sodium salt redissolves in an excess of the latter, but is again reprecipitated by an excess of cupric salt, but under no circumstances completely. It dissolves in caustic potash to a violet solution. The soluble sodium double salt is partially precipitated on heating its aqueous solution, the precipitate redissolving on cooling. The precipitate with excess of cupric sulphate dissolves readily in cold acetic or sulphurous acid, and is temporarily reprecipitated on heating the solution, unless too dilute and too strongly acid, in which case some pyrophosphate crystallizes out on long heating. The same temporary precipitation occurs in a less degree on heating its solution in very dilute nitric acid.

The property of being precipitated from an acid solution on boiling is one which cupric imidodiphosphate shares with the pyrophosphate, and the same is observed with the magnesium salts, but with the difference that the pyrophosphates do not redissolve on cooling, while the imidodiphosphates redissolve either at once or in a short time. It is not possible to effect a complete separation of the two acids in this way, however, for if pyrophosphoric acid be present, more or less imidodiphosphate remains in the permanent precipitate, apparently because of the formation of complex salts containing both acids. The only method for separating the two acids when mixed in approximately equal proportions is to convert them into the sodium salts, and to precipitate repeatedly by alcohol, finally recrystallizing the pyrophosphate from water.

Decomposition of Imidodiphosphoric Acid.—When a soluble imidodiphosphate is boiled with acetic acid, it is converted for the most part into orthophosphoric acid, and to a much less extent into pyrophosphoric acid. The significance of this fact is pointed out in the introduction. A solution of the sodium salt (which analysis has proved to be free from pyrophosphate) in 30–50 parts water is weakly acidified with acetic acid, boiled 7–8 minutes, and cooled. If this solution be made alkaline with caustic soda, and alcohol added, an abundant crystallization of tertiary sodium phosphate is formed, which may be recognized by its crystalline form and by the usual reactions. In this the microscope shows a few crystals of sodium pyrophosphate. The latter acid may be isolated by making use of the fact that a solution of freshly precipitated magnesium pyrophosphate in excess of cold acetic acid is quantitatively precipitated on boiling, in a permanently insoluble form, while magnesium orthophosphate remains dissolved. The above weakly acetic solution is mixed with magnesium acetate in excess, the precipitate dissolved by adding about one-fifth volume of strong acetic acid, and boiled a few minutes. The precipitated granular magnesium pyrophosphate is dissolved in nitric acid, in the manner described for the separation of the decomposition-products of trimetaphosphimic acid, converted into silver salt and then into sodium salt. This, after several precipitations by alcohol, is recrystallized from water. A careful determination of the yield of pyrophosphoric acid in two experiments gave 13.5 and 16 per cent. of the theoretical. For analysis the sodium salt was converted into silver pyrophosphate, which gave :

	Calculated for $Ag_4P_2O_7$.	Found.
P	10.24	10.35
Ag	71.27	70.74

Decomposition of Sodium Trimetaphosphimate by Acetic Acid.

As before pointed out, this salt is not decomposed by acetic acid in the cold, or on short heating. If, however, its solution is heated for two or three hours with 30 per cent. acetic acid and magnesium acetate, under the conditions mentioned under the magnesium salt, a granular precipitate is obtained, consisting of a mixture or double salt of magnesium pyrophosphate and imidodiphosphate, which does not perceptibly redissolve on cooling, while the liquid contains much orthophosphoric acid. The sodium pyrophosphate, separated from this by the above method, showed the characteristic form. For analysis it was converted into the silver salt, and gave :

	Calculated for $Ag_4P_2O_7$.	Found.
P	10.24	10.43
Ag	71.27	70.33

The following paper will be devoted to the description of *tetrametaphosphimic* acid.

WASHINGTON, D. C., June 30, 1896.

Contributions from the Chemical Laboratory of Harvard College.

XCV.—ON CERTAIN DERIVATIVES OF TRICHLORDINITROBENZOL.

By C. Loring Jackson and W. R. Lamar.

For several years the behavior of various reagents with tribromdinitrobenzol, melting at 192°, has been studied in this laboratory,[1] and, as results accumulated, it became of interest to study the corresponding trichlordinitrobenzol melting at 129°.5, to see whether it behaved in the same way as the bromine compound. This extension of the work was prevented by the extreme difficulty in preparing symmetrical trichlorbenzol by any of the known methods until Victor Meyer and Sudborough published[2] in 1894 their admirable method of preparing trichloraniline, by which it can be made in quantity with no great outlay of time or labor. We have accordingly taken up the study of trichlordinitrobenzol melting at 129°.5, discovered some years ago by J. F. Wing and one of us,[3] and in this paper describe its action with aniline, sodic ethylate, and sodium malonic ester, with the last two of which reagents it behaves in many respects differently from the tribromdinitrobenzol. The behavior of the other reagents with this substance, and a similar study of the trichlortrinitrobenzol will be undertaken in the near future in this laboratory.

When heated with aniline, trichlordinitrobenzol gives the same trianilidodinitrobenzol melting at 179°, which was obtained under the same conditions from tribromdinitrobenzol. With sodic ethylate in the cold tribromdinitrobenzol lost two of its atoms of bromine, which were replaced by two ethoxy radicals forming bromdinitroresorcin diethylether melting at 184°. In just the same way cold sodic ethylate in alcoholic solution converts trichlordinitrobenzol into chlordinitroresorcin diethylether which melts at 160°, but here the resemblance ends, for whereas a hot solution of sodic ethylate replaces the atom of bromine in bromdinitroresorcin diethylether by hydrogen forming dinitroresorcin diethylether melting at 133°, under the same conditions the chlordinitroresorcin diethylether was converted into a mixture of dinitrophloro-

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[1] This Journal, **10**, 283; **11**, 93, 541; **12**, 164: **13**, 164; **14**, 331; **16**, 28, 35; **18**, 465.

[2] Ber. d. chem. Ges., **27**, 3151.

[3] This Journal, **9**, 348.

glucin triethylether, $C_6H(NO_2)_2(OC_2H_6)_3$, which melts at 104–105°, and its diethylether, $C_6H(NO_2)_2(OC_2H_6)_2OH$, melting at 166°. The same products were obtained in each case by treating the tribrom- or trichlordinitrobenzol with hot sodic ethylate.

With sodium malonic ester tribromdinitrobenzol gives a rather complex reaction. Two atoms of bromine are removed, one being replaced by the malonic ester radical, and the other by hydrogen, so that the product is bromdinitrophenylmalonic ester, $C_6H_2Br(NO_2)_2CH(COOC_2H_6)_2$. The trichlordinitrobenzol under the same conditions acts more simply, as only one atom of chlorine is affected, and this is replaced by the malonic ester radical, so that the product is dichlordinitrophenylmalonic ester, $C_6HCl_2(NO_2)_2CH(COOC_2H_6)_2$, which melts at 101°. We have not yet succeeded in replacing one of the atoms of chlorine in this substance by hydrogen under the influence of sodium malonic ester, but hope to try further experiments in this direction. The dichlordinitrophenylmalonic ester resembles the bromdinitrophenylmalonic ester in many of its properties. Both give red sodium salts, and by the action of nitric acid both are converted into nitrites. The nitrite of dichlordinitrophenylmalonic ester has the formula, $C_6HCl_2(NO_2)_2CONO(COOC_2H_6)_2$, and seems to be less stable than the corresponding bromine compound. Both the substituted malonic esters also are saponified by boiling with sulphuric acid of specific gravity 1.44, forming the corresponding phenylacetic acids, but the dichlordinitrophenylacetic acid, $C_6HCl_2(NO_2)_2CH_2COOH$, (melting-point 140°) differs in some striking particulars from the bromdinitrophenylacetic acid. The latter is so unstable that five crystallizations from alcohol are enough to remove carbonic dioxide from it, and convert it completely into bromdinitrotoluol. The same transformation takes place more slowly, when it is crystallized from hot water. The dichlordinitrophenylacetic acid, on the other hand, can be crystallized from hot water without alteration. When it was boiled with alcohol a new compound was formed, but very slowly, so that it was necessary to boil the substance with alcohol for some hours in order to convert it into the new body; this, however, was not the expected dichlordinitrotoluol, but the ethyl ester of the substituted acetic acid, $C_6HCl_2(NO_2)_2CH_2COOC_2H_5$, which melted at 67–68°. At first we thought that this formation of the ester must have been caused by the presence of a trace of the sulphuric acid used in saponifying the substituted malonic ester, but on repeating the experiment with a sample, which did not contain a trace of sulphuric acid, the same result was obtained. The formation of an ester from an acid and alcohol alone without the aid of a mineral acid has been observed in a few other cases. These are, pyruric acid, described by L. Simon,[1] and also by Emil Fischer and Speier,[2] and tartaric acid described by Berthelot.[3] The easy formation of the ester from our dichlordinitrophenylacetic acid is the less surprising because Victor Meyer[4] and Goldschmidt[5] have recently called attention to the extraordinary ease with which phenylacetic acid itself is converted into its ester.

Another difference between the dichlordinitrophenylacetic acid and the bromdinitrophenylacetic acid appears in their behavior with alkalies. The bromine compound gives an intense dark green coloration with sodic hydrate, whereas the chlorine compound with the same reagent turns crimson at first, but this color fades in a few seconds, and a nearly white salt of the acid is formed. We are of the opinion from these phenomena that both these intense colors are due to compounds similar to those formed by sodic alcoholates or sodic hydrate on trinitrobenzol, studied by Victor Meyer[6] and by Shukoff,[7] on dinitrobenzoic acid studied by Lobry de Bruyn,[8] and later by him and Van Leent,[9] or on bromdinitrobenzoic acid and a number of related substances by Ittner and one of us.[10]

EXPERIMENTAL PART.

Preparation of Trichlordinitrobenzol.

The trichloraniline used in this preparation was made by

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[1] Thèses, Paris, 1895.

[2] Ber. d. chem. Ges., **28**, 3256.

[3] Ann. de Chim. et de Phys., **68**, 263.

[4] Ber. d. chem. Ges., **28**, 3197. Compare also Shukoff, *ibid*, 3201.

[5] *Ibid*, 3224.

[6] *Ibid*, **27**, 3153.

[7] *Ibid.*, **28**, 1800.

[8] Rec. Tr. chim. Pays Bas, **14**, 89.

[9] *Ibid.*, 150.

[10] *Ibid.*, **28**, 3063. A fuller account of this work, including a study of the product from dinitranisic acid, will appear soon in this JOURNAL.

the excellent method of Victor Meyer and Sudborough[1] as follows: One hundred grams of freshly distilled aniline were dissolved in one kilogram of chloroform, which had been washed to free it from alcohol, and thoroughly dried. The vessel containing this solution was immersed in a bath of ice and water, and dry chlorine passed through the cold liquid, until it was saturated, which occupied from twelve to fifteen hours. It is advisable to introduce the chlorine through a wide tube, as there is danger that a narrow one will be stopped up by precipitated trichloraniline chloride. The precipitate formed by the action of the chlorine was freed from chloroform by means of a filter-pump, dried and washed with water, which removed all the compounds of aniline except the trichloraniline. The yield was good, as 117 grams of trichloraniline were obtained instead of 211 grams, that is 55.4 per cent. of the theoretical amount. The product made in this way was pure enough to be submitted directly to the diazo reaction. It melted at 76° instead of 77°.5. If sufficient care was not taken in washing and drying the chloroform, or if the solution was not cooled during the treatment with chlorine, a more impure product resulted, which it was necessary to purify by distillation.

The trichloraniline was converted into trichlorbenzol as follows: Thirty grams of it were dissolved in 500 cc. of common alcohol and gradually mixed with 17 cc. of strong sulphuric acid (the calculated amount). The liquid was allowed to cool to ordinary temperatures, and then 17 grams of finely powdered sodic nitrite added at one time; after which the mixture was allowed to stand for eight hours. At the end of this time the trichlorbenzol, which had separated, was filtered out and washed with water until free from sodic sulphate. The alcoholic filtrate was then treated with water in the proportion of one volume of water to three volumes of the filtrate, as it had been found that this amount of water precipitated most of the trichlorbenzol, but left the oily impurities in solution. The yield of trichlorbenzol was excellent, 30 grams of trichloraniline gave 25.5 grams of trichlorbenzol

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[1] Ber. d. chem. Ges., 27, 3151.

instead of 27.7 grams, that is 92 per cent. of the theoretical amount.

The trichlorbenzol was converted into trichlordinitrobenzol[1] by dissolving it at ordinary temperatures in nitric acid of specific gravity 1.505, made from nitre and sulphuric acid in the proportion of one molecule of each. After the solid was completely dissolved, it was precipitated by pouring it into cold water, and purified by recrystallization from hot alcohol till it showed the melting-point 129°.5.

Action of Aniline on Trichlordinitrobenzol.

Five grams of trichlordinitrobenzol were mixed with 10.5 grams of aniline, that is a slight excess over the proportion of 6 molecules of aniline to 1 of the trichlordinitrobenzol. The greater part of the solid dissolved in the cold, and the rest went into solution when the mixture was warmed on the steam-bath. The deep-red liquid solidified after it had been heated for an hour on the steam-bath. The solid mass, freed from aniline by treatment with very dilute acid, was recrystallized from alcohol until it showed the constant melting-point, 179°. As this is the melting-point of the trianilidodinitrobenzol, prepared by A. W. Palmer and one of us,[2] by the action of aniline on tribromdinitrobenzol, it seemed unnecessary to submit the substance to analysis. It was obtained in the orange-red prisms described by H. N. Herman and one of us.[3] In this respect, therefore, the trichlordinitrobenzol behaves exactly like the corresponding bromine compound.

Action of Sodic Ethylate on Trichlordinitrobenzol in the Cold.

Ten grams of trichlordinitrobenzol, dissolved in a mixture of 30 cc. of dry benzol and 60 cc. of absolute alcohol, were mixed with the sodic ethylate prepared by treating 2.6 grams of sodium with 65 cc. of absolute alcohol. This gives the proportion of 3 molecules of sodic ethylate to each molecule of trichlordinitrobenzol. The first few drops of the sodic ethylate solution produced a deep wine-red color, but, as more was added, this color grew fainter, fading to a light yellowish red. A considerable evolution of heat was also observed, sufficient to raise the temperature of 155 cc. of the liquid 10°.

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[1] This JOURNAL. **9**, 348.

[2] *Ibid*, **11**, 456.

[3] *Ibid*, **16**, 35.

This is the more remarkable, as no evolution of heat was perceptible in the corresponding reaction of sodic ethylate on tribromdinitrobenzol. In order to make sure that the reaction was complete, the mixture was allowed to stand in a corked flask, at ordinary temperatures, over night, when it was found that a portion of the product had crystallized in clusters of pale yellow needles. The mother-liquor poured off from these crystals was allowed to evaporate spontaneously, and the product of the reaction, after being washed free from sodic chloride with water, was purified by crystallization from hot alcohol, until it showed the constant melting-point, 160°. This substance is the chief product of the reaction; the only other organic product was an oily body which occurred in such small quantity that we were unable to isolate it. The body melting at 160° was dried at 100°, and analyzed with the following result:

0.3192 gram of the substance gave by the method of Carius 0.1600 gram of argentic chloride.

	Calculated for $C_6HCl(OC_2H_5)_2(NO_2)_2$.	Found.
Chlorine	12.22	12.39

The substance is therefore chlordinitroresorcin diethylether, and the action of sodic ethylate on trichlordinitrobenzol is exactly the same as its behavior with tribromdinitrobenzol,[1] which it converts into the bromdinitroresorcin diethylether melting at 184°.

Properties of Chlordinitroresorcin Diethylether.—It crystallizes from alcohol in good sized, yellowish white prisms with square, or nearly square ends, which show a tendency to combine longitudinally, forming twin crystals looking like a grain of wheat, as they taper to fine points at the ends. When crystallized less well it appears in bunches of branching needles. From its solution in benzol it crystallizes in prisms, which effloresce on exposure to the air, and therefore, undoubtedly, contain benzol of crystallization. It melts at 160°. It is practically insoluble in water, whether hot or cold; slightly soluble in ether, carbonic disulphide or cold methyl or ethyl alcohol, much more soluble in hot

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[1] Jackson and Warren, This Journal, **13**, 164.

alcohol; soluble in benzol, or chloroform; freely soluble in acetone, which is the best solvent for it. The three strong acids have no apparent action on it in the cold, nor is it saponified by cold sodic hydrate.

Action of Hot Sodic Ethylate on Trichlordinitrobenzol.

Ten grams of trichlordinitrobenzol were dissolved in 20 cc. of dry benzol, and this solution, while still warm, was mixed with sodic ethylate prepared by the action of 45 cc. of absolute alcohol on 2.6 grams of sodium. This gave the proportion of 3 molecules of sodic ethylate to each molecule of trichlordinitrobenzol. So much heat was given off on the addition of the sodic ethylate that the liquid began to boil. This violent boiling was checked by cooling the flask with running water, and then the mixture was heated gently on the steam-bath for ten minutes. Longer boiling partially decomposed the first product of the reaction by saponifying one or more of the ethoxy groups which it contained. The best results were obtained with very concentrated solutions, as already described. If more of the solvents was used, it was necessary to heat longer to bring the reaction to an end; for instance, when the mixed liquids amounted to 160 cc. we were obliged to heat them for an hour and a quarter, but in such cases the yield was much less satisfactory than in those where a strong solution was used. During the boiling the same phenomena were observed, which had appeared in the corresponding reaction with tribromdinitrobenzol,[1] that is, the red color of the solution steadily increased in intensity, and an inorganic precipitate (in this case sodic chloride) was formed. A curious odor was also observed in the solution, which was in the case of the bromine compound supposed to accompany the replacement of the halogen by hydrogen, but this supposition was incorrect, as it also appeared in this reaction, where no such replacement took place.

After the boiling was finished the solvents were allowed to evaporate spontaneously, and the residue thoroughly washed with water. The consideration of the organic substance contained in these wash-waters will be postponed to the next

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[1] Jackson and Warren, This JOURNAL, 13, 164.

section. The insoluble residue could not be purified by crystallization from alcohol, but by allowing its solution in benzol to evaporate to dryness spontaneously a mixture was obtained of large prismatic crystals and smaller, rather indefinite needles. From this mixture the larger crystals were easily picked out, and these were then purified by recrystallization from alcohol, when they showed the constant melting-point 104–105°. An additional amount of the substance was obtained from an oily product of the reaction, which was found mixed with the original crystals; after standing for three or four weeks it solidified, and was then easily purified by crystallization from alcohol. As the substance gave up its moisture very slowly *in vacuo*, it was dried at about 90°, and then analyzed with the following results:

I. 0.2689 gram of the substance gave on combustion 0.4792 gram of carbonic dioxide and 0.1532 gram of water.

II. 0.3157 gram substance gave 0.5622 gram of carbonic dioxide and 0.1885 gram of water.

III. 0.3316 gram of the substance gave 28.6 cc. of nitrogen at a temperature of 20° and a pressure of 761 mm.

	Calculated for $C_6H(OC_2H_5)_3(NO_2)_2$.	Found. I.	 II.	 III.
Carbon	48.01	48.60	48.57	
Hydrogen	5.33	6.33	6.63	
Nitrogen	9.34			9.87

These numbers do not agree so closely with those calculated from the formula as could be wished, but we could obtain no better on account of the explosive nature of the substance, which rendered its combustion a matter of great difficulty. In fact, only after several attempts and adopting special precautions, could results as good as these be secured. They are near enough to the theoretical, however, to prove that the substance is the dinitrophloroglucin triethylether, and therefore the reaction has run differently from that observed in the case of hot sodic ethylate and tribromdinitrobenzol, as then one of the atoms of bromine was replaced by hydrogen giving dinitroresorcin diethylether.

Properties of Dinitrophloroglucin Triethylether, $C_6H(NO_2)_2$-$(OC_2H_5)_3$.—This substance crystallizes from benzol at first in rhombic plates, but, as the crystallization continues, the acute angles of these plates become more and more strongly truncated, until the plates develop into prisms terminated at each end by two planes at an obtuse angle to each other. These crystals are frequently more than a centimeter long and somewhat less than a centimeter broad. They have a yellowish color and turn dark brown on exposure to the air and light, a change which takes place more rapidly when they are heated to 100°. They melt at 104–105°. They are very freely soluble in alcohol; freely soluble in glacial acetic acid, chloroform, or benzol; soluble in ether, slightly soluble in carbonic disulphide, or in cold methyl or ethyl alcohol, but freely soluble in the two alcohols when they are hot; essentially insoluble in ligroïn, or in water even when hot. The best solvent for it is hot alcohol, or benzol. It dissolves in cold strong sulphuric acid with a yellowish brown color, and water seems to precipitate it unaltered from this solution. It appears to be insoluble, or nearly so, in cold strong nitric acid, but dissolves readily when heated with it. This solution, on cooling, deposits long, slender, pale-yellow crystals, which have not yet been examined more carefully. Strong hydrochloric acid does not act on it in the cold, or even when heated to 100° in a sealed tube with it, but if the temperature is raised to 150°, the ether is saponified, as is shown by the evolution of a gas burning with a green-bordered flame, when the tube is opened, which is undoubtedly ethyl chloride. The other product of the reaction is principally dissolved in the liquid to which it imparts a deep brown-red color. Want of time has prevented us from preparing it in quantity for analysis. It seemed to be a yellow phenol, which sublimed with difficulty. Sodic hydrate, even in boiling solution, acted only slowly and incompletely on the dinitrophloroglucin triethylether, forming a brownish-red solution of the sodium salt of a phenol soluble in water or salt solutions.

Dinitrophloroglucin Diethylether, $C_6H(NO_2)_2(OC_2H_5)_2OH$.

The sodium salt of this substance was formed by the action, already described, of hot sodic ethylate on trichlordinitrobenzol, and was dissolved in the water, with which the original product was washed. It was obtained by acidifying these wash-waters with hydrochloric acid and recrystallizing the dark-brown precipitate from alcohol, till it showed the constant melting-point, 166°. The longer the mixture of trichlordinitrobenzol and sodic ethylate was heated, the larger was the proportion of diethylether formed, which renders it probable that the triethylether is the first product of the action, and that the diethylether is formed from it by a subsequent reaction. The same substance was the principal product when chlordinitroresorcin diethylether was treated with a hot solution of sodic ethylate. It was mixed in this case with a little of the dinitrophloroglucin triethylether just described.

The substance was dried at 100° and analyzed. The results obtained agreed with the numbers calculated for dinitrophloroglucin diethylether better than with anything else, but the agreement was not close enough to make it worth while to publish them. These variations are undoubtedly due to the fact that the substance is very explosive, since these analyses were made with only the ordinary precautions. We have not repeated the combustions under more carefully regulated conditions, because the analyses given below of the salt of this substance establish its composition sufficiently.

Sodium Salt of Dinitrophloroglucin Diethylether,

$C_6H(NO_2)_2(OC_2H_5)_2ONa.2H_2O$.

This salt was made as follows: A quantity of the dinitrophloroglucin diethylether was treated with a solution of sodic hydrate (made from sodium) in quantity insufficient to convert the whole of it into the salt. The dark orange-red solution thus obtained was filtered from the unchanged phenol, concentrated, and then allowed to evaporate spontaneously. The salt thus prepared gave the following results on analysis:

I. 0.5122 gram of the air-dried salt lost, when dried at 100°, 0.0571 gram of water.

II. 0.6242 gram of the salt lost 0.0688 gram of water.

	Calculated for $C_6H(NO_2)_2(OC_2H_5)_2ONa.2H_2O$.	Found.	
		I.	II.
Water	10.91	11.14	11.02

I. 0.4551 gram of the salt dried at 100° gave 0.1100 gram of sodic sulphate.

II. 0.5554 gram of the salt dried at 100° gave 0.1336 gram of sodic sulphate.

	Calculated for $C_6H(NO_2)_2(OC_2H_5)_2ONa$.	Found.	
		I.	II.
Sodium	7.82	7.83	7.79

In making these analyses it was necessary to apply the heat at first with the greatest care, for, if the temperature rose too high before the phenol was decomposed, an explosion took place.

Properties of the Sodium Salt of Dinitrophloroglucin Diethylether. — Crystallized from water it forms good-sized flat prisms either with square ends or terminated by two planes at an obtuse angle, which is sometimes truncated, or even cut off by a number of smaller modifications. It has a brownish-orange color, and when heated to 135° for some time is partially decomposed with the formation of a slight orange sublimate. Its aqueous solution is dark orange red and gives a neutral reaction. It gave striking precipitates with the following reagents:

With salts of *calcium*, *strontium* or *barium* a bright yellow, gelatinous precipitate, if the solution was concentrated.

With *ferric chloride* salmon-colored flocks.

With *plumbic acetate* yellow flocks.

With *mercuric chloride* yellow flocks, but in smaller quantity than with a salt of lead.

Properties of Dinitrophloroglucin Diethylether.—This substance crystallizes from alcohol in sharp, yellowish-white needles. It melts at 166°, and sublimes although very slowly even at 135°. It is very soluble in acetone or chloroform; soluble in benzol, ether, glacial acetic acid or carbonic disulphide; more soluble in methyl than in ethyl alcohol; slightly soluble in hot water, but practically insoluble in cold; essentially insoluble in ligroïn. Alcohol is the best solvent for it. Apparently unaffected by strong hydrochloric acid in the cold; very slightly, if at all, soluble in cold nitric acid, but dissolves when heated with it; cold strong sulphuric acid dissolves it, forming a yellow liquid. Sodic hydrate converts it into the salt already described.

Action of Sodium Malonic Ester on Trichlordinitrobenzol.—Thirty grams of trichlordinitrobenzol (melting at 129°.5) dissolved in 60 cc. of benzol, were mixed with 35.6 grams of malonic ester, previously converted into the sodium salt by treatment with the sodic ethylate made from 5 grams of sodium and 200 cc. of absolute alcohol. These proportions give three molecules of the ester for each molecule of trichlordinitrobenzol. The mixture was allowed to stand at ordinary temperatures in a corked flask for twenty hours and then the dark-red liquid poured into five times its volume of cold water acidified with dilute sulphuric acid, and allowed to stand till the next day. During this second standing the portion of the product which had been precipitated in the aqueous solution, was converted from an oily to a crystalline consistency, and could then be filtered out without difficulty. The larger part of the product, however, was not here, but was dissolved in the benzol, which collected on the bottom of the beaker. This was separated, and mixed with hot alcohol, from which crystals were deposited as the mixture cooled. These crystals and those obtained from the aqueous liquid were purified by crystallization from hot alcohol, until they showed the constant melting-point 101°, when the substance was dried *in vacuo* and analyzed with the following results:

I. 0.3006 gram of the substance gave on combustion 0.4400 gram of carbon dioxide and 0.0866 gram of water.

II. 0.2223 gram of the substance gave by the method of Carius 0.1625 gram of argentic chloride.

III. 0.2411 gram of the substance gave 0.1757 gram of argentic chloride.

	Calculated for $C_6H(NO_2)_2Cl_2CH(COOC_2H_5)_2$.	Found. I.	II.	III.
Carbon	39.50	39.92		
Hydrogen	3.04	3.20		
Chlorine	17.97		18.08	18.02

The substance, like those already mentioned in this paper, is very explosive, so that a good combustion could be obtained only by special precautions, such as mixing the substance with a large quantity of the powdered cupric oxide in a bayonet tube, or using a long copper boat in which the substance was mixed with much powdered cupric oxide, and the successive portions of it separated by dams of the pure oxide. In any case the heat must be applied with the greatest caution. Even with these precautions we did not succeed in getting satisfactory nitrogen determinations, the numbers coming more than one per cent. too high. This we ascribe to the presence of a combustible gas driven over the cupric oxide so rapidly by the explosive burning of the substance that it escaped combustion. We should not mention this observation if it had not been made in other cases during the determination of nitrogen in ethyl esters. The analyses given above show that the substance is the dichlordinitrophenylmalonic ester, formed by the replacement of one atom of chlorine by one malonic ester radical. The action of sodium malonic ester upon trichlordinitrobenzol is different from its behavior with the corresponding bromine compound, as in that case not only is one atom of bromine replaced by the malonic ester radical, but another is replaced by hydrogen, so that the product is the bromdinitrophenylmalonic ester, $C_6H_2(NO_2)_2BrCH(COOC_2H_5)_2$.

The yield of the dichlordinitrophenylmalonic ester is satisfactory. We obtained from 30 grams of trichlordinitrobenzol 23.8 grams of the ester instead of the 43.6 grams calculated from the reaction, that is 54.5 per cent. of the theoretical yield. The real yield is even somewhat better than this, as a certain amount of unaltered trichlordinitrobenzol was usually detected in the mother-liquors. It was not present, however, in sufficient quantity to make it worth while to recover it.

Properties of Dichlordinitrophenylmalonic Ester.—When crystallized from alcohol it forms thick, narrow plates terminated by two planes at an acute angle to each other. Crystallized from benzol or chloroform it appears in stellate groups of small needles. It is white with a slight pearly luster, and melts at 101°. It shows a marked tendency to explode. It is freely soluble in benzol, chloroform or acetone; soluble in alcohol, ether or glacial acetic acid; slightly soluble in carbonic disulphide or ligroïn; essentially insoluble in water.

The best solvent for it is alcohol. It is insoluble in strong hydrochloric acid, whether hot or cold; slightly soluble in hot sulphuric acid diluted with its own volume of water when heated with it, but this solution is accompanied by saponification, as described later in this paper; insoluble in hot, strong nitric acid, but converted by it into the nitrite described in the next section. Sodic hydrate dissolves it, forming a red solution, and we hoped by this action to get the red salt of the dichlordinitrophenylmalonic ester, but found that the sodic chloride was formed, whether the sodic hydrate was used in aqueous or alcoholic solution, and this even when the ester was in considerable excess. From some preliminary analyses we should judge that one atom of chlorine was removed, but the careful study of this reaction must be postponed for the present.

The Nitrite of Dichlordinitrophenylmalonic Ester, $C_6HCl_2(NO_2)_2CNO_2(COOC_2H_5)_2$.—This substance was made as follows: Two grams of dichlordinitrophenylmalonic ester were warmed on the steam-bath with 7 grams of nitric acid (sp. gr. 1.38) for five minutes. The ester did not dissolve, but melted to an oily drop, which as the heating continued took on an amber color, while at the same time an evolution of gas was observed. After the heating was finished, the liquid was allowed to cool and then poured into about three times its volume of cold water, with which it was thoroughly stirred and allowed to stand until the oily particles had settled, when the supernatant liquid was decanted and the oil washed till free from acid. During this washing the oil was frequently stirred under water with a sharp glass rod, when it usually solidified in the course of half an hour. The substance should be brought into the solid state before dissolving it for crystallization, as if this precaution is neglected, after solution and evaporation of the solvent it shows a tendency obstinately to remain liquid. It was purified by crystallization from alcohol, dried and analyzed with the following result:

0.2905 gram of the substance gave by the method of Carius 0.1873 gram of argentic chloride.

	Calculated for $C_6HCl_2(NO_2)_2CNO_2(COOC_2H_5)_2$.	Found.
Chlorine	16.14	15.94

The substance therefore is a nitrite exactly similar to that obtained under the same conditions from the bromdinitrophenylmalonic ester.[1] The yield is essentially quantitative. Two grams of the ester gave 2.2 grams of the nitrite instead of the 2.23 grams required by the theory, that is a yield of 99 per cent.

Properties of the Nitrite of Dichlordinitrophenylmalonic Ester.—When crystallized by spontaneous evaporation from a cold, saturated, alcoholic solution, it forms glistening, compact, white crystals often a millimeter or more in diameter, which seem to be more or less distorted octahedra. It has no definite melting-point, as different portions of the same specimen melted at 87°–89°, if heated very slowly, or at 94°–95°, if heated more rapidly. It seems to be a decomposition rather than a fusion. It is freely soluble in ether, benzol, chloroform, acetone or carbonic disulphide; soluble in methyl alcohol, and somewhat more freely so in ethyl alcohol; moderately soluble in glacial acetic acid; slightly soluble in hot ligroïn; essentially insoluble in cold ligroïn, or in water either cold or hot. Alcohol is the best solvent for it; from benzol, ether, or chloroform we could not succeed in getting it in a crystalline state. It is insoluble in strong hydrochloric acid whether cold or hot; cold strong sulphuric acid does not dissolve it, but when hot a brown solution is formed. A solution of sodic hydrate does not affect it in the cold, but if the mixture be heated, the nitrite at first melts to a bright red oil and then slowly goes into solution. The reddish-yellow liquid thus obtained gives no precipitate when acidified with dilute nitric acid, but the acid liquid gives a strong test for a chloride showing that the solution of the nitrite in the sodic hydrate has been attended with a deep-seated decomposition. Ammonic hydrate has no effect on the nitrite in the cold, and but little when hot, for although the aqueous solution took on a yellowish tinge, the greater part of the nitrite was recovered unaltered, as shown by its decomposition-point 87°–89°. No

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[1] This JOURNAL, 14, 331.

test for a chloride could be obtained in the acidified aqueous solution.

When the nitrite mixed with a slight excess of aniline was gently heated on the steam-bath, it went into solution, and then after heating for ten or fifteen minutes, became nearly solid. After removing the excess of aniline by washing with acidified water, a substance was obtained which crystallized from a mixture of chloroform and alcohol in a mat of white slender needles which did not melt at 340°, and gave no test for chlorine with a copper wire. The acid wash-waters gave a strong test for chlorides. Lack of time has prevented us from studying this substance.

Action of Aniline on Dichlordinitrophenylmalonic Ester.

Aniline did not react on the ester in the cold. If the two substances were heated for about an hour on the steam-bath a red color appeared, but most of the ester was recovered unaltered. When they were heated in an oil-bath to 150°–160° for ten minutes, a reaction took place, as was shown by the formation of aniline chloride, and the other product of the reaction was a red viscous body, which hardened to a varnish on long standing. We have not succeeded in bringing this substance into a crystalline state by any means we could devise, and therefore have not attempted to analyze it. This is the more strange as the anilidodinitrophenylmalonic ester is a well crystallized substance.

Saponification of Dichlordinitrophenylmalonic Ester.

Five grams of the ester (melting-point 101°) were boiled under a return-condenser with 500 cc. of sulphuric acid of specific gravity 1.44, as this strength of acid had given excellent results in many other cases. The ester at first melted, and floated in yellowish oily drops on the surface of the acid, but as the reaction went on a large part of it dissolved in the acid, imparting to it a pale-yellowish color. With the amount of acid used the whole of the organic substance did not go into solution, but as the original ester was replaced by the saponification-product, the drops sank to the bottom of the flask. It was necessary to boil the mixture for three or four hours to obtain complete saponification. At the end of this time the solution was allowed to cool, when the product crystallized out, and was easily purified by one recrystallization from water acidified with a little sulphuric acid. It then melted constant at 140°. Alcohol should not be used in purifying it, as this acts upon it in a way to be described later. A small additional amount of the substance can be obtained by concentrating the acid liquid from which the original crystals were filtered out. The substance was dried at 100° and analyzed with the following result:

I. 0.1463 gram of the substance gave by the method of Carius 0.1419 gram of argentic chloride.

II. 0.2342 gram of the substance gave 19.5 cc. of nitrogen at a temperature of 23° and a pressure of 765.9 mm.

	Calculated for $C_6HCl_2(NO_2)_2CH_2COOH$.	Found. I.	II.
Chlorine	24.07	23.98	
Nitrogen	9.49		9.46

The substance is therefore dichlordinitrophenylacetic acid, and the saponification is exactly similar to that of the bromdinitrophenylmalonic ester.

The yield is not far from quantitative. 5 grams of dichlordinitrophenylmalonic ester gave 3.4 grams of the substituted acetic acid instead of the 3.7 grams required by the reaction, that is, 91 per cent. of the theoretical yield.

The following observation throws some light on the manner in which the saponification takes place. The crude product resulting from an experiment like that described above was mixed with aqueous ammonic hydrate and warmed gently on the steam-bath. About half of the solid went into solution, and this solution, after being freed from the undissolved portion by filtration, gave a precipitate on the addition of nitric acid, which was recognized as dichlordinitrophenylacetic acid by its crystalline form and its constant melting-point, 140°. The undissolved portion, after recrystallization from alcohol, showed the constant melting-point, 67–68°, and was therefore the dichlordinitrophenylacetic ester described later in this paper. From this it follows that one of the two carboxethyl groups ($COOC_2H_5$), in the malonic ester is saponified, and then loses carbonic dioxide before the second carboxethyl group is affected by the acid.

An attempt was also made to saponify the dichlordinitrophenylmalonic ester with a weaker sulphuric acid, in the hope that a different saponification-product might be obtained. The acid used in this case had a specific gravity of 1.195, and therefore contained 25 per cent. of sulphuric acid; the product, however, was the same as before, that is, the dichlordinitrophenylacetic acid, which was recognized by its melting-point, 140°.

Properties of Dichlordinitrophenylacetic Acid, $C_6HCl_2(NO_2)_2CH_2COOH$.—This substance crystallizes from acidified water in clusters of yellowish-white needles often 2 to 3 centimeters long, which show a tendency to twin longitudinally. The crystals are also sometimes arranged in pinnately branching groups, or in forms like a short bushy tree, tapering to a sharp point. It melts at 140°. It is very soluble in glacial acetic acid, or acetone, but is deposited as a white varnish from these solutions; soluble in benzol or chloroform; moderately soluble in ether; practically insoluble in carbonic disulphide, or in ligroïn, hot or cold. It is freely soluble in methyl or ethyl alcohol, but the substance is affected by the alcohol in a way which will be described later. Nearly insoluble in cold water, slightly soluble in boiling water, and this solubility is much increased by the presence of a small amount of sulphuric acid. Water containing some sulphuric acid is the best solvent for it. Neither hydrochloric acid nor nitric acid dissolves it.

An aqueous solution of sodic hydrate dissolves the dichlordinitrophenylacetic acid forming a beautiful crimson liquid, which loses this color almost immediately. With an alcoholic solution of sodic ethylate the same color is obtained, but in this case it is much more permanent, lasting for as much as twenty-five minutes. The addition of water discharges the color instantly. This crimson color is undoubtedly analogous to the colors obtained by the action of sodic hydrate or ethylate on various nitro compounds and studied by Victor Meyer,[1] Lobry deBruyn and Van Leent,[2] and Jackson and Ittner.[3] We are led to this conclusion by the transitory nature

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[1] Ber. d. chem. Ges., 27, 3153.

[2] Rec. Trav. chim. Pays Bas, 14, 150.

[3] Ber. d. chem. Ges., 28, 3063.

of the color, and by the fact that the sodium salt of the dichlordinitrophenylacetic acid (which is described later) is nearly colorless. It is probable that the dark Prussian green color obtained by the action of sodic hydrate on bromdinitrophenylacetic acid[1] is also due to a substance of this class and not the salt of the acid as was supposed when it was described. Ammonic hydrate dissolves the dichlordinitrophenylacetic acid giving a greenish-yellow solution, which after acidification with nitric acid gave no test for a chloride.

Sodium Salt of Dichlordinitrophenylacetic Acid, $C_6HCl_2(NO_2)_2CH_2COONa$.

The salt was made by boiling an aqueous solution of sodic carbonate with an excess of the acid, and filtering out the unaltered acid from the cold solution, which was then concentrated and set aside to crystallize spontaneously. The crystals dried at 100° were analyzed with the following result:

0.1965 gram of the salt gave 0.0436 gram of sodic sulphate.

	Calculated for $C_6HCl_2(NO_2)_2CH_2COONa$.	Found.
Sodium	7.25	7.19

The salt has a pale yellow color and is crystalline. When the powdered salt is brought in contact with water it seems at first to swell, and then dissolves to a pale yellow, neutral liquid. This aqueous solution of the salt gives the following precipitates:

With *ferric chloride* a white flocculent precipitate.

With *cupric sulphate* a greenish-blue precipitate.

With *plumbic acetate* a white curdy precipitate.

With *argentic nitrate* a bluish-white, translucent, gelatinous precipitate.

No precipitates were observed with most of the other common reagents.

Action of Alcohol on Dichlordinitrophenylacetic Acid.

As has been mentioned already the dichlordinitrophenylacetic acid is acted on by alcohol with the formation of a new substance, as was indicated by the fact that the melting-point was lowered several degrees by a single crystallization from

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[1] Jackson and Robinson, This JOURNAL, 11, 541.

this solvent. As this action was not very rapid, we boiled some of the compound with alcohol in a flask with a return-condenser for fifteen hours. At the end of this time the alcohol was allowed to evaporate spontaneously, when the product of the reaction was left as a yellowish varnish. After trying in vain to crystallize this from the commoner solvents, we proceeded as follows: The substance was extracted several times with boiling water containing a little sulphuric acid to remove any of the unaltered acetic acid, and then the residue was dissolved in boiling ligroïn, from which it crystallized on cooling. After this there was no difficulty in recrystallizing it from alcohol. When it had reached the constant melting-point, 67–68°, it was dried *in vacuo* and analyzed with the following results:

I. 0.1596 gram of the substance gave on combustion 0.2195 gram of carbonic dioxide and 0.0463 gram of water.

II. 0.2524 gram of the substance gave by the method of Carius 0.2239 gram of argentic chloride.

III. 0.2950 gram of the substance gave 0.2607 gram of argentic chloride.

IV. 0.2086 gram of the substance gave 0.1856 gram of argentic chloride.

	Calculated for $C_6HCl_2(NO_2)_2CH_2COOC_2H_5$.	Found.			
		I.	II.	III.	IV.
Carbon	37.15	37.50			
Hydrogen	2.48	3.22			
Chlorine	21.98		21.94	21.85	22.00

The poor results obtained from the combustion are due to the explosive nature of the substance. These numbers show that the substance is the dichlordinitrophenylacetic ester, and, therefore, that the reaction is different from that with bromdinitrophenylacetic acid, which is converted by boiling alcohol into the corresponding toluol. In view of this difference, we thought it well to confirm our analyses by preparing the ethyl ester in the usual way. Accordingly, 1 gram of the dichlordinitrophenylacetic acid was dissolved in 10 cc. of absolute alcohol and the solution saturated with dry hydrochloric acid gas. The alcohol was then allowed to evaporate spontaneously, when the ester was left in crystals, which, after being washed free from hydrochloric acid, melted at 67–68°, and were therefore identical with those obtained by the action of hot alcohol.

The formation of the ester from dichlordinitrophenylacetic acid and alcohol alone seemed so strange that we were inclined to ascribe the action to the presence of a trace of sulphuric acid remaining from the acidified water used in crystallizing the acid. To settle this point a specimen of the dichlordinitrophenylacetic acid was recrystallized from boiling water and thoroughly washed. It melted at the right point, 140°, and gave no test for sulphuric acid. It was boiled for several hours with alcohol in a flask fitted with a return-condenser, and, after the alcohol had been evaporated off, extracted repeatedly with boiling water, and then crystallized from ligroïn, when the ester was obtained as shown by the melting-point, 67–68°. This experiment proves that dichlordinitrophenylacetic acid is converted into its ester by alcohol alone without the aid of any mineral acid. In this connection it should be mentioned that several chemists[1] have recently called attention to the great ease with which phenylacetic acid is converted into its ester. None of them, however, seemed to have tried the experiment without the help of a mineral acid. It will be interesting to determine in this way whether phenylacetic acid can be esterified by alcohol alone, or whether our body owes this property to the presence of the negative radicals attached to the benzol ring.

Properties of Dichlordinitrophenylacetic Ethyl Ester, $C_6HCl_2(NO_2)_2CH_2COOC_2H_5$.—The substance crystallizes from alcohol in rather long white needles with nearly, but not quite, square ends. It melts at 67–68°. It is very soluble in ether or acetone; freely soluble in benzol, carbonic disulphide, or chloroform; soluble in glacial acetic acid. From these solvents it is deposited as a varnish. Soluble in methyl or ethyl alcohol; very slightly soluble in cold ligroïn, more soluble in hot, but not freely even in this; essentially insoluble in water, hot or cold. The best solvents for it are alcohol, or hot ligroïn. It is insoluble in strong nitric acid, or in hydrochlo-

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[1] Victor Meyer, Ber. d. chem. Ges., **28**, 3197; Shukoff, *Ibid*, 3201; Goldschmidt, *Ibid*, 3224.

ric acid. With an alcoholic solution of sodic hydrate or sodic ethylate it gave a crimson color, undoubtedly due to a compound similar to that produced by the action of the same reagents on the acid. With aqueous sodic hydrate and a little alcohol it was saponified when heated, but apparently at the same time a portion of the chlorine it contained was removed. We had not time to give this reaction the study it deserves.

The study of these compounds and of the behavior of trichlordinitrobenzol with other reagents will be continued in this laboratory.

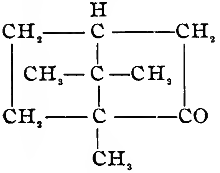
Contributions from the Chemical Laboratory of the Rose Polytechnic Institute.

XIII.—CAMPHORIC ACID.

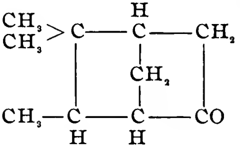
FOURTH PAPER.

By W. A. Noyes.

The formula for camphor, which appears at the present time, to be most in favor, is that of Bredt.[1] A formula more recently proposed by Tiemann[2] does not appear to have been as well received, though he appears to consider that the work done in his laboratory furnishes complete proof that it is correct. These formulæ are as follows:



Bredt.



Tiemann.

Each of these formulæ supposes camphoric acid to be a derivative of glutaric acid. In my last paper[3] several reasons, which appeared conclusive, were given for believing that camphoric acid is a derivative of succinic rather than of glutaric acid. This opinion has received additional support from the work to be described in this paper, and it would seem that Bredt's formula can no longer be considered a possible ex-

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[1] Ber. d. chem. Ges., **26**, 3047.

[2] *Ibid.*, **28**, 1087.

[3] This JOURNAL, **17**, 421.

pression for the structure of camphor. The same line of work which proves the falsity of Bredt's formula, also renders Tiemann's equally untenable. In addition to this, it was pointed out in my last paper[1] that dihydrohydroxycampholytic acid conducts itself in such a manner toward Beckmann's chromic acid mixture as to indicate that the hydroxyl which it contains is tertiary. If this view is correct, the carboxyl of aminolauronic acid must also be tertiary, while that of dihydroaminocampholytic acid, according to the experiments of Walker[2] and myself[3] is secondary. There should, therefore, in accordance with the well-known laws of esterification for secondary and tertiary carboxyl, be a marked difference in the rate of esterification for the two acids. According to Tiemann's formula, however, the rate of esterification for the two acids should be practically identical.

The experiment was tried as follows: A mixture of 10 grams of dihydroaminocampholytic acid, 40 cc. of absolute alcohol and 3 cc. of concentrated sulphuric acid was boiled with a reversed condenser for three hours. A part of the alcohol was then distilled off, the residue was diluted, rendered alkaline with sodium hydroxide, and the ester formed taken up with ether. After distilling off the ether, the ester, which is a strong base, was titrated with dilute sulphuric acid. The amount of ester formed was 5.2 grams. 11 grams of the chloride of aminolauronic acid, treated in exactly the same manner, gave only 0.48 gram of the ester. More than ten times as much of the first acid, therefore, was converted into the ester. The result conclusively disproves Tiemann's formula, while it is in entire accord with the conclusion reached by Walker and myself. It would also agree with Bredt's formula.

Ethyl Ester of Aminolauronic Acid.

When mixtures of the proportions given above are boiled for two or three days, about thirty per cent. of the aminolauronic acid is converted into the ethyl ester. The free ester is a mobile, strongly basic liquid with an ammoniacal, aromatic odor. On neutralizing the ester with sulphuric acid of

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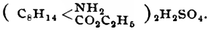
[1] *Loc. cit.*, p. 426.

[2] J. Chem. Soc., **63**, 506, (1893).

[3] This JOURNAL, **16**, 509; and **17**, 421.

25 per cent. a considerable part of the *sulphate* formed separates in difficultly soluble, pearly-white scales.

0.1432 gram of the sulphate gave 0.0663 gram $BaSO_4$.

	Calculated for  $\left(C_8H_{14}<\begin{matrix}NH_2\\CO_2C_2H_5\end{matrix}\right)_2H_2SO_4$.	Found.
S	6.45	6.38

Hydroxylauronic Acid.

The fact that the treatment of aminolauronic acid with nitrous acid[1] gives rise to the formation, along with other products, of isocampholactone, and that no other hydroxy acid could be found among the products of decomposition, would, in the absence of evidence to the contrary, indicate that the amino group is in the γ-position with reference to the carboxyl. While the evidence given in my last paper furnishes satisfactory reasons for believing that the hydroxyl group of the acid corresponding to the lactone is combined with a different carbon atom from that with which the amino group of aminolauronic acid is combined, the preparation of the hydroxy acid corresponding to the latter was of very considerable interest. This has now been effected. When the neutral sulphate of the ester of aminolauronic acid is treated with a strong solution of sodium nitrite it is decomposed with the formation, chiefly, of the ethyl ester of γ-lauronolic acid,[2] (the allo-campholytic acid of Walker[3]) together with a small amount of the ethyl ester of the new hydroxylauronic acid. The two esters may be partly separated by fractional distillation under diminished pressure, but the complete separation of the two acids is best effected, after saponifying the esters with alcoholic potash, and taking up the acids from the acidified solution with ether, by distilling with water-vapor. The hydroxy acid is almost non-volatile and by continuing the current of steam for some time the γ-lauronolic acid may be entirely removed, while the larger part of the hydroxy acid remains behind, dissolved in the hot water. The solution was filtered from a small amount of tarry matter and, when cold, was extracted with ether.

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[1] This JOURNAL, **17**, 432.

[2] *Ibid*, **17**, 433.

[3] J. Chem. Soc., **67**, 341, (1895).

On evaporating the ether and drying *in vacuo* over sulphuric acid the hydroxylauronic acid remains as a viscous, hygroscopic liquid. For analysis the acid was dried for a short time at 105°.

0.1248 gram of the acid gave 0.1068 gram H_2O and 0.2855 gram CO_2.

0.1098 gram of the acid gave 0.0898 gram H_2O and 0.2524 gram CO_2.

	Calculated for $C_8H_{14}<\substack{CO_2H \\ OH}$.	Found. I.	 II.
C	62.79	62.39	62.69
H	9.30	9.51	9.09

The *copper salt*, $\left(C_8H_{14}<\substack{CO_2 \\ OH}\right)_2Cu + H_2O$, was prepared, by precipitation, from the easily soluble calcium salt. When air-dry the salt contains 1 molecule of water of crystallization, but this is partly lost on standing over sulphuric acid. The salt is green and very difficultly soluble in water.

0.1224 gram of the salt lost 0.0051 gram H_2O at 105°.

0.0796 gram of the salt lost 0.00315 gram H_2O at 105°.

	Calculated for $\left(C_8H_{14}<\substack{CO_2 \\ OH}\right)_2Cu + H_2O$.	Found. I.	 II.
H_2O	4.25	4.16	3.96

0.1173 gram of the dry salt gave 0.0235 gram CuO.

0.1000 gram of the dry salt gave 0.0197 gram CuO.

	Calculated for $\left(C_8H_{14}<\substack{CO_2 \\ OH}\right)_2Cu$.	Found. I.	 II.
Cu	15.88	16.00	15.73

If the views which have been expressed are correct, the hydroxyl group of hydroxylauronic acid is that of a secondary alcohol and is in the β position with reference to the carboxyl. A very strong confirmation of this opinion is given by the conduct of the acid toward Beckmann's chromic acid mixture.[1] While this mixture is without effect on dihydrohydroxycampholytic acid in the cold, it darkens quickly when added to hydroxylauronic acid and there is, at the same time, a slow evolution of carbon dioxide. Evidently the mixture converts the secondary hydroxyl into carbonyl and, as the resulting

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[1] Ann. Chem. (Liebig), **250**, 325.

acid is a β-ketonic acid, it undergoes decomposition, in accordance with the well-known law for such acids, yielding carbon dioxide and a ketone. As the hydroxy acid is difficult to obtain, the ketone has not yet been isolated in pure condition.

Dihydro-cis-campholytic Acid.

This acid is readily obtained by reducing cis-campholytic acid with amyl alcohol and sodium. After purification by treatment of the solution of the sodium salt with an excess of potassium permanganate, the acid is an oily liquid, almost insoluble in water, and having an odor somewhat like that of valerianic acid. It boils at 244°. The boiling-point of cis-campholytic acid, which has not yet been given, was also determined and found to be at 255°–256°. The boiling-point of the cis-trans-campholytic acid is 240°–243°, very near to that of the dihydrociscampholytic acid. The specific gravity of the dihydro acid at 20° is 0.9833.[1] The acid is perfectly stable toward a cold solution of potassium permanganate. The composition of the acid was established by analyses, but the record was unfortunately lost in a fire.

The *amide*,[1] $C_8H_{16}CONH_2$, was prepared by treating the acid with phosphorus pentachloride and pouring the product carefully into cooled aqueous ammonia. It crystallizes from alcohol of 30 per cent. in needles, while from strong alcohol it separates in good-sized, rectangular plates. It is remarkably stable toward potassium permanganate, and may even be crystallized unchanged from a boiling, dilute solution of the salt. It melts at 161°.

α-Bromdihydro-cis-campholytic Acid.

This was prepared by treating the acid with phosphorus pentachloride and with bromine, as directed by Baeyer[2] and Aschan.[3] After decomposing the chloride of the acid by warming with formic acid the acid was crystallized from formic acid and the crystals washed with ligroïn. The acid melts at 129°–130°. It crystallizes from formic acid in needles.

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[1] Preparation and determination by Mr. E. B. Harris.

[2] Ann. Chem. (Liebig), **245**, 175.

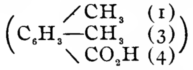
[3] *Ibid.*, **271**, 265.

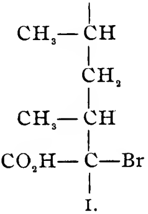
The record of the bromine determinations, which established the composition, was lost.

When α-bromdihydro-cis-campholytic acid is treated with a cold alcoholic solution of potash, hydrobromic acid is removed and cis-campholytic acid is regenerated. The acid was identified by its melting-point, crystalline form and by the melting-point of its amide. This furnishes a new and positive proof that the double union of cis-campholytic acid is in the α-β-position, and gives additional support to the view expressed in my last paper that the two campholytic acids are stereoisomers.

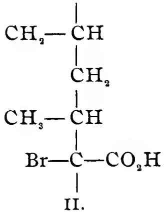
Attempts to reduce cis-trans-campholytic acid by amyl alcohol and sodium or by any other methods have, thus far, been entirely unsuccessful.

Hexahydroxylylic Acid.

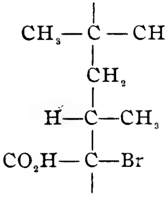
The proof that cis-campholytic acid is regenerated from the α-bromdihydrocampholytic acid, together with the fact that cis-campholytic acid is optically inactive has made it possible to subject Armstrong's formula to a synthetic test, which is nearly or quite conclusive. According to Armstrong's formula cis-campholytic acid must be Δ^1-tetrahydroxylylic acid. The reduction of xylylic acid  $\left(C_6H_3\begin{matrix} /CH_3 & (1) \\ -CH_3 & (3) \\ \backslash CO_2H & (4) \end{matrix}\right)$, would give, apart from enantiomorphic forms, four stereoisomers, corresponding to which there would be four α-bromhexahydroxylylic acids. These would have the configuration represented by the following formulæ, in which only the atoms concerned in the stereoisomerism are shown :



I.

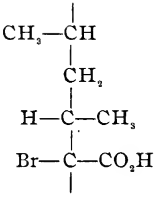


II.



$$\begin{array}{rcl} & | & \\ CH_3- & C & -CH \\ & | & \\ & CH_2 & \\ & | & \\ H- & C & -CH_3 \\ & | & \\ CO_2H- & C & -Br \\ & | & \end{array}$$

III.



$$\begin{array}{rcl} & | & \\ CH_3- & CH & \\ & | & \\ & CH_2 & \\ & | & \\ H- & C & -CH_3 \\ & | & \\ Br- & C & -CO_2H \\ & | & \end{array}$$

IV.

Of these isomers, I and IV, supposing Armstrong's formula to be correct, would give cis-campholytic acid directly when treated with alcoholic potash. II and III would give either cis-trans-campholytic acid or a Δ^6-tetrahydroxylylic acid.

Xylylic acid (melting-point 126°) was reduced with amyl alcohol and sodium, the reduction being several times repeated to secure as complete a conversion as possible. The hexahydroxylylic acid was purified by treatment with potassium permanganate and distillation with water vapor. The acid came over as an oil which soon solidified, the first portions melting a little below and the later portions a little above 60°. The composition of the acid was established by analyses, but the record was burned, and as the point for which the experiments were undertaken has been established, it has not been deemed necessary to repeat the work. From the hexahydro acid the α-brom derivative was prepared, and this also was analyzed. The record of its melting-point was lost and is of little consequence, as it was probably a mixture of stereoisomers. On treatment with alcoholic potash, the main product of the action was a liquid acid which was not cis-trans-campholytic acid, since it was not converted into cis-campholytic acid by the action of dilute sulphuric acid (1 : 1). A very small amount of a solid acid melting at about 100° was found. While it is possible that the product consisted in part of the Δ^6 tetrahydroxylylic acid, it seems scarcely possible that the Δ^1 acid was not also formed. The properties of cis-campholytic acid are so characteristic that the body is easily identified, and it could scarcely have been overlooked, if present. The evidence appears to be conclusive, therefore, that cis-campholytic acid is not Δ^1-tetrahydroxylylic acid and that Armstrong's formula for camphor is not true.

The results described in the latter part of this paper are of such a nature as to render a similar examination of the truth or falsity of Collie's formula for camphoric acid of very great interest. Mr. W. E. Burk has, under my direction, spent a considerable amount of time in attempting the preparation of the neighboring xylylic acid necessary for the purpose. The work has been thus far only partially successful, but will be continued.

DERIVATIVES OF DIHYDRO-CIS-CAMPHOLYTIC ACID.

BY E. B. HARRIS.

The amide of dihydro-cis-campholytic acid has been described above. When treated with an alkaline solution of potassium hypobromite an amine, $C_8H_{15}NH_2$, is formed. The conversion was effected as follows: 8 grams of the amide were placed in a distilling-bulb and a freshly prepared solution of 8.2 grams of bromine in 100 cc. of ten per cent. sodium hydroxide was added. On warming gently the reaction took place, accompanied by some evolution of heat. The amine formed was distilled with water vapor and collected in dilute hydrochloric acid.

The *chloride*, $C_8H_{16}NH_2.HCl$, crystallizes in needles which are easily soluble in water and alcohol and melt with decomposition at 239°.

The *sulphate* crystallizes in white scales which are rather difficultly soluble in water. It resembles somewhat the sulphate of the ethyl ester of aminolauronic acid.

The *chloroplatinate*, $(C_8H_{16}NH_2)_2H_2PtCl_6$, crystallizes from hot water, in which it is difficultly soluble, in fine, light-orange colored needles.

0.0998 gram of the salt gave 0.0287 gram Pt.
0.1120 " " " " 0.0325 " "
0.1587 " " " " 0.0465 " "

	Calculated for $(C_8H_{16}NH_2)_2H_2PtCl_6$.	Found. I.	II.	III.
Pt	29.36	28.75	29.01	29.30

The free amine, $C_8H_{15}NH_2$, is a clear, colorless, mobile liquid with a very characteristic ammoniacal, fishy odor. It is slightly soluble in water, easily in alcohol and ether. It boils at 156°.5. Its specific gravity at 20° is 0.8431.

Alcohol, $C_8H_{15}OH$.

In order to obtain, if possible, the alcohol corresponding to the amine, three grams of the latter were converted into the sulphate by means of dilute sulphuric acid, the solution was rendered slightly alkaline with caustic soda and the theoretical amount of a strong solution of sodium nitrite was added. Decomposition took place slowly with a slight evolution of heat. A greenish yellow oil, having a marked odor of turpentine, separated on top. The products of decomposition were roughly separated by distilling twice with water vapor. The portion which came over first, after separating from the water and drying, consisted of a light, somewhat volatile oil which boiled at about 122°. It was undoubtedly a hydrocarbon, C_8H_{14}. It is evident that the decomposition, as is so often the case with cyclic amines, takes place mainly with the formation of this hydrocarbon instead of the alcohol desired. During the distillation there separated in the condenser a small amount of a white, crystalline, rather volatile substance, which melts at 59°. It was soluble in ether, insoluble in water, and stable toward permanganate. A test with phenylhydrazine indicated that it was not a ketone. The body was not obtained in sufficient amount for analysis.

The portion of the distillate referred to above, which was supposed to contain the alcohol, $C_8H_{15}OH$, was extracted with ether, and after evaporation of the ether the residue was heated to 55°–60° for twenty minutes with 3 cc. of Beckmann's mixture[1] of sulphuric acid and potassium pyrochromate. The ketone formed was extracted with ether, washed with water and sodium hydroxide and, after the removal of the ether, distilled with water vapor. It was then converted into the oxime by treatment with hydroxylamine chloride and sodium carbonate in dilute alcoholic solution. The oxime obtained crystallizes in needles or small prisms, has an odor resembling

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[1] Ann. Chem. (Liebig), **250**, 325.

that of camphor oxime and melts at 112°–113°. The amount obtained was too small for satisfactory purification, but crystallization from a very small amount of alcohol did not change the melting-point.

This oxime proves to be of very unusual interest, because of its very close agreement in properties with the oxime of Kipping's dimethyl-(1.3)-cyclohexenone-(2). Kipping's[1] oxime melts at 114°–115°, and in its other properties agrees with this oxime as far as can be determined. Not much reliance can be placed on the melting-point as a proof of identity in this case, however, since Zilinsky[2] has recently obtained the same oxime, having prepared the ketone by a somewhat different method and gives a melting-point of 104°–105°. We have also prepared the oxime as follows: Pentanetetracarboxylic ester was prepared from trimethylene bromide and malonic ester according to Baeyer's directions;[3] the two methyl groups were introduced as directed by Perkin and Prentice;[4] the resulting ester was saponified with methyl alcoholic potash; the tetracarboxylic acid was decomposed by heating to about 200°, and the resulting dimethylpimelic acid was distilled under diminished pressure. The acid was mixed with twice its weight of lime and, after fractioning, the ketone obtained was converted into the oxime. The oxime obtained melted at 120°–122°.

A comparison of these results seems to indicate that the ketone, or at least, the oxime, was, in each case, a mixture of stereomeric modifications. While the evidence that the oxime derived from cis-campholytic acid is in reality a derivative of the dimethyl-(1.3)-hexanone-(2) is unsatisfactory, there is some probability that it has this structure. The synthesis of the Δ^1-tetrahydro-(1. 2. 3)-xylylic acid, which, if this is true, must have the same structure as campholytic acid, will furnish positive evidence on this point. Experiments for this purpose have already been commenced.

TERRE HAUTE, INDIANA, JULY 31, 1896.

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[1] J. Chem. Soc., **67**, 351, (1895).

[2] Ber. d. Chem. Ges., **28**, 781.

[3] Ann. Chem. (Liebig), **278**, 100.

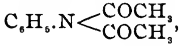
[4] Ber. d. chem. Ges., **24**, 818, 852.

Contribution from the Sheffield Laboratory of Yale University.

ON DIACID ANILIDES.

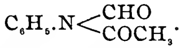
BY H. L. WHEELER.

For convenience of reference, diacid anilides may be divided into two classes. The first class will consist of those which have identical acid groups, such as diacetanilide,



$$\mathrm{C_6H_5.N}<\begin{array}{l}\mathrm{COCH_3}\\ \mathrm{COCH_3}\end{array},$$

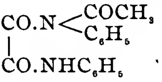
while the second class will contain those with unlike acid groups, and will be referred to as mixed diacid anilides, formylacetanilide, for example,



$$\mathrm{C_6H_5.N}<\begin{array}{l}\mathrm{CHO}\\ \mathrm{COCH_3}\end{array}.$$

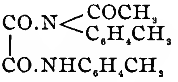
Diacid anilides of the first class can be prepared by acting on the mono acid anilides with acid anhydrides[1] [2] or acid chlorides.[3] They have also been obtained from the sodium salts of the anilides and acid anhydrides[4] and from the mustard oils.[5]

Diacid anilides of the second class have not been obtained by any of the above methods. They could not be prepared by acting on the monoacid anilides[6] or their sodium salts[7] with acid chlorides, while attempts to prepare them by acting on the anilides with acid anhydrides, formanilide, and acetic anhydride, for example, did not give pure products. However, the above method can be used with success in the preparation of what may be called semi-diacid anilides, since oxanilide and oxalparatoluide give monoacetyloxanilide and monoacetyloxalparatoluide,[8] *i. e.*,



$$\begin{array}{l}\mathrm{CO.N}<\begin{array}{l}\mathrm{COCH_3}\\ \mathrm{C_6H_5}\end{array}\\ \mid\\ \mathrm{CO.NHC_6H_5}\end{array}$$

and



$$\begin{array}{l}\mathrm{CO.N}<\begin{array}{l}\mathrm{COCH_3}\\ \mathrm{C_6H_4CH_3}\end{array}\\ \mid\\ \mathrm{CO.NHC_6H_4CH_3}\end{array}$$

In two former papers[9] from this laboratory the action of benzoyl chloride on the silver and mercury salts of the ani-

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[1] Bistrzycki and Ulffers: Ber. d. chem. Ges., **27**, 91.

[2] Tassinari: *Ibid*, R, **27**, 581.

[3] Kay: *Ibid*, **26**, 2853.

[4] Blacher: *Ibid*, **28**, 2356.

[5] Kay: *Ibid*, **26**, 2848.

[6] Pictet: *Ibid*, **23**, 3014.

[7] Paal and Otten: *Ibid*, **23**, 2587.

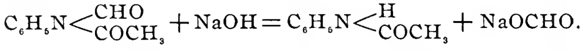
[8] Tassinari: *Loc. cit.*

[9] Wheeler and Boltwood: This JOURNAL, **18**, 381; Wheeler and McFarland, *Ibid*, **18**, 540.

lides was described. It was then shown that these salts could be used for the synthesis of the hitherto inaccessible mixed diacid anilides, and that both silver and mercury formanilide gave the same compound, *i. e.*, formylbenzanilide

$\mathrm{C_6H_5N}{<}\begin{matrix}\mathrm{CHO}\\ \mathrm{COC_6H_5}\end{matrix}$, etc.

In the present paper it will be shown that the action of aliphatic acid chlorides on silver formanilide and mercury acetanilide is perfectly analogous to that of benzoyl chloride; that the formation of mixed diacid anilides is general; and that these diacid anilides react with alkali invariably with the separation of the lower acid radical and formation of the anilide of the higher acid, as follows:



$$\mathrm{C_6H_5N}{<}\begin{matrix}\mathrm{CHO}\\ \mathrm{COCH_3}\end{matrix} + \mathrm{NaOH} = \mathrm{C_6H_5N}{<}\begin{matrix}\mathrm{H}\\ \mathrm{COCH_3}\end{matrix} + \mathrm{NaOCHO}.$$

By this reaction the mixed diacid anilides are shown to be nitrogen derivatives, and, since diacetanilide is formed from the mercury salt of acetanilide in precisely the same manner as the mixed diacid anilides, it is probable that the anilides of both classes have an analogous structure.

In the latter part of this paper a notice is given of the action of acetyl and benzoyl chlorides on silver and mercury benzamide, and it is the intention of the author to extend the work to salts of other amides and imides.

From silver formanilide and mercury acetanilide the following series of diacid anilides have now been prepared in this laboratory:

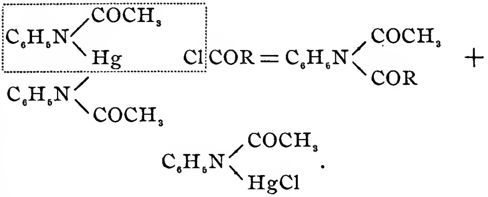
Acetylacetanilide or Diacetanilide,

Formylacetanilide,
Formylpropionanilide,
Formyl-*n*-butyranilide,
Formylstearanilide,
Formylbenzanilide,

Acetylpropionanilide,
Acetyl-*n*-butyranilide,
Acetylisovaleranilide,
Acetylpalmitanilide,
Acetylbenzanilide.

Method of Preparation.

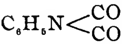
Silver formanilide or mercury acetanilide was suspended in dry ether or benzene and 1 molecular proportion of acid chloride was added. In the case of the mercury salts it was found convenient to use only 1 molecular proportion of acid chloride, since, by this means, the presence of mercuric chloride in the extract was largely avoided. The action then takes place chiefly as follows:



$$\boxed{C_6H_5N\begin{array}{l}\diagup COCH_3\\ \diagdown Hg\end{array}\quad Cl}\,COR = C_6H_5N\begin{array}{l}\diagup COCH_3\\ \diagdown COR\end{array} +$$

$$C_6H_5N\begin{array}{l}\diagup\\ \diagdown COCH_3\end{array}\qquad C_6H_5N\begin{array}{l}\diagup COCH_3\\ \diagdown HgCl\end{array}.$$

The action begins immediately with evolution of heat and is complete in the case of the lower acid chlorides in a few minutes. After filtering from the silver chloride or the halogen mercuric compound, the filtrates in the case of the lower acid derivatives, were shaken with water, and on evaporating the solvent the diacid anilides were obtained as oils. The purification and properties of these products are described below.

Acetylacetanilide or Diacetanilide,  $C_6H_5N<\begin{smallmatrix}COCH_3\\COCH_3\end{smallmatrix}$.—The preparation of this compound has received considerable attention. Bistrzycki and Ulffers[1] have carefully investigated the formation from acetanilide and acetic anhydride and conclude that it is not to be obtained in a pure condition by the method of Reverdin and de la Harpe.[2] They have shown that it can not be obtained from aniline and acetic acid as stated by Gumpert[3], and they also call attention to the fact that Krafft and Karsten[4] have shown that Hofmann[5] did not obtain this compound from phenyl mustard oil and acetic acid. They state that they obtained diacetanilide first in April, 1893. They were anticipated, however, by Kay,[6] who prepared this compound from phenyl mustard oil and acetic anhydride, as well as from acetanilide and acetyl chloride. Its preparation, according to the method of Bistrzycki and Ulffers has been confirmed by Tassinari,[7] while Blacher[8] obtained it from

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[1] *Loc cit.*

[2] Ber. d. chem. Ges., **22**, 1006.

[3] J. prakt. Chem. [2], **32**, 294.

[4] Ber. d. chem. Ges., **25**, 460.

[5] *Ibid*, **3**, 770.

[6] *Loc. cit.*

[7] *Loc. cit.*

[8] *Loc. cit.*

sodium acetanilide and acetic anhydride. The work of the later investigators confirms that of Kay, and they refer to him for the properties of this compound. He obtained this diacid anilide as a clear colorless oil, boiling at 150° at 16 mm. pressure and solidifying to a mass of crystals, which on crystallizing from ligroïn melted at 37°.

The same compound results by acting on mercury acetanilide with acetyl chloride. The product obtained from the benzene solution, in this case, was an oil which boiled at 150° at 17 mm. pressure and the distillate soon solidified to a colorless mass of crystals, which on crystallizing from ligroïn separated in eight-sided plates, melting at 37°. On warming with a dilute alcoholic solution of sodium hydroxide, acetanilide was formed.

Formylacetanilide,  $C_6H_5N<^{CHO}_{COCH_3}$.—This was obtained as an oil which soon solidified. It was crystallized from a mixture of ether and ligroïn, by evaporation under diminished pressure, when beautiful, colorless, prismatic crystals were obtained, melting at 56°.

	Found.	Calculated for $C_9H_9NO_2$.
N	8.59	8.58

Formylacetanilide is readily soluble in alcohol, ether, and benzene, but difficultly in ligroïn. On boiling with dilute sodium hydroxide it dissolves, and, on cooling, acetanilide separates in plates melting at 114°.

Formylpropionanilide,  $C_6H_5N<^{CHO}_{COCH_2CH_3}$.—The product of the action of propionyl chloride on both silver and mercury formanilides, in ether or benzene, either when obtained directly or when first shaken with bicarbonate of soda, was an oil which did not solidify in a freezing-mixture. On attempting to purify it by distillation, at 18 mm. pressure, it decomposed with effervescence, the pressure increased, and, finally, when this ceased, propionanilide distilled over, boiling at 183° at 20 mm. pressure. The decomposition possibly took place as follows:

$$C_6H_5N<^{CHO}_{COCH_2CH_3} = C_6H_5N<^{H}_{COCH_2CH_3} + CO.$$

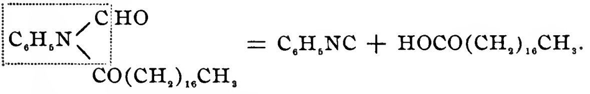
The oil gave propionanilide[1] melting at 105° when boiled with dilute sodium hydroxide.

Formylnormalbutyranilide, $C_6H_5N<\begin{matrix}CHO\\CO(CH_2)_2CH_3\end{matrix}$.—This diacid anilide was obtained only in the form of an oil and, like the preceding, it could not be solidified or distilled without decomposition. When an attempt was made to distil this crude product at 20 mm. pressure, it boiled from 164° to 185°. This fraction was distilled again at 20 mm. pressure, when the larger portion, a clear colorless oil, was collected between 172° and 180°. On standing, this fraction deposited plates, melting from 90 to 92°. The distillate was therefore a mixture of the diacid anilide with butyranilide.[2] The latter was obtained when the oil was boiled with dilute alcoholic sodium hydroxide.

Formylstearanilide, $C_6H_5N<\begin{matrix}CHO\\CO(CH_2)_{16}CH_3\end{matrix}$.—The stearic acid used in this experiment melted from 69° to 70°. From this the chloride was prepared according to the method of Krafft and Bürger.[3] In this case silver formanilide, suspended in ether, was used. On evaporating the ethereal solution minute, flattened, colorless crystals were obtained. These, on crystallizing repeatedly from ether, melted at 61°.

	Found.	Calculated for $C_{25}H_{41}NO_2$.
N	3.34	3.61

Formylstearanilide is extremely soluble in benzene, chloroform, ligroïn, and carbon disulphide, easily in ether, but less readily in cold alcohol. On heating the diacid anilide a decomposition takes place, as follows :



$$C_6H_5N<\begin{matrix}CHO\\CO(CH_2)_{16}CH_3\end{matrix} = C_6H_5NC + HOCO(CH_2)_{16}CH_3.$$

When the alcoholic solution is warmed with potassium hydroxide a bulky mass of colorless needles separates ; these melt from 93° to 94°, and the product is therefore stearanilide.[4]

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[1] Kelbe : Ber. d. chem. Ges., **16**, 1200.

[2] Gerhardt : Ann. Chem. (Liebig), **87**, 166.

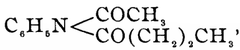
[3] Ber. d. chem. Ges., **17**, 1380.

[4] Pebal : Ann. Chem. (Liebig), **91**, 152.

Acetylpropionanilide,  $C_6H_5N{<}\begin{matrix}COCH_3\\COCH_2CH_3\end{matrix}$.—The product in this case was distilled at 18 mm. pressure when a clear colorless oil was obtained, boiling from 159° to 160°, which did not solidify in a freezing-mixture.

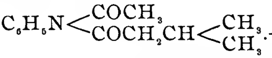
	Found.	Calculated for $C_{11}H_{13}NO_2$.
N	7.46	7.33

Acetylpropionanilide is readily soluble in ether and benzene. When the analyzed substance was warmed with dilute sodium hydroxide and the product crystallized from dilute alcohol, plates of propionanilide were obtained, melting at 105°.

Acetylnormalbutyranilide,  $C_6H_5N{<}\begin{matrix}COCH_3\\CO(CH_2)_2CH_3\end{matrix}$, was obtained as a clear, colorless oil, boiling at 163° under 18 mm. pressure.

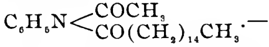
	Found.	Calculated for $C_{12}H_{15}NO_2$.
N	7.18	6.83

When warmed with sodium hydroxide in alcohol it gave butyranilide melting from 90° to 92°.

Acetylisovaleranilide,  $C_6H_5N{<}\begin{matrix}COCH_3\\COCH_2CH{<}\begin{matrix}CH_3\\CH_3\end{matrix}\end{matrix}$.—The isovaleryl chloride used in this experiment boiled from 113 to 116°. The diacid anilide was an oil which was distilled at 18 mm. pressure. The fraction boiling at 161.5° to 167° was collected and redistilled at the same pressure, the larger portion then boiled between 164° and 165°.

	Found.	Calculated for $C_{13}H_{17}NO_2$.
N	6.46	6.39

The product obtained on boiling this with alcoholic sodium hydroxide was crystallized from dilute alcohol and finally from a mixture of ligroïn and benzene. It then melted at 115° and and was therefore isovaleranilide.[1]

Acetylpalmitanilide,  $C_6H_5N{<}\begin{matrix}COCH_3\\CO(CH_2)_{14}CH_3\end{matrix}$.—The palmitic acid used in this case melted from 61° to 62°. It was converted into the chloride according to the directions of

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[1] Chiozza: Ann. Chem. (Liebig), 84, 109.

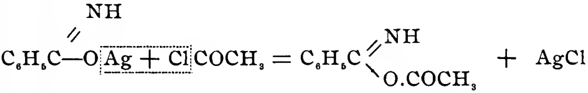
Krafft and Bürger.[1] The diacid anilide was obtained as an oil, which readily solidified. It was dissolved in cold ligroïn, filtered from a small amount of acetanilide (?), and the solution was then evaporated to dryness, the residue dissolved in alcohol, and the diacid anilide precipitated with a small amount of water. It was then crystallized several times from ether, a rather unsatisfactory operation on account of its great solubility. It was thus obtained as a compact mass of colorless, indistinct, microscopic crystals, melting from 60° to 61°.

	Found.	Calculated for $C_{24}H_{39}NO_2$.
N	3.54	3.75

On warming this product with alcoholic potassium hydroxide it gave palmitanilide[2] melting from 90° to 91°.

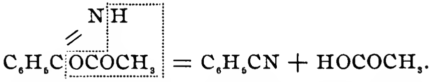
Experiments with Silver and Mercury Benzamide.

It would be expected that the silver and mercury salts of the amides would react with acid chlorides in an analogous manner to the corresponding salts of the anilides, and that diacid amides would result as the chief products. This, however, is not the case with either silver or mercury benzamide. Although silver benzamide reacts with alkyl[3] halides precisely like silver formanilide,[4] *i. e.*, in both cases imidoethers result, on the other hand, with acid chlorides, silver and mercury benzamide give chiefly benzonitrile. This reaction, in the case of the silver salts, if represented as a direct double decomposition, would be as follows:



$$C_6H_5\overset{\overset{NH}{/\!/}}{C}—O\boxed{Ag + Cl}COCH_3 = C_6H_5C\genfrac{}{}{0pt}{}{/\!/ NH}{\diagdown O.COCH_3} + AgCl$$

and



$$C_6H_5\overset{\overset{N\boxed{H}}{/\!/}}{C}\boxed{OCOCH_3} = C_6H_5CN + HOCOCH_3.$$

This apparently parallel reaction with alkyl halides would not be surprising if it were not for the entirely opposite reactions of the salts of the anilides.

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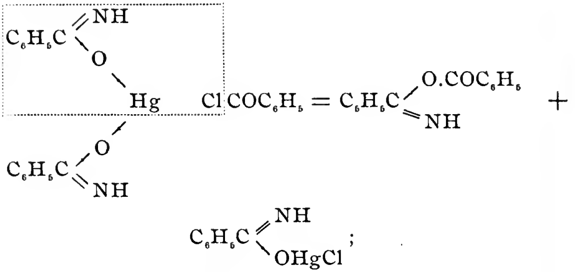
[1] *Loc. cit.*

[2] Hell and Jordanow: Ber. d. chem. Ges., **24**, 943.

[3] Tafel and Enoch: Ber. d. chem. Ges., **23**, 104.

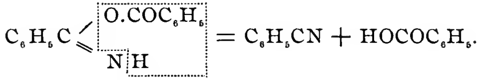
[4] Comstock and Kleeburg: *Ibid*, **12**, 493.

In the case of the action of benzoyl chloride on mercury benzamide, using molecular proportions of the acid chloride, the yield of benzonitrile was about 72 per cent. of the calculated. A direct double decomposition in this case again would be represented as follows :



$$\begin{array}{l} C_6H_5C{<}^{NH}_{O} \\ \qquad\qquad \rangle Hg \quad Cl\,COC_6H_5 = C_6H_5C{<}^{O.COC_6H_5}_{NH} + \\ C_6H_5C{<}^{O}_{NH} \\ \qquad\qquad\qquad\qquad C_6H_5C{<}^{NH}_{OHgCl}\ ; \end{array}$$

and



$$C_6H_5C{<}^{O.COC_6H_5}_{NH} = C_6H_5CN + HOCOC_6H_5.$$

While hitherto there has been no reason to assign to the salts of the amides a structure different from those of the anilides, this must now be done if the action of acid chlorides on these salts is a direct double decomposition, as shown above. For this reason these methods of representing the reactions are objectionable. It is far more probable that it is not the structure of the salts which varies in these tautomeric reactions, but that it is the mechanism of the reactions which undergoes change in different cases. It is probable in some cases that unstable addition-products[1] occur which break up into simpler products, and in other cases that double decompositions take place. The chief course of the reaction being influenced, not only by the union of the atoms or groups in the molecules reacting, but also by their chemical and physical nature and spacial arrangement.

NEW HAVEN, June, 1896.

[1] Nef: Ann. Chem. (Liebig), **287**, 269 ; and Proc. Amer. Acad., May, 1892, 169.

Contribution from the Chemical Laboratory of the Massachusetts Institute of Technology.

XIV.—IODOMETRIC DETERMINATION OF SELENIOUS AND SELENIC ACIDS.

BY JAMES F. NORRIS AND HENRY FAY.

The methods already in use for the volumetric determination of selenious acids are those of Muthmann and Schaefer,[1] and Gooch and Peirce.[2] The former method has been studied by Gooch and Reynolds,[3] and found to be inaccurate. The method of Gooch and Peirce depends upon the reduction of a known weight of potassium iodide in sulphuric acid solution by selenious acid in presence of arsenic acid. The difference between the arsenious acid equivalent to the potassium iodide and the amount found is a measure of the selenious acid. Selenic acid is first reduced by boiling with potassium bromide and sulphuric acid under definite conditions.

The method here proposed requires fewer reagents, occupies less time, and gives more accurate results. The determination depends on the reaction between sodium thiosulphate and selenious acid in presence of hydrochloric acid. So far we are unable to state the complete reaction which takes place, but have found that one molecule of selenious acid is exactly equivalent to four molecules of sodium thiosulphate. After standing about twenty-four hours, part of the selenium is precipitated. In neutral solution the reaction takes place slowly and is not complete after standing a day. In a strong neutral solution there is immediate precipitation of selenium, and the reaction becomes strongly alkaline. In this solution no sulphates were found. It is proposed to make a more complete study of this reaction.

The reagents used were carefully purified. Resublimed iodine was sublimed from one-third of its weight of potassium iodide and dissolved in potassium iodide free from iodate. This precaution was necessary as the titrations were made in acid solution. A hot concentrated solution of potassium iodide was boiled five minutes with the addition of a small quantity of hydrochloric acid, the solution cooled rapidly and

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[1] Ber. d. chem. Ges., **26**, 1008.

[2] Am. J. Sci., **1**, [4], 31.

[3] *Ibid*, **50**, 254.

the precipitate washed with alcohol to remove free iodine. The potassium iodide gave no reaction with starch when acidified with hydrochloric acid.

As the commercial sodium thiosulphate gave a different iodine-value in acid and neutral solution, it was found necessary to recrystallize it to remove the sulphite, although the presence of the latter was not indicated by barium chloride. The sodium thiosulphate was standardized against resublimed iodine and pure sodium arsenite.

The selenious acid was prepared from commercial selenium by evaporating to dryness with concentrated nitric acid. The selenium dioxide thus obtained was reduced by sodium sulphite and hydrochloric acid, and the pure selenium was again oxidized by evaporating to dryness with nitric acid, and the residue resublimed. In order to prevent reduction the oxide was sublimed in a small beaker, covered with a watch-glass, and containing a drop of strong nitric acid. By this method long, perfectly white needles of selenium dioxide can be obtained which are free from selenic acid. About 2 grams were weighed accurately, dissolved in water and diluted to 500 cc.

The selenic acid was prepared by dissolving about 2 grams of selenium dioxide in 200 cc. of water and adding a strong solution of potassium permanganate until a permanent pink color remained after heating one-half hour at 60° C. Sulphurous acid was then added until only a small amount of manganese dioxide remained, and the solution filtered and diluted to 500 cc. Sodium thiosulphate titrated in the presence of a definite portion of this solution acidified with hydrochloric acid, gave the same iodine-value as without its presence, thus showing the absence of selenious acid.

The flasks and burettes were calibrated according to the method of Morse and Blalock.[1]

Determination of Selenious Acid.

A definite portion of selenious acid was measured off, diluted with ice-water and 10 cc. hydrochloric acid (1.12 sp. gr.) An excess of one-tenth normal solution of sodium thiosulphate was added and titrated back with iodine solution.

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[1] This JOURNAL, 16, 479.

One molecule selenious acid, SeO_2, is equivalent to four molecules of thiosulphate, $Na_2S_2O_3.5H_2O$. It was found necessary to have enough hydrochloric acid present to set free all of the thiosulphuric acid. If the solution is cold a large excess of hydrochloric acid does not affect the titration. The following is a series of eight consecutive determinations :

SeO_2 taken.	SeO_2 found.	SeO_2 taken.	SeO_2 found.
0.0829	0.0829	0.1366	0.1367
0.0829	0.0829	0.1366	0.1368
0.1242	0.1242	0.1656	0.1659
0.1242	0.1242	0.2070	0.2071

It will be seen that the error varies from 0.00 to 0.18 per cent., the average being 0.06 per cent. The method is therefore one of the most accurate of iodometric methods and can be used conveniently for the standardization of sodium thiosulphate. The solution of selenious acid is entirely stable.

Determination of Selenic Acid.

As selenic acid does not react with sodium thiosulphate, it is first reduced by boiling with hydrochloric acid and titrated as above. It was found necessary to modify the method of Gooch and Evans[1] for the reduction by hydrochloric acid, as there was invariably loss of selenium.

To a measured portion of selenic acid is added 25 cc. concentrated hydrochloric acid and the solution diluted to 100 cc. The solution is boiled for one hour, precaution being taken not to allow the volume to go below 75 cc., cooled, diluted with ice-water and the selenious acid determined by titration. The following results were obtained consecutively :

SeO_3 taken.	SeO_3 found.	SeO_3 taken.	SeO_3 found.
0.1011	0.1009	0.1598	0.1595
0.1011	0.1008	0.1598	0.1595
0.1067	0.1067	0.2023	0.2024
0.1067	0.1065	0.2665	0.2662

Determination of a Mixture of Selenious and Selenic Acids.

Two portions of a solution containing a known quantity of selenious and selenic acids were measured off. In one the selenious acid was determined by direct titration; in the other the total selenium, after reduction of the selenic acid, was determined. On heating the solution in the reduction of selenic acid, some selenium is precipitated, which goes into solution

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[1] Am. J. Sci., **50**, 400.

when the chlorine is evolved. The method was tested by the following determinations:

SeO_2 taken.	SeO_2 found.	SeO_3 taken.	SeO_3 found.
0.0467	0.0467	0.1013	0.1015
0.0467	0.0466	0.1013	0.1016
0.0934	0.0933	0.0506	0.0504
0.1868	0.1865	0.1012	0.1015

Boston, Mass.

NOTE.

To the Editor: In the July number of the Journal there is a preliminary notice on the "Aluminum Alcoholates" by Mr. H. W. Hillyer, dated May 29. I beg to state that on May 2 I read before the Russian Chemical Society a paper "On the Action of Amalgamated Aluminum on Absolute Alcohols," of which the following abstract appeared in the "Proceedings of the Section of Chemistry of the Russian Physico-Chemical Society" ("Journal of the Russian Physico-Chemical Society," Vol. **28**, p. 412), and also in the "Chemiker Zeitung, Vol. **20**, No. 57, p. 563: "Amalgamated aluminum not only removes the last trace of moisture from alcohols, as has been observed by Wislicenus and Kaufmann (Ber. d. chem. Ges., **28**, 1323, 1983), but it also reacts with the alcohols forming aluminum alcoholates identical with the compounds described by Gladstone and Tribe (Trans. of the Chemical Society, 1881, p. 1). The following alcoholates have been prepared by heating the alcohols with amalgamated aluminum on the water-bath; their boiling-points have been determined for the first time:

		Melting point.	Boiling point 12 mm. press.	Al_2O_3 found.	Calculated for
Aluminum	trimethylate	Decomposes when heated.		43.67%	$Al(CH_3O)_3$, 42.50%
"	triethylate	132–136°	207–209°	32.13%	$Al(C_2H_5O)_3$, 31.47%
"	tripropylate	99–105°	263–264°	26.31% 25.65% 25.63%	$Al(C_3H_7O)_3$, 25.00%
"	triisobutylate	210–212°	250·254°	21.17%	$Al(C_4H_9O)_3$, 20.73%

The alcoholates burn in the air with a brilliant flame, and readily absorb water, the alcohols being regenerated. The investigation will be continued. It is proposed to investigate the action of amalgamated aluminum on secondary and tertiary alcohols, the reactions of aluminum alcoholates, and the action of other amalgamated metals on alcohols."

Yours truly,

W. Tistschenko.

St. Petersburg, Imp. University,
Chemical Laboratory, Aug. 3, 1896.

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AMERICAN CHEMICAL JOURNAL.

Contribution from the Laboratory of Analytical Chemistry of the University of Michigan.

ON THE DIFFUSION OF SULPHIDES THROUGH STEEL.

BY E. D. CAMPBELL.

In 1893 the author read a paper on the diffusion of sulphide of iron through steel before the American Institute of Mining Engineers. In this paper[1] five experiments were described, in which the rapidity with which the sulphide of iron used diffused through steel at a bright red heat, was strikingly shown.

In these experiments, bars of soft steel 2.5 cm. thick, 5 cm. wide and 15 cm. long, were used. The steel had the following composition: Carbon, 0.17 per cent.; silicon, 0.00 per cent.; phosphorus, 0.11 per cent.; total sulphur, 0.074 per cent. The sulphide of iron used in the above experiments was a sample of the ordinary fused sulphide used for the generation of hydrogen sulphide; it contained 20.62 per cent. sulphur.

The first purpose of the experiments was to decide whether or not an unquestioned chemical compound could diffuse through steel at a bright red heat. The statement has been made that, because carbon will diffuse through steel at a bright red heat, the diffusing carbon must be in the elemental

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[1] Trans. Am. Inst. Min. Eng., **23**, 621.

condition. If we could get sulphide of iron to diffuse through steel, then the statement that, because carbon will diffuse, therefore the diffusing carbon must be in the elemental condition, is without weight. The diffusing element may or may not be in a chemically combined form.

A brief description of two of the experiments above mentioned will suffice to show the extent to which the work was carried at that time. In one case a hole 12 mm. in diameter and 30 mm. deep was drilled in one edge of one of the above described bars. This hole was filled with 10 grams of sulphide of iron, and closed by driving in a short steel plug, turned to accurately fit the hole. The bar, so prepared, was then placed in a muffle furnace, brought to a bright red heat, and maintained at this temperature for four hours. An examination of the bar showed the hole to be nearly empty, except for a thin film. Drillings taken from the bar at various points, some within less than 2 mm. of the original hole, showed no perceptible increase in the percentage of sulphur in the bar. The scale, formed by the oxidation of the iron at the temperature employed, showed portions containing 2.604 per cent. of sulphur. It was evident from this that the sulphide had diffused through the bar.

In the second case the bar was prepared like the first one, except that the hole containing the sulphide of iron, instead of being plugged, was left open, and the bar was so placed in a Hoskins muffle furnace, that the interior of the hole could be observed through a small chimney in the top of the muffle. The bar was brought to a bright red heat and the sulphide was noticed apparently to settle rapidly, almost as soon as thoroughly melted. When most of the sulphide had diffused the bar was quickly withdrawn from the furnace and quenched in water; a distinct odor of hydrogen sulphide was perceived on quenching the bar. Drillings of the bar taken in the immediate vicinity of the hole showed no increase of sulphur above that originally present.

In the fall of 1893 further experiments were undertaken to determine the conditions best suited to the diffusion. A different sample of sulphide of iron from that employed in the above experiments was used at this time. The results obtained were rather unexpected for it was found that, when a bar prepared like those previously described was heated, little or no diffusion took place. The temperatures to which the bar was heated, whether oxidizing or reducing, were varied without apparently influencing the result. The work was again taken up in the fall of 1894 and experiments carried on for several months with apparently little or no better success than those of 1893. The identical bars used in the first experiments were employed, but the sulphide used failed to diffuse to any appreciable extent. It was not until the beginning of the present year that the property of diffusing through steel was found to be peculiar to an oxy-sulphide of iron instead of a normal sulphide. This peculiarity is proved and illustrated by the work described below.

A normal sulphide of iron, FeS, was prepared as follows: About 450 grams of ordinary fused sulphide was placed in a clay crucible, contained in a Hoskins gasoline furnace; the crucible containing the sulphide was covered with a crucible cover, perforated with a large hole; on top of this cover was cemented a second inverted crucible, having a hole about 20 mm. in diameter in the bottom. The second crucible extended above the top of the furnace, and through it sulphur could be introduced without disturbing the crucible containing the molten sulphide. By this means it was easy to maintain the molten sulphide in an atmosphere of sulphur for any desired length of time. Experiments made by keeping the molten sulphide in an atmosphere of sulphur for varying lengths of time showed that all oxide present was reduced, and the composition became constant when normal ferrous sulphide was obtained.

The steel, employed for the diffusion tests described in this work, was kindly furnished by Mr. M. J. Moore, chemist of the Illinois Steel Co., Joliet, Ill. A Bessemer steel billet having the following composition: Carbon, 0.10 per cent.; silicon, 0.009 per cent.; sulphur, 0.091 per cent.; phosphorus, 0.103 per cent.; manganese, 0.52 per cent., was heated and drawn down under the hammer to a thickness of 2.5 cm. and a width of 5 cm. This bar was then cut into pieces 5, 10, and 15 cm. long, weighing about 500, 1,000, and1, 500 grams, respectively. The short pieces were the ones employed in the diffusion tests to be described. The holes for containing the sulphide were in all cases drilled vertically in the narrow side of the bar; the holes were 12 mm. in diameter and 3 cm. deep, thus leaving about 6 mm. of metal on each side of the hole and 2 cm. beneath. The holes were placed at varying distances from the ends of the bar, these distances being stated under each experiment. When a hole after being filled with the sulphide, was plugged, this was done by accurately fitting a short tapered steel plug to the hole, and then driving it in with a heavy hammer. In examining the interior of a plugged hole after diffusion, it was almost always found necessary to drill out the plug, as it would be firmly welded in.

The furnace used for heating the bars was an assay muffle-furnace heated with gasoline. The muffle was 10 cm. high, 15 cm. wide, and 25 cm. long, provided at the back end with a small chimney, 10 cm. high, to increase the draught of air through the muffle when an oxidizing atmosphere was desired. Owing to the weight of the bars and thinness of the muffle bottom it was found desirable to reinforce the latter with a heavy false bottom 1 cm. thick. When an oxidizing atmosphere was desired the chimney was left open and the front of the muffle loosely closed with the door. When a reducing atmosphere was wanted the chimney was covered with a piece of mica, two or three large pieces of charcoal placed in the muffle, and the door closed and luted with fire clay. Bars heated to a bright red heat for several hours in a muffle so prepared, showed no signs of oxidation other than a slight blueing of the surface.

Experiment 1.—The hole in a bar 15 cm. long was filled with 20 grams of normal ferrous sulphide, FeS, and the bar so placed in the muffle that the open hole could be observed through the chimney. The muffle was then brought to a bright red heat, requiring thirty-five minutes. In fifteen minutes more the sulphide was observed to melt down; the temperature was maintained at a bright red with an oxidizing atmosphere for one hour and twenty-five minutes longer. The flame was then turned out and the bar allowed to cool slowly. The sulphide was found to have simply melted down in the hole but with no evidence of diffusion. In two or three other instances where normal sulphide of iron was used in open or in plugged holes the same results were obtained.

Seeing, from Experiment 1, that the normal sulphide of iron, FeS, would not diffuse, we prepared a sub-sulphide in the following manner: 175 grams of the normal ferrous sulphide was melted in a crucible with the inverted crucible for a cover, arranged in the same manner as for making the normal sulphide. When the normal sulphide was perfectly liquid a little sulphur was added to insure complete reduction of any oxide that might be present, then very fine pure iron wire, tied up in little bundles of about 10 grams each, was dropped in. At first the iron was very rapidly absorbed, but absorption became slower, and, although the temperature was increased almost to a white heat, finally ceased, and apparently unattached bundles of wire were observed immersed in the liquid sulphide. The crucible was then drawn from the furnace and the liquid sulphide poured into a flat iron mold. This sulphide was hard, brittle, and of a steel-gray color with a slight yellow tinge. The analysis of the sulphide showed the following composition:

	Per cent.
SiO_2	0.10
Al_2O_3	1.66
Fe	75.59
S	22.66

Assuming the sulphur and iron to be combined as a mixture of ferrous sulphide, FeS, and subsulphide, Fe_2S, the above would give:

	Per cent.
SiO_2	0.10
Al_2O_3	1.66
FeS	5.84
Fe_2S	92.41
	100.00

Experiment 2.—A bar 5 cm. long was prepared with two holes, equally distant from the center and ends; each hole was filled with 12 grams of the above subsulphide and one hole plugged. The bar was placed in the furnace upon two sup-

ports made by wrapping small pieces of iron, 2.5 cm. long, 6 mm. wide, and 4 mm. thick, with platinum foil. These supports were used to prevent any oxide, formed during the operation, from coming in contact with the muffle bottom, and also to prevent absorption by the muffle bottom of any diffused sulphide, experiments having shown that this absorption took place to a very marked degree. The bar was heated to a bright red heat in an oxidizing atmosphere for two hours and fifteen minutes. The sulphide in the open hole had sunk very slightly, while that in the plugged hole showed no sign of diffusion.

Experiments 1 and 2, having shown that neither normal ferrous sulphide, FeS, nor a subsulphide approximately Fe_2S, would diffuse, we next made an oxysulphide in the following manner: 400 grams of ordinary fused sulphide, such as is used for making hydrogen sulphide and containing 23.6 per cent. of sulphur, was ground and intimately mixed with 13 per cent. of its weight of fine magnetic oxide of iron, Fe_3O_4. This mixture was put into a fine-grained, clay crucible, and melted as quickly as possible; although the crucible was not kept in the furnace more than five minutes after the sulphide had melted, the molten sulphide was observed to have penetrated in many places completely through the crucible. The crucible was withdrawn and the sulphide poured into a cold iron mold. Although the crucible was kept in the furnace so short a time after the sulphide was melted, it absorbed almost one-half its weight of molten sulphide before the latter could be poured out. The oxysulphide obtained gave the following results on analysis:

	Per cent.
SiO_2	0.81
Al_2O_3	1.61
MnO	0.15
Fe	66.07
S	21.68
	90.32

Undetermined oxygen = 9.68 per cent.

Combining the sulphur as ferrous sulphide, FeS, and the remaining iron as ferrous oxide, FeO, gives:

	Per cent.
SiO_2	0.81
Al_2O_3	1.61
MnO	0.15
FeS	59.62
FeO	36.16
	98.46

The above calculation would make the molecular ratio of ferrous sulphide, FeS, to ferrous oxide, FeO, in the oxysulphide, 2.7 to 2. These results would indicate the probable existence of an oxysulphide of iron, Fe_2OS, derived from ferrous sulphide, FeS, by the replacement of one-half of the sulphur by oxygen. But, owing to the extreme rapidity with which this oxysulphide, when melted, diffuses through the walls of the retaining crucible, it is extremely difficult to obtain the pure oxysulphide free from unchanged normal sulphide, FeS. The properties of the sulphide obtained above are illustrated by the following experiments :

Experiment 3.—This was undertaken to show the rate and completeness of the diffusion of the above oxysulphide. A bar 5 cm. long was used with two holes, equally distant from the center and ends. Each hole was filled with 9.65 grams of oxysulphide and one of the holes tightly plugged, the other being left open so that the diffusion could be watched as it took place. The bar was supported upon the platinum supports, the open hole being directly beneath the chimney of the muffle.

9.65 grams of the same oxysulphide was placed in a small, covered, porcelain crucible, which was then placed near the bar in order to determine whether or not the oxysulphide lost weight by heat alone. The furnace was lighted and the temperature of the bar raised in an oxidizing atmosphere. The bar attained a dull red heat in thirty minutes and a full red in fifty minutes. At this time the sulphide in the open hole was observed to melt and to commence to disappear rapidly ; in from ten to fifteen seconds from the time the sulphide was observed to begin diffusing, diffusion appeared to be complete, except for a small piece, a few mm. in diameter, left in the bottom of the hole. The heat was turned off five minutes after this time, and the bar allowed to cool. On drilling into the plugged hole the sulphide appeared to have diffused practically completely. A rather thin scale of oxide was formed on the surface of the bar, and this, on removal and analysis showed 0.50 per cent. of sulphur. It will thus be seen that the oxysulphide had diffused through the steel, and the greater part of the sulphur been oxidized by the air at the temperature at which the operation was conducted. The results of the first experiments described in 1893 proved that when that sulphide diffused through steel there was practically no retention of sulphur by the metal. The oxysulphide in the porcelain crucible placed near the bar of steel, melted in the crucible but without change in weight.

Experiment 4.—This was planned to demonstrate that when diffusion of the oxysulphide takes place, the diffusion extends throughout the entire length of the bar and not merely through the thin-walled metal between the holes and the sides of the bar. A bar 10 cm. long was used with the hole 12 mm. from one end. In this hole was placed 12 grams of oxysulphide of iron, the hole being left open. At the further end of the bar a strip of sheet asbestos about 3 cm. wide was so fastened that the ends of the strip were in contact with the top and bottom of the bar for a distance of about 2 cm. The asbestos was retained firmly in position by a wire passing around it. No portion of the asbestos was within less than 6 cm. of the hole containing the oxysulphide, the object being to apply an absorbent material to two points of the bar as far removed as possible from the diffusing sulphide. If the sulphide diffused as far as this material it must have diffused through the entire bar. The bar, with the asbestos attached, was placed upon platinum supports and the temperature brought to a bright red in an oxidizing atmosphere. In forty-five minutes from the time of lighting the furnace, the bar had attained the full heat, the sulphide had melted and diffused, and the flame was turned out. The portions of the asbestos in contact with the bar, both at the top and at the bottom, were found black and to be saturated with oxide of iron due to the oxidation of the diffused sulphide.

In order to study the behavior of other sulphides than that of iron, cuprous sulphide was made by heating pure copper wire in a crucible, covered, and treated as in the preparation of the normal sulphide of iron. When the copper was full red, sulphur was added, and the temperature raised almost to white heat with frequent additions of sulphur for a little over two hours. In this way a nearly normal cuprous sulphide was obtained, as an analysis of the product showed 78.44 per cent. of copper, the theory for the normal sulphide, Cu_2S, being 79.8 per cent.

Experiment 5.—The bar used in this experiment was 5 cm. long with the hole equally distant from the ends, and of the usual size. In this was placed 12 grams of cuprous sulphide, and the hole was plugged. The bar, placed upon platinum supports, was kept at a bright red in an oxidizing atmosphere for two hours and forty-five minutes. On drilling into the hole the cuprous sulphide was found simply to have melted down, without diffusion. The scale on the outside of the bar was analyzed, but found to contain no copper; no evidence of diffusion could be discovered.

Experiment 6.—This was made to determine whether or not the oxysulphide of iron, when mixed with cuprous sulphide, would diffuse and, if it did diffuse, whether cuprous sulphide would be carried along with it.

A bar 5 cm. long was used with two holes equally distant from the end and center. In one hole was placed 6 grams of cuprous sulphide together with 6 grams of oxysulphide of iron, both sulphides being ground and mixed before introducing into the hole, which was then tightly plugged. In the parallel hole was firmly pressed 4 grams of ignited asbestos, this hole also being plugged. The bar so prepared was raised on platinum supports and brought in an oxidizing atmosphere to a bright red heat, at which temperature it was kept for two hours. The scale which was formed on the outside of the bar, by oxidation, was much smoother and stronger than when iron alone was present. The scale was divided into three portions, that from the bottom, middle, and top of the bar, weighing respectively 25, 19, and 24 grams. On drilling into the first hole the sulphides had apparently diffused except for a lining of cuprous sulphide, Cu_2S, in the lower portion of the hole. On opening the hole containing the asbestos the latter was found to be soaked for 6–7 mm. in depth, the lower portion of the asbestos being apparently unchanged. This altered portion of the asbestos was removed, weighed, and analyzed. The bar was then weighed and two holes drilled in it, one hole between the two original holes, but near the top; the drillings from these holes were mixed and analyzed to find the amount of copper retained by the bar. The distribution of the copper after the diffusion is best shown in the following table:

	Weight. Grams.	Percentage of copper.	Weight of contained copper. Grams.
Bar	400	0.026	0.106
Asbestos	6	8.06	0.483
Top scale	24	2.47	0.593
Middle scale	19	1.94	0.368
Bottom scale	25	6.91	1.730
Total			3.28

The 1.420 grams of copper unaccounted for in the above table as the difference between the total copper added and that recovered, undoubtedly constituted the lining in the lower portion of the hole. A determination of the per cent. of sulphur (2.92) in the scale showed the presence of 1.990 grams out of 2.600 grams of sulphur originally present in the sulphides. The analysis of the asbestos containing diffused sulphide, showed: iron, 24.28 per cent.; copper, 8.10 per cent.; sulphur, 9.98 per cent. If the iron shown in this had been derived from the oxysulphide diffusing without decomposition and the copper from cuprous sulphide, also diffusing without change, then the theoretical percentage of sulphur which would have accompanied the amount of iron and copper shown by analysis, would have been 10.12 per cent., whereas that actually found was 9.98 per cent. The latter figure would go to prove almost conclusively that not only does the oxysulphide of iron diffuse unchanged but that the cuprous sulphide passes also without decomposition through the steel.

Experiment 7.—This experiment, like No. 4, was intended to show that when diffusion of cuprous sulphide was brought about by means of the oxysulphide of iron the diffusion also took place throughout the entire length of the bar. The bar used was 10 cm. long with a hole 12 mm. from each end, thus leaving 5 cm. of steel between the two holes. In one hole was placed 6 grams of copper sulphide with 6 grams of oxysulphide of iron, both ground and mixed, and the hole then plugged ; the other hole was filled with ignited asbestos and then plugged. The bar, raised upon platinum supports, was brought in an oxidizing atmosphere to a bright red heat and kept here for three hours. Upon opening the first hole the sulphides were found to have nearly all diffused. The upper part of the asbestos was found to be converted into a hard, dark-colored mass, weighing 1.2 grams and containing 0.276 gram of copper, thus demonstrating the distance to which the copper sulphide may be carried by the diffusing oxysulphide of iron.

On sawing a vertical section through the hole originally containing the sulphides, it was found to be lined in the lower portion with cuprous sulphide, Cu_2S. On polishing this section, etching, and examining microscopically, the outline of the original hole appeared to be perfectly sharp, and there was no evidence that the steel had been attacked by the sulphides which must have entered the metal at this point.

The next sulphide operated upon was that of nickel. This was prepared by heating pure nickel wire under the same conditions as those used in making cuprous sulphide. The metal was heated and kept in an atmosphere of sulphur until it had taken up all the sulphur with which it would combine. Several experiments proved that when nickel is heated with sulphur, and the sulphide produced kept melted in an atmosphere of sulphur, the sulphide, Ni_4S_3, is the result.

Experiment 8.—To determine whether nickel sulphide, like cuprous sulphide, could be made to diffuse by mixing it with oxysulphide of iron. The bar used was 5 cm. long prepared with two holes, as in Experiment 6, one filled with asbestos and plugged, the other with 6 grams of nickel sulphide and 6 grams oxysulphide of iron, both ground and mixed before being placed in the hole, which was afterwards plugged. The bar, upon platinum supports, was heated in the usual manner and kept at a bright red for two hours and fifty minutes. On drilling into the hole, practically all of the nickel sulphide seemed to have remained in it after melting down. The scale formed on the bar was divided into two parts, that from the lower and that from the upper portion of the bar, the scale from the lower portion weighing 24 grams and showing 0.26 per cent. of nickel or 0.062 gram, while that from the upper portion, 23 grams in weight, gave 0.10 per cent. of nickel or 0.023 gram; thus it will be seen that although there was 4.26 grams of nickel in the nickel sulphide used, only 0.085 gram diffused through the bar. The asbestos showed no change in appearance.

The above experiments were selected from 40 diffusion tests, extending over a period of about ten months, distributed in three or four intervals during the past three years. It did not seem desirable to describe more than the above experiments as they suffice to demonstrate the peculiar property of diffusion of oxysulphide of iron, which ultimately became the object of the research. We might offer the following possible explanation of the observed phenomena. The oxysulphide being an extremely mobile liquid at the temperature at which the experiments were performed would readily be absorbed by any porous body. The rapidity of its absorption by the crucible, while being made, shows this. If steel is at all porous at a bright red heat then the oxysulphide would diffuse through these pores and be drawn rapidly into any porous absorbent material, such as asbestos or scale, from the superficial oxidation of the bar. The retention of so small an amount of copper by the bar after diffusion takes place, shows that although pores may exist in the steel, their volume is extremely minute compared with that of the metal. The tendency of the diffusing sulphide to accumulate towards the lower part of the bar would show the influence of gravity on the diffusing sulphide, and that it diffuses in a liquid and not gaseous form.

The fact that pure cuprous sulphide will not diffuse, although a mixture of pure cuprous sulphide and oxysulphide of iron will do so can be explained only on the assumption that pure cuprous sulphide is not sufficiently mobile when liquid to enter the extremely fine pores in the steel, but that mobility is increased sufficiently by diluting with the extremely mobile oxysulphide of iron, thus enabling absorption to take place, and diffusion through the bar.

The failure of the greater part of nickel sulphide, Ni_4S_3, to diffuse even when mixed with oxysulphide of iron, would clearly show the greater difficulty of obtaining this body in a sufficiently finely divided state to enter the pores of the steel.

The experimentation in the above work was carried on by my successive private assistants, W. G. Wallace, C. R. Rose, F. Thompson, and E. B. Hart, and here I acknowledge my obligations to them for the care and patience with which they have conducted the above research.

ANN ARBOR, MICH., July 11, 1896.

ON THE INFLUENCE OF HEAT TREATMENT AND CARBON UPON THE SOLUBILITY OF PHOSPHORUS IN STEELS.

BY E. D. CAMPBELL AND S. C. BABCOCK.

It has been well known for some time that the brittleness of steel, due to the presence of phosphorus, is more marked when the percentage of carbon is high than when there is but little carbon present, and that with the same percentage of carbon the brittleness is more marked when the metal is hardened than when it is in its annealed or normal state. Since the above is true, it would seem that there must be some relationship between the carbon and phosphorus compounds in steel, and that the chemical condition in which phosphorus exists in steel is capable of being changed by varying the heat treatment. With a view to determining whether chemical evidence could be obtained to prove that phosphorus may exist in steel in at least two forms, our research was undertaken.

Three specimens of steel were used in this work:

No. I was a soft steel containing 0.10 per cent. carbon and 0.119 per cent. phosphorus.

No. II was a mild steel containing 0.37 per cent. carbon and 0.160 per cent. phosphorus.

No. III was a Bessemer steel containing 0.73 per cent. carbon and 0.114 per cent. phosphorus.

Annealed samples were obtained by placing specimens in a muffle furnace containing pieces of charcoal to prevent oxidation, bringing the whole to a bright red heat, then packing the muffle with a mixture of wood ashes and charcoal, closing everything as tight as possible, and allowing to remain till cold. The steel was considered in its normal state as it came from the mill. The hardened specimens were obtained by heating pieces in a muffle furnace to bright red heat and quenching in cold water. Samples for analysis of all these specimens except No. III hardened were obtained by drilling. The No. III hardened was reduced by pounding in a steel mortar until it was all passed through a sieve with 20 meshes to the linear inch.

The phosphorus soluble in neutral mercuric chloride is determined in the following manner: Five grams of steel together with 35 grams of finely ground mercuric chloride are introduced into an eight-ounce Erlenmeyer flask with 130 cc. water. Carbon dioxide is then passed in till all air is displaced, in order to avoid oxidation of ferrous chloride, and the flask tightly stoppered and shaken for some time until the solution of the steel is complete. The annealed and normal steels dissolve quite readily, solution usually being complete within an hour. The hardened metal is much less readily soluble, so that it is usually found best to allow the solution to stand over night before filtering. When the solution of the iron is complete, the precipitation of mercury associated with any insoluble compound is filtered out (using the pump to hasten the operation) and washed with hot water till the filtrate gives no test for ferrous iron with potassium ferricyanide. The filtrate is examined for phosphorus in solution by adding 10 cc. of a solution of ferric chloride, then adding 4 grams of sodium acetate and heating till the precipitate of basic acetate separates, carrying ferric phosphate with it. The basic acetate precipitate is dissolved in hot hydrochloric acid (1–3), washed through with hot water, concentrated, and finally boiled down with excess of nitric acid till all hydrochloric acid is oxidized. The solution of ferric nitrate thus obtained is then diluted slightly, ammonia added in excess, cleared up with nitric acid and the phosphoric acid precipitated, with the usual precautions, with ammonium molybdate. The ferric chloride used was prepared by dissolving 8.15 grams of pure iron wire containing 0.050 per cent. phosphorus in hydrochloric acid, oxidizing by cautious addition of chloric acid, and diluting to 250 cc. 10 cc. of this solution contained 0.326 gram iron, 1 cc. free hydrochloric acid, phosphorus enough to give 0.01 gram precipitate of ammonium phosphomolybdate, for which amount allowance was made in the determinations given in the appended table.

The determination of the phosphorus insoluble in mercuric chloride, but soluble in 4-per cent. hydrochloric acid (40 cc. hydrochloric acid diluted in 1000 cc.) is made by taking filter-paper containing the precipitated and washed mercury from the above determinations, introducing into an Erlenmeyer flask and shaking well for ten minutes with 100 cc. of the cold dilute acid. The mercury and the paper are separated by filtering and washing with hot water. The filtrate is boiled down with addition, toward the last of the operation, of an excess of nitric acid, and the phosphoric acid determined, after neutralization with ammonia and subsequent acidification with nitric acid, by addition of ammonium molybdate.

The phosphorus insoluble in neutral mercuric chloride is determined by taking the washed precipitate of mercury obtained by dissolving a second sample and removing it as completely as possible from the filter-paper. The filter is charred and ignited in a porcelain crucible at as low a heat as possible. The mercury is introduced into a large combustion-boat, which is then put into a large combustion-tube and the mercury volatilized in a stream of carbon dioxide by cautiously heating the tube. The vapors of mercury are condensed by drawing the gas through a Wolff bottle containing water. After the volatilization of the mercury, the residue in the boat is added to the small portion obtained by igniting the filter-paper in a porcelain crucible, the whole treated with nitric acid (1.40), evaporated to dryness, and baked to oxidize the phosphorus thoroughly. The residue is dissolved in hydrochloric acid (1.20), filtered to remove silica, boiled down with excess of nitric acid, and the phosphoric acid precipitated in the usual manner with ammonium molybdate. This determination gives the total amount of phosphorus insoluble in neutral mercuric chloride, from which, by subtracting the amount soluble in 4-per cent. hydrochloric acid, we obtain the amount of phosphorus insoluble in neutral mercuric chloride in 4-per cent. hydrochloric acid.

The table of results is as follows:

Steel.	Per cent. carbon.	Per cent. phosphorus.	Heat treatment.	Per cent. phosphorus soluble in neutral $HgCl_2$.	Per cent. phosphorus insoluble in $HgCl_2$ but soluble in 4 per cent. HCl.	Per cent. phosphorus insoluble in either $HgCl_2$ or 4 per cent. HCl.	Per cent. of the total phosphorus found in		
				A.	B.	C.	A.	B.	C.
I	0.10	0.119	A	0.014	0.060	0.044	11.8	50.4	37.0
I	"	"	N	0.020	0.054	0.044	16.9	45.4	37.0
I	"	"	H	0.015	0.049	0.055	12.6	41.1	46.2
II	0.37	0.160	A	0.044	0.072	0.045	27.5	45.0	28.1
II	"	"	N	0.030	0.103	0.028	18.7	64.1	17.5
II	"	"	H	0.005	0.052	0.104	3.1	32.5	65.0
III	0.73	0.114	A	0.045	0.065	0.005	39.4	57.0	4.4
III	"	"	N	0.027	0.063	0.024	23.7	55.2	21.0
III	"	"	H	0.001	0.030	0.088	0.8	26.3	77.1

The inspection of the above table brings out the following facts:

1. With very low percentage of carbon, the effect of heat treatment upon the solubility of phosphorus is slight, probably if carbon were entirely absent there would be no effect.

2. With increase of carbon the effect of hardening is to diminish the solubility of the phosphorus.

3. With high percentage of carbon the solubility is increased by slow cooling.

These three facts would point very strongly to the probable formation at a high temperature of a difficultly soluble compound of iron with carbon and phosphorus, which is transformed on slow cooling into an easily soluble one. Since the difference in the chemical behavior of phosphorus in hardened and annealed steels is fully as marked as is that of carbon under the same conditions, it would seem not improbable that the heat absorbed or evolved in the transformation of one form into another might account for one of the other retardations (A_2 or A_3 of F. Osmund) in the same way that the transformation of carbon into cement carbon accounts for the recalescence A.

Further work will be done in this laboratory in order to determine, if possible, the composition of the compounds indicated in the above work, and the temperature at which the transformation of one form into another takes place.

ANN ARBOR, MICH., JULY 11, 1896.

Contribution from the Kent Chemical Laboratory of the University of Chicago.

ON MALONIC NITRILE AND SOME OF ITS DERIVATIVES.

BY B. C. HESSE.

Malonic nitrile, prepared in 1886 by L. Henry,[1] was studied by him to but a slight extent. He showed that on distillation it did not polymerize; that with cold concentrated hydrochloric acid malonic acid was readily formed; whereas in sealed tubes at 150°, it was split into chloracetic acid and carbon dioxide. With ammoniacal silver nitrate he obtained a salt which contained an amount of silver approaching that required by the formula $C_3Ag_2N_2$. So far as has been recorded syntheses by means of the salts of malonic nitrile have not been made.

The work to be described in the following pages was carried out under the supervision of Professor Nef of this university. Its object is to study some of the derivatives of malonic nitrile and to ascertain, if possible, whether in its salts the metal is bound to nitrogen or to carbon. Judging from the work on acetoacetic ester and its congeners as well as that on malonic ester, the 1.3 diketones and the nitroparaffins, it seemed quite unlikely that the metal is bound to carbon. That it is bound to nitrogen appears very probable because of the work on prussic acid and the cyanides.[2]

Cyanacetamide.

Preparation.— Cyanacetamide was prepared according to Van't Hoff's method[3] from cyanacetic ester and aqueous am-

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[1] Compt. Rend., **102**, 1394.

[2] Nef, (1895): Ann. Chem. (Liebig), **287**, 265-359.

[3] Van't Hoff, (1874): Ber. d. chem. Ges., **7**, 1382.

monia. The best yield as well as the purest product is obtained by slowly pouring cyanacetic ester (one molecule) into two molecules of 28-per cent. ammonia water, both reagents being at 0°. The ester dissolves and the amide soon separates out as a closely felted mass of crystals; the mass is now cooled to —15° and transferred to a Hirsch funnel, washed with ice-water until the odor of ammonia is only slight, spread on clay plates, dried in the air and finally at 100°. The yield varies from 70 to 75 per cent. of the theory.

Properties.—Thus prepared, cyanacetamide is a white substance crystallizing in hexagonal plates, melting without decomposition at 120°. It cannot be distilled either at ordinary or at reduced pressure without decomposition. It is soluble in 6.5 parts of cold water, 55 parts of cold alcohol, and is not very soluble in ether, chloroform or ligroïn. It dissolves in caustic soda solution with slow evolution of ammonia.

The fact that cyanacetamide is less soluble in alcohol than in water suggested that alcoholic ammonia would give a better yield. This is not the case, since with two molecules of a 16-per cent. alcoholic ammonia only 28 per cent. of the theoretical yield of the amide was formed, while with one molecule of alcoholic ammonia no separation whatever took place.

The clear solution of the ester in the aqueous ammonia followed by precipitation of amide has suggested the existence of an intermediate unstable addition-product which by loss of alcohol yields amide. This view has apparent support, at least, in the fact that the yield with alcoholic ammonia is only one-third of that obtained in the aqueous solution, although the solubility in water is very nearly ten times greater than in alcohol. The reason for this may be that in alcoholic solutions loss of alcohol by this addition-product with subsequent formation and precipitation of amide is prevented by the surrounding alcohol, a condition of things not found in the aqueous solution.

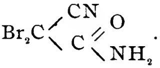
Sodium Cyanacetamide.—Dry cyanacetamide suspended in dry and alcohol-free ether is not attacked by sodium. On adding a few drops of alcohol reaction sets in at once, a light yellow salt being formed. It is necessary to add a few drops of alcohol from time to time. The reaction being completed the salt is removed from the ether and dried over paraffin *in vacuo.*

On analysis 0.4199 gram substance gave 0.2911 gram Na_2SO_4.

	Calculated for $C_3N_2H_3NaO$.	Found.
Na	21.70	22.48

Two atoms of sodium cannot be taken up.

The monosodium salt in chloroform suspension readily reacts with bromine, but the reaction-products were not further investigated.

Dibromcyanacetamide, 

$$Br_2C\left\langle\begin{matrix} CN \\ C\left\langle\begin{matrix} O \\ NH_2 \end{matrix}\right. \end{matrix}\right. .$$

Cyanacetamide in cold aqueous solution, treated with one molecule of bromine reacts at once. An oil separates, which after standing, becomes crystalline when scratched. Hydrobromic acid and ammonium bromide are also formed. The crystalline body thus obtained is not, as would be expected, monobromcyanacetamide,[1] but is the dibrom derivative. It is formed to the extent of 50 to 60 per cent. of the theory. After recrystallizing from benzene until a constant melting product was obtained, the substance was analyzed.

0.1705 gram substance gave 0.0931 gram CO_2, and 0.0155 gram H_2O.

0.2164 gram substance gave 23.0 cc. N at 743.6 mm. and 19°.

0.1656 gram substance gave 0.2558 gram AgBr.

0.2018 gram substance gave 0.3135 gram AgBr.

	Calculated for $Br_2C_3H_2N_2O$.	Found.
C	14.87	14.89
H	0.83	1.02
N	11.57	12.00
Br	66.11	65.74 ; 66.11

Dibromcyanacetamide, recrystallized from benzene, melts at 120°.5 without decomposition. Heated dry to 160° it gives off a slight amount of bromine ; at 210° the evolution of bromine is marked.

Dibromcyanacetamide is very soluble in cold ether and in

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[1] *cf.* Ann. Chem. (Liebig), **280**, 334.

cold alcohol; cold benzene dissolves but little, while boiling benzene dissolves it readily; chloroform, cold or boiling, dissolves it more readily than does benzene; cold or boiling ligroïn or carbon disulphide dissolves but very little.

With potassium cyanide in concentrated aqueous solution, a concentrated alcoholic solution of dibromcyanacetamide becomes warm and deposits a white crystalline substance and potassium bromide. With potassium iodide iodine is liberated.

Malonic Nitrile.

Perfectly dry cyanacetamide in fine powder, intimately mixed with an equal weight of phosphorus pentachloride, is introduced into a distilling flask, whose volume is about four times that of the mixture. The bulb is connected with a Brühl's apparatus, which is then exhausted; the mixture is heated with a water-bath, and the reaction begins at about 90°, hydrochloric acid being given off in great quantities. When the liquid is boiling quietly and no more gas evolution takes place, the water-bath is replaced by a metal bath and the dark brown liquid is distilled *at once*. The distillate has generally to be redistilled twice in order to free it from traces of oxychloride of phosphorus. The yield of the purified product is upwards of 70 per cent. of the theory. The above proportion corresponds to 5 molecules of amide to 2 molecules of pentachloride. Proportions which allowed the formation of phosphorus oxychloride to take place to a great extent, rarely gave over 30 per cent. of the theoretical yield.

Malonic nitrile is a pure white, ice-like solid, melting at 29°, and boiling at 219°–220° at ordinary pressures, 99° at 11 mm. and 109° at 20 mm. On standing, even in the dark, it becomes colored. A specimen of Kahlbaum's preparation which was at least two years old, had become entirely black and, on attempting to distil it at ordinary pressure, it decomposed with great violence, emitting white fumes having the odor of ammonia and of prussic acid. In its freshly prepared aqueous solution malonic nitrile has a neutral reaction; on standing for a day it becomes quite colored, and in two weeks has become brownish and acid in reaction. Malonic nitrile has an odor faintly resembling acetamide.

0.0699 gram substance gave 26.7 cc. N at 21° and 741.6 mm.

0.1403 gram substance gave 0.0393 gram H_2O, and 0.2774 gram CO_2.

	Calculated for $C_3H_2N_2$.	Found.
C	54.54	53.92
H	3.03	3.11
N	42.42	42.61

In the combustion, malonic nitrile forms a very hard charcoal, which is burned with great difficulty. This probably explains the low result for carbon.

In the cold the malonic nitrile is soluble in about 7.5 parts of water, 2.5 parts of alcohol, 5 parts of ether, 10 parts of glacial acetic acid, 10 parts of chloroform and 15 parts of benzene. It requires more than 150 parts of cold ligroïn (boiling-point 70°–80°) for solution. It can be extracted from its aqueous solutions by ether, and these ethereal solutions must be dried with sodium sulphate, as the small amount of caustic lime in the fused calcium chloride is sufficient to turn the nitrile yellow. Sodium hydrate solution extracts malonic nitrile from ether.

Malonic nitrile dissolved in the smallest quantity of water at 20° and poured into a 30-per cent. solution of sodium hydrate (2¼ molecules) also at 20°, and this mixture at once poured into the calculated amount of 25-per cent. sulphuric acid cooled with ice, and then extracted with ether, all the malonic nitrile is recovered. The recovered substance is tinged a very slight brown, but is not contaminated enough to materially affect the melting-point, which is found to be 28°–29°.

An excess of cold concentrated caustic soda after a long time converts malonic nitrile into malonic acid and much colored amorphous substance.

An ethereal solution of malonic nitrile shaken up with a concentrated aqueous solution of sodium carbonate for a long time, turns brown and deposits a brown amorphous flaky substance. The aqueous solution does not yield malonic nitrile on acidifying ; on boiling ammonia is evolved.

Malonic Nitrile and Bromine.

The action of bromine on malonic nitrile, either molten or in aqueous solution, is complex, as oils and crystalline and amorphous solids are produced. Satisfactory observations with regard to the nature of the oils and the amorphous bodies could not be made because of the difficulties in the way of isolating homogeneous products. In the following only the crystalline bodies, which form from 20 to 25 per cent. of the reaction-products, will be described.

Monobrommalonic Nitrile,  $\begin{matrix}H\\Br\end{matrix}\!>C(CN)_2$. — Ten grams of malonic nitrile dissolved in as small a quantity of water as possible, were treated with 24.8 grams (2 atoms) of bromine. The temperature of the solution rose at once, but was controlled by the tap water. After reaction had apparently ceased, the product was warmed on the water-bath until nearly all color of bromine had disappeared. The product is an oil heavier than and insoluble in water. The oil was extracted by ether and dried with sodium sulphate. On distilling off the ether a reddish brown oil remains, which when scratched becomes a magma of white crystals and red oil. The crystals were removed from the mixture and recrystallized from chloroform until a constant melting product was obtained. The yield of pure substance is small, about five grams or 25 per cent. of the theoretical.

On analysis:

0.2613 gram substance gave 45.6 cc. N at 22°.5 and 741.5 mm.

0.2182 gram substance gave 0.1981 gram CO_2, and 0.0188 gram H_2O.

0.1817 gram substance gave 0.2362 gram AgBr.

	Calculated for C_3HBrN_2.	Found.
C	24.82	24.75
H	0.69	0.91
N	19.31	19.33
Br	55.17	55.32

Monobrommalonic nitrile is a white crystalline solid melting between 65° and 66°. It is not very soluble in water or ligroïn, but is quite soluble in alcohol, ether, benzene, chloroform or carbon disulphide.

To 5 grams of monobrommalonic nitrile dissolved in 85 cc. of absolute ether were added 5.5 grams (slightly more than one molecule) of silver nitrite, and the whole boiled for eight hours. At the end of this time the contents of the flask had a strong odor of nitrous fumes. After separation of the solid material from the ether, the latter was distilled off and the residue gave 0.8 gram of white crystalline substance melting at 118°–119°. The melting-point could not be raised by repeated crystallization. On analysis it was shown to be nearly all dibromcyanacetamide. The desired nitro-malonic nitrile had evidently not been formed.

An aqueous solution of monobrommalonic nitrile reacts at once with lead oxide, turning red and depositing lead bromide. If lead oxide be present in slight excess metallic lead is formed.

It also reacts with alkalies, lime and a silver cyanide giving off a sharp odor resembling cyanogen bromide, and amorphous red and yellow products are formed.

Dibrommalonic Nitrile, $Br_2C(CN)_2$, is prepared in a manner similar to that of the monobrom derivative. It is accompanied by much more oil and amorphous matter than is monobrommalonic nitrile, and consequently the yield is smaller. The product of the reaction is likewise an oil which is separated from the water; the water solution is extracted with ether, the ethereal solution and the oil are mixed, washed with a little water, dried with sodium sulphate and the ether distilled off. At this point a small quantity of crystals melting at 109° were obtained; the remaining oil on standing *in vacuo* over paraffin for some days partially solidified. After separating the crystals from the adhering reddish oil,[1] they were washed with much cold chloroform and finally recrystallized from boiling chloroform until the melting-point remained constant. The yield from 10 grams of nitrile is 6.5 grams, or about 17 per cent. of the theoretical.

The white crystals melting at 123°.5 to 124°, gave on analysis the following results:

0.2444 gram substance gave 0.1424 gram CO_2, and 0.0123 gram H_2O.

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[1] The oil could not be made to yield any homogeneous oils or solids. It readily lost bromine on heating, liberated iodine from potassium iodide, distilled *in vacuo* with decomposition, giving a small quantity of white plates; cold or boiling alkalies did not produce cyanide, but merely gave off a sharp odor resembling that of cyanogen bromide.

0.1436 gram substance gave 16.3 cc. N at 18°.5 and 742.4 mm.

0.1165 gram substance gave 0.1951 gram AgBr.

	Calculated for $C_3N_2Br_2$.	Found.
C	16.07	15.88
H	0.00	0.56
N	12.50	12.85
Br	71.43	71.27

Dibrommalonic nitrile is quite easily soluble in alcohol, ether and boiling chloroform, and not very soluble in benzene or in ligroïn.

Silver Salt of Malonic Nitrile.—This silver salt was prepared by L. Henry[1] from ammoniacal silver-nitrate solution and malonic nitrile. He published no analytical data, but says that the amount of silver contained in it approaches that required by the formula $C_3Ag_2N_2$. This salt was prepared by pouring a cold aqueous solution of malonic nitrile (one molecule) into a cold solution of ammoniacal silver nitrate (2 molecules). The resulting white precipitate is agitated violently and set aside in a dark place for ten minutes. The salt is then filtered by means of a Hirsch funnel, washed with water until free from nitric acid, spread on clay plates and dried at 100° to 110° for several hours.

Silver determinations were made in two separate preparations and the carbon and hydrogen in a third.

0.1091 gram substance gave 0.1043 gram AgCl.

0.1326 gram substance gave 0.1293 gram AgCl.

0.6719 gram substance gave 0.3596 gram CO_2, and 0.0145 gram H_2O.

0.6999 gram substance gave 0.3790 gram CO_2, and 0.0170 gram H_2O.

0.4732 gram substance lost 0.0017 gram when heated to 110°–115° for three hours, and for three hours more to 130°–135°.

	Found.			
C	14.59	14.76		
H	0.24	0.27		
Ag			72.13	73.47

Moisture 0.36 per cent.

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[1] L. Henry : Compt. Rend., 102, 1394.

The salt is evidently a mixture of mono- and disilver malonic nitrile, for which the calculated percentages are:

	C_3HAgN_2.	$C_3Ag_2N_2$.
C	20.86	12.85
H	0.56	0.00
Ag	62.42	77.14

The analysis corresponds roughly to a mixture of about 25 per cent. of the monosilver salt, and 75 per cent. of the disilver salt; the presence of water either as such or as water of constitution is also excluded. The presence of disilver salt is shown by the behavior of the salt towards alkyl iodides.

The precipitate obtained as above described is at first white, but rapidly changes to yellow, and, after drying on a clay plate, is yellowish brown. It is soluble in an excess of ammonia from which dilute nitric acid reprecipitates it; an excess of the precipitant redissolves the salt. Heated dry to 210° it explodes with a flash of light and a slight noise, an odor resembling that of cyanogen being given off.

Silver Malonic Nitrile and Alkyl Iodides.

Diethyl Malonic Nitrile, $(C_2H_5)_2C(CN)_2$.—Silver malonic nitrile, when acted upon by ethyl iodide, pure or diluted with ether, gives diethylmalonic nitrile, ethyl isocyanide, and amorphous substances.

To 56 grams of ethyl iodide, cooled in ice, were carefully added 25 grams of silver malonic nitrile in 5 gram portions. Slight reaction takes place in the cold, the odor of isocyanide being very noticeable. This mixture is allowed to stand at the temperature of the room for seven hours, and is then heated on a bath of boiling water for twenty-one hours longer. The reaction-product was distilled with steam, the distillate extracted with ether, and the ether dried with calcium chloride; the light-brown residual oil, 4.5 grams, has an odor of isocyanide. Distillation *in vacuo* gave a liquid boiling at 91°–93° at 24 mm., which solidified on standing; after recrystallizing many times from water, 1.7 grams of a pure product (melting-point 44°) were obtained.

0.1203 gram substance gave 0.3004 gram CO_2 and 0.0926 gram H_2O.

0.0867 gram substance gave 18.0 cc. N at 22° and 747 mm.

	Calculated for $C_7H_{10}N_2$.	Found.
C	68.85	68.10
H	8.19	8.55
N	22.95	23.23

The yield of diethylmalonic nitrile is 15.6 per cent. of the theoretical.

Thirty-two grams of silver salt and 2.5 molecules of ethyl iodide, diluted with 3 volumes of absolute ether, were heated in a sealed tube at 100° for five hours, and the residue extracted with absolute ether gave finally 0.9 grams of diethylmalonic nitrile, melting at 45°, or 6.4 per cent. of the theoretical yield. The ether which was distilled off was shaken with concentrated hydrochloric acid until all odor of isonitrile disappeared ; the acid solution was evaporated on the water-bath. The white deliquescent crystalline residue melted at 78° while ethylammonium chloride melts at 80° and is also deliquescent. This substance, whose weight was 0.4 gram, was therefore regarded as ethylammonium chloride. The yield is 4.3 per cent. of the total amount possible.

Besides these substances there was also formed a large amount of a reddish amorphous organic substance, probably polymerized ethyl isocyanide, which is insoluble in ether and was not further examined.

That the substance melting at 44° is diethylmalonic nitrile is shown by its conversion into diethylcyanacetamide by boiling with sodium ethylate in absolute alcohol solution, and the conversion of the latter into diethylcyanacetic and diethylacetic acids. These experiments will be described more fully further on.

Diethylmalonic nitrile is a white crystalline substance soluble in alcohol, ether, benzene, ligroïn, chloroform, acetone, and acetic ether ; it is not soluble in cold water but dissolves in a small quantity of hot water, from which it crystallizes on cooling. Its aqueous and alcoholic solutions are neutral to litmus paper. It melts at 44° and is volatile with steam; boiled with alcoholic potash no ammonia or cyanide is formed.

One-half gram of the substance boiled with 15 cc. of carefully prepared absolute alcohol, containing two-tenths gram sodium, for twenty minutes, cooled and poured into water, extracted with ether, gave 0.45 gram of diethylcyanacetamide, which will be described later on.

One gram of diethylmalonic nitrile dissolved in 60 cc. of absolute alcohol containing 0.25 gram sodium, and allowed to stand at the temperature of the room for two hours, poured into water and extracted with ether, gave 1.1 grams of a yellow oil having a mint-like odor, and in other respects fully resembling the oil obtained by the action of ethyl iodide upon malonic nitrile and sodium ethylate in alcoholic solution. This oil will be shown later to consist of diethylmalonic nitrile and its alcohol addition-product, diethylcyanacetimidoethyl ether. This formation of imido ether from nitrile and alcohol in the presence of sodium ethylate demonstrates the additive power of the nitrile group in this compound toward alcohol and furnishes another instance of the formation of free imido ethers directly from the nitriles,[1] of which the substances described by Schmidtmann[2] are also very striking examples. The oil prepared in this way, after some time, acquired a slight odor of isonitrile, which disappeared if the flask remained uncorked for some time.

Dimethylmalonic nitrile, $(CH_3)_2C(CN)_2$.—To 70 grams of methyl iodide, cooled to —10°, were added 25 grams of silver malonic nitrile in 5-gram portions. The odor of isocyanide was soon detected and on gradually warming up to 35° the reaction became very violent. After the violence of the reaction had subsided the mixture was heated to 50° for six hours to insure completion of the reaction. The mass was now distilled with steam, the distillate extracted with ether, the ether dried, and distilled off.

The oily residue distilled at 62°–66° at 22 mm. and yielded 2.5 grams of a crystalline distillate. These crystals, after several crystallizations from ligroïn, melted at 32°.

0.1233 gram substance gave 0.0713 gram H_2O and 0.2882 gram CO_2.

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[1] Nef (1895): Ann. Chem. (Liebig), **287**, 280, 322.

[2] Schmidtmann (1896): Ber. d. chem. Ges., **29**, 1193, 1174. Although Schmidtmann does not say so, yet there can be no doubt that these bodies are imido ethers.

0.1211 gram substance gave 32.9 cc. N at 22° and 737.8 mm.

	Calculated for $C_5H_6N_2$.	Found.
C	63.83	63.74
H	6.38	6.42
N	29.79	30.01

Further evidence that this substance is dimethylmalonic nitrile was obtained by converting it into dimethylmalonic acid by heating in sealed tubes with concentrated hydrochloric acid at 100° for two hours.

Dimethylmalonic nitrile is a white crystalline substance melting at 32°–32°.5, quite easily soluble in alcohol, ether, acetone, and acetic ether, not so easily soluble in chloroform, benzene, and ligroïn, and quite insoluble in water. Its alcoholic solution is neutral to litmus. Boiling with caustic soda produces no ammonia.

The formation of dialkylmalonic nitriles and of alkyl isocyanide suggests two points of attack in the silver malonic nitrile molecule, or that the compound partially decomposes into silver cyanide, and the latter reacting with the alkyl iodide produces the isonitrile. If the latter were true then there would be positive evidence as to the position of the metal in the substance since in silver cyanide the metal is bound to nitrogen.[1] This is hardly probable, since the formation of isonitrile takes place at 20°.

On the first assumption we may have two possibilities: namely, that the metal is bound to carbon or to nitrogen. The first of these is rendered unlikely because, in order to explain the formation of isonitrile, addition of alkyl iodide to the nitrile group would have to be supposed, a supposition for which there is no foundation in fact. On the second supposition the constitution to be assigned to the disilver salt would be

$$AgN : C : C : C : NAg.$$

A substance with so many consecutive double linkings would of necessity be a very reactive body.

By the addition of alkyl iodide to the double bonds between the carbon atoms the intermediate product

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[1] Nef (1895): Ann. Chem. (Liebig), **287**, 269 et seq.

$$\mathrm{AgN : \underset{I}{\overset{|}{C}} \cdot \underset{R_2}{\overset{\|}{C}} \cdot \underset{I}{\overset{|}{C}} : NAg}$$

would be formed which, by loss of silver iodide, would give dialkylmalonic nitrile. The formation of isocyanide would be explained by the direct replacement of the silver by alkyl or by addition of alkyl iodide to the double bonds between nitrogen and carbon with subsequent loss of silver iodide. In either case, of which the first is the more likely, the compounds

RN : C : C : C : NR or AgN : C : C : C : NR

would be formed which could decompose with the formation of isonitrile. The isonitrile at that temperature and in the nascent state would undergo polymerization to a great extent.[1]

It is well known that silver salts react more readily by direct replacement than do the sodium salts. Consequently, the sodium derivatives of malonic nitrile with alkyl iodide should form little or no isonitrile. As a matter of fact no isocyanide is found.

These facts render the constitution given for disilver malonic nitrile very probable.

Malonic Nitrile and Sodium.

Although Schmidtmann[2] has succeeded in isolating the pure monosodium malonic nitrile, the following attempts to prepare the disodium compound will not be without interest :

To 11.5 grams of malonic nitrile dissolved in 200 cc. of absolute ether were added 8.0 grams (2 atoms) of sodium ; if the nitrile is perfectly pure and dry *no reaction* of any consequence takes place. On adding a few drops of alcohol a reaction is set up at once and continues for a long time, during which a yellowish-white heavy salt, mixed with a white and lighter substance is deposited. Whenever the evolution of gas slackens a few drops more of alcohol are added to increase the action. In all, 10 cc. of alcohol were added, an amount corresponding very nearly to 1 molecule. The salt was filtered off, washed with ether, and dried. Its weight was

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[1] Nef (1895): Ann. Chem. (Liebig), **287**, 357.

[2] Schmidtmann (1896): Ber. d. chem. Ges., **29**, 1171.

27.13 grams. The ether filtrate contained less than 0.75 gram of dissolved material; hydrochloric acid precipitated nothing but sodium chloride and the filtrate from this contained a very small quantity of a brownish oil with a very penetrating odor. The total weight of the material taken is 27.5 grams and 27.13 grams of salt were obtained, so that very little, if any, of the nitrile escaped conversion into the salt.

Cyanides were not present in the salt.

Sodium determinations were made in two different preparations of this substance.

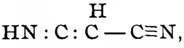
I. 0.5864 gram substance gave 0.4951 gram Na_2SO_4 = 27.38 per cent. Na.

II. 0.5432 gram substance gave 0.4712 gram Na_2SO_4 = 28.13 per cent. Na.

C_3HNaN_2	requires	26.13	per cent.	Na.
C_3Na_2N	"	41.82	" "	Na.
$NaOC_2H_5$	"	33.82	" "	Na.

The analysis as well as the appearance of the product make it likely that it is a mixture of at least two substances. At any rate, it reacts with alkyl iodides as though it contained both mono- and disodium malonic nitriles. A mixture of monosodium malonic nitrile and sodium ethylate in equivalent molecular proportions—the most probable composition of the product—could react as disodium malonic nitrile. Such a mixture contains 29.4 per cent. sodium, an amount not very different from that actually found.

The product obtained is a light yellow powder turning red on exposure to moist air. It dissolves readily in water, giving a yellow solution; it is slowly, but completely, soluble in alcohol. Its aqueous solution gives with silver nitrate at first a black precipitate, due probably to an excess of sodium ethylate. After removing the black precipitate, a white one is obtained on further addition of the reagent, having the same characteristics as described for the salt obtained from malonic nitrile and ammoniacal silver nitrate.

Decomposed by acids, the odor of prussic acid is obtained, and a brownish oil containing malonic nitrile melting at 27°–29° can be extracted by ether; with dilute sulphuric acid the oil separates out at once, but with hydrochloric acid there is no separation of oil. Heated in dry condition the salt gives off ammonia and the charred residue contains cyanide and traces of carbonate. This formation of prussic acid by dilute acids is in favor of the view that the metal is bound to nitrogen, the regeneration of malonic nitrile not being a serious objection to this view, since it is not impossible that at the moment of liberation from its sodium salt malonic nitrile is  $HN:C:\overset{H}{C}—C\equiv N$, of which the greater part rearranges to $CH_2(CN)_2$, while a small part escapes such rearrangement and decomposes, giving prussic acid as one of the decomposition-products.

The formation of cyanide by heating the dry, salt while not conclusive evidence, is at least of value as indirect evidence, since in cyanides the metal is bound to nitrogen.[1]

Sodium Malonic Nitrile and Ethyl Iodide.—Ten grams of the above mentioned salt were heated in a sealed tube with four molecules of ethyl iodide at 100° for eight hours. On opening the tube not a trace of isocyanide odor could be detected; prussic acid was present in the tube, as was shown by its odor, as well as by drawing air through the tube and then through caustic soda solution and showing the presence of the cyanide in the latter. The liquid contents of the tube were taken out and mixed with ether as long as any precipitate formed, which was then filtered out; the solid part of the contents of the tube was dissolved in water as far as possible, and the solution extracted with ether. The two ethereal solutions were mixed and dried with sodium sulphate. After distilling off the ether there remained an oil which on distilling *in vacuo* gave an oil boiling from 85° to 120° at 14 mm. and a solid which was identified as diethylcyanacetamide. The oily distillate was dissolved in ether, shaken out with sodium hydrate solution to remove any monoalkylated nitrile. The sodium hydrate solution after washing with ether, was poured into dilute sulphuric acid. The ether extract of this acid solution was only a very small quantity of an oil with a sharp odor. The ethereal solution which had been washed

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[1] Nef (1895) : Ann. Chem. (Liebig), **287**, 269.

with alkali, was washed with water, dried and distilled. The distillate boiled at 87°–88° at 13 mm. and solidified in a freezing-mixture. After several recrystallizations from water it melted at 44° and possessed all the properties of diethylmalonic nitrile.

The yield was 2.5 grams, or 31.9 per cent. of the theoretical. The presence of prussic acid is probably due to the decomposition of monoethylmalonic nitrile.[1]

Sodium Malonic Nitrile and Methyl Iodide.—Eleven grams of sodium malonic nitrile and 57 grams of methyl iodide (four molecules) were heated in a sealed tube to 100° for 8 hours. The contents of the tube did not have any odor of isocyanide, but contained much prussic acid, which was verified in the same way as in the preceding experiment. The contents of the tube were treated in the same way as before with the additional operation of removing iodine from the ether by aqueous sodium thiosulphate. After drying and distilling *in vacuo*, an oil boiling from 50° to 70° at 11 mm., and a small quantity of a solid crystalline body were obtained. The oil was dissolved in ether and washed with sodium hydrate solution as before. Again on acidifying this alkaline solution and extracting with ether a small quantity of an oil with a sharp odor was obtained. The ethereal solution which had been washed with alkali, after distilling off the ether as before, left an oil which was almost colorless and solidified when placed on ice. After several recrystallizations from ligroïn it melted constantly at 32°–32°.5. It is dimethylmalonic nitrile, and the yield is 36 per cent. of the theory.

The solid crystalline body obtained during the distillation *in vacuo* was very small in quantity ; it was found to be made up of two parts, one soluble in ether, and the other insoluble. Nothing was done with it because of the very small quantity formed.

THE ACTION OF CHLORFORMIC ESTERS AND OF ALKYL IODIDES UPON AN ALCOHOLIC SOLUTION OF MALONIC NITRILE AND SODIUM ALCOHOLATE.

a. The Action of Chlorformic Ethyl Ester.

Sodium Dicyanacetic Acid Ethyl Ester.—Five grams of

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[1] P. Henry : Jahresbericht (Fittica), 1889, 639.

malonic nitrile dissolved in a small quantity of absolute ethyl alcohol were poured into 175 cc. of alcohol cooled to —15° and containing 1.75 grams (one atom) of sodium. To this mixture were added 8.5 grams (one molecule) of ethyl chlorformate. The temperature rose to +5°, and the liquid became turbid at once; the contents of the flask were cooled to —10° as rapidly as possible and then allowed to rise slowly to +10°. The liquid was neutral to litmus paper, although the odor of ethyl chlorformate was still noticeable. After vigorous agitation of the liquid the separated salt was filtered off and identified as sodium chloride; its weight was 1.9 grams or 90 per cent. of the theoretical yield. The alcohol was distilled off from the filtrate at 30–40° and 35 mm. pressure. The distillate was slightly acid and became turbid with silver nitrate. The residue was extracted with ether to remove the unchanged malonic nitrile. This ethereal extract contains, besides malonic nitrile, a substance which gives a yellowish precipitate directly with silver nitrate, and this precipitate when dried and heated on platinum foil leaves behind a fluffy, bluish-black residue. The precipitate is not due to sodium dicyanacetic ether, as will be shown later on.

The slightly yellowish residue, insoluble in ether, was extracted with boiling acetic ether, which left a small amount of sodium chloride undissolved. The acetic ether was removed by distillation, and the residue, weighing 4.2 grams or 70 per cent. of the theory, was almost white. It was purified once more by solution in 7 parts of warm alcohol and precipitating by 50 parts of ether; the crystalline precipitate is filtered off, washed with fresh ether, dried on a clay plate and then placed over paraffin *in vacuo* for 36 hours.

0.1863 gram substance gave 29.5 cc. N at 748.2 mm. and 24°.5.

0.1861 gram substance gave 0.3098 gram CO_2 and 0.0607 gram H_2O.

0.3728 gram substance gave 0.1640 gram Na_2SO_4.

	Calculated for $C_6H_5N_2O_2Na$.	Found.
N	17.50	17.53
C	45.00	45.40
H	3.13	3.62
Na	14.37	14.27

Sodium dicyanacetic ether has already been isolated, having been obtained by Haller[1] from sodic cyanacetic ether and cyanogen chloride. The salt obtained as above described has all the properties of Haller's salt: it is not soluble in chloroform, ether, ligroïn or benzene; it is soluble in about 8 parts of cold acetic ether, and the solubility is not much increased by heating. Heated dry an odor resembling that of isonitrile is first observed, and finally ammonia is given off; the residue does not contain cyanide. With boiling concentrated caustic soda this salt does not evolve ammonia, only when all the water has been driven off and the residue begins to fuse is ammonia noticeable. It does not react with dilute (1.5) sulphuric acid, but with concentrated acid it reacts at once. It dissolves in boiling concentrated hydrochloric acid from which it is again deposited unchanged in thick prisms upon cooling, and no ammonium or sodium chlorides could be detected in this deposit. The behavior towards caustic soda and hydrochloric acid is sufficient evidence of the extreme stability of this compound towards hydrolyzing agents and also shows the firm linking of the metal.

Silver nitrate produces a white curdy precipitate, which when dried has only a slight yellow tint. The dry salt heated on platinum foil gives off combustible gases having the odor of ethyl isocyanide; the residue is grayish and compact.

b. The Action of Methyl Chlorformate.

Sodium Dicyanacetic Acid Methyl Ester.—Five grams of malonic nitrile dissolved in a small quantity of absolute methyl alcohol were poured into 175 cc. of methyl alcohol containing 1.75 grams (one atom) of sodium and cooled to —15°. To this mixture 7.1 grams (one molecule) of methyl chlorformate were added at once. The temperature rose to 0°, but was soon lowered to —15°. The mixture became turbid almost immediately, and in a few moments the liquid was neutral. The greater part of the alcohol was recovered by distillation at ordinary pressure. The residual liquid, which had become slightly acid in reaction, was poured into water and extracted with ether, dried with calcium chloride,

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[1] Alb. Haller (1890): Compt. Rend., 111, 53-55.

and the ether distilled off. The residue is a reddish-brown oil which does not distil without decomposition at ordinary pressure, but at 10 mm. and 100° colorless malonic nitrile distils over. There remains in the bulb a mass of charcoal and white crystals. The reddish-brown oil from ethereal solution, on standing a few days, deposits crystals which are apparently monoclinic tablets, melting with partial decomposition at 206°. They give a neutral solution with boiling water, from which on cooling the substance separates out. Hot or cold ether does not take up much of it; hot alcohol dissolves it readily, cold does not. Aqueous caustic soda dissolves it readily, and from this solution it is precipitated by dilute sulphuric acid. A solution of sodium carbonate does not dissolve it. Boiling hydrochloric acid dissolves it and on cooling deposits it unchanged. A boiling solution of caustic soda does not give any ammonia; when fused with caustic soda it gives off ammonia. The amount of substance formed was about 0.05 gram.

The oil obtained from this ether was mainly malonic nitrile and contained in addition a substance giving directly with silver nitrate a yellowish precipitate which, when dried and heated on a platinum foil, swelled up and left a bluish-black mass, just as the similar substance formed in the case of ethyl chlorformate. It is not due to the presence of the sodium compound whose reaction-product with silver nitrate behaves very differently, as will be shown later.

The aqueous solution after extraction with ether was evaporated *in vacuo*, the residue extracted once more with ether, and finally with boiling acetic ether, leaving sodium chloride undissolved. There were obtained 2.9 grams of the sodium compound, or 53 per cent. of the theoretical yield. This salt was purified and dried in exactly the same manner as the corresponding ethyl compound.

0.3195 gram substance gave 0.1537 gram Na_2SO_4.

0.0838 gram substance gave 14.3 cc. N at 750.6 mm. and 17°.5.

0.1189 gram substance gave 0.1784 gram CO_2 and 0.0241 gram H_2O.

	Calculated for $C_5H_8N_2O_2Na$.	Found.
C	41.09	40.91
H	2.05	2.25
N	19.18	19.57
Na	15.75	15.60

This substance has already been isolated by Haller.[1] In addition to the description thereof given by him, it may be added that the salt is precipitated from its alcoholic solution by benzene, ligroïn, chloroform and ether; it is insoluble in acetic ether. Its behavior towards acids and alkalies, both cold and boiling, is the same as that of the corresponding ethyl derivative. The silver salt, obtained by treating the aqueous solution of the sodium compound with silver nitrate, when dried is slightly yellow, and when heated on platinum foil leaves a compact grayish residue.

c. The Action of Methyl Iodide.

Ten grams (one molecule) of malonic nitrile, dissolved in a small quantity of cold methyl alcohol, were poured into 500 cc. of cold absolute methyl alcohol containing 7 grams (two atoms) of sodium. After connecting the flask with a return-condenser, 49 grams ($2\frac{1}{4}$ molecules) of methyl iodide were added. The liquid warmed up spontaneously, but was cooled with tap water. After a few moments the flask was heated to 60° on a water-bath until the alkaline reaction disappeared. Total time of the reaction was about five minutes. The alcohol was distilled off at ordinary pressure until sodium iodide began to separate out. The remaining liquid was poured into much water, extracted with ether, the ether washed with sodium hydrate and then with water to remove any unchanged malonic nitrile and any monoalkylated product, and finally dried with calcium chloride. The light-brown oil remaining after distilling off the ether was distilled *in vacuo*. The distillate came over at 74°–76° and 22 mm.; its weight was 10.6 grams. This oil has a fragrant mint-like odor, is soluble in 8 parts of water, is decomposed by boiling with water or with methyl alcohol, giving an alkaline vapor. The aqueous solution on treatment with dilute hydrochloric acid deposits an oil suggesting the presence of imido ethers.

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[1] Alb. Haller (1890): Compt. Rend., 111, 53–56.

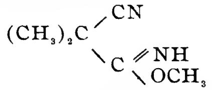
On analysis:

I. 0.0788 gram substance gave 16.5 cc. N at 19°.5 and 745 mm.

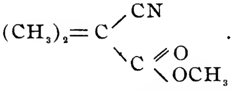
II. 0.0787 gram substance gave 16.6 cc. N at 22° and 747.4 mm.

Per cent. N found, I. 23.63; II. 23.61.

Calculated for dimethylmalonic nitrile 29.79 per cent.

Calculated for  $(CH_3)_2C\left\langle\begin{array}{l}CN\\ C\left\langle\begin{array}{l}NH\\ OCH_3\end{array}\right.\end{array}\right.$, 22.22 per cent.

This analysis therefore indicates the presence of about 82 per cent. of imidoether.

Methyl Dimethyl Cyanacetate,  $(CH_3)_2{=}C\left\langle\begin{array}{l}CN\\ C\left\langle\begin{array}{l}O\\ OCH_3\end{array}\right.\end{array}\right.$.—To prove the presence of imidoether 5 grams of the oil were dissolved in 40 cc. of water, filtered, and treated with an excess of cold hydrochloric acid. The oil which separated was filtered off, dissolved in ether, and dried with calcium chloride. On distilling *in vacuo* 2.45 grams of a colorless oil boiling at 78° and 24 mm. were obtained. The aqueous filtrate was extracted with ether, the ethereal solution washed with water, dried with calcium chloride and distilled *in vacuo*, when 0.8 gram of a colorless oil boiling from 76–78° at 20 mm. was obtained.

Nitrogen determinations were made in these oils. The oil which separated from the aqueous solution gave the following results:

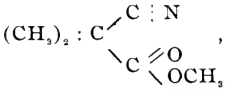
I. 0.1896 gram substance gave 20.5 cc. N at 30°.5 and 741 mm.

II. 0.1647 gram substance gave 18.0 cc. N at 30° and 739 mm.

The oil extracted by ether:

III. 0.2020 gram substance gave 21.0 cc. N at 27°.5 and 741 mm.

I = 11.49 per cent.
II = 11.62 per cent.
III = 11.23 per cent.



Calculated for $(CH_3)_2:C(C\vdots N)(C(=O)OCH_3)$, N = 11.02 per cent.

The oil is therefore the methyl ester of dimethylcyanacetic acid. The ammonium chloride obtained by evaporation of the aqueous solution corresponded to 3.74 grams of imido ether. The amount of imido ether obtained was 86 per cent. of this.

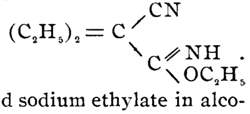
To prove that in the oil obtained by the action of methyl iodide upon the alcoholic solution of malonic nitrile and sodium methylate, the two methyl groups are bound to the same carbon atom, a portion of this oil was converted into dimethylmalonic acid by heating with an excess of concentrated hydrochloric acid in a sealed tube to 100° for two hours. Besides ammonium chloride, methyl chloride and some carbon dioxide, large quantities of a white crystalline substance soluble in ether were formed. This last substance after repeated recrystallization from water and ether, melted with decomposition and evolution of gas at 188°. These properties, as well as the following analysis, show the substance to be dimethylmalonic acid, already described by Thorne.[1]

0.1123 gram substance gave 0.1852 gram CO_2 and 0.0696 gram H_2O.

	Calculated for $C_5H_8O_4$.	Found.
C	45.45	44.97
H	6.06	6.88

d. The Action of Ethyl Iodide.

Diethyl Cyanacetimidoethyl Ether,



$(C_2H_5)_2=C(CN)(C(=NH)OC_2H_5)$.

—By acting upon malonic nitrile and sodium ethylate in alcoholic solution with ethyl iodide at 72°, the proportions and the operation being the same as in the preceding experiment, an oil giving indications of the presence of imido ethers and a solid which will be shown to be diethyl cyanacetamide were obtained.

On analysis of the oil

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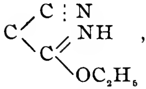
[1] Thorne (1881): J. Chem. Soc., **39**, 544.

I. 0.1708 gram substance gave 30.6 cc. N at 23°, and 742.1 mm.

II. 0.1366 gram substance gave 24.5 cc. N at 23°.5, and 748.2 mm.

Found I. = 19.81 per cent. N; II. = 19.96 per cent. N.

Calculated for $(C_2H_5)_2$:  $C\left\langle\begin{matrix} C \vdots N \\ C \overset{\displaystyle NH}{\diagup\!\!\diagup} \\ \diagdown OC_2H_5 \end{matrix}\right.$, N = 16.66 per cent.

Calculated for $(C_2H_5)_2 : C : (CN)_2$, N = 22.95 per cent.

This analysis corresponds to a mixture of about equal parts of nitrile and imidoether. Since it has been shown that diethylmalonic nitrile on standing with alcoholic sodium ethylates gives an oil similar to the above it seemed probable that the formation of imidoether could be increased by retarding the reaction, thus allowing the nitrile, which may be formed, to become converted into imidoether under the influence of the unacted upon sodium ethylate.

This was verified in a special experiment where the reaction was allowed to take place at ordinary temperatures. Six hours were required to complete the reaction. From this mixture the oil was recovered as in the preceding cases and analyzed.

0.1226 gram substance gave 19.5 cc. N at 18°, and 740.3 mm. = 17.96 per cent. N.

This analysis corresponds to a mixture of 80 per cent. of imidoether and 20 per cent. of nitrile.

The almost complete conversion of this oil into imidoether was effected as follows: Twelve and one-half grams were dissolved in 180 cc. of absolute ethyl alcohol containing 0.75 gram sodium and allowed to stand at the temperature of the room for twenty-eight hours. The oil was then recovered in the usual way. Ten grams boiling at 90°–91° at 15 mm. were obtained; on redistillation, 8.2 grams boiling at 90°–91° at 15 mm. were obtained. The residue in the flask was oily without the slightest sign of a crystalline solid, which shows the absence of any diethyl cyanacetamide.

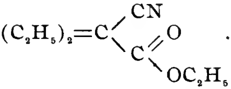
On analysis

0.2060 gram substance gave 31.7 cc. N at 23°, and 743.2 mm.

0.1644 gram substance gave 0.3888 gram CO_2, and 0.1408 gram H_2O.

	Calculated for $C_9H_{16}N_2O$.	Found.
C	64.27	64.49
H	9.52	9.51
N	16.66	17.04

Judging from the analysis and the steadiness of the boiling-point, the oil was apparently the pure imido ether. That such was not the case was shown when the oil was converted into

Diethylcyanacetic Ethyl Ether, 
$(C_2H_5)_2{=}C(CN)C({=}O)OC_2H_5$.—To 7.8 grams of the imido ether dissolved in 65 cc. of-33 per cent. alcohol were added 8 cc. (2 molecules) of concentrated hydrochloric acid. The temperature of the liquid rose somewhat, but was controlled by tap water. After a short time a considerable quantity of colorless oil separated out. The mixture was now poured into water, extracted with ether, the latter washed with sodium carbonate solution, and then with pure water. After drying, distillation *in vacuo* gave 4.0 grams of colorless oil (analyzed) boiling between 100° and 101° at 15 mm., and 3.0 grams boiling between 99° and 100° and 101°–102°.

On analysis

0.1182 gram substance gave 10.3 cc. N at 23°.5, and 739.2 mm.

0.1774 gram substance gave 0.4275 gram CO_2, and 0.1422 gram H_2O.

	Calculated for $C_9H_{15}NO_2$.	Found.
C	63.90	65.71
H	8.87	8.96
N	8.28	9.57

The oil is evidently the desired substance containing traces of another compound richer in carbon and nitrogen than itself, in all probability diethylmalonic nitrile. In order to test this 5.25 grams of the oil were dissolved in 90 cc. of absolute ethyl alcohol containing 0.4 gram sodium, and the mixture allowed to stand at the temperature of the room for thirteen days. The liquid was now poured into water, treated with an excess of hydrochloric acid, and extracted with ether as before. The second distillation *in vacuo* yielded 3.1 grams of an oil boiling at 100–101° at 14 mm.

On analysis

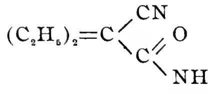
0.1874 gram substance gave 14.4 cc. N at 21°, and 745 mm.

0.1630 gram substance gave 0.3816 gram CO_2, and 0.1293 gram H_2O.

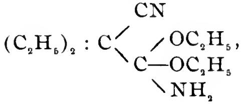
	Calculated for $C_9H_{15}NO_2$.	Found.
C	63.90	63.84
H	8.87	8.81
N	8.28	8.61

Diethylcyanacetic ether is a colorless oil with a fragrant odor, entirely different from the refreshing mint-like odor of the imido ether. It is not very soluble in water and its solubility in 33-per cent. alcohol is less than that of the imido ether.

Although the diethylcyanacetimidoether described above has not been obtained in a perfectly pure state, yet it cannot be doubted that if the mixture of nitrile imido ether and alcoholic sodium ethylate had been allowed to stand longer, no unchanged nitrile would have remained. The only slightly contaminated specimen of diethylcyanacetimidoethyl ether is a colorless mobile oil possessing a fragrant and refreshing mint-like odor. It is only slightly soluble in water, and can be boiled without decomposition with water and ethyl alcohol.

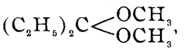
Diethylcyanacetamide,  $(C_2H_5)_2{=}C\begin{matrix}CN\\ C\begin{matrix}O\\ NH_2\end{matrix}\end{matrix}$.—This substance is formed in the preparation of diethylmalonic nitrile from the sodium salt and ethyl iodide in sealed tubes; in the action of ethyl iodide upon malonic nitrile and sodium ethylate in alcoholic solution; and when diethylmalonic nitrile is boiled with absolute alcohol containing 1.3 per cent. of sodium.

In this last method the alcohol had been made absolute with the greatest of care and it is not reasonable to suppose that the formation of amide is caused by the presence of water or of sodium hydrate. This is probably due to the intermediate production of the dialkylamidoether,



$$(C_2H_5)_2:C\left\langle\begin{array}{l}CN\\ C\left\langle\begin{array}{l}OC_2H_5,\\ OC_2H_5\\ NH_2\end{array}\right.\end{array}\right.$$

which at the boiling-point of alcohol must lose ethyl ether and form the amide. Such a loss of ether is not improbable since Mackenzie[1] has shown that the compound



$$(C_2H_5)_2C{<}\begin{array}{l}OCH_3\\ OCH_3\end{array},$$

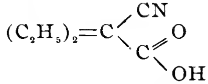
on standing over sulphuric acid in a desiccator, loses ether, and that with acid it forms benzophenone.

Diethylcyanacetamide melts at 120°, is white, and crystallizes in plates. It is soluble in alcohol, ether, and chloroform, and not very soluble in ligroïn or benzene.

0.1516 gram substance gave 0.1187 gram H_2O, and 0.3337 gram CO_2.

0.1194 gram substance gave 21.3 cc. N at 21°, and 746.9 mm.

	Calculated for $C_7H_{12}N_2O$.	Found.
C	60.00	60.02
H	8.57	8.69
N	20.00	20.05



Diethylcyanacetic Acid, $(C_2H_5)_2{=}C\left\langle\begin{array}{l}CN\\ C\left\langle\begin{array}{l}O\\ OH\end{array}\right.\end{array}\right.$.—This substance has been made (1) from the oil obtained by the action of ethyl iodide upon malonic nitrile and sodium ethylate in alcoholic solution, (2) from diethylmalonic nitrile and (3) from diethylcyanacetamide by heating in sealed tubes with concentrated hydrochloric acid to 100° for two hours. In all cases a brownish oil floats on top of the hydrochloric acid in the tube. The oil is separated, the acid solution is mixed with

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[1] (1896) Chem. News, **73**, 268.

enough water to dissolve the ammonium chloride, and shaken out with ether. The ethereal solution and the separated oil are mixed and shaken out with a solution of sodium carbonate. This carbonate solution, after being washed with fresh ether, is acidified, and again shaken out with ether; the ether washed with water, dried, and distilled. There is obtained a colorless oil boiling between 162° and 164°, at 18 mm. The oil soon solidifies to a white, hygroscopic, ice-like solid. It melts at 57° and distils undecomposed at ordinary pressure, a rather striking property of a cyanogen acid. The cyanogen group is very stable, not being affected by concentrated hydrochloric acid in a sealed tube at 120° for one hour, nor by heating with alcoholic potash in a sealed tube to 100° for three hours. A silver salt is obtained when sodium hydrate is added to a mixture of the acid and silver nitrate. The salt crystallizes from boiling water in glistening needles, which are not affected by light.

0.1847 gram substance (free acid) gave 0.1302 gram H_2O, and 0.4012 gram CO_2.

0.2534 gram substance gave 22.5 cc. N at 18°, and 749 mm.

	Calculated for $C_7H_{11}NO_2$.	Found.
C	59.57	59.23
H	7.80	7.83
N	9.93	10.15

By heating with concentrated hydrochloric acid in a sealed tube to 160° for eight hours diethylcyanacetic acid is quantitatively converted into

Diethylacetic Acid.—This acid was isolated in the same way as the preceding acid, except that it was distilled at ordinary pressure, boiling from 189–191°.[1] The portion coming over between 189°.5 and 190°.5 was analyzed.

0.1766 gram substance gave 0.1624 gram H_2O, and 0.3998 gram CO_2.

	Calculated for $C_6H_{12}O_2$.	Found.
C	62.07	61.73
H	10.35	10.22

The acid also forms the peculiar silver salt so characteristic of diethylacetic acid.[2]

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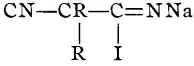
[1] Saytzeff (1878): Ann. Chem. (Liebig), **193**, 351. [2] *Ibid.* p. 353.

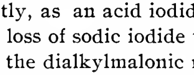
The conversion of diethylcyanacetic acid into diethylacetic acid furnishes the proof that in all those substances yielding diethylcyanacetic acid the two ethyl groups are bound to one and the same carbon atom.

In the foregoing reasons have been given for considering that the metal in metallic derivatives of malonic nitrile is bound to nitrogen. On this basis the alcoholic solution of malonic nitrile and sodium alcoholate must be regarded as containing monosodic malonic nitrile,[1] $CN{-}CH{=}C{=}NNa$. The alkyl iodide, adding itself to the double bond between the two carbon atoms, produces, with loss of sodic iodide, monoalkylated malonic nitrile, $CN{-}CHR{-}CN$, which, in the presence of the excess of sodium ethylate, must immediately be converted into the sodium salt, $CN{-}CR{=}C{=}NNa$; the latter then gives, by absorption of alkyl iodide,



$$\mathrm{CN{-}\underset{\substack{|\\ R}}{CR}{-}\underset{\substack{|\\ I}}{C}{=}NNa}\ (A).$$

The product (*A*) by loss of sodic iodide, yields dialkylmalonic nitrile. The formation of the monimido ether,



$$\mathrm{CN{-}CR_2{-}\underset{\substack{|\\ OR}}{C} : NH},$$

which, as has been seen, is, in the case of methyl—as well as of ethyl iodide, the chief product of the reaction, can be explained (1) on the assumption that the above intermediary product (*A*) reacts directly, as an acid iodide,[2] with the alcohol present, *i. e.*, before loss of sodic iodide takes place, or (2) on the assumption that the dialkylmalonic nitrile first formed in the reaction subsequently adds, in part, one molecule of methyl or of ethyl alcohol in view of the presence of sodium alcoholate. Since it has been shown that diethylmalonic

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[1] There are no facts as yet known which in any way prove that a disodium salt of malonic nitrile or of malonic ether exists, and, on the whole, the existence of such salts seems at present improbable. We know with certainty that with an excess of sodium ethylate, cyanamide gives only the monosodium salt, $NaHN{-}CN$, notwithstanding that this compound readily gives a disilver salt, $Ag_2N{-}CN$.

The action of alkalies, mild and caustic, on malonic nitrile, as well as a careful study of the behavior of the salts of malonic nitrile and of monoalkylated malonic nitriles towards acids, acyl and alkyl chlorides, will be continued in this laboratory.

J. U. NEF.

[2] *Cf.* Nef (1895): Ann. Chem. (Liebig), **287**, 263, 315, 317–18, 343.

nitrile does actually, although very slowly, absorb ethyl alcohol with formation of the monimidoether in case some sodium ethylate is at hand, it is manifestly impossible, with the experimental data as yet available, to come to a decision as to the actual course of the generation of the monimidoether.

The formation of imido ethers, however, under the circumstances just mentioned, makes it necessary to take the possibility of their presence into consideration in all cases where the Conrad-Limpach method is applied to substances containing nitrile groups.

Contribution from the Kent Chemical Laboratory of the University of Chicago.

ON THE "BECKMANN REARRANGEMENT."

I. CHLORIMIDOESTERS.

BY JULIUS STIEGLITZ.

In 1882 Hofmann[1] discovered that acid bromamides, RCONHBr, undergo a peculiar rearrangement when heated with aqueous alkali, yielding derivatives of the isocyanates CO : NR, or their hydrobromic acid addition-products, the bromformamides, BrCONHR, the bromine atom having apparently exchanged places with the alkyl radicle R.

A similar exchange was soon afterwards observed by Beckmann[2] to occur when oximes are treated with phosphorus pentachloride or other anhydrizing reagents. Hoogewerff and Van Dorp[3] pointed out later the similarity between the reactions discovered by Hofmann and what has become known as the "Beckmann rearrangement" of the oximes. Lengfeld and Stieglitz[4] then found that the acid bromamides undergo the same rearrangement on treatment with a methyl-alcohol solution of sodium methylate, giving urethanes and other derivatives of the isocyanates.

As far as known at present, this peculiar rearrangement of acid bromamides is effected only by alkaline solutions, that of the oximes only by anhydrizing reagents; these facts would indicate that at some, perhaps early, stage of these reactions, in the one case hydrobromic acid, in the other case water

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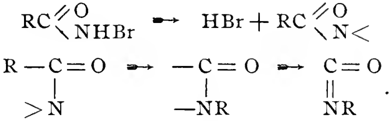
[1] Hofmann : Ber. d. chem. Ges., **14**, 2725; **15**, 408. [2] *Ibid*, **19**, 988, etc.

[3] Recueil d. Travaux chim. d. Pays-Bas, **6**, 373; **8**, 173, etc.

[4] This JOURNAL, **15**, 215, 504.

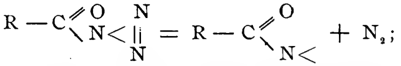
is formed. It has become desirable to determine to what extent, if at all, the remaining hydrogen atom in the group—CONHBr is necessary for effecting the rearrangement of the acid bromamides. The hydrogen atom might influence the reaction in a number of ways, the most important of which need alone be mentioned here. The alkali might cause a direct loss of hydrobromic acid, producing the body $(RCO)N<$ with a univalent nitrogen atom, whose reactivity[1] must then be the cause of the peculiar separation of the alkyl R from the carbon atom holding the nitrogen: the very reactive univalent nitrogen atom taking the alkyl away from the carbon atom, isocyanates must result, and these have actually been obtained,[2] as the first tangible products of the reaction:



$$\mathrm{RC}\begin{matrix}/\!\!/\mathrm{O}\\ \backslash\mathrm{NHBr}\end{matrix} \rightarrow \mathrm{HBr} + \mathrm{RC}\begin{matrix}/\!\!/\mathrm{O}\\ \backslash\mathrm{N}<\end{matrix}$$

$$\begin{array}{ccccc} R-C=O & \rightarrow & -C=O & \rightarrow & C=O \\ | & & | & & \| \\ >N & & -NR & & NR \end{array}.$$

This interpretation of the reaction has become yet more worthy of study because of the peculiar behavior of the acid azides $(RCO)N<\begin{smallmatrix}N\\ \|\\ N\end{smallmatrix}$, discovered by Curtius. These bodies when warmed even with *neutral* reagents, such as water or alcohol,[3] lose two atoms of nitrogen and give the *same* derivatives of the isocyanates which are obtained from the acid bromamides; here too one would expect the first product of the decomposition to be the body $(RCO)N<$ containing a very reactive univalent nitrogen atom, and in fact identical with the body mentioned above, and of course giving the same derivatives (*e.g.*, urethanes) of the isocyanates:

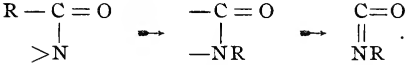


$$R-C\begin{matrix}/\!\!/O\\ \backslash N<\end{matrix}\begin{matrix}N\\ \|\\ N\end{matrix} = R-C\begin{matrix}/\!\!/O\\ \backslash N<\end{matrix} + N_2;$$

[1] Comparable with, and perhaps greater than, the analogous reactivity of bivalent carbon, as shown by Nef, in numerous reactions: Ann. Chem. (Liebig), **270**, 267, etc.

[2] Hofmann: Ber. d. chem. Ges., **15**, 412.

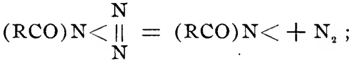
[3] Curtius: Ber. d. chem. Ges., **27**, 778: J. prakt. Chem., **50**, 289.



$$\begin{array}{c} R-C=O \\ | \\ >N \end{array} \rightarrow \begin{array}{c} -C=O \\ | \\ -NR \end{array} \rightarrow \begin{array}{c} C=O \\ \| \\ NR \end{array}.$$

The rearrangement of the acid bromamides and of the acid azides, yielding, as they do, identical products, does not seem to me capable of any other interpretation equally applicable to both classes of bodies.[1]

It may be remarked here that the formation of derivatives of the isocyanates is not the only indication of the preliminary formation of the product (RCO)N< with a univalent nitrogen atom, that the acid azides, $(RCO)N_3$, show. By reducing in alkaline solution, nitrogen is given off and symmetrical diacylhydrazines,[2] RCONHNHCOR, are formed, a most peculiar reaction for which no explanation has been suggested. But the reaction is easily understood, if (RCO)N< is really first formed: two molecules uniting by means of the reactive univalent nitrogen atoms would give azodiacyl (RCO)N = N(COR), which taking up two hydrogen atoms must yield (RCO)NHNH(COR), the diacylhydrazines actually obtained. Again, when reduced in acid solution, the acid azides lose nitrogen and give acid amides, a reaction which also appears very simple according to:



$$(RCO)N<\begin{array}{c}N\\ \|\\ N\end{array} = (RCO)N< + N_2;$$

$$(RCO)N< + H_2 = RCONH_2.$$

In order to determine, for the reasons presented, the influence of the hydrogen atom in the acid bromamide group—CONHBr, E. E. Slosson[3] is investigating under my direction the be-

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[1] *Note by J. U. Nef.*—Dr. Stieglitz having informed me of the contents of this paper, has requested me to call attention to a fact which at once struck me as being of special importance in connection with it. The rearrangement assumed here is analogous to that of the isonitriles to nitriles at 230°:

$$R-N:C< \rightarrow N ¦ C.R$$
$$R-(CO).N< \rightarrow CO:NR$$

—for instance, of phenyl isocyanate, $C_6H_5N:C$, to benzonitrile, $N ¦ CC_6H_5$. This change is best explained on the basis that bivalent carbon at 230° possesses sufficient energy to pull off alkyl (or alphyl) from nitrogen and thus give rise to the formation of the nitrile. I have, it may be mentioned, obtained during the past year, strong indications of the existence of the NH derivatives (containing univalent nitrogen) in connection with the work on the nitroparaffins with Mr. L. W. Jones.

[2] Curtius: *loc. cit.* [3] Preliminary report and note: Ber. d. chem. Ges., **28**, 3265.

havior of the acid chloranilides and analogous bodies, which are considered to have the constitution (RCO)NClR. As yet neither Mr. Slosson nor any other chemist who has worked with these bodies has ever observed a "Beckmann rearrangement" of any acid chloralkylamine, RCO(NClR). Nor has any rearrangement of the acid dibromamides, $(RCO)NBr_2$, been yet recorded. As far as known, therefore, the presence of the hydrogen atom in —CONHBr is essential for the rearrangement of the acid bromamides by alkaline solutions, a result in perfect accord with the interpretation of this reaction given above.[1]

In pursuance of the same purpose of determining the effect of the substitution of an alkyl radicle for the hydrogen atom mentioned, I have recently begun an investigation of the chlorimidoesters, RC(NCl)OR, isomeric with the acid chloralkylamines, RCO(NClR). It was not determined by those who studied the action of alkalies on the acid bromamides, whether the metal salts first formed,[2] before rearrangement occurs, have the constitution RCO(NBrMe') or RC(NBr)OMe': the alkyl derivatives mentioned correspond to these two forms, and it was necessary to examine both. Chlorimidoesters have been till now known only in the carbonic acid series, Sandmeyer[3] having prepared chlorimido-

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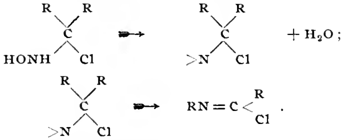
[1] *Note.*—The behavior of the oximes $R_2C{=}NOH$ in suffering rearrangement with anhydrizing reagents and the influence of stereoisomerism on their rearrangement are apparently not in accord with the interpretation of "Beckmann's rearrangement" presented. But the similarity in the behavior of the acid bromamides and the acid azides (and the isonitriles) is so striking that it may be suspected that a very close study of the oximes will reveal a similar cause of rearrangement in their case. It need only be mentioned, that when using phosphorus pentachloride, for instance, the addition of hydrochloric acid to an oxime may lead to a substance $R_2C{<}^{Cl}_{NHOH}$ which can lose water under the influence of the phosphorus pentachloride in the way required, giving by the same series of changes indicated above, acid anilide chlorides, the actual products of the reaction:

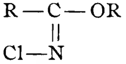


Of course this question and the problem of influence of stereoisomerism must be subjected to crucial experimental investigation.

[2] Hoogewerff and Van Dorp: *loc. cit.*; Hofmann: *loc. cit.*

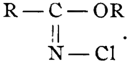
[3] Ber. d. chem. Ges., **19**, 862.

ethyl and methyl carbonate, $ClN{=}C(OR)_2$ by the action of chlorine on a mixture of potassium cyanide, water and alcohol. These esters could throw little light, as yet, on the question of rearrangement, the exchange always being observed to take place between the halogen atom and an alkyl attached to the carbon atom, united to the nitrogen atom. In the case of chlorimidoesters of the type RC(NCl)OR, which I have prepared, such an exchange would be possible. Their study was inviting also, because they were at one time supposed to be intermediate products[1] in the rearrangement of alkylsynhydroximic acids, R.C(NOH)OR, by means of phosphorus pentachloride, and because there can be but little doubt that they will be found to exist in two stereoisomeric forms, the "syn" and "anti" forms:



$$\begin{array}{l}\mathrm{R-C-OR}\\ \qquad \| \\ \mathrm{Cl-N}\end{array}$$

and



$$\begin{array}{l}\mathrm{R-C-OR}\\ \qquad \| \\ \qquad \mathrm{N-Cl}\end{array} .$$

The compounds prepared by me belong perhaps to the "anti" series, but until stereoisomers have been discovered, it would not be advisable to make this distinction in naming them. As yet only the preparation of and the action of heat on chlorimidoethyl benzoate have been studied with any degree of completeness; in a later report the action of alkalies, chloranhydrides, etc., will be described.

Experimental Part.

Chlorimidoethyl Benzoate, $C_6H_6C(NCl)OC_2H_5$, can be readily obtained from the hydrochloride of benzimidoether by the action of hypochlorites. It was found best to effect the reaction in the following way: A mixture of sodium hypochlorite and free hypochlorous acid was made by passing 22 to 25 grams chlorine into a solution of 20 grams sodium hydroxide in 180 grams water, kept in a freezing-mixture. As soon as prepared—on standing decomposition is liable to occur—the hypochlorite solution was brought into a separating-funnel and 5 grams of powdered benzimidoethylether hydrochloride added in several portions, the vessel being vigorously rotated for a

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[1] Werner: Ber. d. chem. Ges., **25**, 33; and **29**, 1146; Lossen: Ann. Chem. (Liebig), **281**, 298.

few minutes. Having extracted the product, an oil, with ligroïn (boiling-point 40°–60°), the extract was filtered and dried with a little solid potassic hydrate for a short time. By avoiding any absorption of moisture, the ligroïn could be nearly all distilled off on the water-bath without any decomposition of the product; the last portions of the solvent were removed in a vacuum-desiccator. A colorless, mobile oil remained, of a peculiar, not disagreeable odor; the oil showed no signs of solidifying, either on long standing or treating with a freezing-mixture or various organic solvents. Prepared in this way, the body is pure chlorimidoethyl benzoate (Analyses I and II of different preparations), and the yield is quantitative (5 grams gave 4.7 grams; the theoretical yield is 4.95 grams), according to the equation:

$$C_6H_5C(NH_2)Cl(OC_2H_5) + NaOCl = C_6H_5C(NCl)OC_2H_5 + H_2O + NaCl.$$

By using a smaller excess of hypochlorites or working with less care, some imidoethyl benzoate is liable to remain with the chlorimide. If the hypochlorite solution contains free chlorine, the ligroïn gives some chlorhydrocarbons, which remain with the chlorimide in a vacuum at ordinary temperature. The new compound was readily analyzed by means of its reaction with hydriodic acid:

$$C_6H_5C(NCl)OC_2H_5 + 2HI = C_6H_5C(NH)OC_2H_5HCl + I_2.$$

Owing to the insolubility of the chlorimide in water, it was found necessary to use an alcoholic solution for analysis: 1 to 2 grams of potassium iodide was dissolved in 2 or 3 cc. water, 20 cc. pure alcohol and about 10 drops of dilute acetic acid added, and this mixture poured on the weighed substance.

I. 0.208 gram substance required 22.31 cc. $\frac{N}{10}$ thiosulphate.

II. 0.210 gram substance required 22.50 cc. $\frac{N}{10}$ thiosulphate.

III. 0.1932 gram substance required 20.71 cc. $\frac{N}{10}$ thiosulphate.

	Calculated for $(C_9H_{10}O)NCl$.	Found. I.	II.	III.
Cl	19.32	19.01	19.00	19.01

Though chlorimidoethyl benzoate, like chlorimidoethyl carbonate, is decomposed on heating at ordinary pressure, it was found to distil unchanged in a vacuum. It boils at 130°–132° (uncorr.) at 16 mm. pressure. Analysis III. and the course of the distillation show that practically no decomposition occurs, only a very slight change being observed at the end of the distillation, due to the action of the cork of the distilling-flask on the chlorimide. By fractional distillation of the mixtures which at first were sometimes obtained in preparing chlorimidoethyl benzoate, the pure substance can be easily isolated. Chlorimidoethyl benzoate is readily soluble in ligroïn, ether, chloroform and alcohol, insoluble in water and aqueous acids and alkalies. It is a comparatively stable substance, as shown by its distilling at 130° under reduced pressure. Partly owing to its insolubility in water, it is very slowly decomposed by aqueous hydrochloric acid, litmus being bleached only in the course of half an hour. After some hours benzoic ether is formed, according to the following reactions:

$$C_6H_6C(NCl)OC_2H_5+2HCl=C_6H_5C(NH_2)Cl(OC_2H_5)+Cl_2,$$

and

$$C_6H_5C(NH_2)Cl(OC_2H_5)+H_2O=NH_4Cl+C_6H_5COOC_2H_5.$$

Aqueous ammonia shows no evolution of nitrogen, while other chlorimides react instantly. Aqueous alkali leaves the oil unchanged at ordinary temperatures, even after days. The influence of solubility is shown by using the same reagents in alcoholic solution: a few drops of aqueous ammonia added evolve nitrogen; hydrochloric acid gives at once a strong evolution of chlorine. That the insolubility in water is not the only cause of the comparative stability of the chlorimide is shown by the behavior of bromimidoethyl benzoate described below.

All attempts to separate or convert ethyl chlorimidobenzoate into two stereoisomers have been as yet unsuccessful. Although the boiling-point is not perfectly constant, rising two degrees, the slight change is most likely due to the action of the stopper on the chlorimide; no fractions of different properties were obtained. Stereoisomers are now being sought for by attempting to prepare solid chlorimidoesters, and by trying other methods of preparation. If, in preparing chlorimidoethyl benzoate, ether is used in place of ligroïn, and the solution is dried with calcium chloride, a small deposit of white needles is always observed, as a layer covering the calcium chloride. The same needles are obtained from the oil left on distilling off the ether; the solid being insoluble in ligroïn, can be separated in this way from the oil. The crystals were in all cases the hydrochloride of imidoethyl benzoate, $C_6H_5C(NH_2)Cl(OC_2H_5)$, decomposing[1] at 130° into ethyl chloride and benzamide (melting-point 128°) and giving no iodine with hydroiodic acid. Their formation is evidently due to the action of a small quantity of hydrochloric acid on the chlorimide (see above), imidoethyl benzoate hydrochloride being stable in the absence of water.

The action of heat on chlorimidoethyl benzoate was studied first to see if it would cause a rearrangement into ethyl phenylimidochlorformate,

$$\left(C_6H_5C(OC_2H_5)NCl \quad \rightarrow \quad ClC(OC_2H_5)NC_6H_5\right)$$

which at the temperature employed would give ethyl chloride and phenyl isocyanate;[2] the metal salts of acid bromamides, which may have an analogous constitution to that of this ether, undergo the rearrangement on heating the aqueous solution.

Four grams of chlorimidoethyl benzoate was very slowly heated in a distilling-flask connected with a condenser, and placed in a small open air-bath. As soon as the decomposition began, the air-bath was quickly removed, but the reaction once started continues very rapidly to the end, the whole mass boiling violently in a few moments. No explosion ever occurred. A strong odor of benzonitrile was perceptible both in the oily distillate and the brown, semi-solid residue; benzonitrile was extracted from both by means of ligroïn. It was fully identified by converting it into benzthiamide:[3]

$$C_6H_5CN + H_2S = C_6H_5CSNH_2.$$

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[1] Pinner: Ber. d. chem. Ges., **16**, 1654, etc.

[2] Lengfeld and Stieglitz: This Journal, **16**, 74.

[3] Cahours: Jahresbericht, *1847–8*, 595.

The benzthiamide obtained had all the properties of some made synthetically. On mixing the two preparations their melting-point (116°) remained constant.

Benzonitrile is the chief product (1.5 grams were obtained) of the action of heat on chlorimidoethyl benzoate. Its formation shows that the chief course of the decomposition must be

$$C_6H_5C(NCl)OC_2H_5 = C_6H_5CN + ClOC_2H_5.$$

The ethyl hypochlorite is decomposed at the temperature of the reaction, yielding hydrochloric acid and other products which were not examined. The wash-water of the distillate mentioned above gave the reactions of hydrochloric acid.

After removing benzonitrile by means of ligroïn from the brown residue left by the distillation, strong alcohol dissolved all but a small quantity of crystals, which may be called *X*. This will be discussed below. On evaporation the alcoholic solution gave white crystals embedded in a brown resin. By treatment with small portions of ether, a solid was obtained, which, after recrystallization from warm chloroform, showed the melting-point (128°) and the other properties of benzamide. On mixing with some benzamide, the melting-point did not change. Benzamide was obtained in second largest quantity; its formation evidently is due to the action of hydrochloric acid (produced by decomposition of ethyl hypochlorite as shown above) on chlorimidoethyl benzoate, the imidoethyl benzoate hydrochloride formed first, decomposing[1] into ethyl chloride and benzamide:

$$C_6H_5C(NCl)OC_2H_5 + 2HCl = C_6H_5C(NH_2)Cl(OC_2H_5) + Cl_2;$$
$$C_6H_5C(NH_2)Cl(OC_2H_5) = C_6H_5CONH_2 + ClC_2H_5.$$

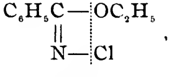
From the ethereal solution of the brown resin, no further homogeneous substance could be obtained. However, by heating the resin in a test-tube, cooling rapidly and adding water, a solution resulted which gave a plain aniline reaction with Jacquemin's reagents, but not with calcium hypochlorite solution, showing that only minute quantities of aniline could have been formed. The crystals called *X*, after repeated recrystallization from hot toluene or benzene, gave a very small quantity of a substance melting at 210°. Recrystallization

[1] Pinner: *loc. cit.*

from chloroform raised the melting-point to 227°–230° (heating rapidly). The body showed the crystal form of carbanilide (melting-point 235°), but a mixture of it with carbanilide melted 30° to 40° lower than carbanilide did. The substance is consequently not carbanilide. It could, however, be shown that it is a derivative of phenyl isocyanate (perhaps benzoylphenylcarbamide), although the amount obtained (50 mg.) was too small to be more closely studied for the present. On subliming the substance carefully in a test-tube, the odor and effect of phenyl isocyanate are unmistakable. If a few drops of water are now added, the presence of aniline is indicated by Jacquemin's reagent (calcium hypochlorite and ammonium sulphide). Carbanilide treated in the same way gave the same results. There can be no doubt, therefore, that a very small quantity of an aniline derivative is obtained by heating chlorimidoethyl benzoate at ordinary pressure. Whether it is obtained primarily from this substance or from one of its decomposition-products, will be further investigated. It is evident, however, that the chief effect of heat on chlorimidoethyl benzoate is to decompose it into ethyl hypochlorite and benzonitrile:

$$C_6H_5C(NCl)OC_2H_5 = C_6H_5CN + ClOC_2H_5,$$

a direct exchange of the phenyl group and the chlorine atom, if it takes place at all in chlorimidoethyl benzoate, occurring only to a very slight extent. It is possible that the oil under investigation is an "anti" compound,



$$\begin{array}{l} C_6H_5C - \vdots OC_2H_5 \\ \quad\ \ \| \qquad \vdots \\ \quad\ N - \vdots Cl \end{array},$$

and it remains to be seen whether a stereoisomer can be obtained, in which this exchange could occur more easily.

Bromimidoethyl Benzoate was prepared in the hope that, having a higher molecular weight, it might prove to be a solid body. It was obtained by the action of sodium hypobromite on the chloride of benzimidoether. To an excess of sodium hypobromite solution prepared from 9.2 grams bromine (8 molecules), 4.6 grams sodium hydroxide (16 molecules), and 40 grams water, 1.3 grams of the chloride of ethylimidobenzoate (1 molecule) was added, and the mixture shaken for a few minutes. An oil was extracted with low-boiling ligroïn, the extract dried with solid potassium hydrate, and then allowed to evaporate at ordinary temperature in a vacuum-desiccator. 1.5 grams (the theoretical yield would be 1.6 grams) of a pale yellow oil remained, which refused to crystallize. Analysis showed the body to be nearly pure bromimidoethyl benzoate.

I. 0.194 gram substance required 16.33 cc. $\frac{1}{10}$-N. thiosulphate.

II. 0.190 gram substance required 15.93 cc. $\frac{1}{10}$-N. thiosulphate.

III. 0.4486 gram substance gave 25.2 cc. nitrogen over 30 per cent. caustic potash, at 754.3 mm. and 15°.8 C.

	Calculated for $C_9H_{10}ONBr$.	Found.	
Br	35.09	33.67	33.54
N	6.14		6.53

Bromimidoethyl benzoate is far less stable than the corresponding chlorine compound. Water decomposes it gradually, reproducing the imidoether as first product. Hydrochloric acid gives bromine at once; concentrated aqueous ammonia is decomposed with evolution of nitrogen, reactions which prove that the greater stability of the chlorimide towards these reagents is not entirely due to its insolubility in them. It is probably owing to this instability, to the fact that the reaction

$$C_6H_5C(NH)OC_2H_5 + HOBr \rightleftarrows C_6H_5C(NBr)OC_2H_5 + H_2O,$$

is reversible to some extent, that the bromimide prepared in the above manner always contains a small quantity of imidoethyl benzoate. On heating, bromimidoethyl benzoate behaves like the chlorimide, giving benzonitrile as the chief decomposition-product. As it proved to be an oil, no further experiments were made with it.

CHICAGO, *August*, 1896.

MENTHENE NITROSOCHLORIDE AND SOME OF ITS DERIVATIVES.[1]

BY W. O. RICHTMANN[2] AND EDWARD KREMERS.

In connection with the study of the nitrosochlorides of menthene several observations have been made with regard to the melting-point of the same, that appear grossly inconsistent. Sieker, who first prepared the nitrosochloride of menthene, stated that it melted at 113° C.[3] Other observations made in this laboratory seem to indicate that the melting-point is somewhat higher. The highest melting-point of the nitrosochloride of menthene yet obtained in this laboratory was observed by Mr. Urban. It was that of a purified compound, melting at 128° C.[4]

In addition to these deviations Baeyer has made the statement that the hydrocarbon, $C_{10}H_{18}$, prepared from a tertiary menthol yields "dasselbe bei 146° C. schmelzende nitrosochlorid wie gewöhnliches menthen."[5]

It would seem either that the observations made in this laboratory were on impure material, or that Baeyer's nitrosochloride of menthene differs somewhat, though only stereometrically, from the nitrosochloride of menthene, prepared from menthene that was obtained by the dehydration of menthol.

Since the observations made in this laboratory were based upon material obtained at different times, sometimes only in very small quantities, also from menthene prepared with the aid of different dehydrating reagents, it seemed very desirable, in order to prevent the multiplication of similar incongruities, to make a thorough study of the physical constants of menthene and its nitrosochloride.

Preparation of Menthene.

A.—Mr. Helbing[6] prepared menthene by dehydrating menthol with anhydrous copper sulphate in the following manner: 500 grams of menthol and 750 grams of anhydrous copper sulphate were heated in a copper flask connected with

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[1] Read at the Montreal meeting of the American Pharmaceutical Association.

[2] Fred. Pabst Fellow in Pharmaceutical Chemistry.

[3] This JOURNAL, **14**, 292.

[4] *Ibid.*, **16**, 395.

[5] Ber. d. chem. Ges., **26**, 2561.

[6] Graduation Thesis: "Nitrosochloride of Menthene and some of its Derivatives." 1894. Not published.

a reflux condenser over a free flame for from eight to ten hours. The resulting mixture was distilled with water-vapor. The oily layer of the distillate, after separation by means of a separatory funnel, was dried with anhydrous copper sulphate and then fractionated six times. The first fractionation was in fractions of 5° each; the second, third, and fourth fractionations of 1° each, and the fifth and sixth fractionations of one-half degree each. In all but the first fractionation, where an ordinary distilling-bulb was used, a "Loebel and Henninger" column was employed.

B.—The menthene employed by W. R.[1] in the second series of experiments was prepared by the dehydration of menthol in the following manner: 100 grams of menthol and 200 grams of coarsely powdered acid potassium sulphate were heated together in a round-bottomed flask, connected with a reflux condenser, for from ten to twelve hours on a paraffin-bath at a temperature of 180–200° C. The mixture thus obtained was treated in the same manner as that obtained by Mr. Helbing, as was also the resulting menthene.

C.—In a third series of experiments, menthene was obtained by means of anhydrous copper sulphate as dehydrating agent, as given under *A* of this paper. This process of dehydration was employed, now that sufficient data of the physical constants of menthene had been obtained because (1) of the larger quantities used with greater ease of manipulation; (2) the more complete dehydration of a menthol at each dehydration, and (3) the greater percentage yield of menthene.

Inasmuch as the principal object in this series of experiments was to obtain a large quantity of Δ^4-terpene-3-one, the fractionation of the menthene was not conducted with any particular care. The fractional crystallization of the nitrosochloride of menthene, however, was of some interest, and the results will therefore be recorded.

The change in the fractions of the menthene obtained by the two previously mentioned processes during the last three fractionations, as indicated by the boiling-point, specific gravity, rotatory power, and yield, are shown in the following table:

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[1] Graduation Thesis. Unpublished results.

Table I.

Fourth fractionation.				
B. P.	Sp. gr.	α.	$[\alpha]_D$.	Per-cent'ge yield.
A.				
Below 165°				
165-6°				
166-7°	0.8130			3.1
167-8°	0.8123	+24°.30	+28°.83	16.5
168-9°	0.8128	+22°.01	+27°.08	17.8
B.				
Below 165°				3.4
165-6°	0.8103	+23°.91	+29°.51	15.4
166-7°	0.8113	+23°.93	+29°.50	15.1
167-8°	0.8136	+23°.48	+28°.86	8.9
168-9°	0.8147	+22°.67	+27°.82	12.8

Fifth fractionation.				
B. P.	Sp. gr.	α.	$[\alpha]_D$.	Per-cent'ge yield.
Below 165°				
165 -165°.5				
165.5-166°				
166 -166°.5				
166.5-167°	0.8140	+22°.60	+27°.76	1.7
167 -167°.5	0.8113	+24°.05	+29°.60	2.3
167.5-168°	0.8118	+24°.01	+29°.57	15.7
168 -168°.5	0.8123	+23°.81	+29°.34	12.7
168.5-169°	0.8130	+22°.67	+27°.89	7.1
Below 165°				
165 -165°.5				
165.5-166°				
166 -166°.5	0.8106	+23°.75	+29°.30	3.2
166.5-167°	0.8106	+23°.88	+29°.46	5.1
167 -167°.5	0.8114	+23°.93	+29°.49	13.3
167.5-168°	0.8117	+23°.80	+29°.34	14.7
168 -168°.5	0.8125	+23°.45	+28°.86	12.2
168.5-169°	0.8140	+22°.96	+28°.81	4.3

Sixth fractionation.				
B. P.	Sp. gr.	α.	$[\alpha]_D$.	Per-cent'ge yield.
Below 165°				
165 -165°.5				
165.5-166°				
166 -166°.5				
166.5-167°				
167 -167°.5				
167.5-168°	0.8118	+24°.48	+30°.17	14.1
168 -168°.5	0.8130	+24°.20	+29°.76	11.0
168.5-169°	0.8148	+23°.41	+28°.73	2.1
Below 165°				
165 -165°.5				
165.5-166°				
166 -166°.5	0.8103			5.2
166.5-167°	0.8103	+23°.98	+29°.60	7.4
167 -167°.5	0.8113	+24°.04	+29°.63	15.1
167.5-168°	0.8117	+24°.08	+29°.66	12.0
168 -168°.5	0.8125	+23°.88	+29°.39	5.7
168.5-169°	0.8135	+23°.90	+28°.76	2.7

In this table, as in all that are to follow, it is to be understood that the specific gravity and rotatory power were taken at a temperature of 20° C., and the latter in a 100-mm. tube, unless otherwise stated. The atmospheric pressure as observed during the last three fractionations by means of a mercury barometer, was as follows :

Table II.

No. of fraction.	A. mm.	B. mm.
4	735	735
2	734	735
6	739	739

Menthene Nitrosochloride.

All of the menthene nitrosochloride was prepared according to the following formula : 45 cc. of menthene, 45 cc. of glacial acetic acid, and 33 cc. of ethyl nitrite were mixed in an Erlenmeyer flask, which was placed in a freezing-mixture. While the flask is constantly being shaken in the freezing-mixture, a solution of 18 cc. of concentrated hydrochloric acid in an equal volume of glacial acetic acid is allowed to enter the flask, drop by drop, from a separatory funnel. After all of the acid in the funnel has entered the flask the entire mixture in the flask is shaken continuously for about fifteen minutes, when it is packed in a freezing-mixture and allowed to remain for an hour.

The crystals which have formed during this time are now filtered off by means of a force filter, and the mother-liquid is again placed in the freezing-mixture for the separation of more crystals. After having remained in the freezing-bath during the night, the second crop of crystals is removed, and the mother-liquid again cooled as before. In the course of a week or two a third and sometimes even a fourth crop of crystals may be obtained.

Each crop of crystals, after having been well drained on a force filter, is washed successively with small quantities of alcohol to remove the last portions of the mother-liquid. The crystals are dried on porous plates. The yield of the various crops, together with the physical constants of each, are given in the following table :

Table III.

No. of crop.	B. P. of menthene.	M. P.	$[\alpha]_D$.	Percentage yield.
A.				
1	166.5–167°			
1	167–167°.5			
1	167.5–168°	113–114°	+20.64°	21.11
1	168–168°.5	107–108°		21.99
1	168.5–169°			
2	166.5–167°			
2	167–167°.5			
2	167.5–168°	106–107°		3.05
2	168–168°.5	109–110°		4.50
2	168.5–169°			
3	all	114–115°		3.05
4	"			
B.				
1	166.5–167°	112–113°	+ 9.65°	27.36
1	167–167°.5	112–113°	+ 9.84°	24.41
1	167.5–168°	112–113°.5	+ 8.26°	22.56
1	168–168°.5			
1	168.5–169°			
2	166.5–167°	107–108°	Inactive	2.67
2	167–167°.5	107–108°	"	4.34
2	167.5–168°	108–109°	"	5.05
2	168–168°.5			
2	168.5–169°			
3	all	115–116°	Inactive	4.31
4	"	116–117°	"	3.27
C.				
1	all	112–113°	+7.234°	21.21
2	"	113–115°	Inactive	4.80
3	"	115.5–117°	"	3.00
4	"			

In order to purify the menthene nitrosochloride thus obtained it was precipitated from its solution in chloroform by means of alcohol. 18 grams of the menthene nitrosochloride were dissolved in 90 grams of chloroform. The solution was filtered and then 30 grams of alcohol were added to the filtrate. The resulting mixture was shaken frequently during ten minutes, and then the precipitated menthene nitrosochloride was filtered off with the aid of a force filter. 30 grams of alcohol were again added to the filtrate and then the process was repeated as before.

After the second crop had been removed, the filtrate was placed under the blast to evaporate for two hours. The crystals which separated were removed as before. From this filtrate still a fourth crop separated upon standing forty-eight hours. Each crop of crystals, after draining for some time on a force filter, was washed with a small quantity of alcohol, and after draining again, were placed upon a porous plate to dry.

In the table below, the yield and physical constants of each crop are given. The specimens *A* were obtained from the first crop of menthene nitrosochloride that had been prepared from menthene boiling at 167.5–168° C.; while the others, *B*, were obtained from the first crop of menthene nitrosochloride that had been prepared from menthene boiling at 167–167°.5 C.

Table IV.

Crop.	M. P.	$[\alpha]_D$.	Percentage yield.
A.			
1	113 –114°	+ 1.015°	33.47
2	108.5–109°	+16.715°	26.39
3	110 –111°	+31.234°	16.61
4	113.5–115°		2.77
B.			
1	121 –122°	— 2.4508°	32.44
2	118 –119°	+ 3.7556°	19.52
3	117 –118°	+16.4434°	24.02
4	117 –118°		1.17

It becomes evident from these figures that the menthene nitrosochloride, when prepared by the process previously given (page 765) is a mixture. Possibly the menthene from which it is prepared is itself a mixture.

It is remarkable that the first fraction (*B*), which is slightly lævogyrate has a higher melting-point than any of the other fractions, also that the second and third fractions, although differing widely in rotatory power, differ but slightly in their melting-points.

As the quantity of lævogyrate nitrosochloride of menthene obtained in series *B* was very small, the same experiments were continued in series *C*, as follows: The second crop, Table III., being entirely inactive, it was thought that perhaps it might be a mixture of some quite strongly dextrogyrate and much more or less strongly lævogyrate nitrosochloride of menthene. The process for fractional crystallization, as given on page 767, was employed with the following results :

Table V.

Fraction.	M. P.	$[\alpha]_D$.	Percentage yield.
C.			
1	115.5–116°	Inactive	18.21
2	114 –114°.5	"	22.24
3	114 –114°.5	"	12.96
4	112.5–113°	"	8.48
5	118 –119°	"	4.65

As all of the fractions thus obtained are inactive, either the nitrosochloride is composed of inactive molecules or, if it is a mixture of dextro- and lævogyrate nitrosochlorides, as was supposed, then the process for fractional crystallization, as given above, does not serve to isolate the two forms.

The same experiment was now tried on an optically active nitrosochloride of menthene; *viz.*, crop 1, Table III.

Table VI.

Fraction.	M. P.	$[\alpha]_D$.	Percentage yield.
1	121.5–122°.5	—0.9784°	18.60
2	121 –122°	+0.9304°	10.25
3	119.5–120°	+1.7506°	11.80
4	116 –117°.5	+0.5763°	29.80

In Tables V. and VI. it is to be noticed that there is a gradual falling off of the melting-points from the first to the fourth fractions ; and in Table V. a very sudden rise in the melting-point occurs in the fifth fraction. A fifth fraction was not obtained in Table VI, and consequently no observation for a like phenomenon could be made.

The first fraction of Table VI. was slightly lævogyrate, which was the variety much sought after, but it was too small in amount to work with. Only about 65 per cent. of the substance used recrystallized during this process. The experiments could not be repeated, as the remainder of crop

1, Table III., had already been employed in the preparation of nitrosomenthene.

These experiments indicate the presence of two, and possibly three, nitrosochlorides of menthene when prepared by the process given on page 765. The two known forms are the dextrogyrate and lævogyrate nitrosochlorides, while the third may be composed of inactive molecules, or the mixture of the dextro- and lævogyrate forms previously spoken of, but for the separation and isolation of which no satisfactory method has yet been found.

Menthene Nitrolbenzylamine.

A. The three purified fractions of menthene nitrosochloride, Table III., were converted into benzylamine base. 5 grams of each of the fractions, with 5.25 grams of benzylamine and 30 cc. of alcohol were heated in a round-bottomed flask connected with a reflux condenser, on a water-bath until solution was effected. The solutions were filtered and then set aside to crystallize. The crystals were separated from the mother-liquid and then recrystallized from alcohol. The melting-points of the purified products thus obtained were found to be 106°.5, 105°.5, and 105°.5, respectively. In an approximately 5-per cent. solution each was found to be optically inactive.

It is of interest to note that the menthene nitrosochlorides, differing by at least 30°, should all yield an optically inactive benzylamine base. It would be less surprising if the loss of optical activity had occurred in the dehydration of menthol to menthene or in the preparation of the nitrosochloride from the latter.

Nitrosomenthene.

Nitrosomenthene was prepared by heating 50 grams of menthene nitrosochloride with 250 cc. of a 10-per cent. alcoholic potash solution, in a round-bottomed flask, connected with a reflux condenser, on a water-bath, for from one to one and one-half hours. The resulting mixture was filtered, and the residue washed with alcohol to remove all the soluble portion. Water was now added to the filtrate to precipitate the nitrosomenthene. The mixture was allowed to stand for twelve hours. The yellow flocculent precipitate, which had risen to the surface, was collected, washed with a small quantity of dilute alcohol, and drained with the aid of a force filter.

The nitrosomenthene thus obtained was very impure and was purified—*A*, by two recrystallizations from hot alcoholic solution; and *B*, by distillation with water-vapor—and collected in fractions.

No determination of the physical constants of the purified nitrosomenthene *A* were made. Those of the four fractions of *B* are given in

Table VII.

Fraction.	M. P.	$[\alpha]_D$.	Yield.
1	62 –64°	—9.123°	About 25 per cent.
2	63.5–64°.5	—3.655°	" 25 " "
3	64 –65°	—4.683°	" 25 " "
4	64.5–65°	—4.7915°	" 25 " "

The first and second fractions were impure, as shown by their color, which was somewhat yellowish, while the third and fourth fractions were pure white; also by their somewhat lower melting-points, and varying specific rotatory power.

It was of interest to know whether the differences in the physical constants of menthene nitrosochloride would cause similar differences in those of the nitrosomenthene. In order to make these observations, nitrosomenthene was prepared from the purified menthene nitrosochloride (see Table IV.). The resulting observations are given in the following tables: Table VIII. giving the physical constants of the nitrosomenthene before, and Table IX. after recrystallization from alcohol:

Table VIII.

Fraction.	M. P.	$[\alpha]_D$	Yield.
1	67 –68°	—1.253°	86.5 per cent.
2	67 –68°	—3.186°	85.9 " "
3	66.5–67°.5	—6.717°	85.2 " "

Table IX.

Fraction.	M. P.	$[\alpha]_D$.	Yield.
1	67 –67°.5	—6.414°	47.8 per cent.
2	67 –67°5	—10.225°	49.2 " "
3	66.5–67	—10.148°.	48.7 " "

A comparison of Tables IX. and IV. shows that the difference in melting-points is practically lost, but that the sign of rotation of the menthene nitrosochlorides is reversed in splitting off the hydrochloric acid, and that the greater the positive rotation of the nitrosochloride the greater the negative rotation of the nitrosomenthene. An inactive nitrosomenthene was obtained from inactive menthene nitrosochloride, Table V. The melting-point was the same as that of the specially optically active variety; *viz.*, 65–67°. The same process as given under (*B*) was employed.

Menthylamine Nitrate.

The menthylamine was prepared by the reduction of nitrosomenthene with acetic acid and zinc dust. The nitrate of the base was separated by means of sodium nitrate, but for some reason only a very small quantity was obtained (about 10 grams from 100 grams of nitrosomenthene). This was too small a quantity to proceed with for experimentation on the alcohol $C_{10}H_{18}O$, which compound we had expected to obtain from the menthylamine nitrate.

Ketone, $C_{10}H_{16}O$.

15 grams of purified nitrosomenthene were dissolved in 30 cc. of concentrated hydrochloric acid, to which was added 30 cc. of water. The mixture was heated in a round-bottomed flask, connected with a reflux condenser, on a water-bath, for fifteen minutes, until the oily layer ceased to separate. The mixture was distilled with water-vapor. The purified oil was separated from the water and then dried with anhydrous sodium sulphate. The oil was of a light straw color, but became darker very rapidly on standing, and had a decided odor of mint. The physical constants of the oil are given in the following table :

Table X.

B. P.	Percentage yield.	Sp. gr.	α.	[α]$_D$.
Below 205°	6.3			
205–206°	10.0	0.9148		
206–207°	37.1	0.9157	—1.2063°	—1.3173°
207–208°	40.2	0.9163	—1.2083°	—1.3189°
208–210°	1.2			
210–212°	1.6			
212–215°	1.2			
215–218°	0.8			
218 +	1.4			

The inactive nitrosomenthene obtained from the inactive menthene nitrosochloride was also converted into the ketone. The physical constants of the main fraction, together with those of the corresponding fraction of the ketone from the general source are given in

Table XI.

Source.	B. P.	Sp. gr.	α.	[α]$_D$.
Mixed NOCl's	207–208°	0.9163	—1.2063°	—0.3173°
Inactive NOCl's	207–208°	0.9159	+0.3938°	+0.4299°

A slight difference in the specific rotatory power will be noticed. The one being dextro- and the other lævogyrate.

Upon comparison, it will be seen that the boiling-point of this ketone, $C_{10}H_{16}O$, as given above, is somewhat lower than that observed by Kremers and Urban. They found the boiling-point to be 210–212°, but worked with much smaller quantities.

The boiling-point of this ketone, $C_{10}H_{16}O$, is but a few degrees higher than that of menthone, (204–205° C.), the corresponding ketone richer by two hydrogen atoms.

Ketone Hydrosulphide.

Crystals of the hydrosulphide were very easily obtained by passing hydrogen sulphide into a solution of the ketone (1 volume) in alcohol (4 volumes) and subsequently adding strong ammonia water. On standing for twelve hours very fine needles appeared. These were separated by means of a force filter, washed with alcohol, and then dried on porous plates. The melting-point of the crystals was 212–215°. They were soluble in chloroform and hot methyl alcohol, slightly soluble in ether, benzene, petroleum ether, and hot ethyl alcohol. The mother-liquid which possessed a decided *buchu* odor, was set aside for further crystallization. Two more crops of crystals were obtained. The melting-point of each was lower than that of the preceding one.

The several crops were mixed and dissolved in chloroform and allowed to crystallize. When dried they melted at 206–208°. A sulphur determination gave the following results :

0.2786 gram substance yielded 0.5802 gram $BaSO_4 =$ 0.0796 gram $S = 28.57$ per cent.

Calculated for		Found.
$C_{10}H_{16}O.H_2S$	17.205 per cent.	28.57 per cent.
$C_{10}H_{16}O.2H_2S$	29.090 " "	

The result, although somewhat low, is decidedly in favor of the addition of 2 molecules of hydrogen sulphide.

Nitroso Derivative of Ketone.

Baeyer's formula for the preparation of nitrosopulegone was employed, but did not give a very large yield. Two cc. of the oil were dissolved in an equal volume of petroleum ether (boiling-point 65° C.) and then 1 cc. of ethyl nitrite added. The mixture contained in a test-tube is immersed in a freezing-mixture and stirred with a glass rod, which had been dipped in concentrated hydrochloric acid. After stirring for fifteen minutes the mixture was allowed to remain in the freezing-mixture for another fifteen minutes, when the white amorphous precipitate which had formed was removed with the aid of a force filter. After drying it melted at 115–115°.5 with slight decomposition, as shown by the compound turning brown. The yield was so small that no other work could be done with the compound.

Ketone and Phenylhydrazine Hydrochloride.

The hydrazone of the ketone was very easily prepared by dissolving 5 cc. of the oil in 12.5 cc. of alcohol and then 6.05 grams of phenylhydrazine hydrochloride and an excess of sodium bicarbonate added. On standing over night without heating, or heating with a reflux condenser on a water-bath for fifteen minutes and then cooling, the entire mass crystallized.

To purify the crystals they were dissolved in warm alcohol and allowed to recrystallize. Decomposition occurred so rapidly that only a very small quantity was obtained. This melted at 73.5–74°, with slight decomposition and evolution of a colorless gas. On cooling, the substance in the tube was of a bright green color. When remelted no further change was noticed. It melted at 72.5-73° and became green upon cooling. Fischer's precaution that in determining the melting-points of hydrazones they should be heated rapidly in order to avoid error, was carefully observed.

To obtain larger quantities for combustion a modification of the above method of preparation was adopted. The hot alcoholic solution, after being filtered, was gradually diluted with water until a slight turbidity resulted. After standing fifteen minutes a large quantity of fine silky crystals had separated. These were removed with the aid of a force filter, washed with dilute alcohol, drained and dried (melting-point 73.5–74° C.) The crystals decomposed within twenty-four hours with the evolution of gas. A spongy, dark-green, resinous mass remained.

The pure crystals gave the following results for nitrogen with the Will and Varentrapp method :

A. 0.2348 gram yielded 0.02387 gram N = 10.15 per cent.

B. 0.2330 gram yielded 0.02352 gram N = 10.095 per cent.

	Calculated for $C_6H_5NHN : C_{10}H_{16}$.	Found.	
		I.	II.
N	11.57	10.15	10.095

Although somewhat too low, the above figures indicate that the formula $C_{10}H_{16} : NNHC_6H_5$ is correct and that a hydrazone is formed.

An attempt was also made to determine the nitrogen by means of the Kjeldahl method, but no satisfactory results were obtained. E. Lawes[1] finds that, contrary to previous reports, nitrogen in glucozone, phenylhydrazine, and antipyrine cannot be determined by the Kjeldahl method.

Ketone and Substituted Phenylhydrazine.

By using substituted phenylhydrazines it was hoped to obtain a more stable compound with the ketone, and the follow-

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[1] Chem. Centralb., 1892, 2, 628.

ing were tried: (*a*) acetylphenylhydrazine hydrochloride; (*b*) orthotoluylphenylhydrazine hydrochloride; and (*c*) paratoluylphenylhydrazine hydrochloride.

Both processes given under Δ^4-terpenehydrazone were tried with each substance; no positive results, however, were obtained.

Ketone and Nitrosochloride Reaction.

An attempt was made to prepare a nitrosochloride of the ketone (it having a double bond, Δ^4, in the ring). The formula used in preparing menthene nitrosochloride was employed. Several trials yield only negative results. During the experiments nitrous acid fumes were given off.

Reduction of Ketone.

In order to reduce the ketone, Beckmann's process was employed. 15 cc. of the oil (boiling-point 207–208°) were dissolved in 50 cc. of anhydrous ether. Metallic sodium in excess is gradually added and the mixture heated in a flask with a reflux condenser, on a water-bath, for four hours. The liquid portion, upon cooling, was decanted, and the residue washed with several successive portions of ether. Both portions of ether were placed in a separatory funnel and an equal volume of water added; the mixture was shaken occasionally and placed in a cool place for half an hour. The ethereal layer was then separated and allowed to evaporate spontaneously. Small, white crystals formed. These were separated from the reddish-brown oil, which had a decided odor of mint.

The oil was again heated in the same manner as above, excepting that instead of allowing the ethereal solution to evaporate it was distilled with water-vapor. The first portion which came over was entirely ether. The oil which distilled over was collected, dried, and exposed to a freezing-mixture. Nothing separated. The oil was light-yellow in color and of a minty odor.

A very heavy, reddish-brown, gummy residue remained in the distilling flask. It readily dissolved in hot alcohol, and from the solution crystals began to separate after standing several months.

None of the above compounds were obtained in sufficient quantities to work with. The experiment was repeated on a larger scale (using 150 cc. of the ketone and corresponding quantities of the other substances), and petroleum ether (boiling-point 65–70° C.) was used as the solvent. The same results were obtained as when anhydrous ether was used, except that crystals separated from the hot methyl-alcohol solution of the gummy residue very easily.

Oily Portion.

The oil which had a specific gravity of 0.9019 and $[\alpha]_D$ —0.8144° was fractionated (see Table XII). Most of it distilled over between 207–208° C., which fraction was colorless and of a mint-like odor. It is to be observed that this compound differs very slightly in its physical constants from the original ketone.

Molecular Coëfficient of Refraction.

This physical constant was determined by means of Pulfrich's total reflectometer, and calculated from the following formula for the coëfficient of refraction (according to Lorentz),

$$\left(R = \frac{n^2 - 1}{(n^2 + 2)\,d}\right)$$

in which

n = index of fluid examined (obtained from tables for refractometer) from angles read.

d = density of fluid examined.

R = coëfficient of fluid.

M = molecular weight of fluid examined.

MR = molecular coëfficient of fluid examined.

Observed : $n = 1.466921$ (20° C).

$d = 0.9103$.

Then $R = 0.304769824$.

M, in the case of the supposed alcohol = 154.

M, in the case of the original ketone = 152.

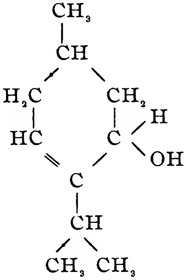
Then $MR = 46.93$ for the alcohol and 46.36 for the ketone.

The factors used in determining the molecular refraction according to Conrady are :

1. C (in C—C)= 2.501 ;
2. C (in C=C)= 1.707 additional ;
3. O (in O—H)= 1.521 ;
4. O (in C=O)= 2.287 ;
5. H= 1.051.

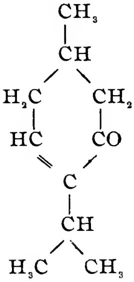
From these factors the calculated molecular refraction would be :

Alcohol.



C_{10}	(1)	25.01
	(2)	1.707
H_{18}	(3)	18.908
O	(4)	1.521
		47.146

Ketone.



C_{10}	(1)	25.01
	(2)	1.707
H_{16}	(3)	16.816
O	(4)	2.287
		45.820

	Alcohol.	Ketone.
Calculated	47.146	45.820
Found	46.935	46.325

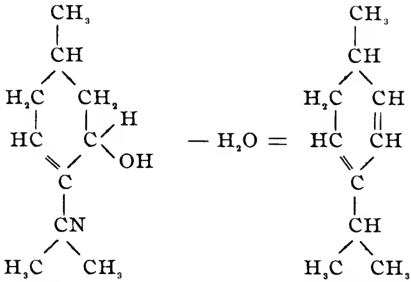
The figures seem to be in favor of the alcohol formula, but they do not vary greatly from the calculated results for the ketone. Chemical reactions seem to indicate that the supposed alcohol consists mainly of unchanged ketone.

Dehydration of Alcohol, $C_{10}H_{18}O$.

The supposed alcohol was treated the same as under *B* in the dehydration of menthol. The resulting oil, when fractionated, distilled over for the most part between 204°–206°, which fraction had a specific gravity of 0.9100 and $[\alpha]_D$—1.3919°. All of the fractions were colorless and possessed a mint-like odor.

Nitrochloride Reaction.

The above compound, which was supposed to be the hydrocarbon $C_{10}H_{16}$ ($\Delta^{2.4}$-Terpadiene), formed according to the following equation:



Alcohol.
Δ^{4}-Terpene-3-ol.

Hydrocarbon.
$\Delta^{2.4}$-Terpadiene.

was treated with ethyl nitrite, concentrated hydrochloric acid, and glacial acetic acid, but no crystals were obtained upon several repeated trials.

Combustion of the oil gave the following results:

A. 0.2147 gram substance yielded
   0.5918 gram CO_2 = 0.1614 gram C = 75.13 per cent. C.
   0.2075 gram H_2O = 0.02305 gram H = 10.74 per cent. H.

B. 0.1991 gram substance yielded
   0.5210 gram CO_2 = 0.1421 gram C = 71.39 per cent. C.
   0.1925 gram H_2O = 0.0214 gram H = 10.75 per cent. H.

C. 0.1909 gram substance yielded
   0.5228 gram CO_2 = 0.1426 gram C = 74.70 per cent. C.
   0.1848 gram H_2O = 0.0205 gram H = 10.77 per cent. H.

	Calculated for $C_{10}H_{16}$.	Found. I.	II.	III.
C	88.24	75.13	71.39	74.70
H	11.76	10.74	10.75	10.77

That the oil cannot be a hydrocarbon is certain from the the above figures, since they admit of nearly 15 per cent. of oxygen.

Further proof was found in the fact that both an oxime (melting-point 67–68° C.) and a hydrosulphide (melting-point 212-214°) were obtained.

Crystals Obtained during Process of Reduction of Ketone.

The several lots of crystals which separated showed varying melting-points. All were, therefore, recrystallized from hot methyl alcohol, when they showed a melting-point of 160–162° C. Upon analysis the following results were obtained :

A. 0.2445 gram substance yielded
0.6451 gram CO_2 = 0.1759 gram C = 71.96 per cent. C.
0.2384 gram H_2O = 0.0265 gram H = 10.82 per cent. H.

B. 0.2024 gram substance yielded
0.5297 gram CO_2 = 0.14445 gram C = 71.86 per cent. C.
0.1993 gram H_2O = 0.02215 gram H = 10.94 per cent. H.

A test for sodium was made, but no appreciable amount was found. 0.2213 gram, after ignition, left no perceptible residue. Wallach, in the reduction of carvone to dihydrocarveol obtained a pinacone. These results agree neither with the formula for the alcohol, $C_{10}H_{17}OH$, nor for the corresponding pinacone. Molecular-weight determinations of this substance will next be made. The investigation along other lines will also be continued.

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ON TETRAMETAPHOSPHIMIC ACID.

BY H. N. STOKES.

Trimetaphosphimic acid and its decomposition-products have been described in the preceding article on the phosphorus nitrogen compounds.[1] In the present paper some account is given of the next higher member of the series, *tetrametaphosphimic acid*, $P_4N_4O_8H_8$, which results from the decomposition by water of tetraphosphonitrilic chloride, $P_4N_4Cl_8$.[2] The molecular weight of the chloride having been established with certainty, that of the acid follows directly. Although the free acid crystallizes with 2 molecules of water, the silver salts and the acid potassium and ammonium salts are anhydrous and conform to the above formula.

Notwithstanding the proximity of these two acids in the series, and the general similarity of the chloronitrides from which they are derived, they differ exceedingly, trimetaphosphimic acid being extremely soluble, uncrystallizable, undergoing rapid spontaneous decomposition, and yielding but two series of salts; while tetrametaphosphimic acid is very difficultly soluble, highly crystalline, permanent when dry, offers marked resistance to the action of acids and forms three series of salts, $P_4N_4O_8H_6M'_2$, $P_4N_4O_8H_4M'_4$ and $P_4N_4O_8M'_8$. Those metals which form insoluble salts are precipitated from solutions of their chlorides or nitrates even by the free acid, but a very slight excess of either being required to make the precipitation complete. As is the case with trimetaphosphimic acid, the eight-atom silver salt exists in a white and a yellow modification, the former, however, being very unstable; these may be regarded as corresponding to the tautomeric forms $(PN(OH)_2)_4$ and $(PO.NH.OH)_4$. Under the action of stronger acids it is ultimately converted into orthophosphoric acid and ammonia, but its great stability, and the instability of the intermediate products, have rendered the isolation of the latter impossible.

Experimental data for a discussion of the constitution of the acid are therefore almost wholly wanting. Presumably the phosphorus atoms in the nucleus P_4N_4 are united by nitrogen atoms, but whether they constitute a ring of eight

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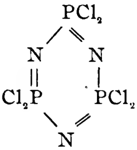
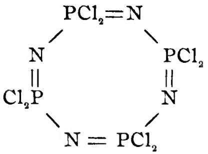
[1] This JOURNAL, **18**, 629.

[2] *Ibid.*, **17**, 275; Ber. d. chem. Ges., **28**, 437.

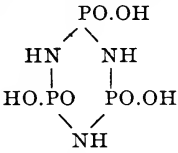
atoms cannot be decided definitely in the absence of intermediate decomposition-products. It is quite likely that the reason of the greater stability of the acid may be found in steric considerations, and in this connection it is interesting to observe that while $P_4N_4O_8H_8$ is much more stable than $P_3N_3O_6H_6$, the reverse is true of the chloronitrides, for while $P_4N_4Cl_8$ also resists the action of boiling water and can be distilled with steam, it is perceptibly easier to saponify than $P_3N_3Cl_6$. If we assume the formulas



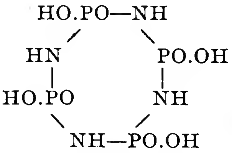
and



for the chloronitrides, and



and



for the acids, it is obvious that the nitrile configuration is more stable in a ring of six than in one of eight atoms, while for the group—NH—PO(OH)—NH—the reverse is true. The same appears in the different action of aqueous ammonia on the chloronitrides, two atoms of chlorine in $P_3N_3Cl_6$, and two only, being readily replaced by NH_2, forming a stable chloramide, while $P_4N_4Cl_8$ under the same conditions gives no chloramide, but the ammonium salt of tetrametaphosphimic acid.[1]

Experimental Part.

Preparation by Tetrametaphosphimic Acid.—Tetraphosphonitrilic chloride can be saponified by alcoholic alkalies, but the yield of tetrametaphosphimic acid is poor, owing to the formation of ethers, which, however, can be decomposed by

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[1] This JOURNAL, 17, 286, 290.

prolonged treatment. Satisfactory results are obtained by using an ethereal solution, which is agitated, in the manner described under tetrametaphosphimic acid, with either water, ammonia or a solution of ammonium acetate.

Decomposition by Water.—As tetrametaphosphimic acid is not perceptibly attacked by cold hydrochloric acid, water may be used when it is desired to obtain the free acid directly. One part $P_4N_4Cl_8$ is dissolved in 15 volumes alcohol-free ether and gently agitated with 5 volumes water. Within half an hour needles of the free acid begin to separate from the aqueous portion, and after many hours the latter has become converted into a thick pasty mass of needles suspended in dilute hydrochloric acid. Chlorhydrines are formed as intermediate products, and these remain dissolved in the ether. It is not necessary to continue the agitation until they are completely decomposed; as soon as a few drops of the ether leave a residue wholly soluble in water, the ether is decanted and the aqueous portion filtered, the crystals being washed with 10-per cent. hydrochloric acid or alcohol. The ethereal portion, containing the chlorhydrines, is evaporated cautiously. The chlorhydrines which remain as an oil from which crystals separate after complete removal of the ether, are dissolved in a little cold water and warmed, with addition of dilute hydrochloric acid, in which tetrametaphosphimic acid is much less soluble than in pure water. The separation of the acid is nearly complete after a few minutes. This portion is better crystallized than that obtained directly, but is otherwise the same. The acid may be recrystallized from hot water, but this is quite unnecessary. Yield, about theoretical.

Decomposition by Ammonia.—The ethereal solution of the chloronitride is shaken for a short time with aqueous ammonia. This does not give chloramide as is the case with $P_3N_3Cl_6$, but produces at once neutral ammonium tetrametaphosphimate, $P_4N_4O_8H_4(NH_4)_4+4H_2O$, which is precipitated by adding alcohol and washed with dilute alcohol. The decomposition is complete in a few minutes.

Decomposition by Ammonium Acetate.—One part chloronitride, dissolved in 15 volumes ether, is agitated with a solution of 4 parts ammonium acetate in 8 parts water. After several hours crystals begin to separate. The final product is a mixture of acid ammonium salt with some neutral salt and some free acid, and is nearly insoluble in the strong salt solution. It is washed with alcohol, dissolved in dilute ammonia and reprecipitated by alcohol. Yield, theoretical. Ammonium acetate is to be preferred to sodium acetate, as the sodium salt does not precipitate well with alcohol.

Chlorhydrines.—None of these were isolated. The oil left on distilling off the ether solidifies to plates as soon as the ether is completely removed. The crystalline substance is much more soluble in ether than the chloronitride, even momentary exposure to ether-vapor causing it to liquefy. It dissolves in cold water to a clear solution from which, in a few minutes, or sooner on warming, tetrametaphosphimic acid is deposited. On one occasion the flask containing the chlorhydrines was placed in hot water and a current of dry air passed through. Some hydrochloric acid was given off, and on treatment with water incomplete solution occurred, a portion being converted into a sandy powder, which, under the microscope, was seen to consist of short spindle-shaped crystals. This acid was insoluble in boiling water, and warm ammonia converted it without dissolving into an acicular ammonium salt, difficultly soluble in water and insoluble in an excess of ammonia; nitric acid dissolved this salt, which was reprecipitated by ammonia in a bulky amorphous form like precipitated alumina, which quickly changed to needles. This ammonium salt was very slowly attacked by hot concentrated sulphuric acid and contained 27.96 per cent. phosphorus and 13.28 per cent. nitrogen ($P : N = 4 : 4.2$). Lack of material prevented further study of this finely crystallized acid, of the nature of which I can form no conjecture.

Tetrametaphosphimic Acid, $P_4N_4O_8H_8 + 2H_2O$.—The free acid may be prepared by the first method above described. It is not readily obtained pure by decomposing most of its soluble salts, as even in the presence of a large excess of acid more or less acid salt is deposited. Thus on dissolving neutral ammonium salt and adding a large excess of hot 5-per cent. nitric acid, nearly pure acid salt was obtained. It may also be prepared by boiling the silver salt with much water, containing about the requisite amount of hydrochloric acid for its decomposition, and precipitating by further addition of the same acid to the filtrate.

The analytical methods are the same as those employed for trimetaphosphimates, but much longer heating with strong sulphuric acid is necessary, because of its greater stability.

Analyses of four air-dried preparations gave :

	Calculated for $P_4N_4O_8H_8 + 2H_2O$.	Found. (1)	(2)	(3)	(4)
P	35.23	35.01	35.27	35.38	35.20
N	15.94	15.93	....	15.99	15.92
H	3.41	....	....	3.55	3.59

(1) P : N = 4 : 4.02.

(3) P : N : H = 4 : 4.06 : 12.43. From chlorhydrine.

(4) P : N : H = 4 : 4 : 12.64. First method, from aqueous portion.

The crystal water is not given off *in vacuo* over sulphuric acid. At 100° it loses weight rapidly, then slowly, but the total loss never reaches the theoretical, a portion of the water being taken up in producing intramolecular changes.

Loss calculated for $2H_2O$	10.22
(1) Loss after 24 hours (weight constant)	9.37
(2) Loss after 78 hours (weight constant)	8.91

If rapidly heated to 130–40° the loss is still less, and is soon replaced by a gain ; after thirty hours at this temperature a net *increase* of 11.15 per cent., corresponding to somewhat more than 2 molecules H_2O was observed, which must have come from the atmosphere. The product consisted of unchanged acid, with ammonium phosphate and apparently pyrophosphate.

Tetrametaphosphimic acid forms colorless needles, either single or in radiating groups, and visible without a lens ; they appear to consist of flat rectangularly terminated prisms. 100 parts water at 20° dissolve 0.64 part crystallized acid ; in boiling water it is somewhat more soluble, but is insoluble in alcohol. From its saturated aqueous solution it is partially precipitated by adding one of the stronger acids, and more rapidly if heated ; 100 parts by weight of 10-per cent. nitric acid at 20° dissolve only 0.26 part of the crystallized acid, but on decomposing its salts in the cold by an excess of acid, it frequently dissolves completely and separates out later. Its saturated aqueous solution does not coagulate albumen. Boiling alkaline solutions cause no evolution of ammonia. Its stability towards acids is illustrated by the following: 0.1 gram, dissolved in 200 cc. water with 8 cc. strong nitric and some hydrochloric acid, was evaporated to dryness on the water-bath, whereby a large part was recovered unchanged; ten minutes heating would have sufficed for the total decomposition of the same quantity of trimetaphosphimic acid. Nitrous acid has no perceptible action.

Di-Potassium Tetrametaphosphimate, $P_4N_4O_8H_6K_2$.—The free acid dissolves easily in cold dilute caustic potash; on strongly acidifying with acetic acid the solution remains clear, but on warming the above salt is deposited as a heavy sandy powder, consisting of microscopic thick rectangular (quadratic?) prisms with basal planes. It is very difficultly soluble even in boiling water.

The air-dried substance lost nothing at 100° and gave:

	Calculated for $P_4N_4O_8H_6K_2$.	Found.
P	31.61	31.26
K	19.93	20.05

P : K = 4 : 2.03.

The tetra-potassium salt formed large flat obliquely terminated plates, very soluble, and was not isolated.

Tetra-Sodium Tetrametaphosphimate, $P_4N_4O_8H_4Na_4 + 2\frac{1}{2}$ (?) H_2O.—The acid is suspended in a little water, and an excess of dilute caustic soda added, whereby complete solution occurs. The separation of the neutral salt soon begins in the form of obliquely terminated flat prisms, sometimes single, sometimes in twins or quadruplets; the filtrate deposits more on heating, but in imperfect forms, broader at one end than at the other. Sometimes nothing separates from the alkaline solution until it is heated. On the contrary, strong caustic soda converts the solid acid in the salt without dissolving it. The salt is rather difficultly soluble in cold, quite easily in hot water, but much less soluble in the presence of an excess of alkali, and the latter throws it down from its saturated aqueous solution. Sodium carbonate gives the same salt.

The substance, pressed out without washing and dried *in vacuo*, lost nothing at 100° and gave :

	Calculated for $P_4N_4O_8H_4Na_4 + 2\frac{1}{2}H_2O$.	Found. (1)	(2)
P	27.62	27.61	27.71
Na	20.50	21.23	20.80

(1) P : Na = 4 : 4.14 ; (2) P : Na = 4 : 4.05.

Alcohol precipitates this salt in a slimy form, which filters with difficulty.

A solution of the tetra-sodium salt, strongly acidified with acetic acid gave a deposit of granules, probably the acid salt. A salt with more than 4 atoms of sodium[1] was not observed.

Tetra-Ammonium Tetrametaphosphimate, $P_4N_4O_8H_4(NH_4)_4 + 4H_2O$.—Strong ammonia converts tetrametaphosphimic acid into this salt without dissolving it ; from its solution in weaker ammonia it is precipitated by alcohol. It usually forms well developed flat monoclinic prisms with pinakoid and basal planes, the base being occasionally replaced by a set of many small planes. It is easily soluble in water, but difficultly in strong ammonia. Its solution undergoes partial decomposition into acid salt on evaporating. It loses nothing *in vacuo*, and analysis gave :

	Calculated for $P_4N_4O_8H_4(NH_4)_4 + 4H_2O$.	(1)	Found. (2)	(3)
P	27.19	27.12	....	27.25
N	24.61	24.74	....	24.66
H	6.15	....	5.94	....

(1). P : N = 4 : 8.12 ; (3). P : N = 4 : 8.00.

Di-Ammonium Tetrametaphosphimate, $P_4N_4O_8H_6(NH_4)_2$.—This salt forms whenever a solution of the neutral salt is strongly acidified, and was at first mistaken for the free acid, which it somewhat resembles. It forms four- and six-sided prisms with base (tetragonal ?), closely resembling the acid potassium salt and, like this, is very difficultly soluble even in boiling water. It separates on heating a solution of the neutral salt with acetic acid in excess (Analyses 1 and 2); or with a stronger acid, in which case it may be slightly contaminated with free acid. The preparation under Analysis 3

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[1] Compare the behavior of trimetaphosphimic acid toward excess of alkali.—This JOURNAL, **18**, 642.

was crystallized from a large excess of hot 5-per cent. nitric acid. It contains no crystal water. Analysis gave:

	Calculated for $P_4N_4O_8H_6(NH_4)_2$.	Found. (1)	(2)	(3)
P	35.42	34.41	35.10	35.20
N	24.04	24.32	24.33	23.17

$$P : N \begin{cases} (1) = 4 : 6.26 \\ (2) = 4 : 6.15 \\ (3) = 4 : 5.82 \end{cases}$$

Barium Tetrametaphosphimate, $P_4N_4O_8H_4Ba_2 + 2H_2O$.—A solution of the di- or tetra-ammonium salt in 500 parts cold or, better, boiling water is precipitated by an excess of barium chloride. The salt forms a voluminous precipitate consisting of microscopic needles, branched or forked, insoluble in water, and undecomposed by acetic acid. These have approximately the composition of neutral salt, with a slight deficiency of barium.

The air-dried salt lost nothing at 100° and gave:

	Calculated for $P_4N_4O_8H_4Ba_2 + 2H_2O$.	Found. (1)	(2)
P	20.28	20.17	20.18
Ba	44.83	42.91	42.39

(1). P : Ba = 4 : 1.93, from acid ammonium salt.

(2). P : Ba = 4 : 1.90, from neutral ammonium salt.

Basic barium salts of indefinite properties seem to exist, but no indication of an acid salt could be obtained.

No satisfactory results were obtained with *magnesium* salts, a large variety of crystalline and amorphous precipitates being obtained under different conditions.

Manganese salts give with free tetrametaphosphimic acid a flocculent precipitate of neutral manganese tetrametaphosphimate; on adding a mineral acid this is decomposed, according to the proportion of the latter, into acid salt or free acid, or a mixture of both. The acid salt forms handsome pinkish rectangular plates, often superposed at various angles, and is one of the most characteristic salts obtained.

Ferric chloride gives no precipitate with a cold dilute solution of the neutral ammonium salt; on warming a white amorphous precipitate forms, which is soluble only on warming with much hydrochloric acid, from which solution, on cooling, the free acid separates.

Tetra-Silver Tetrametaphosphimate, $P_4N_4O_8H_4Ag_4$.—If to a cold solution of tetrametaphosphimic acid silver nitrate be added the resulting precipitate is white, curdy, and, under the microscope, granular or amorphous ; formed in the presence of some alcohol it is even flocculent. These amorphous precipitates, after drying, slowly change to needles, and this occurs at once if they be boiled under water. The salt is obtained at once in crystalline form if a slight excess of silver nitrate be added to a hot solution of tetrametaphosphimic acid in 200–300 parts water. It requires but a slight excess of silver nitrate to bring about complete precipitation, the liberated nitric acid exercising a scarcely perceptible solvent action. Neutral ammonium salt may be used, but the addition of a little nitric acid is essential, otherwise the product is yellowish from contamination with the eight-atom silver salt.

When precipitated hot the salt sometimes consists of thick needles with tufts or brushes at each end, sometimes of long pointed plates, more rarely of rhombic plates, and in no case are they well formed or very characteristic. An acid salt could not be obtained, but the neutral salt always shows a slight deficiency of silver.

The air-dried substance lost nothing at 100° and gave :

	Calculated for $P_4N_4O_8H_4Ag_4$.	Found. (1)	(2)	(3)	(4)	(5)	(6)
P	16.68	16.78	17.04	17.04	16.68	16.84	16.74
N	7.55	....	....	....	....	....	7.62
Ag	58.04	....	57.06	56.13	57.09	57.09	57.40

$$P : Ag \begin{cases} (2) = 4 : 3.85 \\ (3) = 4 : 3.79 \\ (4) = 4 : 3.94 \\ (5) = 4 : 3.90 \end{cases} \quad (6)\ P : N : Ag = 4 : 4.02 : 3.95$$

Octa-Silver Tetrametaphosphimate, $P_4N_4O_8Ag_8$.—If an ammoniacal solution of a tetrametaphosphimate be added to an excess of silver nitrate, a yellowish flocculent precipitate forms, which is insoluble in ammonium nitrate and which does not change on boiling under its mother-liquor or under pure water. On drying at 100° it became grayish olive-colored, apparently because of the separation of some silver oxide. It gave the figures under 1, 2 and 3.

If a solution of a neutral tetrametaphosphimate be added to ammoniacal silver nitrate containing the least possible excess of ammonia, a nearly white flocculent precipitate forms in small amount, which is soluble in ammonium nitrate solution on gently warming; from this solution an orange-yellow semi-crystalline body is thrown out on boiling for a moment. The latter is obtained in greater abundance by boiling the original filtrate from the silver-nitrate precipitate. It seems to be merely the crystalline modification of the above amorphous yellow salt. It gave the figures under Analysis 4. The nearly white modification is obtained in greater amount by using a solution of silver oxide in ammonium nitrate solution. It shows a considerable deficiency of silver (P : Ag = 4 : 6.7) and seems to be less stable than the corresponding white hexa-silver trimetaphosphimate, as it cannot be obtained entirely free from the yellow modification. The yellow form also shows a slight deficiency of silver, and unlike the tri-metaphosphimate, it cannot be converted into a red form.

The yellow salts, dried at 100°, gave:

	Calculated for $P_4N_4O_8Ag_8$.	Found.			
		(1)	(2)	(3)	(4)
P	10.59	10.47	10.88	10.80	10.89
Ag	73.69	71.86	71.60	71.96	72.21

$$\text{P : Ag}\begin{cases}(1) = 4 : 7.90\\(2) = 4 : 7.57\\(3) = 4 : 7.66\\(4) = 4 : 7.63\end{cases}$$

1–3, amorphous.
4, semi-crystalline.

U. S. GEOLOGICAL SURVEY,
WASHINGTON, July, 1896.

NOTE.

AUGUST KEKULÉ.

Friederich August Kekulé von Stradonitz, one of the greatest chemists of this century, died on the 13th of July last. Kekulê was born on the 7th of September, 1829, at Darmstadt. As in early life he exhibited marked excellence in mathematics and drawing, his parents wished him to become an architect, but, being attracted by the lectures of Liebig, he turned to chemistry. Later he went to Paris, where he worked with Dumas, Würtz, and Gerhardt. Then he went to London, where he enjoyed the friendship of Williamson. In 1856 he became Privatdocent at Heidelberg; in 1858 he was appointed professor in the University of Gent; and in 1865 he became Hofmann's successor in the University of Bonn, where he remained until the end of his life—a period of thirty-one years.

Kekulé has exerted a powerful influence upon the thoughts of chemists during the past thirty years. He first showed how the general application of ideas, previously put forward by Frankland, Williamson, and others, helped to clear up many problems of constitution that were not clear in the light of the theory of types. He showed that the four types to which chemists were then referring chemical compounds for purposes of classification were themselves to be referred back to fundamental differences between the typical atoms, and that it was possible to go beyond the types—"back to the elements themselves"—and show how the elements are combined. The conceptions of constitution now held were worked out in a clear way for the first time by Kekulé, and, while these conceptions were not original with him, it is to him that we owe their general acceptance.

Kekulé's name is most frequently heard in connection with the famous hypothesis of benzene, proposed by him in 1865. It is generally recognized that this hypothesis has contributed more than any other single thought to the progress of chemistry during the past thirty years. In 1890 the chemists of the world met at Berlin, under the auspices of the German Chemical Society, to do honor to Kekulé by celebrating the twenty-fifth anniversary of the birth of the benzene theory. No other chemist has been thus honored during his life-time. The account of the meeting[1] is most interesting to every chemist; and the reading of it will show in what esteem Kekulé's work is held.

For years past Kekulé has not been very actively engaged in experimental work. Perhaps the principal reason for this was his poor health. When he began his career Liebig told him that he would never succeed unless he gave himself up to his work to such an extent as to ruin his health. Whatever effect this may have had upon him, it is certain that overwork in his early days did ruin his health.

A full account of Kekulé's life will appear in the *Berichte der deutschen chemischen Gesellschaft.*

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[1] Ber. d. chem. Ges., **23**, 1205–1312.

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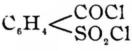
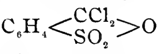
INVESTIGATIONS ON THE TWO ISOMERIC CHLORIDES OF ORTHOSULPHOBENZOIC ACID.

BY IRA REMSEN.

In earlier articles[1] the preparation and general properties of the two isomeric chlorides of orthosulphobenzoic acid were described, and evidence was presented which clearly shows that the chloride melting at the higher temperature (76°) has the symmetrical structure represented by the formula  $C_6H_4{<}\substack{COCl \\ SO_2Cl}$. There was, however, very little direct evidence available bearing upon the structure of the chloride melting at 21.5°–22.5°, and, although it seemed highly probable that it has the unsymmetrical structure represented by the formula  $C_6H_4{<}\substack{CCl_2 \\ SO_2}{>}O$, this view lacked a firm experimental basis. Work upon the two chlorides has been continued since the articles referred to were published, and a number of facts of interest have been established. The only piece of evidence bearing upon the structure of the low-melting chloride is that furnished by the action of ammonia upon it. Experiments described below show that the observation first made by A. D. Chambers in this laboratory that ammonia converts the low-melting chloride into the ammo-

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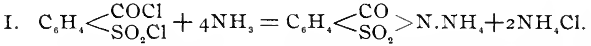
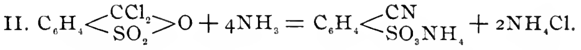
[1] This JOURNAL, 17, 309, 311, 330, 347.

nium salt of orthocyanbenzenesulphonic acid is correct, while it has repeatedly been shown that ammonia converts the symmetrical or high-melting chloride into the ammonium salt of benzoic sulphinide (saccharin). The two reactions are, therefore, to be represented by the following equations :



$$\text{I.}\quad C_6H_4{<}\begin{matrix}COCl\\SO_2Cl\end{matrix} + 4NH_3 = C_6H_4{<}\begin{matrix}CO\\SO_2\end{matrix}{>}N.NH_4 + 2NH_4Cl.$$

Symmetrical chloride. Ammonium salt of benzoic sulphinide.

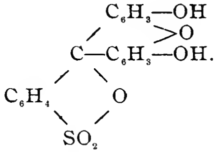


$$\text{II.}\quad C_6H_4{<}\begin{matrix}CCl_2\\SO_2\end{matrix}{>}O + 4NH_3 = C_6H_4{<}\begin{matrix}CN\\SO_3NH_4\end{matrix} + 2NH_4Cl.$$

Unsymmetrical chloride. Ammonium orthocyanbenzenesulphonate.

While the latter equation represents the principal action of ammonia upon the unsymmetrical chloride when proper precautions are taken, it does not represent all that takes place, for the ammonium salt of benzoic sulphinide is always formed to some extent. This appears to be due to a partial transformation of the unsymmetrical in the symmetrical chloride in the presence of aqueous ammonia.

In some of the experiments described below great precautions were taken to purify the two chlorides, and it is believed that the products obtained and described are individuals, each free from its isomer. Starting with these pure substances the action of various reagents upon them was carefully studied. While with ammonia, aniline, and the toluidines they give isomeric products, with water, phenols, and benzene, in the presence of aluminium chloride, both yield the same products, which are in some cases those corresponding to the symmetrical arrangement, and in others those corresponding to the unsymmetrical arrangement. Thus, with water, both give orthosulphobenzoic acid, the reaction taking place more readily with the unsymmetrical than with the symmetrical chloride. With ordinary phenol both yield the symmetrical product, the diphenyl ether of orthosulphobenzoic acid $C_6H_4{<}\begin{matrix}COOC_6H_5\\SO_2OC_6H_5\end{matrix}$. On the other hand, with resorcinol both yield sulphonfluoresceïn, which, in all probability, considering its close resemblance to ordinary fluoresceïn, has the unsymmetrical structure represented by the formula



As has been shown by Saunders and myself,[1] the symmetrical chloride gives first the chloride, $C_6H_4{<}\begin{matrix}COC_6H_5\\ SO_2Cl\end{matrix}$, and then orthobenzoyldiphenylsulphone, $C_6H_4{<}\begin{matrix}COC_6H_5\\ SO_2C_6H_5\end{matrix}$, when treated with benzene in the presence of aluminium chloride. It has now been found that the product of the action of benzene and aluminium chloride on the low-melting or unsymmetrical chloride is orthobenzoyldiphenylsulphone, as in the case of the symmetrical chloride.

Obviously, the careful study of this peculiar case is of interest from the point of view of the hypothesis of tautomerism. Here we have the two definite isomeric substances in crystallized form and with characteristic properties. Both have been purified so that repeated recrystallizations effect no change in the crystalline form or in the melting-points, and yet these two substances act in what appears to be an entirely irresponsible way, making it impossible to predict in any unstudied case whether a symmetrical or an unsymmetrical product will be formed. Further, one of these chlorides does not pass over into the other under any ordinary circumstances—certainly not under the influence of heat. As will be seen, special experiments were undertaken in the hope of effecting such transformation, but without success.

The relations of the two anilides derived from the two chlorides have been investigated and methods devised for the transformation of one into the other. The reactions studied are of such a character as to leave no room for doubt that the two anilides are what they were supposed to be when the first articles on this subject were written, that is to say, one is the

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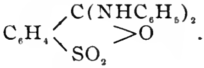
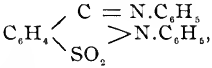
[1] This JOURNAL, **17**, 347.

normal symmetrical anilide, $C_6H_4<\begin{matrix}CONH.C_6H_5\\ SO_2NH.C_6H_5\end{matrix}$, while the other is the unsymmetrical anilide,  $C_6H_4\begin{matrix}C(NHC_6H_5)_2\\ SO_2\end{matrix}>O$.

Both are converted into the dianil of the formula,



$$C_6H_4\begin{matrix}C = N.C_6H_5\\ SO_2\end{matrix}>N.C_6H_5,$$

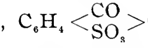
by phosphorus oxychloride and by phosphoric anhydride ; and the same product is formed by the action of phosphorus pentachloride on the infusible or unsymmetrical anilide. When the dianil is boiled with glacial acetic acid or with alcoholic potash the unsymmetrical anilide is formed from it. Other transformations of these anilides will be described which go to show that they are closely related substances, both containing two aniline residues.

IV.—PURIFICATION OF THE CHLORIDES, AND ACTION OF VARIOUS REAGENTS UPON THEM.

BY IRA REMSEN AND S. R. MCKEE.

In the preparation of the mixture of the two chlorides by the action of phosphorus pentachloride upon the acid potassium salt of orthosulphobenzoic acid, certain material improvements have been introduced by which the yield is increased to about 95 per cent. The process as now carried out is as follows :

The acid potassium salt, in quantities of 75–100 grams, is placed in a porcelain dish with 2½ molecules phosphorus pentachloride, and rubbed with a pestle until the action is over, when the whole mass is liquid. This liquid mass is then transferred to a flask, and the phosphorus oxychloride distilled off under diminished pressure. In this operation a small quantity of phosphorus pentachloride collects in the tube, showing that it is present in slight excess. The oxychloride may be evaporated off, as in the former method, by heating the dish on a water-bath for about three hours, if it is preferred, as the yield was practically the same in both cases. When the oxychloride is driven off the mass is transferred to a tall glass cylinder, containing 200–250 cc. of water and washed by vigorously churning it with a glass rod terminating in a ring. After two or three washings it was poured into a beaker and placed in a freezing-mixture, when it soon became completely solid. To prevent the formation of a solid cake and also to facilitate the freezing, it should be stirred and broken up with a spatula. It is then thoroughly ground up in a mortar with ice-water, transferred to a filter, and washed with ice-water, with the aid of a pump. In this way the chlorides can be freed from potassium chloride and phosphorus compounds. After drying as far as possible with the pump, the mass can be further dried by placing it between layers of drying-paper, and pressing with a plate, or rolling a glass rod over it. Care must be taken, however, not to touch it with the hands, or anything that is warm. If the mass is now placed in a beaker, and kept in a desiccator over calcium chloride, in a cool place, it remains a dry solid, and can be handled very easily. The wash-water should be evaporated, for the purpose of recovering a small quantity of the acid potassium salt it contains.

Several experiments were made to see if the chlorides could with advantage be extracted with ether after distilling off the phosphorus oxychloride, but no distinct advantage was gained. In two cases, however, when 2 molecules of phosphorus pentachloride was used and the chlorides extracted with ether, crystals of another substance were deposited in small quantity from the ether extract, before the chlorides separated. These were thought to be the anhydride of orthosulphobenzoic acid,  $C_6H_4<\substack{CO \\ SO_3}>O$, and an investigation by Mr. Sohon, of this laboratory, has proved that the assumption was correct, and that the substance is formed in large amount when a smaller quantity of phosphorus is used.

Separation of the Two Chlorides.

1. The Pure High-melting Chloride.—Heretofore this substance has been obtained by dissolving the mixed chlorides in chloroform, shaking this solution with ammonia, separating the chloroform solution, and evaporating. Ammonia acts much more easily on the low-melting than on the high-melting chloride, and thus it is possible to get rid of the former.

Shaking the mixed chlorides with aqueous ammonia was tried, and it was found that nearly all the low-melting constituent could be destroyed in this way. By repeating this several times, and then crystallizing from ligroïn, the high-melting chloride can be prepared in pure condition. This substance melts, according to Remsen and Saunders,[1] at 76°–77° (uncorr.), but a product has been obtained by the above method, which melts somewhat higher. A portion melting at 76°–77° was alternately shaken with dilute ammonia, and crystallized from ligroïn (boiling-point 90°–125°) nine times. The melting-point gradually rose until the sixth crystallization, when it was 79°–79°.5 (uncorr.); but after that there was no further rise. The thermometer used was correct for the boiling-point of water.

It has been found that when the mixed chlorides are dissolved in ether, shaken with dilute ammonia, and the solution in ether evaporated, the high-melting chloride can be obtained very easily. So that the best method, and the one now used, is to shake the mixed chlorides with dilute aqueous ammonia until nearly all the low-melting constituent is destroyed; then dissolve in ether, cool down to about 0° by adding ice, and shake with dilute ammonia. The ether solution is separated, dried over calcium chloride, and most of the ether distilled off. From the residue good crystals of the chloride, melting at 79°–79°.5, are obtained.

2. *The Pure Low-melting Chloride.*—By fractional crystallization of the mixed chlorides from petroleum ether in the cold, Remsen and Saunders[2] obtained a small quantity of the low-melting chloride in pure condition (melting-point 21°.5–22°.5.) After various attempts to effect a separation of the two chlorides during the past year, a method has been devised which gives satisfactory results, though it is somewhat tedious. It is as follows: A portion of the mixed chlorides is dissolved in absolute ether, placed in a cool place, and allowed to stand for about a day, when nearly all of the ether will have evaporated, and there will be a separation of crystals of

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[1] This JOURNAL, 17, 347.

[2] *Loc. cit.*

the high-melting chloride. The oily portion, consisting mainly of the low-melting chloride, is drained off and dissolved in ligroïn (boiling-point 90°–125°). This solution is placed in an Erlenmeyer flask, and a current of dry air drawn through the flask. The liquid must be kept cold, however, or else the substance will not crystallize; and for this purpose a refrigerating-box was devised. This is made of galvanized iron, and consists of an outer and an inner chamber, with a space of about four inches between them. The outer chamber has a cover, and is surrounded by a thick layer of cotton. When this is filled with broken ice the temperature of the inner chamber can be kept at 0° for several days. The flask containing the solution is placed in the inner chamber, and this covered with cotton, or a piece of asbestos board with small holes cut in it for the passage of the glass tubes leading into the flask. The air is dried with sulphuric acid and calcium chloride. After a time two kinds of crystals are noticed, stout columns and radiating tufts of fine needles. The columns melt at 70°–75°, and the needles at 22°–23° (uncorr.) As a rule the columns do not appear until some time after crystallization begins, owing to the fact that part of the high-melting chloride has already been removed by crystallization from ether. When evaporation has proceeded far enough, the mother-liquor is poured off, and the columns removed with a properly constructed spatula. If this is done carefully, very little is left except the radiating tufts. These are then redissolved in ligroïn and the process repeated. Sometimes the columns are observed in the second crystallization, if the solution is evaporated far enough; if so, they are removed as before. As a rule the substance was recrystallized twice after columns ceased to appear, and all the low-melting chloride used in the experiments, hereafter described, was thus treated. After the final crystallization, the mother-liquor should be washed out with cold ligroïn, and the crystals removed and dried. The crystals thus obtained melted at 21°.5–22°.5 (uncorr.), and the melting-point was not lowered by recrystallization. In no case should the solution of the chlorides be saturated, even at 0°, for the solution then becomes cloudy, and the substance does not crystallize so well.

When the high-melting chloride is removed, it is best, in all crystallizations, to add three or four individual crystals of the low-melting chloride when crystallization is just about to begin, for without this, in some cases, only an oil is obtained.

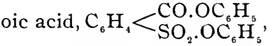
Petroleum ether of different boiling-points was tried, but nothing gave as satisfactory results as ligroïn, boiling-point 90°–125°. Moreover, it was found necessary to purify the commercial ligroïn, as the chlorides absorb something from it and become darkened in consequence. It was shaken in a large separating-funnel with strong sulphuric acid until it almost ceased to color the acid, washed with hot water, then with a hot, dilute solution of sodium hydroxide, then with hot water until free from alkali; then dried over calcium chloride, and filtered.

Action of Water on the Pure Chlorides.

Remsen and Saunders[1] showed that both of the pure chlorides are decomposed by water, yielding orthosulphobenzoic and hydrochloric acid, but noted no difference in the rate of action. The following experiment shows that there is a difference, and that the low-melting chloride is acted on by water about three times as rapidly as the high-melting. 0.8 gram of each of the chlorides was placed in a small flask, and 50 cc. of water added. The flasks were shaken and placed aside. Every twenty-four hours 10 cc. of the water was removed and titrated with silver nitrate and 10 cc. of pure water added. The results were as follows:

	Pure high-melting chloride. Decomposition.		Pure low-melting chloride. Decomposition.	
	Daily.	Total.	Daily.	Total.
1	3.96	3.96	11.87	11.87
2	5.66	9.60	21.30	32.20
3	5.48	15.08	17.77	50.78
4	4.71	19.80	14.08	64.91

Action of Phenol.

By heating the high-melting chlorides and the mixed chlorides with phenol, Remsen and Saunders[2] obtained the normal diphenyl ether of orthosulphobenzoic acid,  $C_6H_4<\begin{matrix}CO.OC_6H_5\\SO_2.OC_6H_5\end{matrix}$, and a red substance which was not investigated. The work

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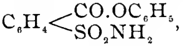
[1] *Loc. cit.*

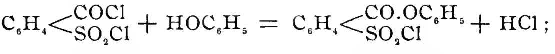
[2] *Loc. cit.*

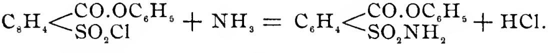
was repeated, and the diphenyl ether obtained, but no considerable amount of the red-colored substance, although special efforts were made to get it. After the action was over, instead of treating with sodium hydroxide, ammonia was added. The whole mass at once became oily, and, on standing for some time, solid. From this a new substance was obtained, as will be shown below. The action of phenol was tried at various temperatures, ranging from 40° to 120°, but the temperatures at which the largest yields and the cleanest products were obtained was 40°–45°. In every experiment with phenol the red color was observed, even with the purest specimens of the chlorides.

1. *Action on the High-melting Chloride.*—5 grams of the chloride (melting-point 79° -79°.5), was heated with 4 grams (2 molecules) phenol for five hours at 40°–45°, and then dilute ammonia added. After stirring for some time the oily mass became solid; it was then filtered, washed, and dried. The yield was 4.175 grams. This, when crystallized from alcohol, gave the diphenyl ether and the new substance described below.

Phenyl Orthosulphaminebenzoate.—When the solid substance, obtained above, was dissolved in alcohol, water added slowly till crystallization was just about to begin, and the solution then allowed to cool slowly, crystals of the diphenyl ether (melting-point 117°–118°) separated. After filtering, the mother-liquor was evaporated and a little more water added, when it became cloudy. On cooling slowly, feathery crystals separated, which melted at 128°–130°, and on crystallization melted quite sharply at 131°–132° (uncorr.). This substance proved to be an amide of the formula


$C_6H_4<\begin{smallmatrix}CO.OC_6H_5\\SO_2NH_2\end{smallmatrix}$, formed by the following reactions :


$$C_6H_4<\begin{smallmatrix}COCl\\SO_2Cl\end{smallmatrix} + HOC_6H_5 = C_6H_4<\begin{smallmatrix}CO.OC_6H_5\\SO_2Cl\end{smallmatrix} + HCl\,;$$


$$C_8H_4<\begin{smallmatrix}CO.OC_6H_5\\SO_2Cl\end{smallmatrix} + NH_3 = C_6H_4<\begin{smallmatrix}CO.OC_6H_5\\SO_2NH_2\end{smallmatrix} + HCl.$$

The analyses were as follows:

I. 0.1527 gram gave 0.1241 gram $BaSO_4$ (Carius method).

II. 0.1532 gram gave 0.1251 gram $BaSO_4$ (Carius method).

III. 0.314 gram gave 0.01637 gram nitrogen (absolute method).

	Calculated for		Found.	
	$C_{13}H_{11}SO_4N$.	I.	II.	III.
S	11.55	11.16	11.22	....
N	5.05	....	....	5.21

The second sulphur determination was made by Mr. Ragland, and the nitrogen determination by Mr. Mackay, of this laboratory.

The intermediate product could not be isolated. Several attempts were made to get the corresponding acid by boiling with water after the action was over, and also to prepare the anilide, but these were unsuccessful; only orthosulphobenzoic acid and the fusible and infusible anilides could be obtained. The presence of the phenol complicated matters very much, and besides, the action of phenol on the original chloride could never be made complete.

At higher temperatures the yield of the phenyl orthosulphaminebenzoate was smaller, though a small quantity was obtained even at 100°. It seems, then, very probable that part of the action, at least, gives an intermediate product, and that at a higher temperature the action goes to the full extent. The diphenyl ether, however, is formed at the lowest temperature at which the action takes place; at 40°–45° about equal quantities of each are formed.

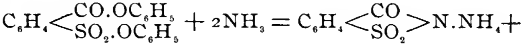
2. *Action on the Mixed Chlorides.*—When the mixed chlorides were used, the same two substances were obtained, though there was proportionally a somewhat smaller yield of phenyl orthosulphaminebenzoàte.

3. *Action on the Low-melting Chloride.*—2 grams of the low-melting chloride was heated with 1.6 grams phenol for five hours, at 40°–45°, and the product treated as above. Both substances were obtained and in approximately equal quantities. It was hoped that an isomeric substance would be formed, but there was not the slightest indication of this.

Decomposition of the Diphenyl Ether.

1. *Decomposition with Ammonia.*—The diphenyl ether is not acted on by strong ammonia under ordinary pressure, even

when boiled. When heated in a sealed tube for two hours at the temperature of the water-bath, the action is very slight, but, when heated in a sealed tube at 125° for four hours, the decomposition is complete. There is formed a dark-colored solution, which gives off phenol when heated. By heating with water all the phenol can be driven off, and on evaporating to a small bulk, crystals of a sweet-tasting substance separate. When these are dissolved in water and the solution acidified, there is a large deposit of benzoic sulphinide. The substance formed is the ammonium salt of the sulphinide,  $C_6H_4{<}\substack{CO \\ SO_2}{>}N.NH_4$, and the reaction is, in all probability, to be represented thus:



$$C_6H_4{<}\substack{CO.OC_6H_5 \\ SO_2.OC_6H_5} + 2NH_3 = C_6H_4{<}\substack{CO \\ SO_2}{>}N.NH_4 + 2C_6H_5OH.$$

2. *Decomposition with Hydrochloric Acid.*—Portions of the diphenyl ether were heated with concentrated hydrochloric acid in a sealed tube, at 100°, at 125°, and at 150° for several hours without action. When, however, it was heated to 200° for six hours, there was complete decomposition. The dark-colored liquid, when evaporated, gave a strong odor of phenol, and when the phenol was all driven off, the solution was evaporated to dryness to expel the hydrochloric acid. The solid residue, when dissolved in water, gave a strong acid reaction. The solution was neutralized with barium carbonate, boiled with animal charcoal, and evaporated. Good crystals were obtained, answering to the description of the neutral barium salt of orthosulphobenzoic acid made and described by Remsen and Dohme.[1]

I. 0.3394 gram when heated lost 0.0328 gram water.

II. 0.3394 gram gave 0.212 gram $BaSO_4$.

	Calculated for $C_7H_4SO_5Ba + 2H_2O$.	Found.
H_2O	9.65	9.66
Ba	36.72	36.74

3. *Decomposition with Potassium Hydroxide.*—A portion of the diphenyl ether was heated for some time on a water-bath

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[1] This JOURNAL, 11, 332.

with a moderately concentrated solution of potassium hydroxide, but as there seemed to be no action, it was boiled for about twenty minutes. Still there was no action, as was shown by filtering and evaporating the filtrate. When treated with alcoholic potash, however, and heated, the whole went into solution, and almost immediately there was a deposit of fine needles. The odor of phenol was also very pronounced, when the filtrate was acidified. The substance was recrystallized from alcohol and analyzed. In appearance the crystals corresponded to the neutral potassium salt of orthosulphobenzoic acid, made and described by Remsen and Dohme.[1]

I. 0.220 gram heated at 185° lost in weight 0.0181 gram.
II. 0.220 gram gave 0.1255 gram K_2SO_4.

	Calculated for $C_7H_4SO_5K_2 + 1\frac{1}{2} H_2O$.	Found.
H_2O	8.86	8.23
K	23.57	25.55

Action of Resorcinol.

1. *Action on the High-melting Chloride.*—A portion of the pure high-melting chloride was heated with resorcinol (2 molecules) for four hours, at 75°–80°, the action taking place readily at that temperature. The whole mass became soft, and hydrochloric acid was given off freely. At the end of this time it had become quite stiff. The temperature was then raised to 90°, and the heating continued about two hours longer. The evolution of hydrochloric acid had about ceased, and the mass had become quite hard. On adding sodium hydroxide, the whole went into solution. This solution was very dark-colored, but, on distilling, it gave a beautiful fluorescence, and on adding acid a yellowish-brown mass was precipitated. This was redissolved, heated with animal charcoal, filtered and precipitated by acid, when the color became brownish yellow. It was dried in the air on a plate, and then in a desiccator. A portion was heated at 125°–130° for three hours, but lost no water.

I. 0.1467 gram gave 0.329 gram CO_2 and 0.0498 gram H_2O.
II. 0.1509 " " 0.338 " " " 0.0506 " "
III 0.1553 " " 0.0948 " $BaSO_4$ (Carius method).

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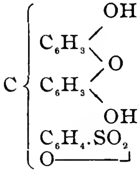
[1] *Loc. cit.*

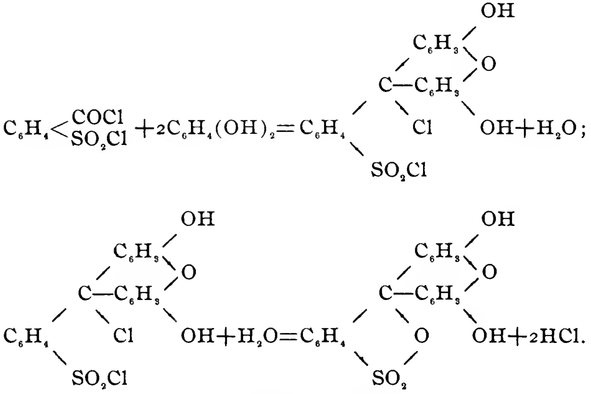
	Calculated for $C_{19}H_{12}O_6S$.	Found. I.	II.	III.
C	61.96	61.16	61.09	...
H	3.26	3.77	3.73	...
S	8.70		...	8.39

The combustions were made by the lead chromate method as modified by DeRoode,[1] but it was found necessary to mix the substance with potassium bichromate in a boat, to burn it. Sulphonfluoresceïn dried in the air contains a molecule of water which it gives off at 125°–130°. The specimen analyzed in this case was dried in a desiccator.

Assuming that this fluoresceïn is analogous to the ordinary fluoresceïns the formula is:



The formation of this substance from the symmetrical chloride can be accounted for in this way:



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[1] This JOURNAL, **12**, 226.

2. *Action on the Low-melting Chloride.*—When the low-melting chloride was heated with resorcinol, at the same temperature, reaction took place in the same way, and when sodium hydroxide was added the whole mass went into solution, just as before, and gave a fluorescent substance. This was precipitated by acids, and acted in every way just as the substance above described.

Action of Aniline.

1. *Action on the High-melting Chloride.*—Remsen and Kohler[1] showed that when the high-melting chloride is treated with aniline only the fusible anilide is obtained. Their work was repeated and confirmed, there being no evidence of the formation of any other substance.

2. *Action on the Low-melting Chloride.*—In accordance with the work of Remsen and Kohler, it was expected that the action of aniline on the pure low-melting chloride would give only the infusible anilide, but the results were different. 0.8 gram of the chloride was dissolved in ether in a small flask, and a dilute ether solution of aniline added slowly, the flask being kept in cold water. Action took place at once. The ether was evaporated off, and the solid residue washed with dilute hydrochloric acid. The residue went into solution in dilute sodium hydroxide, and was precipitated at once as a flocculent mass, on addition of acid. It crystallized from alcohol in fine needles, which melted at 194°–195°, and acted in every way like the fusible anilide. From the wash-water, on evaporation, there was obtained about an equal quantity of crystals of the infusible anilide, melting at 250°–270°, with decomposition. The experiment was repeated, and the flask kept in a freezing-mixture, but with the same results.

1 gram of the chloride was treated with aniline in the presence of water, and the same substance obtained in apparently the same proportions. The only explanation of this seems to be that, in the presence of aniline, there is a partial transformation of the low-melting into the high-melting chloride, as the product used could not have contained more than the merest trace of the high-melting chloride. Further evidence

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[1] This JOURNAL, **17**, 330.

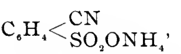
of a transformation is presented in the section dealing with the action of ammonia.

The thought that the formation of the fusible or symmetrical anilide as well as of the infusible or unsymmetrical anilide is due to the imperfect purification of the low-melting chloride used in the experiment is absolutely not to be considered. Every precaution was taken in the purification, and we assert that as used here the chlorides were pure chemical individuals.

Action of Ammonia.

1. *Action on the High-melting Chloride.*—Remsen and Saunders[1] showed that when ammonia acts on the high-melting chloride it is converted into the ammonium salt of benzoic sulphinide. The following experiments confirm their results and show that nothing else is formed :

3 grams of the chloride was dissolved in ether, cooled to 0° by adding ice, and shaken for some time with very dilute ammonia. The ether solution was dried over calcium chloride and the ether evaporated. From this 2.6 grams of the chloride was recovered unchanged. The water, when evaporated, gave crystals of ammonium chloride, and also of the ammonium salt of benzoic sulphinide. When acidified it gave a small precipitate of benzoic sulphinide. This experiment was repeated and much more concentrated ammonia used. Very little of the chloride was recovered from the ether, but from the water, on evaporation, crystals were obtained as above and in large quantity. These had a sweet taste, and when dissolved in water and acid added, there was a copious precipitate of benzoic sulphinide. There was no evidence of the formation of any other substance.

2. *Action on the Low-melting Chloride.*—The work of Remsen and Saunders, and also that of Chambers, of this laboratory, made it extremely probable that when ammonia acts on the low-melting chloride at low temperatures, the ammonium salt of orthocyanbenzenesulphonic acid,  $C_6H_4{<}\begin{matrix}CN\\SO_2ONH_4\end{matrix}$, is formed. This substance has been under investigation during the past year by Mr. Karslake, of this labor-

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[1] *Loc. cit.*

atory. The following experiments are of interest in this connection. 0.8 gram of the pure chloride was dissolved in ether, the solution cooled to 0°, and very dilute ammonia added. After shaking for some time, the solution being kept at 0°, the water was drawn off and evaporated nearly to dryness. A few crystals separated, and when these were dissolved in water, and acid added, there was after a time a very small precipitate of benzoic sulphinide. The ether solution was dried with calcium chloride and evaporated nearly to dryness. From this crystals were obtained which resembled the high-melting chloride. These melted at 75°–78°, and when heated with water they gave off hydrochloric acid.

The experiment was repeated with 2 grams of the chloride. When the ammonia solution was drawn off, a rapid current of air was passed through it to expel any ether; it was then filtered, evaporated to a small volume, and allowed to stand over night. The next morning there was a good deposit of botryoidal crystals, similar in every way to those obtained by Chambers and by Karslake. The ether solution was dried with calcium chloride and evaporated. From this was obtained 0.54 gram of the pure high-melting chloride (melting-point 79°–80° uncorr.) These experiments show that in the presence of ammonia, the low-melting is partially converted into the high-melting chloride. This transformation also accounts for the small amount of benzoic sulphinide obtained in the first experiment, as the high-melting chloride is slowly acted upon by very dilute ammonia. The difference between this case and that of the action of aniline is this, that aniline acts readily on both chlorides, and hence both the fusible and infusible anilides are formed from the low-melting chloride.

Action of Benzene and Aluminium Chloride.

1. *Action on the High-melting Chloride.*—Remsen and Saunders[1] showed that when benzene and aluminium chloride act on the high-melting or mixed chlorides, at ordinary temperatures, orthobenzoylbenzenesulphone chloride is formed, and that, when the action is continued at higher temperatures, orthobenzoyldiphenylsulphone is formed. Their work was

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[1] *Loc. cit.*

repeated, and, under the same conditions, both of the substances just mentioned were obtained. Moreover, the yields were unsatisfactory just as they had observed.

2. *Action on the Low-melting Chloride.*— 3 grams of the chloride was dissolved in about 15 grams of benzene, and 3–4 grams of aluminium chloride added in portions. Reaction took place at once, and was so vigorous that the vessel had to be plunged into cold water to prevent too violent action. In about ten minutes action ceased, but on heating momentarily in a water-bath, at about 60°, action began again. This was repeated at intervals for about fifteen minutes, when all the action seemed to be over, and a dark-colored heavy layer had separated at the bottom. The whole was then poured into warm water containing a little hydrochloric acid. In a short time a yellowish, oily layer separated at the bottom of the dish, and, when the water was poured off, this soon solidified. It was ground in a mortar, and, when washed and dried, weighed 3.6 grams. Some of this was crystallized from alcohol, and then melted at 181°–183°, but on recrystallization it melted at 182°–184° (uncorr.). In every way it agreed with orthobenzoyldiphenylsulphone. In the mass there was also a little orthobenzoylbenzenesulphone chloride, as was shown by extracting with ether and crystallizing. The reaction proceeded very smoothly, and was more satisfactory than in the case of the high-melting chloride.

The experiment was repeated with 2 grams of the chloride, and the temperature kept down to the freezing-point of benzene. The action was not so vigorous as before, and when it was over the benzene solution was poured into cold water. Instead of evaporating from the water, the benzene layer was poured off and quickly evaporated from a watch-glass. A gummy substance remained, but on washing with alcohol, the gum was easily dissolved. The residue, when crystallized from alcohol, melted at 183°–185° (uncorr.). It was hoped that from the low-melting chloride a substance isomeric with orthobenzoyldiphenylsulphone might be obtained, but there was not the slightest indication of the formation of such a substance.

Other Attempts to Effect a Transformation.

1. *By Heat.*—It was hoped that by heating the low-melting chloride it might be possible to change it into the high-melting form. Accordingly, two portions were heated in sealed tubes, the first for seven hours at about 80°, and the second for twelve hours at about 90°. Each of these was then dissolved in ligroïn, and recrystallized, but only crystals of the low-melting chloride could be obtained.

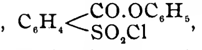
2. *By the Action of Water.*—A portion of the low-melting chloride was shaken in a large test-tube with water for about one-half hour, then dried, dissolved in ligroïn, and crystallized, but there was no evidence of crystals of the high-melting chloride.

Conclusion.

The results of this investigation may be summed up thus:

1. It has been shown that both the chlorides can be obtained in quantity in pure condition.

2. Water and other agents act on the low-melting chloride much more easily than on the high-melting chloride.

3. Phenol gives two products with each of the chlorides, the diphenyl ether  $C_6H_4<\begin{matrix}CO.OC_6H_5,\\SO_2.OC_6H_5\end{matrix}$ and the chlorphenyl ether,  $C_6H_4<\begin{matrix}CO.OC_6H_5\\SO_2Cl\end{matrix}$, but no isomeric product.

4. The diphenyl ether can be decomposed by various agents, but no difference was found in the relations of the two phenol residues to the rest of the compound.

5. Resorcinol gives sulphonfluoresceïn with both chlorides.

6. With aniline the high-melting chloride gives only the fusible anilide, but the low-melting chloride gives both the fusible and infusible anilides. This is accounted for by a partial transformation of the low-melting into the high-melting chloride.

7. Ammonia gives only the ammonium salt of benzoic sulphinide with the high-melting chloride, but the low melting chloride is partly transformed by it into the high-melting form, and partly into ammonium orthocyanbenzenesulphonate,  $C_6H_4<\begin{matrix}CN\\SO_2ONH_4\end{matrix}$.

8. Benzene and aluminium chloride give the same product with both of the chlorides.

V.—THE RELATIONS OF THE ANILIDES.

BY IRA REMSEN AND J. R. HUNTER.

Preparation of the Two Anilides.

The best method for the preparation of the anilides was found to be that given below:

25 grams of the mixed chlorides are dissolved in absolute ether in a 500 cc. Erlenmeyer flask. 38.6 grams aniline, also in solution in absolute ether, are added slowly to the chlorides, the solution being constantly stirred. The temperature of the solution is to be kept down by placing the flask in cold water. A white precipitate appears as soon as the aniline is added. When the reaction is over, the ether is distilled off on the water-bath. To avoid bumping, as far as possible, the flask should be shaken constantly during the distillation. The yellowish-white residue consists of a mixture of the two anilides and aniline hydrochloride. Sometimes the residue has an oily appearance, and it usually contains a slight excess of aniline. Cold water acidulated with hydrochloric acid is then added, the mass thoroughly stirred, and the whole allowed to stand several hours. This treatment removes the aniline salts, and leaves the mixture of the two anilides. Some of the infusible anilide will be dissolved in the water with the salts of aniline, hence this should be recovered by evaporating the water to a small volume, when the anilide will crystallize out, the aniline hydrochloride remaining in solution. This anilide is frequently colored, but can be purified by boiling with animal charcoal in dilute alkaline solution.

To separate the two anilides the following method is satisfactory: The mixture is dissolved in hot alcohol, and this solution is cooled as rapidly as possible by putting the vessel in cold water. Under these conditions the fusible anilide crystallizes in thin white needles, while the infusible variety always crystallizes in short thick prisms. By rotating the vessel the fusible anilide will be disseminated through the alcohol, and may be poured off from the infusible prisms which will quickly settle to the bottom.

Under the conditions described above there is usually formed a small amount of the anil, and sometimes a considerable quantity of it appears. Since this is insoluble in a cold, dilute solution of sodium hydroxide, while the anilides are soluble in that reagent, the latter can be readily separated from the former by that means.

If the molecule of alcohol with which the infusible anilide crystallizes from solution in alcohol is undesirable, the crystals should be dissolved in dilute solution of sodium hydroxide, and the solution acidified, when the anilide will crystallize without water or alcohol of crystallization.

Action of Phosphorus Oxychloride on the Anilides.

1. *On the Infusible Anilide.*—Remsen and Kohler[1] observed that phosphorus oxychloride acts on the infusible anilide, but the products were not isolated. The experiment was repeated. To avoid the action of the oxychloride on rubber or cork a small condenser is fitted over the neck of a tubulated retort. In this apparatus the infusible anilide is then boiled with an excess of the oxychloride, until all of the anilide is dissolved. This is attended by liberation of hydrochloric acid, and the solution becomes quite yellow. When the reaction is complete, the excess of the oxychloride is removed by distillation under diminished pressure. There is left in the retort a light-brown, viscous liquid. While still warm the retort is turned about so that this residue is spread over as much surface as possible. Water is then added, and the retort set aside until the brown viscous mass has disappeared. An insoluble, almost white, material remains, which dissolves in hot alcohol, forming a yellow solution. After repeated crystallizations it melts sharply at 189°.5 C. (uncorr.). An analysis of this product gave the following results :

I. 0.2002 gram gave 0.4997 gram CO_2, and 0.078 gram H_2O.

II. 0.2015 gram gave 0.5020 gram CO_2, and 0.0795 gram H_2O.

III. 0.2443 gram gave 0.1645 gram $BaSO_4$.

IV. 0.1683 gram gave 0.1132 gram $BaSO_4$.

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[1] This JOURNAL, 17, 343.

	Calculated for				Found.			
	$C_{19}H_{14}N_2SO_2$.	I.	II.	III.	IV.	V.	VI.	VII.
C	68.26	68.07	67.94	...	...	...	...	...
H	4.19	4.33	4.38	...	...	...	...	...
S	9.58	...	...	9.25	9.21	...	...	...
N	8.41	...	...	...	...	8.63	8.61	8.5

The combustions were made by the lead chromate method, as described by DeRoode,[1] the sulphur determinations by the method of Carius, and the nitrogen determinations by the absolute method, excepting the last one (VII), which Mr. E. Mackay, of this laboratory, kindly made for me by the method of Kjeldahl.

Considerable difficulty was experienced in obtaining satisfactory results for carbon, although the appearance and the melting-point of the compound indicated its purity. Afterward a possible explanation was found in the fact that a little of the anil described by Remsen and Coates,[2] was found to result under the conditions of the experiment. Its formation will be explained below.

When pure this compound has a bright lemon-yellow color, and the crystals obtained from alcohol are beautifully formed arborescent plates, very brittle. It is only slightly soluble in ether, or chloroform, but is readily soluble in benzene, glacial acetic acid, and acetone. When crystallized from either of the last two solvents named, monoclinic prisms of great briliancy are obtained, the faces developed being usually ∞P, $\infty P\bar{\infty}$, $0P$, P, and $2P\breve{\infty}$.

2. *On the Fusible Anilide.*—This same compound is formed by the action of phosphorus oxychloride on the fusible anilide, the details of the experiment being the same as above given. Some anil is formed in this case also.

Efforts to get a crystallized product from the brown viscous residue, by using various solvents, were unsuccessful. It appears from the following experiments that this residue is really a solution of the yellow product in phosphoric acid. To a small amount of phosphoric acid prepared by adding a very little water to phosphoric anhydride some of the pure yellow product, was added and the mixture heated. A clear solution was effected, having the same consistency and color as the

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[1] This JOURNAL, **12**, 226.

[2] *Ibid*, **17**, 321.

residue obtained above; and when water was added to this, it acted in much the same way.

On comparing the empirical formula arrived at by analysis of this yellow product with that of the anilide, from which it is derived, the equation,

$$C_{19}H_{16}SO_3N_2—H_2O=C_{19}H_{14}SO_2N_2,$$

shows their relation. It thus appears that the action of the oxychloride is one of dehydration.

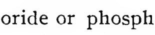
The Action of Phosphorus Pentoxide.

1. *On the Infusible Anilide.*—It seemed reasonable to expect that the same compound would result if either of the anilides should be treated with a strong dehydrating agent. Accordingly, some infusible anilide was mixed with phosphorus pentoxide in a test-tube and then heated for two hours in an air-bath to 130°–150°, the test-tube being closed by a Bunsen valve. The mass had become slightly yellow in color. When cold, water was added to dissolve the phosphoric acid and anhydride, and the portion insoluble in water was found to have the same crystalline form, when deposited from alcohol, and to melt at the same temperature, as the product from the other experiments with phosphorus oxychloride.

2. *On the Fusible Anilide.*—When the fusible anilide is treated with phosphorus pentoxide, as just described, the same yellow compound is formed.

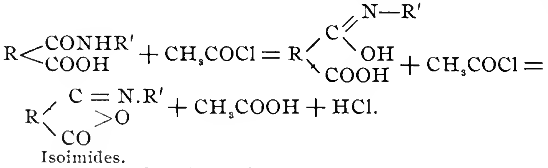
Neither acetyl chloride nor acetic anhydride effect this dehydration of the anilide.

Hoogewerff and Van Dorp[1] have effected the formation of some isoimides by treating dibasic acid derivatives of the general formula,



$$R{<}{\begin{matrix}CONHR'\\COOH\end{matrix}},$$

with either acetyl chloride or phosphorus oxychloride, the reaction with the former being represented by the equations,



Isoimides.

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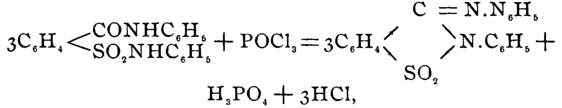
[1] Rec. Trav. chim., **12**, 12; also **13**, 93.

With the oxychloride of phosphorus the reaction would be similar. In all cases examined R′ was CH_3, C_2H_5, or $CH_2.C_6H_5$, while R was the residue of camphoric and phthalic acids, respectively. Clearly the rôle of the oxychloride in these reactions is the same as that which it plays in the reactions with the anilides, the equation,

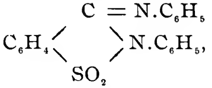


$$3C_6H_4<\begin{matrix}CONHC_6H_5\\SO_2NHC_6H_5\end{matrix} + POCl_3 = 3C_6H_4\begin{matrix}C = N.N_6H_5\\ \\SO_2\end{matrix}\!\!>N.C_6H_5 +$$

$$H_3PO_4 + 3HCl,$$

in all probability represents the reaction with the fusible anilide.

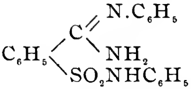
3. *Structure of the Compound.*—From the methods of formation already described, especially those involving the use of the fusible anilide, the formula for which may be regarded as established, it follows that the formula



$$C_6H_4\begin{matrix}C = N.C_6H_5\\ \\SO_2\end{matrix}\!\!>N.C_6H_5,$$

represents the structure of the new compound. It thus appears to be a dianil of orthosulphobenzoic acid.

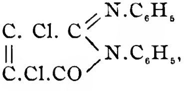
Jesurun[1] obtained this same compound by the action of aniline on orthocyanbenzenesulphone chloride. He thinks the first product formed is a benzamidinesulphanilide,



$$C_6H_5<\begin{matrix}C\begin{matrix}=N.C_6H_5\\-NH_2\end{matrix}\\SO_2NHC_6H_5\end{matrix}$$

and that this loses ammonia, forming this dianil, to which he gives the above structural formula.

The grouping of the two aniline residues in this dianil is the same as that given by Anschütz and Beavis[2] for dichlormaleïc dianil, the formula of which is,



$$\begin{matrix}C.\ Cl.\ C\begin{matrix}=N.C_6H_5\\ \end{matrix}\\ \|\quad\quad\quad\;\; >N.C_6H_5,\\ C.Cl.CO\end{matrix}$$

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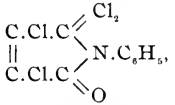
[1] Ber. d. chem. Ges., **26**, 2292.

[2] *Ibid*, **28**, 58.

which is formed by the action of aniline on dichlormaleïc anildichloride,

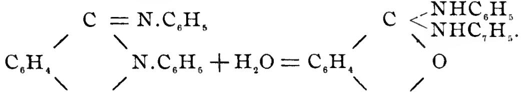


prepared by the action of phosphorus pentachloride on succinanil.[1]

It seems reasonable to expect the formation of analogous derivatives of the anil described by Remsen and Coates. Preliminary experiments have been made with this end in view, but as yet without success. The problem is still under investigation.

4. *Chemical Properties of the Dianil.*—(*a*) It was mentioned above that the compound can be crystallized from glacial acetic acid. For this purpose the solution must not be heated longer than is necessary to effect solution. If the solution is boiled for two or three hours in a flask connected with a reflux condenser, none of the dianil will separate on cooling, but instead, slender, white needles will appear. These are crystals of the infusible anilide. The identity was established by the melting-point, crystalline form when recrystallized from alcohol and from water, ready solubility in dilute cold alkaline solution, from which the characteristic granular crystals of the infusible anilide separate when the solution is acidified. The infusible anilide itself assumes the acicular habit when crystallized from glacial acetic acid. In order further to test the identity some of the needles were treated with phosphorus oxychloride, and the dianil together with some of the ordinary anil was obtained, just as when the granular, infusible anilide was used.

This conversion of the dianil into the infusible anilide is accompanied by a change in color of the acetic acid solution, from a darker to a much lighter shade of yellow. The reaction is represented by the equation,



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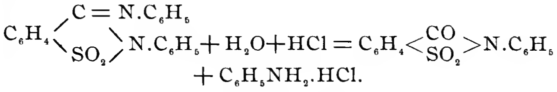
[1] Ann. Chem. (Liebig), **263**, 156.

The yield is quantitative.

(*b*) The crystals of the dianil can be boiled with a water solution of sodium hydroxide, either dilute or concentrated, without undergoing change. When boiled for about an hour with alcoholic potash it passes into solution. If now the alcohol is evaporated almost completely, no precipitate is formed on addition of water. If, however, the solution is acidified, crystals of the infusible anilide appear on standing, provided the solution is sufficiently dilute. If the solution is quite concentrated, the anilide is precipitated at once by the acid.

The effect of boiling the dianil with alcoholic potash is to cause the dianil to unite with the elements of water and form the infusible anilide. It is worthy of note that these elements arrange themselves in the more stable grouping of the infusible, rather than the fusible anilide, which is less stable.

(*c*) When concentrated hydrochloric acid is added to the dianil the yellow color of the latter changes from yellow to white. If the acid is filtered off at once, and the residue washed with cold water, the yellow color reappears. If, however, the dianil is boiled with the acid for about an hour, the insoluble residue remains white after the acid is completely removed, and when crystallized from alcohol it forms slender, white needles. These are crystals of the anil described by Remsen and Coates.[1] In the hydrochloric acid solution there is some aniline hydrochloride. This reaction is to be represented by the equation,



$$C_6H_4\left\langle\begin{matrix}C = N.C_6H_5\\ SO_2\end{matrix}\right\rangle N.C_6H_5 + H_2O + HCl = C_6H_4<\begin{matrix}CO\\ SO_2\end{matrix}>N.C_6H_5 + C_6H_5NH_2.HCl.$$

It was mentioned above that some of this anil is always formed during the action of phosphorus oxychloride on the anilides. In the light of the above reaction its presence is explained.

Action of Phosphorus Pentachloride on the Infusible Anilide.

When the infusible anilide is added slowly to a heated solution of phosphorus pentachloride in chloroform, reaction sets in at once, and generally the solution changes to a light

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[1] *Loc. cit.*

yellow color. Usually about twice as much of the pentachloride as of the anilide is necessary to effect complete solution of the latter. In the first experiment tried, 2.5 grams of the pentachloride were used to 1 gram of the anilide, and the heating was continued only as long as was necessary to effect complete solution of the anilide. On cooling, radiating tufts of fine, white needles separated, completely filling the liquid. More chloroform was added, and the heat applied till all the needles were dissolved. But the needles did not separate again even when most of the chloroform had evaporated. The last traces of chloroform were then driven off by heating gently for some time, and the yellow, viscous residue was treated as a brown residue from the experiment with the oxychloride. Some of the anil was found present, though the chief product was the yellow dianil. The final products of this reaction are the same as those formed by the action of phosphorus oxychloride on the infusible anilide.

This experiment was repeated under the same conditions as before, and under varied conditions, though always without obtaining the fine white needles. The final products were the same each time.

From the results of these experiments it will readily be seen that it is possible to pass from the fusible anilide to the infusible anilide, by passing first to the yellow dianil and then, by boiling this with glacial acetic acid or an alcoholic solution of potassium hydroxide, to the infusible anilide.

Again, from the dianil one can obtain the anil by boiling with concentrated hydrochloric acid. And since the anil, when boiled with aniline, passes over to the fusible anilide, it is therefore possible to pass in the opposite direction, from the infusible to the fusible anilide.

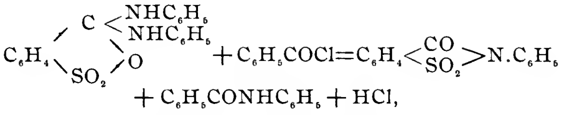
The Action of Benzoyl Chloride on the Infusible Anilide.

Five grams infusible anilide were boiled with an excess of benzoyl chloride until it dissolved. The excess of the benzoyl chloride was removed as completely as possible by distillation under diminished pressure, and the residue boiled with water. After this water had become cold, and without separating it from the insoluble residue, sodium carbonate was added to alkaline reaction and the vessel was heated gently on the water-bath to about 60° C. This solution was then poured off from the undissolved residue, and acidified, when benzoic acid was precipitated.

The residue insoluble in sodium carbonate solution was then dissolved in alcohol and boiled with animal charcoal. From this solution plates of a dirty yellow color separated. These, when purified by repeated recrystallization, became white, and assumed the acicular habit, melting sharply at 190°.5 (uncorr.). They proved to be the anil.

The mother-liquor from the above was then evaporated to dryness and the residue boiled with about 750 cc. water, and this water, while still hot, was drawn off from the part insoluble in the water, which had melted to a brown oil. By repeatedly boiling this residue with water almost all of it was finally dissolved. From this water on cooling, a white precipitate was deposited. When crystallized from alcohol, this forms small globular-shaped tufts of white needles, but these have not yet been identified, partly from lack of material, partly from lack of time.

From the water filtrate from this white precipitate, after evaporating to a very small volume, a small quantity of benzanilide was obtained, which was identified by its melting-point, crystal form, and by comparison with a specimen of benzanilide. The equation,



$$C_6H_4\left\{\begin{matrix} C<^{NHC_6H_5}_{NHC_6H_5} \\ >O \\ SO_2 \end{matrix}\right. + C_6H_5COCl = C_6H_4<^{CO}_{SO_2}>N.C_6H_5 + C_6H_5CONHC_6H_5 + HCl,$$

represents the reaction so far as yet understood.

A second experiment gave the same results as the one just described. No trace of the product mentioned by Remsen and Kohler,[1] as giving rise to the infusible anilide on addition of aniline, was obtained in either case. It is possible that this product might be isolated by keeping the temperature as low as possible during the reaction.

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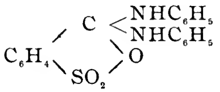
[1] This JOURNAL, 17, 342.

From the results obtained in this investigation it is clear that the two aniline residues are intact in the infusible anilide. This fact, together with the further fact that this anilide is derived only from the liquid, or unsymmetrical, chloride, by the action of aniline, leaves but little if any doubt that the structure of the anilide is correctly represented by the formula,

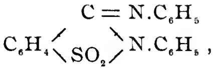


first proposed by Remsen and Coates.[1]

Summary.

The results arrived at in this investigation may be briefly summarized as follows:

1. Orthosulphobenzodianil, having the structure represented by the formula,



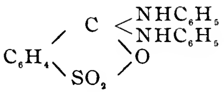
is obtained by the action of phosphorus oxychloride or phosphoric anhydride on either anilide, and by the action of phosphorus pentachloride on the infusible anilide.

2. The infusible anilide is regenerated from this dianil on boiling the latter with glacial acetic acid or with alcoholic potash.

3. The anil of orthosulphobenzoic acid is obtained by boiling this dianil with concentrated hydrochloric acid.

4. Benzoyl chloride acts on the infusible anilide, forming benzanilide and the anil of orthosulphobenzoic acid.

5. The two aniline residues are intact in the infusible anilide, and this anilide has the structure represented by the formula,



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[1] *Ibid*, 17, 320.

VI.—ORTHOCYANBENZENESULPHONIC ACID.

By Ira Remsen and W. J. Karslake.

The object of the work described below was to investigate the substance first obtained by Chambers in this laboratory as a product of the action of aqueous ammonia on the chlorides of orthosulphobenzoic acid, and supposed to be the ammonium salt of orthocyanbenzenesulphonic acid, $C_6H_4<\substack{CN \\ SO_2ONH_4}$, formed from the unsymmetrical chloride, in the same way that the ammonium salt of orthocyanbenzoic acid, $C_6H_4<\substack{CN \\ COONH_4}$, is formed from phthalyl chloride, as shown by Hoogewerff and Van Dorp.[1]

Preparation of Ammonium Orthocyanbenzenesulphonic Acid.

As the result of a large number of experiments the following method was finally adopted: 30 grams of the mixed chlorides prepared according to the directions of Remsen and McKee,[2] were dissolved in about 125 cc. ether and placed in a 500 cc. separating-funnel. Finely crushed ice was added and the whole shaken. About 100 cc. of the ice-cold water was now added and then dilute ammonia (1 : 5) in small portions at a time, care being taken to shake thoroughly after each addition until a slight excess remained after shaking for about two minutes. Meantime crushed ice was frequently added so that there was always some present. The water solution was now drawn off, washed once or twice with ether, filtered, and evaporated to crystallization upon the water-bath. 9 grams of impure ammonium orthocyanbenzenesulphonate were obtained, which is a yield of 30 per cent. Generally, however, the yield obtained by this method in later experiments was from 20 to 25 per cent. A word should also be said in regard to the crystallization of solutions from which the ammonium orthocyanbenzenesulphonate is to be obtained. At first the ammoniacal water solution was evaporated upon the water-bath to small bulk, so that, upon cooling, large quantities of ammonium chloride and the ammonium salt of benzoic sulphinide separated out with the ammonium ortho-

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[1] Rec. Trav. chim., **11**, 84; **12**, 12; **13**, 13.

[2] See p. 794.

cyanbenzenesulphonate. The mass thus obtained, after being drained by the aid of the suction-pump, was treated in a beaker with small quantities of cold water which dissolved the ammonium chloride and the ammonium salt of benzoic sulphinide much more rapidly than it did the compact nodules of the ammonium orthocyanbenzenesulphonate. At its best, however, this is a poor method of separation, although at times, even later, it was found advantageous to resort to it. The method of treating the well-drained and perfectly dry mass with absolute alcohol, filtering from the undissolved ammonium chloride and evaporating to crystallization, was also tried, but did not give satisfactory results. It was found that the best method consists in evaporating the solution to such a concentration that crystallization begins only after the perfectly cold solution has stood for a few hours. It seems that some time is required for the ammonium orthocyanbenzenesulphonate to arrange itself in crystalline form, that it has a tendency to form supersaturated solutions. It was frequently noticed that, if the solution was too concentrated, the ammonium chloride and the ammonium salt of benzoic sulphinide would separate first, while, if the same solution was not so concentrated, the ammonium orthocyanbenzenesulphonate separated first. As thus obtained, however, by the above described methods, the salt is still very impure, being contaminated with a quantity of some chlorine compound from which it is extremely difficult to separate it. Although it was taken for granted that this impurity was ammonium chloride, and, indeed, in many cases there can be no doubt that ammonium chloride was present, still a further study in regard to this point seems desirable in order to find out if *only* ammonium chloride is present. After a large number of experiments it was found that alternate recrystallizations from absolute alcohol and from water furnished the salt in pure condition, although, even by this method, at least 5 or 6 crystallizations were required. Repeated recrystallization from absolute alcohol alone gives good results. As thus obtained the salt crystallizes from alcohol in beautiful transparent needles arranged in rosettes, while from water it separates in botryoidal masses composed of radiating, transparent needles.

It is insoluble in ether and chloroform, very soluble in water and hot alcohol, but much less so in cold alcohol, from which it crystallizes best. Upon comparing some of this salt with some previously obtained by Chambers it was found to be identical with it. Of the crystals,

I. 0.2014 gram gave 0.2376 gram $BaSO_4$ = 16.11 per cent. S.

II. 0.1988 gram gave 25.80 cc. nitrogen at 24° C., and 762.9 mm. = 14.58 per cent. N.

III. 0.2125 gram gave 0.2490 gram $BaSO_4$ = 16.10 per cent. S.

	Calculated for $C_6H_4<\begin{matrix}CN\\SO_2ONH_4\end{matrix}$		Found. I	II.	III.
$C_7H_8O_3$	140	70.00			
S	32	16.00	16.20	....	16.09
N_2	28	14.00	....	14.58	....
	200	100.00			

Analyses I. and II. are those of Mr. Chambers. The nitrogen was determined by the absolute method and the sulphur by the Carius method.

In several experiments in which solutions were evaporated to crystallization in order to obtain the ammonium orthocyanbenzenesulphonate, large, beautiful, transparent plates separated which became dull and opaque after standing for some time in the air. They were first obtained from a solution of the nearly pure salt which had been put in a desiccator over concentrated sulphuric acid for evaporation and crystallization in the cold. They were again obtained from a solution of 0.8 gram pure salt, which had been dissolved in 20 cc. of water and boiled with a return-condenser for 2½ hours. Lastly, they were obtained, and then in large quantity, upon evaporating the first water solution in order to obtain the first deposit of ammonium orthocyanbenzenesulphonate. The plates were mechanically separated, and dissolved in water for recrystallization. From this solution ammonium orthocyanbenzenesulphonate in its well-known form separated, and not the plates. Of the few plates which were obtained in the first observation analyses were made:

I. 0.4657 gram gave 0.5600 gram $BaSO_4$ = 16.52 per cent. S.
II. 0.4060 gram gave 0.4735 gram $BaSO_4$ = 16.02 per cent. S.

They suffered no loss upon heating to 190° C. The sulphur determinations were made by the Liebig method. Repeated experiments under apparently the same and other conditions were made, in order to obtain enough of the salt for a complete analysis, but the plates were not obtained again.

From these few observations, and from the analyses, it would seem, however, that they were another crystalline form of ammonium orthocyanbenzenesulphonate, but further study upon this point is required.

Sodium Salt,  $C_6H_4<\begin{smallmatrix}CN\\SO_2ONa\end{smallmatrix}+H_2O$.—This salt has already been described by Jesurun,[1] who made it by treating orthocyanbenzenesulphone chloride with sodium hydroxide. It is also formed by treating one molecule of the ammonium salt with one molecule of sodium hydroxide and evaporating to crystallization upon the water-bath. It crystallizes from concentrated solutions in large, transparent, prismatic plates containing one molecule of water of crystallization.

Of the crystals,

I. 0.2097 gram gave 0.2227 gram $BaSO_4$=14.59 per cent. S.
II. 0.1134 gram gave 0.1193 gram $BaSO_4$=14.45 per cent. S.
III. 0.2228 gram gave 0.2372 gram $BaSO_4$=14.62 per cent. S.
IV. 0.1920 gram lost 0.0158 gram at 150°=8.23 per cent. H_2O, and gave 0.0613 gram Na_2SO_4=10.34 per cent. Na.

	Calculated for  $C_6H_4<\begin{smallmatrix}CN\\SO_2ONa\end{smallmatrix}+H_2O$.		Found.			
			I.	II.	III.	IV.
$C_7H_4NO_3$	150.0	67.27	....	....	....	....
S	32.0	14.35	14.59	14.45	14.62	....
Na	23.0	10.31	....	....	....	10.34
H_2O	18.0	8.07	....	....	....	8.23
	223.0	100.00				

There was no further loss in weight upon heating to 195° C. Analysis I. is that of Mr. Chambers of the salt which he made.

Potassium Salt,  $C_6H_4<\begin{smallmatrix}CN\\SO_2OK\end{smallmatrix}$.—This salt is made by treating the ammonium salt with the calculated quantity of

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[1] Ber. d. chem. Ges., **26**, 2288.

potassium hydroxide. It is much less soluble than the corresponding sodium salt, and crystallizes from moderately dilute solutions in small, transparent needles radiating from a common centre. In habit it is not unlike the ammonium salt. It is very easily prepared. Of the crystals,

I. 0.2128 gram gave 0.0830 gram K_2SO_4=17.61 per cent. K.

II. 0.2295 gram gave 0.0903 gram K_2SO_4=17.66 per cent. K.

III. 0.2550 gram gave 0.2824 gram $BaSO_4$=15.22 per cent. S.

	Calculated for $C_6H_4<^{CN}_{SO_2OK}$.		Found. I.	II.	III.
$C_7H_4NO_3$	150.0				
S	32.0	15.16	....	....	15.22
K	39.1	17.67	17.61	17.66	....
	221.1				

The salt lost nothing in weight when heated to 190° C.

Barium Salt, $\left(C_6H_4<^{CN}_{SO_3}\right)_2 Ba + 2H_2O$. — Considerable difficulty was experienced in preparing this salt. There seemed to be a strong tendency on the part of the nitrile group to undergo saponification, thus giving rise to the formation of mixtures. The analyses given below are of some crystals which were used in the attempt to prepare the free acid. These were obtained by treating the ammonium salt with only three-fourths of the calculated quantity of barium hydroxide, and gently heating upon the water-bath until no more ammonia was given off. It was then filtered, evaporated to small bulk, and crystallized from dilute alcohol. It separated in little tufts composed of white silky needles. They were washed with alcohol to free them from any of the ammonium salt which might be present. Of the air-dried crystals,

I. 0.1065 gram gave 0.0459 gram $BaSO_4$ = 25.37 per cent. Ba.

II. 0.1882 gram gave 0.0812 gram $BaSO_4$ = 25.56 per cent. Ba.

III. 0.1006 gram lost 0.0070 gram at 135° C = 6.96 per cent. H_2O, and gave 0.0438 gram $BaSO_4$ = 25.59 per cent. Ba.

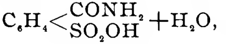
	Calculated for $(C_6H_4<^{CN}_{SO_3})_2Ba+2H_2O$.		Found. I.	II.	III.
$C_{14}H_8N_2O_6$	300.0	....	....	....	....
Ba	137.0	25.51	25.34	25.36	25.59
$2H_2O$	36.0	6.71	....	....	6.96
	473.0				

As stated above, this salt was used in the attempt to prepare free orthocyanbenzenesulphonic acid. It was dissolved in water, and dilute sulphuric acid carefully added until no further precipitation of barium sulphate took place. It was then filtered, evaporated to a small bulk on the water-bath, and placed in a desiccator over sulphuric acid. A syrupy, transparent mass was obtained, which slowly solidified into very fine needles arranged in rosettes. These were then washed with ether containing a little alcohol, and finally with ether alone. They melted at 181°–182° uncorrected. Of the crystals,

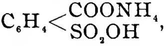
0.1880 gram gave 0.2037 gram $BaSO_4$=14.91 per cent. S.

The formulas,

$$C_6H_4<\begin{matrix}CN\\SO_5OH\end{matrix}+2H_2O,$$

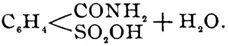


$$C_6H_4<\begin{matrix}CONH_2\\SO_2OH\end{matrix}+H_2O, \text{ and}$$



$$C_6H_4<\begin{matrix}COONH_4\\SO_2OH\end{matrix},$$

all agree for 14.62 per cent. S by theory. Upon comparison, however, of its melting-point and method of crystallization with the orthobenzaminesulphonic acid described by Fahlberg and Barge,[1] and by Jesurun,[2] there can be little doubt of the identity of the two substances. Therefore its formula is probably



$$C_6H_4<\begin{matrix}CONH_2\\SO_2OH\end{matrix}+H_2O.$$

Not enough of the salt was obtained for a water determination. Other attempts were made to isolate the free acid by other methods but without success. Jesurun also failed to isolate it.

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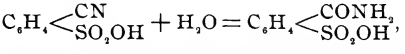
[1] Ber. d. chem. Ges., **22**, 759.

[2] *Loc. cit.*

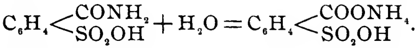
Transformation of Orthocyanbenzenesulphonic Acid into Orthobenzaminesulphonic Acid.

This transformation is most easily effected by boiling with excess of dilute alkalies. Hence it is, that in the preparation of the above described cyan salts, it is essential that not more than the calculated quantity of base should be used. In most cases thereaction proceeds in a normal manner according to the following equation:



$$C_6H_4<\genfrac{}{}{0pt}{}{CN}{SO_2OH} + H_2O = C_6H_4<\genfrac{}{}{0pt}{}{CONH_2}{SO_2OH},$$

and there stops, no further hydrolysis taking place to produce the corresponding ammonium salt as here represented:



$$C_6H_4<\genfrac{}{}{0pt}{}{CONH_2}{SO_2OH} + H_2O = C_6H_4<\genfrac{}{}{0pt}{}{COONH_4}{SO_2OH}.$$

Few salts, however, were obtained, to which no formulas could be assigned.

Ammonium Salt, $C_6H_4<\genfrac{}{}{0pt}{}{CONH_2}{SO_2ONH_4}$.—This salt has already been prepared by Fahlberg and Barge,[1] and described as crystallizing from alcohol in white needles which melt at 255°–256°. Jesurun[2] described it later as crystallizing from water in granular crystals containing 1 molecule of water of crystallization. These descriptions do not agree with the salt we obtained by boiling 3 grams of ammonium orthocyanbenzenesulphonate with dilute hydrochloric acid for eight hours with a return-condenser. On evaporating to dryness on the water-bath several times to drive off most of the hydrochloric acid, there were obtained, by crystallization from a water solution, thin, transparent needles which contained no water of crystallization and melted at 219°–220° uncorr. A sulphur determination was made by the Liebig method. Of the crystals,

0.1918 gram gave 0.2058 gram $BaSO_4 = 14.74$ per cent. S.

The formula $C_6H_4<\genfrac{}{}{0pt}{}{CONH_2}{SO_2ONH_4}$ requires 14.68 per cent. S.

Potassium Salt, $C_6H_4<\genfrac{}{}{0pt}{}{CONH_2}{SO_2OK} + H_2O$.—This salt was made by boiling, with a return-condenser, 3 grams of the am-

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[1] *Loc. cit.*

[2] *Loc. cit.*

monium cyan salt with excess (3.5 grams) of dilute potassium hydroxide for five hours.

From a moderately concentrated solution there separated transparent, monoclinic (?) prisms, which were once recrystallized from water. Of these crystals,

I. 0.2409 gram lost 0.0169 gram below 135° = 7.01 per cent. H_2O.

II. 0.1727 gram lost 0.0119 gram below 135° = 6.88 per cent. H_2O, and gave 0.0588 gram K_2SO_4 = 15.28 per cent. K.

III. 0.1103 gram gave 0.0376 gram K_2SO_4 = 15.32 per cent.

	Calculated for $C_6H_4<\substack{CONH_2\\SO_2OK} + H_2O$.	Found.		
		I.	II.	III.
K	15.21	...	15.18	15.32
H_2O	7.00	7.01	6.88	....

There was no further loss in weight upon heating to 200° C.

Sodium Salt, $C_6H_4<\substack{CONH_2\\SO_2ONa} + 2H_2O$. — This salt was made just as the corresponding potassium salt by using sodium hydroxide, and was found to crystallize in transparent prismatic plates from moderately concentrated solutions. Of the crystals,

I. 0.3653 gram lost 0.0509 gram below 150° = 13.95 per cent. H_2O, and gave 0.1002 gram Na_2SO_4 = 8.89 per cent Na.

II. 0.1894 gram lost 0.0263 gram below 150° = 13.88 per cent. H_2O, and gave 0.0533 gram Na_2SO_4 = 9.12 per cent. Na.

	Calculated for $C_6H_4<\substack{CONH_2\\SO_2ONa} + 2H_2O$.	Found.	
		I.	II.
Na	8.88	8.89	9.12
$2H_2O$	13.85	13.95	13.88

No further loss in weight occurred on heating to 195° C.

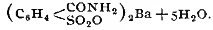
Barium Salt, $\left(C_6H_4<\substack{CONH_2\\SO_2O}\right)_2 Ba + 5H_2O$.—This salt was made by boiling the ammonium cyan salt for five hours with a large excess of barium hydroxide. The excess of barium hydroxide was then precipitated with carbon dioxide and the filtered solution evaporated to small bulk. It was found that crystallization did not easily take place even from syrupy solutions, while from dilute alcohol the salt separated in white, arborescent needles arranged in rosettes. Of these crystals,

I. 0.2490 gram gave 0.0928 gram $BaSO_4 = 21.90$ per cent. Ba.

II. 0.3375 gram lost 0.0477 gram below 140° = 14.13 per cent. H_2O, and gave 0.1262 gram $BaSO_4 = 21.98$ per cent. Ba.

III. 0.2169 gram gave 0.0812 gram $BaSO_4 = 22.01$ per cent. Ba.

IV. 0.2596 gram lost 0.0386 gram below 150° = 14.44 per cent. H_2O.

	Calculated for	Found.			
	 $(C_6H_4<^{CONH_2}_{SO_2O})_2Ba+5H_2O$.	I.	II.	III.	IV.
Ba	21.85	21.90	21.98	22.01	....
$5H_2O$	14.35	....	14.13	....	14.44

No further loss in weight took place upon heating to 195° C.

A calcium salt was made in the same manner as the corresponding barium salt, and was found to crystallize in transparent needles. An analysis gave 10.34 per cent. calcium and 19.08 per cent. water lost at 185° C. No formula was found to agree with these results.

A basic lead salt was also made for which no formula could be calculated. It was made by heating the ammonium cyan salt upon the water-bath with a large excess of freshly precipitated lead hydroxide until no more ammonia was given off, and then filtering. Upon cooling there separated crystals composed of white needles, arranged more or less in rosettes. The air-dried salt lost nothing upon heating to 190° and gave the following results:

I. 0.2379 gram gave 0.2068 gram $PbSO_4 = 59.34$ per cent. Pb.

II. 0.1658 gram gave 0.1440 gram $PbSO_4 = 59.33$ per cent. Pb.

III. 0.1860 gram gave 0.1614 gram $PbSO_4 = 59.29$ per cent. Pb.

IV. 0.2735 gram gave 0.1634 gram $PbSO_4 = 6.31$ per cent. S.

V. 0.2772 gram gave 0.1634 gram $PbSO_4 = 6.22$ per cent. S.

Analysis III. was of a second preparation of the salt. The lead was determined by ignition of the salt with addition of sulphuric acid and the sulphur by the Carius method.

Transformation of Orthocyanbenzenesulphonic Acid into Orthosulphobenzoic Acid.

This transformation was effected by heating 2 grams of the ammonium cyan salt with 15 cc. of hydrochloric acid (2 : 1) in a sealed tube for six or seven hours at 190° C. On evaporating to crystallization the characteristic rhomboidal plates of the acid ammonium salt of orthosulphobenzoic acid separated. Of these crystals,

0.4529 gram gave 0.4827 gram $BaSO_4 = 14.64$ per cent. S.

The formula, $C_6H_4<\substack{COOH \\ SO_2ONH_4}$ requires 14.61 per cent. sulphur.

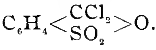
To further identify this salt it was treated with a slight excess of potassium hydroxide, then acidified with hydrochloric acid and allowed to crystallize. The well-known orthorhombic plates of the acid potassium salt of orthosulphobenzoic acid were obtained, of which,

0.2839 gram gave 0.1032 gram $K_2SO_4 = 16.33$ per cent. K.

The formula, $C_6H_4<\substack{COOH \\ SO_2OK}$ requires 16.35 per cent. potassium.

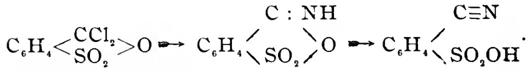
Conclusion.

From this investigation it is clear that orthocyanbenzenesulphonic acid is formed as one of the products of the action of ammonia upon the mixed chlorides of orthosulphobenzoic acid. Moreover, its formation can hardly be explained upon any other hypothesis than that it is derived from a chloride possessing the unsymmetrical formula



$$C_6H_4<\substack{CCl_2 \\ SO_2}>O.$$

It, therefore, appears highly probable that by the action of ammonia an imide is first formed which, being unstable under the existing conditions, passes over by intra-molecular change into orthocyanbenzenesulphonic acid, thus:



$$C_6H_4<\substack{CCl_2 \\ SO_2}>O \rightarrow C_6H_4\substack{\diagup C:NH \diagdown \\ \diagdown SO_2 \diagup}O \rightarrow C_6H_4\substack{\diagup C\equiv N \\ \diagdown SO_2OH}.$$

Johns Hopkins University,
November, 1896.

Contribution from the Sheffield Laboratory of Yale University.

XLVI. ON THE NON-EXISTENCE OF TWO ORTHOPHTHALIC ACIDS.

BY H. L. WHEELER.

An article on the existence of two orthophthalic acids by W. T. H. Howe, formerly of this laboratory, appeared in the May number of this Journal (page 390). The work described in that article has been repeated, as far as its character would permit, and *it has been found to be impossible to prepare the so-called new or β-phthalic acid by the methods given there.* Every attempt to prepare an acid melting at 184°, *i. e.*, the so-called new or β-acid, from pure materials, resulted only in the formation of the well-known orthophthalic acid melting at or near 203°. Not only has it been found that the methods given by Howe for the preparation of the alleged β-phthalic acid give pure ordinary phthalic acid, but also that his entire experimental work with reference to the new acid, as far as it has been found possible to carry it, is absolutely incorrect.

It will also be shown that the errors are not confined to the experimental work, but that the calculated figures for several analytical results are wrong, and, that in two of these cases, although the analyses of the α- and β- derivatives agree with each other, they do not agree with the correctly calculated figures. Again, statements of Ador and Graebe have not been accurately quoted, and this would lead the reader to incorrect conclusions. Too much stress has been laid on the variation of melting-points of phthalic acid obtained by different observers, since Ador has shown that the melting-points observed by previous investigators were low owing to their having obtained impure samples of the substance. Ador does not state that phthalic acid obtained by "boiling" the anhydride with water melted at 203°, but that by repeated recrystallizations from water such an acid was obtained. Howe further mis-states Ador's work when he says "the acid precipitated from the salts apparently does melt at 180°." What Ador really says is that the *impure* acid precipitated from its salts melts at that temperature. The following is Ador's statement on this subject: "Bei dieser Gelegenheit muss ich die Angaben der Lehrbücher über den Schmelzpunkt der Phtalsäure (182°) corrigiren. Unreine Phtalsäure schmilzt sogar noch niedriger, bei etwa 170°, durch Ausfällen der Salze dargestellte allerdings bei circa 180°; aus dem reinen Anhydrid durch Wasser gewonnen, mit Thierkohle gereinigt und wiederholt umkrystallisirt, schmelzen ganze Krystalle bei 213°, ihr Pulver bei 203° C.''

The next statement to be corrected is that Graebe assumed that 184°, the melting-point given by Lossen, was the correct one for phthalic acid. What Graebe said was that between Lossen's statement and that of Ador, the former was the more correct, *i. e.*, "Lossen's Angabe is die richtigere," since as Graebe goes on to state "Gewöhnlich findet man den Schmelzpunkt etwas höher, bei 190° bis 195°." Graebe then calls attention to the fact that large crystals of phthalic acid, which form according to Ador, melts the highest, could be melted even below 184° if heated for some time.[1] [2]

After giving the above incorrect statements in the introduction to his article, Howe further remarks that "very probably certain low melting-points have been due to an admixture of an acid salt which is precipitated together with

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[1] It is well known that the melting-point of orthophthalic acid is really its decomposition-point, *i. e.*, the acid loses water and passes into the anhydride, the melting-point of the anhydride being about 128°. It would be expected that this decomposition might be produced at different temperatures according to the length of time the substance is heated, according to the quantity of substance taken and according to the condition, both physical and chemical, of the sample. Such indeed has been found to be the case. It is therefore not surprising that, if phthalic acid be heated above 128°, different melting-points are obtained under varying conditions.

[2] The author is indebted to Professor Remsen for calling his attention to the following note (This JOURNAL, **3**, 30.) on the melting point of phthalic acid, which was not known to the author when the above was written. "The fusing point of phthalic acid has been the subject of considerable discussion, the last statement bearing upon it having come from E. Ador (Annalen der Chemie, **164**, 239). Ador says tha crystallized phthalic acid melts at 213° and the powder of the same substance at 203° The discrepancies in the statements on record seems to be due to the fact that when the acid is heated, it is partly converted into its anhydride before its fusing point is reached. The presence of the anhydride tends to lower the fusing point, and this is the lower the more anhydride there is formed. If the acid is heated slowly, or if it be used in the form of powder more anhydride is formed and the fusing point is lower. Some special experiments were made with the pure acid to test the correctness of this view. Small quantities were heated in U-tubes placed in paraffin baths at the temperature of 140° and 170°. In both cases anhydride was formed and the fusing point of the acid considerably lowered. Under exceptional conditions the fusing point of pure phthalic acid may be observed as high as 213°, but usually it will be found to vary considerably. To test the purity of the acid, it is advisable to make the anhydride and then crystallize this, when pure, from water.—I. R."

the acid under certain conditions of concentration," and on page 394 he again states that by acidifying concentrated alkaline solutions of phthalic acid a white crystalline precipitate is thrown down. "This is identical in appearance with the pure acid, but it melts at 175°–180°, and upon drying and extracting with alcohol a residue of an acid salt remains." This is also incorrect, because the writer has prepared the acid salt of phthalic acid and mixed it with varying proportions of the acid without observing that it produced such an effect on its melting-point. The acid salt itself did not melt below 270°. [Compare also Eighth Experiment below.]

EXPERIMENTAL WORK.

Attempts to Prepare the β-Acid by the First Method.

Howe states that "to prepare the pure β-acid, the anhydride is dissolved in cold dilute sodium hydroxide, the solution cooled to 0°, slowly precipitated with hydrochloric acid and dried over sulphuric acid." The attempts to prepare the β-acid according to these directions were conducted as follows:

First Experiment.—Finely powdered phthalic acid anhydride[1] was dissolved in cold, very dilute sodium hydrate and filtered. During these operations the temperature of the solutions did not rise above $+5°$. It was then cooled in a freezing-mixture to $-3°$, and cold dilute hydrochloric acid was slowly and cautiously added in excess. During the neutralization the temperature of the solution did not rise above $+1°$. The solution was so dilute that after an excess of hydrochloric acid was added, no immediate precipitate separated, but, on standing, a well crystallized product was obtained in small amount. This was filtered, washed with ice-water and prepared for a melting-point determination by drying, in the air, and then pulverizing the material. This specimen, according to Howe, should melt at 184°, but, when the heating was started at an ordinary temperature, it showed absolutely

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[1] Phthalic acid anhydride, manufactured by H. Trommsdorff, of Erfurt, Germany, was used in these experiments.

no signs of melting below 193°, finally melting with effervescence at 200°.[1]

Another portion of the same material was taken, and the heating was started at 180°; it then melted at 203° and showed no signs of melting below 197°.

Another portion dried over sulphuric acid gave a melting-point of 206° when the heating was started at 197°. Finally, another portion of this material was placed in the melting-point apparatus at 75°, heated rapidly up to 128°, and then half an hour was taken to heat the material up to 184°; even then no trace of melting could be observed below 190°, when it slowly began to melt, and at 193°.5 effervescence took place.

These melting-points show that nothing but ordinary phthalic acid was obtained in this experiment, and that the melting-point of the acid varies according to the length of time employed in heating.

Second Experiment.—Finely powdered phthalic acid anhydride (4.0 grams) was dissolved in a five per cent. solution of sodium hydrate (4.0 grams of sodium hydrate) at + 6°. The solution was cooled to — 4° and slowly precipitated by adding a 20 per cent. solution of hydrochloric acid *drop by drop*. The neutralization was conducted at temperatures ranging from — 4° to + 1°. The solution was made stongly acid and then allowed to warm up to + 6°. It was filtered, washed with ice-water, and one portion dried in the air, the other over sulphuric acid. The portion dried in the air melted at 201°, while that dried over sulphuric acid, the melting-point being determined by a different observer, melted at 200°. There-

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[1] The melting-points given in this paper were taken in the usual manner unless otherwise stated. The contents of the melting-point flask were 78.5 cc. and in this flask 37 cc. of concentrated sulphuric acid were placed. The thermometer was made of normal glass. It was obtained from Drs. Bender and Hobein, of Munich, and it was graduated in degrees ranging from — 29° to 360°, the 200° mark was 1.4 of a degree too low according to a "Prüfungs-Bescheinigung," which accompanied the thermometer. The thermometer was further tested by taking a melting-point of paranitroacetanilide. This substance was prepared from the base and crystallized from strong alcohol. The second and third crystallizations began to show signs of melting at 207°.5, and then melted together at 208°.5, as near as could be judged. The generally accepted melting-point of paranitroacetanilide is 207°. This result therefore confirms the statement in the "Prüfungs-Bescheinigung." *The correction has not been applied to the melting-points given in this article.*

fore in this experiment also nothing but ordinary phthalic acid was obtained.

Third Experiment.—In this experiment 20 grams of anhydride were dissolved in 30 grams of sodium hydrate in 170cc. of water, and the solution was precipitated with 20 per cent. hydrochloric acid without carefully cooling. The product thus obtained was dried in the air and portions placed in two capillary tubes, one of which had a diameter of 1.0 mm., while the other was oval-shaped and measured 3.0 mm. by 2.0 mm. The portion in the smaller tube melted at 193°, while that in the larger tube melted at 197°, although they were side by side in the melting-point apparatus.

Again portions of the same material were placed in two tubes as follows: One tube was 1 mm. in diameter, the other 3.0 mm. by 4.0 mm. These tubes were placed side by side and the melting-points determined as 198°, at which temperature the substance in the smaller tube melted with effervescence. The heating was then discontinued, and not until the effervescence in the one tube had almost ceased, did the other begin.

This experiment shows that nothing but ordinary phthalic acid was obtained, and that the melting-point of this acid depends not alone on the time taken in heating, but that it also may vary with the amount of substance used.

Fourth Experiment.—In this experiment a much stronger solution of sodium hydrate was used to dissolve the anhydride than that used in the previous cases. The solution cooled to 0° was then very slowly precipitated with hydrochloric acid. A product was thus obtained, which, when dried over sulphuric acid, melted in powdered form at 204°, the crystals at 205°. This material was therefore the ordinary acid, and since no evidence was found that the anhydride gave anything else when treated according to Howe's directions, further attempts to prepare the so-called β-acid by this method were abandoned.

Attempts to Prepare the β-Acid by the Second Method.

Howe's second method for preparing the "new acid" is as follows: "The α-acid is converted into the β-isomer by boiling with a 30 per cent. sodium or potassium hydroxide solution for four or five hours, then precipitating and drying as mentioned above."

Fifth Experiment.[1]—35 grams of the ordinary or "α-acid," which had been obtained by the previous attempts to prepare the "β-acid" were boiled with a 30 per cent. solution of sodium hydroxide, the calculated quantity of sodium hydroxide to convert the acid into its sodium salt being previously added. The boiling was continued without interruption for five hours and a half. A portion of the solution, which on cooling became semi-solid, was then taken, diluted with 3 to 4 volumes of water and cooled in a freezing-mixture of ice and concentrated hydrochloric acid. The solution was then neutralized with 20 per cent. hydrochloric acid, so carefully that the temperature did not rise to 0° during the entire operation. A well crystallized product separated soon after an excess of acid was added. This was filtered, washed with ice-water and dried by pressing on paper and exposure to the air at ordinary temperature. It then melted sharply from 203°-4°, and was therefore pure ordinary phthalic acid.

Further attempts to prepare the compounds melting at 184° and described as β-phthalic acid from pure phthalic acid or its anhydride were deemed useless, and experiments along these lines were therefore abandoned. It seemed of interest, however, to see if pure phthalic acid was affected by strong acids, since Howe states that "strong acids partially change the α- into the β-acid."

Sixth Experiment.—A portion of the pure phthalic acid, melting at 203°, from the fifth experiment was digested with concentrated hydrochloric acid for an hour at ordinary temperature; water was then added without trying to avoid the rise in temperature that was produced. The product when dried showed absolutely no appreciable change in the melting-point.

Seventh Experiment.—In this experiment the pure phthalic acid was dissolved in a large excess of concentrated sulphuric

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[1] In the performance of this experiment the author was assisted by Prof. H. L. Wells, to whom he wishes to express his thanks.

acid at ordinary temperature, in which it is readily soluble; water was then poured into the acid, when the solution of course boiled, and, on cooling, a well crystallized product was obtained, and, when dried, melted unaltered at 203° to 205°. Strong acids therefore do not "partially" change ordinary pure phthalic acid into a "β-acid."

Eighth Experiment.—A portion of the semi-solid mass from the fifth experiment, which consisted of the sodium salt of phthalic acid, suspended in a strong solution of sodium hydrate, and in which it is difficultly soluble, was treated directly with strong hydrochloric acid; this brought about solution and then gave a precipitate of the acid salt as stated, but the precipitate thus produced remained unaltered even at the boiling-point of sulphuric acid, while it is stated by Howe that this precipitate melts from 175° to 180°.

The Analytical Results.

Howe's results obtained with the aniline salts are remarkable, as both agree with an error in calculation for carbon that is almost two per cent. too low. They are as follows:

	Calculated for $C_{20}H_{20}N_2O_4$.		Found.	
	Correct.	Incorrect.	α-Salt.	β-Salt.
C	68.18	66.30	65.92	66.01
H	5.68	5.53	5.72	5.63

In the case of the brucine salts the error is even greater. Here the analyses of the two products agree only with each other, and the determinations found are over four per cent. too high.

	Calculated for $C_{54}H_{58}N_4O_{12}$.		Found.	
	Correct.	Incorrect.	α-Acid (?).	β-Acid (?).
C	67.92	78.81	72.22	72.35
H	6.07	6.52	6.82	6.89

Since there is so great a variation in the case of the carbon between the theory as given and the analyses as reported, it is possible that a typographical error has occurred and each of the figures 8 should be read as a 2. This seems possible, since a typographical error in the references occurs on the first page of the article, where a figure 2 has been printed as a 9. The reference in question is number 3, and instead of Ber.

d. chem. Ges., **19**, 579, should read Ber. d. chem Ges., **12**, 579.

The error in the case of the α-naphthylamine salts is about one per cent. for carbon, and seems again to be typographical since both preparations agree with the correct theory.

	Calculated for $C_{28}H_{24}N_2O_4$.		Found.	
	Correct.	Incorrect.	α-Salt.	β-Salt.
C	74.34	73.34	74.22	74.15
H	5.31	5.21	5.42	5.51

Conclusion.

Since it has been shown in this article that the β-phthalic acid does not exist, or rather cannot possibly be prepared from pure materials by the methods given by Howe in his article, it follows that the number of derivatives described by him also can not be prepared by his methods, and it is naturally impossible to repeat the rest of his experimental work on the derivatives of the alleged new acid. If one removes the foundation of a piece of work, naturally the whole structure falls to the ground. It may be said in conclusion that the results of the present investigation show that the methods given by Howe, when carefully followed, do not give any clue whatever to the real nature of the compounds which he prepared. The work described in this article was undertaken at the request of Prof. H. L. Wells.

NEW HAVEN, OCTOBER, 1896.

Contributions from the Laboratory of Analytical Chemistry of the University of Michigan.

A PURE CARBIDE OF IRON.

BY E. D. CAMPBELL.

The first definite carbide of iron described was that obtained by Sir F. Abel and Mr. Deering,[1] who isolated it by acting upon thin sheets of annealed steel with a mixture of dilute sulphuric acid and potassium dichromate. The results of analyses of residues thus obtained, while not agreeing very closely, led the authors to assign the formula Fe_3C to the carbide existing in annealed steel. Later Dr. Müller,[2] by the action of dilute sulphuric acid upon annealed steel recov-

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[1] Proceedings Inst. Mech. Eng., 1885, p. 30.

[2] Stahl und Eisen, No. 5.

ered about one-half of the carbon in the steel in the form of a carbide, also agreeing approximately with the formula Fe_3C. Osmond and Werth,[1] by acting upon steel electrolytically in dilute hydrochloric acid solution, according to the method first proposed by Weyl, obtained a dark residue containing thin metallic plates, which they proved both microscopically and chemically to be identical with the carbide first isolated by Abel. The latest and most exhaustive work that has appeared was that by J. O. Arnold and A. A. Read.[2] These authors prepared five samples of steel of varying carbon content, and, after carefully annealing them, submitted them to electrolytic action in hydrochloric acid solution for varying lengths of time. The carbonaceous residue adhering to the bars was scraped off, and, after washing till free from ferrous chloride, was rinsed into a porcelain boat and subsequently burned in a stream of oxygen for the determination of carbon, the iron being determined in the residual ferric oxide. In this way the weight of steel dissolved in the different experiments varied from 3.466 grams to 10.238 grams, yielding residues weighing from 0.0697 gram to 0.8912 gram. The percentage of carbon in the residues obtained varied from 6.60 to 7.83 per cent., 6 out of 8 determinations lying between 6.60 and 6.97 per cent., the theoretical percentage of carbon for the compound Fe_3C being 6.67 with 93.33 per cent. of iron. These residues were described as varying in color from "dull grey, silver plates mixed with greyish-black powder" to "silver grey plates." The proportion of carbon in the residues varied from 71.31 to 94.90 per cent. of the total amount in the steel.

The following research was undertaken to determine if a purer carbide than any heretofore isolated could not be obtained, and whether a formula so simple as CFe_3 should be assigned to it. The steel used in the work was a sample of crucible cast steel containing 1.29 per cent. of carbon. This steel was rolled into bars 5 cm. wide and 1.5 cm. thick, then cut into lengths of 30 cm. These pieces were annealed in the following manner: The bottom of an ordinary assay muffle

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[1] Annales des Mines, 1885, Vol. 2.

[2] J. Chem. Soc., 1894, **65**, 788.

furnace was covered to the depth of 6 or 8 mm. with crushed coke. Upon this was placed sheet asbestos, then the bars were introduced. On top of the bars sheet asbestos was also placed, and the rest of the space in the muffle completely filled with a mixture of one part charcoal to five of wood ashes. The whole of the space in the front of the muffle was filled with this mixture and the door closed. The muffle was then brought to a bright red heat, the fires banked, and the whole allowed to cool slowly. At the end of sixty hours the bars were still warm.

The bars, after annealing, were freed from scale by grinding on an emery wheel, and were then cut into strips from 5 to 6 mm. in thickness. These strips were then cut in two, giving for the final pieces used in the work small bars about 15 cm. long, 15 mm. wide, and from 5 to 6 mm thick.

The electrolysis of the bars was carried on in a manner quite similar to that used by Arnold and Read, but with such modifications of the apparatus as were thought suited to the larger samples used in the work. Each bar was sawed near one end about half way through, thus practically making a small hook, by means of which the bar could be easily hung to a small platinum wire stirrup soldered to a copper wire hook about 10 cm. long. Twelve of these hooks with their attached bars were hung to a ring of heavy copper wire about 10 cm. in diameter, which was fastened to a large retort stand, and connected with the positive pole of 4 storage batteries, connected in series, and having an electromotive force of about 8 volts. The negative pole consisted of a small platinum cylinder suspended in a porous cup standing in the centre of the circle of bars.

An ammeter and resistance box were introduced into the circuit so that the current passing through the bars could at any time be easily read and controlled. The bars and porous cup, during the electrolysis, were nearly immersed in 4 per cent. hydrochloric acid (1 volume of hydrochloric acid, sp. gr. 1.20, to 12 of water) contained in a large beaker, about 2 liters being used each time.

The method of operating found most satisfactory was as follows: When the bars were hung in position a current of 1 ampere was started through the system, and allowed to act over night, usually about fifteen or sixteen hours. A small brown deposit, varying in amount, was noticed accumulating around the negative pole and, according to whether this was present in large or small amounts, the current would be found to have fallen to from 0.6 to 0.9 amperes. In the morning the bars were all removed from the acid and placed in a large dish of water. They were then taken and the residue adhering to the surface of the bars brushed off by rubbing with a small brush made by binding together a large number of strands of fine No. 28 pure aluminium wire. After the bars were brushed clean they were placed under water and allowed to remain until afternoon, when the system was again set up, fresh acid being used each day. An aluminium wire brush was used, as earlier work showed that a brush made of rubber or bristles was quickly cut by the sharp crystals, and the residue contaminated with organic material. The small pieces of aluminium, which were broken off by the vigorous rubbing necessary to remove the carbide, were easily removed by dissolving in potassium hydroxide.

When the carbide had been brushed from all of the bars it was collected in a small beaker, washed well by decantation with distilled water, then treated with warm 10 per cent. potassium hydroxide until all particles of aluminium were dissolved. The potassium hydroxide was then decanted, and the carbide again well washed with distilled water by decantation. During these latter decantations the material was thoroughly stirred, and the solution decanted before any very fine or light matter had time to settle. This was done until only a heavy, bright steel-gray powder remained in the beaker. This carbide was then thrown on a smooth lintless filter, washed with alcohol, then with ether, dried, weighed, and placed in bottles for further investigation.

The original weight of the twelve bars operated upon was 1352.3 grams. At the end of 29 electrolyses the weight was 776.5 grams, showing 575.8 grams of steel to have been dissolved. The actual weight of carbide recovered, not including what must have been lost in washing by decantation, to remove uncombined carbon, was 55.1 grams, or 9.66 per cent.

of the steel dissolved. Had all of the carbon in the steel been recovered as the carbide CFe_3, there would have been 19.35 per cent. of carbide. Thus the amount actually recovered was one-half that present in the steel. Part of the loss was undoubtedly due to a mechanical action in washing the carbide to insure perfect freedom from uncombined carbon, although probably the greater part of the loss was due to compounds dissolved by hydrochloric acid.

The carbide obtained by the above process consisted of a bright steel-gray powder, which, on examination with a microscope, was found to be made up of thin plates or scales. The specific gravity determined on a sample of about 15 grams at 23° was 6.944. The carbon was determined in two samples of 5 grams each recovered at different times, the method used being that of decomposition with slightly acid potassium cupric chloride, and subsequent combustion of the carbon in oxygen. The iron was determined gravimetrically as ferric oxide and checked volumetrically. The carbide showed the following composition :

	Per cent.
Carbon	6.646 and 6.625
Iron	93.255
Phosphorus	0.026
Manganese	none

This carbide is gradually, but completely, converted into ferric oxide and carbon by oxidation in moist air.

5.0263 grams, placed in a watch-glass, was alternately moistened with distilled water and dried in an air-bath at about 80° C. once or twice each day until the weight became constant.

This required about six weeks. The result was a brownish-red powder weighing 7.066 grams, thus showing a gain in weight by oxidation of 2.040 grams. This oxidized product, on treatment with hydrochloric acid, left an insoluble black residue which, on combustion, gave 4.64 per cent. of carbon, equal to 6.64 per cent. of the original carbide. The theoretical amount of oxygen necessary to convert the iron in 5.0263 grams of carbide to Fe_2O_3 is 2.009 grams, whereas the gain in weight was 2.040 grams. The slight excess is probably due to water combined with the carbon, the ferric oxide being anhydrous.

The carbide was, practically, completely soluble in hot moderately concentrated hydrochloric acid, so that it was thought desirable to study the products of solution, as they would probably throw some light on the constitution of the body from which they were derived.

The gaseous products of solution were obtained in the following manner: A small generating flask, having a capacity of about 150 cc., was fitted with a 3-hole rubber stopper. Through one hole passed a tube connected with a carbon dioxide generator, rendering it possible to displace all of the air in the flask by carbon dioxide. Through a second hole passed a long funnel, provided with a stop-cock, and drawn out at its lower end to a fine opening. Through the third hole passed the outlet tube, which was surrounded by a short reflux condenser, and was fused to a 3-way stop-cock. One arm from the 3-way stop-cock opened into the air, the other was connected with one tip of a specially constructed Hempel gas burette, graduated to 200 cc. and accurately calibrated. The second tip of the Hempel burette was connected by means of capillary tubing to a Hempel storage pipette filled with mercury, but containing 3 or 4 cc. of 1 to 1 potassium hydroxide. The burette was water-jacketed and filled with mercury.

In collecting the gas, the sample of 0.600 gram of carbide was first introduced into the generating flask and covered with a small amount of water. The level-bulb of the collecting burette was then lowered until the solution of potassium hydroxide in the storage pipette was drawn over to the stopcock of the burette, which was then reversed and the air in the burette completely expelled by raising the level-bulb until the mercury completely filled the burette and just reached the three-way stop-cock between the generating flask and the burette. In this way the entire space beyond the 3-way stopcock was filled with mercury. The 3-way stop-cock was then turned so as to connect the generating flask with the outside air, and carbon dioxide run into the flask until complete absorption by potassium hydroxide showed all of the air in the flask to have been displaced. The supply of carbon dioxide was then shut off, and the 3-way stop-cock turned so as to connect the generating flask with the collecting burette. The stop-cock of the funnel which had been previously filled with 1 to 1 hydrochloric acid was then opened, and a little hydrochloric acid allowed to run into the flask, which was then heated until action set in. As soon as gas began to be evolved, the stop-cock of the collecting burette was opened so that the gases might pass over, the mercury in the level-bulb being kept level with that inside of the burette, thus avoiding any excessive internal pressure. When the collecting burette was nearly filled with gas the stop-cock of the burette was reversed, and this gas driven over into the storage pipette, and then the stop-cock brought back again to its original position, and the collection continued.

Solution could be easily completed in about an hour by gradually increasing the amount of hydrochloric acid added, and bringing the contents of the flask to active ebullition. When solution was complete the 3-way stop-cock was closed, the funnel filled with hot water, and the flame withdrawn from under the flask. As the steam condensed, the flask drew in sufficient water to nearly fill it. The 3-way stop-cock was then opened to once more connect with the collecting burette, the mercury in the level-bulb lowered, until all of the gas in the generating flask had been drawn over to the burette, water being allowed to run in through the funnel during the operation. When the last of the gas had been transferred to the collecting burette, its stop-cock was reversed, and all of the gas passed over into the storage pipette, and allowed to stand until the carbon dioxide was completely absorbed. When the carbon dioxide was all removed, the gas was passed back from the storage pipette into the collecting burette, and its volume read, and corrections made for temperature, pressure, and vapor-tension, the volume being reduced to standard conditions, dry gas at 0° C. and 760 mm. pressure. In this way about 150 cc. of gas were obtained from each solution.

This gas was analyzed first for the total carbon dioxide obtained by combustion of both paraffins and olefins. This combustion was effected in the usual manner by mixing 12–14 cc. of the gas with enough air to make 100 cc. exploding in an explosion pipette, and determining the carbon dioxide by absorption with potassium hydroxide.

The volume of the olefins was determined by operating directly in the 200 cc. collecting burette. After sufficient gas had been drawn off in a second burette for the determination of total carbon dioxide from paraffins and olefins, the gas remaining in the collecting burette was measured; then by means of a small funnel attached to one tip of the burette, about 2 cc. of 1 to 1 potassium hydroxide was introduced into the burette.

When the mercury was so protected, a few small drops of bromine were allowed slowly to run into the burette, thus filling it with vapor of bromine, which soon formed the dibrom derivatives with the olefins. When all of the bromine had been absorbed the entire volume of gas, together with the solution of potassium hydroxide in the burette, was passed into the storage pipette, and sufficient mercury to fill the connecting capillary was forced over; then the storage pipette was pinched off. The mercury in the collecting burette was now emptied, and the burette and mercury thoroughly washed with water, then with dilute sulphuric acid to neutralize any potassium hydroxide, and finally with water again. The mercury was then replaced, the burette connected with the storage pipette once more, and the gas returned and measured, the loss in volume giving the volume of the olefins.

The residual gas contained hydrogen and the paraffins. A sample of this gas was transferred to a second burette, mixed with air, and exploded for the determination of the carbon dioxide derived from the paraffins. The volume of carbon dioxide derived from the olefins was taken as the difference between the results obtained in the first and second explosions.

Owing to the fact that the paraffins are higher members than methane, the volume of hydrogen could not be determined by the contraction in the explosions, so that the method proposed by the author,[1] that is, direct absorption of the hydrogen with 1 per cent. palladious chloride was re-

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[1] This JOURNAL, 18, 294.

sorted to. Samples of the gas, from which the olefins had been removed, were passed into absorption pipettes filled with palladious chloride, and heated until absorption of the hydrogen was complete. As soon as the absorption of hydrogen in one sample was about complete the residual gas was returned to the burette and a second sample of gas drawn in and mixed with it. The combined gases were then returned to a pipette filled with fresh palladious chloride, and the absorption continued. This method of removal of hydrogen and accumulation of paraffins was continued until sufficient of the paraffins was obtained for satisfactory explosions.

Owing to the fact that dilute mixtures of the paraffins with air do not readily explode on sparking, a small measured amount of pure hydrogen was introduced, each time allowance being made, of course, for this contraction. The paraffins obtained by this method gave an explosion for every volume of gas burned, almost exactly two volumes of carbon dioxide, accompanied by a contraction of 2.5 times the gas burned, and an oxygen consumption of almost exactly 3.5 volumes, thus indicating that ethane C_2H_6 was probably the paraffin present.

The volume of hydrogen was obtained by taking a sample of the gas from which the olefins had been removed, mixed with an accurately measured amount of nitrogen, and passing into palladious chloride, keeping the gas over palladious chloride for periods of time varying from two to fourteen hours. A measured amount of nitrogen was introduced, since the volume of paraffins, after the removal of the hydrogen, would be so small as to render the reading inconvenient if not impossible.

In the following table the amount of gases which was obtained from one gram of the carbide is given :

Gas evolved.	Hydrogen in cc.	Total CO_2.	CO_2 from paraffins.	CO_2 from olefins.	Volume of olefins.
250.51	208.10	71.87	35.68	36.20	
250.51	208.10		34.80	37.00	
250.77		75.09	30.10	45.09	9.32
251.80		71.05			9.47
250.77			31.89	43.20	9.93
251.90	213.10	70.80	30.40	40.40	9.88
251.90	213.10	71.87	35.68	36.20	

The above "total CO_2" would contain only enough carbon to account for about 60 per cent. of the carbon in the carbide dissolved, thus showing that nearly 40 per cent. was present in the form of some hydrocarbon, which was either condensed or remained in solution in the generating flask. The strong odor, both of the solution in the generating flask and especially of the potassium hydroxide used in the storage pipette for the removal of the carbon dioxide, showed that butane was undoubtedly present, and it is probable that the greater part of the carbon unaccounted for was lost in this form. The most striking feature in the above table is the volume of carbon dioxide derived from the olefins compared with the volume of the olefins. It will be noted that this ratio is a little more than 4 to 1, thus indicating the almost certain predominance of butylene, C_4H_8, probably mixed with a little dibutylene, C_8H_{14}.

As early as 1864 Hahn,[1] and again in 1877, Cloëz[2] showed, by dissolving cast irons in dilute hydrochloric or sulphuric acid, that a portion of the carbon passed off with the hydrogen as ethylene, C_2H_4, propylene, C_3H_6, butylene, C_4H_8, and dibutylene, C_8H_{14}. This they showed by passing the gas through bromine and purifying and fractionally distilling the dibrom derivatives thus obtained.

At the time of Hahn's and Cloëz's work no definite carbide of iron had been isolated, and no possible explanation offered for the presence of the gaseous products of solution of a mixture of hydrogen, olefins and paraffins. We would recall two well-known facts before offering a possible explanation for the composition of the gas evolved in dissolving iron containing carbon. The first of these is the tendency of the olefins with the general formula, C_nH_{2n}, to combine with nascent hydrogen to form the corresponding paraffins, C_nN_{2n+2}; and also the tendency of some of the higher olefins, especially butylene, C_4H_8, and those of higher molecular weight to form condensation products. It would seem not unreasonable to assume that iron is capable of forming a series of what we might properly term ferro-carbons analogous to the olefin series of hydrocarbons; that this series has the general formula,

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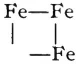
[1] Ann. Chem. (Liebig), **129**, 57.

[2] Compt. rend., **85**, 1003.

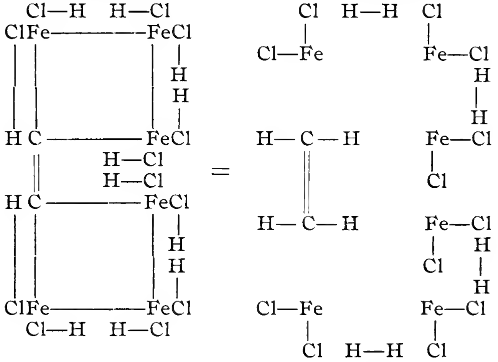
C_nFe_{3n}, in which the group  $\begin{array}{ll}\mathrm{Fe{-}Fe} & \\ | \quad\; | & \\ \quad\;\mathrm{{-}Fe} & \end{array}$ replaces H_2 in the olefin series C_nH_{2n}; that, when these ferro-carbons are acted upon by an acid, such as hydrochloric or sulphuric acid, the first reaction is the substitution of two hydrogen atoms for the two iron atoms, united to the carbon atom, thus producing the analogous olefin, C_nH_{2n}, free hydrogen being liberated between the iron atoms. Thus the primary products of solution of these ferro-carbons would be olefins, C_nH_{2n}, and hydrogen, but, owing to the tendency of the olefins to combine with nascent hydrogen, the secondary reaction producing a greater or less proportion of paraffins would take place.

That this is probably the case is rendered the more probable from the fact that the proportion of paraffins to olefins varies somewhat with varying conditions of solution.

The first reaction in the case of the simplest of these ferro-carbons, C_2Fe_6, when dissolved in hydrochloric acid, is as follows:

$$C_2Fe_6 + 12HCl = C_2H_4 + 6FeCl_2 + 4H_2.$$

Or the reaction may be graphically represented as follows:



The secondary reaction between hydrogen and the olefins would be one of direct addition to form the homologous paraffins.

Further work upon the relation of iron to carbon in continuation of what has been carried on in this laboratory during the past four years, will be prosecuted in the hope of giving greater weight to the above hypothesis, and of determining if possible the conditions governing the formation of the various ferro-carbons, and the influence of their compounds upon the physical properties of the iron or steel in which they occur.

I wish here to express my obligations to my two assistants, Messrs. Walter Scotten and Firman Thompson, for the care with which they carried on the laboratory work in the recovery and analysis of the above carbide.

ANN ARBOR, MICHIGAN,
OCTOBER 23, 1896.

THE ALKALI TRIHALIDES.

BY CHARLES H. HERTY AND HOMER V. BLACK.

It has been shown by one of us[1] that the so-called compounds PbICl, $PbI_2.2PbCl_2$, $PbI_2.5PbCl_2$, described by Labouré,[2] Poggiale,[3] and Miss Field,[4] are not true chemical compounds, but isomorphous mixtures of lead iodide and lead chloride. This suggested the thought that possibly the mixed trihalides of the alkali metals were also isomorphous mixtures and not true chemical compounds.

To determine this point it was deemed best to study one of the series of rubidium trihalides described by Wells.[5]

Messrs. Eimer and Amend have kindly furnished us with a quantity of rubidium iodide sufficient for the investigation.

The method of work consisted in determining the composition of the successive crops of crystals obtained from a solution of the ingredients in quantities suitable for giving as the first crop the member of the series under investigation.

Our work has been confined to rubidium dibromiodide. To prepare this substance 10 grams of rubidium iodide were dissolved in 6.6 cc. of water. To this solution was added very cautiously 8 grams of bromine. At first separation of iodine occurred. On stirring, this completely dissolved, the solution

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[1] This JOURNAL, **18**, 293.
[2] J. Pharm. [3], **4**, 328.
[3] Compt. Rend., **20**, 1180.
[4] J. Chem. Soc., **63**, 540.
[5] Am. J. Sci., **43**, 475.

becoming warm. On cooling and standing for several hours, quite a large crop of crystals was obtained. These crystals resembled in every way those obtained by Wells. They were quickly dried between folds of paper and immediately placed in a desiccator. They were designated "A."

The mother-liquor from "A" was allowed to evaporate spontaneously, and thus a second crop of crystals was obtained, similar to "A." These were designated "B."

Further evaporation of the mother-liquor from "B" gave a third crop of crystals, similar to "A" and "B." These were slightly mixed with crystals of a normal halide, from which they were carefully separated. The third crop was designated "C."

In these substances rubidium was determined by heating the substance in a porcelain crucible. Only rubidium bromide remained in each case after the heating. Bromine and iodine were determined by treating the water solution of the substance with sulphurous acid, just sufficient for decolorization, precipitating the halides with excess of a standard solution of silver nitrate, weighing the precipitated silver halides, and determining the excess of silver in the filtrate by ammonium thiocyanate. The results of the analysis are given below:

	A.	B.	C.	Calculated for $RbBr_2I$.
Rb	22.99	22.92	22.88	22.95
Br	39.64	41.23	40.41	42.97
I	37.07	35.94	36.66	34.08
Total	99.70	100.09	99.95	100.00

From these results it is evident that the three successive crops of crystals are identical, proof being thus given that the substance is not a mixture, but a true chemical compound.

When this salt is dissolved in water, dissociation takes place as is shown by the odor of the solution. Complete dissociation, however, does not take place immediately, for when silver nitrate is added to the dilute water solution of the substance, the precipitate is at first quite dark. This gradually changes to the lighter color of silver bromide and silver iodide. Not enough of this dark precipitate was obtained in satisfactory condition for analysis, but it seems probable that the substance has the composition $AgBr_2I$.

The stability of the salt $RbBr_2I$ is quite marked in the absence of moisture.

1.4047 grams $RbBr_2I$ on standing in a desiccator 16 days lost only 3.3 milligrams. On standing 38 days the loss was only 7.1 milligrams.

The effect of atmospheric moisture in accelerating the decomposition of this salt is well shown in the following table:

Time of standing.	Condition of experiment.	Per cent moisture in air.	Weight of salt. Gram.
	Original weight of salt		0.8678
2 days.	In open vessel		0.8655
1 day more.	" desiccator		0.8650
1 " "	" "		0.8649
1 " "	" open vessel		0.8644
1 " "	" " "	69 per cent.	0.8642
1 " "	" " "	69 " "	0.8640
2 days "	" " "	92 " "	0.8632
2 " "	" " "	93 " "	0.8627
4 hours "	" desiccator		0.8626
20 " "	" "		0.8625
5 days "	" "		0.8622
21 " "	" "		0.8582

The addition of a slight quantity of sulphurous acid to the water solution of the salt produces a precipitation of iodine, which is redissolved on further addition of the reagent.

Finally to 10 grams of rubidium iodide dissolved in 6.6 cc. of water was added 4 grams of bromine, one-half of the quantity of bromine used in the preparation of rubidium dibromiodide. From the solution thus obtained only rubidium triiodide crystallized as the first crop.

UNIVERSITY OF GEORGIA,
JUNE 27, 1896.

ACTION OF WATER OF THE HUBB COAL MINE UPON CAST IRON.

BY FRANK W. DURKEE.

In 1872 the Hubb Coal Mine, in Cape Breton, Nova Scotia, was abandoned. Soon it filled with water; but in the time between December, 1894, and April, 1895, the Dominion Coal

Company (Limited), the present owners of the mine, pumped the water out. Then, it was found, that the cast iron which had formerly been used for purposes of construction within the mine, had, while lying beneath the mine water, through this long period, undergone radical changes. For instance, the cast iron T-rails in the car tracks, while retaining their original size and shape, were no longer strong and fairly tough like cast iron. A man could break them across his knee, or beat them into fragments with a tack hammer. They were soft enough to be easily cut with a knife. A cross-section, prepared by the use of an ordinary saw, was grayish-brown in color. The internal half of the section, however, was lighter in color than the external, and softer in texture. Where the surfaces of the original castings were not covered by films of a reddish-brown ferric oxide, they were grayish-brown like the cross-sections. The transformed cast iron was magnetic, porous, and several times lighter than the same bulk of cast iron. Brought in contact with a piece of white paper it left a mark like that of a lead pencil. In a word, the greater part of the cast iron that was in the Hubb mine at the time it was filled with water, had been changed, by chemical action, into masses looking like graphite and shaped like the original castings. While the changes described above had been going on in the cast iron, the surfaces of wrought iron structures had been deeply corroded by the mine waters, but the iron in the deep-seated portions still remained perfect. Consequently the wrought iron structures in the mine had diminished considerably in size, but internally had not become porous like the cast iron. Steel structures had wasted away but slightly, and were perfect beneath their surfaces. The waters of the Hubb mine attack white cast iron less readily than gray, wrought iron slowly, and steel with much difficulty.

Changes in cast iron, in some ways, not unlike those that have taken place in the Hubb mine, have been described by Deslongchamps,[1] who found that the cast iron cannon balls, which had been taken from the sea off the coast of Normandy, had lost two-thirds of their weight, contained no metallic

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[1] J. chim. Méd., 13, 89.

iron, and were soft enough to be cut with a knife. Berzelius states[1] that some of the cast iron cannon balls, which had been taken from a vessel, sunk fifty years before near Carlscrona, were changed to their very centers into a gray, porous, graphite substance, which, after exposure to the air for fifteen minutes, became hot enough to drive out the adhering moisture. Other cannon balls in the same lot were changed, as above described, only through a part of their diameters. In the opinion of Berzelius and Karsten, these changes have been produced by the action of oxygen and carbon dioxide from the atmosphere, which have been dissolved in the sea water, and they describe the product as a mixture of graphite, ferric oxide, ferrous carbonate, silica, and the carbide of iron, FeC_3. Karsten has also shown that a mixture of graphite, silicon, and the carbide, FeC_3, is produced by treating gray cast iron with a ten per cent. solution of sulphuric acid. Mallet has found[2] that cast iron yielded more readily to the action of impure waters at the mouths of rivers which empty into the sea, than to the action of pure sea water. The chemical changes that take place under the last mentioned conditions, Mallet summarized as follows: $FeO + H_2O$, $Fe_2O_3 + FeO + H_2O$, and $FeCO_3$, are at first produced. These substances are then attacked by H_2S, forming FeS and $6(FeS + FeS_2)$. The sulphides are transformed by the oxygen of the air into $2Fe_2O_3 + SO_3 + 6H_2O$ and $FeSO_4 + 6H_2O$.

It is noticeable, in all the instances hitherto investigated, where cast iron has been transformed by natural means into the product above described, that the transformation has been effected under sea water, or in a mixture of sea water and fresh water, where the conditions are different from those that might be expected to exist in a submerged Nova Scotia coal mine. Consequently, to find by what means the cast iron of the Hubb mine had been changed to a mass resembling graphite, and the chemical character of the new substance, further investigation seemed necessary.

Through the kindness of the Dominion Coal Company

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[1] Gmelin's Handbook, 5, 218.

[2] Action of Air, Water, Etc., upon Cast Iron, Wrought Iron and Steel, British Assoc. Reporter, 1839 and 1841.

(Limited), several pieces of the transformed cast iron, together with pieces of wrought iron and steel, from the submerged mine, have been obtained for use at our laboratory, and, at the same time, six gallons of the mine water. From the center of a piece of transformed cast iron, a sample of the original cast iron has been obtained. In addition to the sample of cast iron just mentioned, four samples of the transformed cast iron have been selected for analysis and numbered I., II., III. and IV. for convenience. No. I. contained nothing but the light colored central part of the transformed cast iron, mentioned in the description of a cross-section of a rail; II., the outer, harder, and darker part of the piece from which I. came; III., the outside of the piece from which the gray cast iron was taken; and IV., the cross-section of a T-rail. The samples were not dried artificially, but were ground in an agate mortar, and transferred at once to glass-stoppered weighing-tubes. Analyses of these samples should disclose much of the chemical character of the transformed cast iron.

The samples have been analyzed and the calculations made by the following methods: Carbon and water have been determined by combustion with lead chromate and oxygen. In the case of the cast iron, the carbon has first been separated by the use of the double chloride of copper and ammonium.

Water mechanically held has been found by heating weighed quantities of the samples in an air-bath at 105° for four hours.

The first step in the determination of silicon and silicon dioxide in the samples, has been to oxidize the remaining silicon to silicon dioxide by fusion with sodium carbonate and potassium nitrate in a platinum crucible. The silicon dioxide resulting, has then been determined in the usual way.

Another weighed portion of the same sample, freed from water by gently heating in a porcelain boat with a small Bunsen flame, has then been transferred to a combustion furnace and treated with chlorine according to Drown's[1] method for the determination of silicon in cast iron. Afterwards the residue in the boat has been removed to a platinum crucible, mixed with sodium carbonate and potassium nitrate, and

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[1] Journal of Institute of Mining Engineers, 7, 346.

fused. On cooling the fused mass has been treated in the usual way for the determination of silicon dioxide. The weight of the silicon dioxide, found in the second determination, subtracted from the weight of the silicon dioxide obtained by fusion before the treatment with chlorine, gives the weight of the silicon dioxide that has been produced by the oxidation of the silicon in the original samples. From the weight of silicon dioxide thus obtained by difference, the weight of silicon in the samples has been calculated. The weight of silicon dioxide, obtained before the treatment with chlorine, minus the weight of the silicon dioxide, found as above by difference, gives the weight of the original silicon dioxide in the samples.

Phosphorus has been determined by the molybdate method with final precipitation as ammonium magnesium phosphate. In sample IV., which contained arsenic, the phosphorus and arsenic have been precipitated together by boiling with molybdate solution, and afterwards weighed together as magnesium pyrophosphate and magnesium pyroarseniate. In a very dilute solution of a separate portion of IV. the arsenic itself has been estimated by the use of Marsh's apparatus and standard arsenical mirrors. The arsenic has then been calculated as arsenical pyrites and magnesium pyroarseniate. The magnesium pyroarseniate subtracted from the magnesium pyrophosphate and magnesium pyroarseniate give the magnesium pyrophosphate obtained from the samples, and this has been calculated as phosphoric anhydride.

Calcium had been determined by the oxalate method; magnesium by the pyrophosphate method; and manganese by Gibbs's pyrophosphate method.

The total amount of sulphur in the samples has been determined in the usual way after fusion with sodium carbonate and potassium nitrate. The sulphur, combined with a metal or metals to form sulphide, has been determined by Blair's[1] modification of Fresenius' method. The sulphur has been calculated as ferrous sulphide. Sulphur, in the sample, above that in combination with metals to form sulphides, has been calculated as sulphur trioxide.

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[1] Blair's Chem. Anal. of Iron, p. 63.

Iron has been determined by Marguerite's potassium permanganate method. Unfortunately, on account of the presence of considerable carbon and iron or less metallic iron in the samples, it has been impossible to determine the part of each sample that is ferric oxide. But this failure seems to be of little importance, since inspection of the samples alone is sufficient to show that ferric oxide is present only in small quantities, and therefore, the oxygen above that necessary to form ferrous oxide can safely be neglected.

Oxygen, above that in combination with silicon to form silicon dioxide, with hydrogen to form water, with sulphur to form sulphur trioxide, with calcium to form calcium oxide, with magnesium to form magnesium oxide, with manganese to form manganese monoxide, and with phosphorus to form phosphoric anhydride, has been determined by difference, after first assuming that the sulphide, found by direct experiment in the samples, was ferrous sulphide, and that the arsenic in IV. was combined with iron to form arsenical pyrites. If this assumption is true, it follows, for there is no carbonate in the samples, that all the oxygen in excess of that mentioned above, neglecting traces of ferric oxide, must be combined with the iron to form ferrous oxide. Therefore, to find what per cent. this oxygen is of the whole substance, it only remains to add together the percentage of each sample, that is, silicon dioxide, silicon, carbon, water, ferrous sulphide, sulphur trioxide, phosphoric anhydride, calcium oxide, magnesium oxide, manganese monoxide, arsenical pyrites, and iron above that combined with sulphur and arsenic, and to subtract the sum from one hundred. The difference, which is the percentage of oxygen in the samples above that already mentioned, has been calculated as ferrous oxide. The percentage of each sample, that is, iron combined with carbon to form carbide, FeC_3, and metallic iron, has been found by subtracting the sum of the percentages of the iron in ferrous sulphide, arsenical pyrites, and ferrous oxide from the total percentage of iron in the sample.

The analytical results below show the composition of the sample of gray cast iron and of I., II., III. and IV. These results have been calculated in per cent., and, in most cases, are averages obtained by duplicate determinations. The specific gravities of the samples, water standard, are first given.

Gray Cast Iron.

Specific gravity 6.9.

Silicon.	Carbon.	Sulphur.	Phosphorus.	Calcium.	Magnesium.	Manganese.	Iron.	Total.
1.74	3.46	0.15	0.38	0.76	0.24	0.63	92.54	99.90

Transformed Cast Iron.

	I.	II.	III.	IV.
Specific gravity.	2.1	2.5	2.5	2.3
Silicon dioxide	17.97	12.25	10.62	27.81
Silicon	0.57	1.67	0.83	
Carbon	18.21	13.33	9.71	15.21
Water mechanically held	3.04	3.53	4.70	3.29
Water combined	5.40	5.21	7.78	4.49
Ferrous sulphide	0.33	0.38	1.25	0.96
Sulphur trioxide	1.41	2.73	3.02	0.75
Phosphoric anhydride	2.34	1.65	1.88	2.36
Calcium oxide	1.36	1.25	0.99	trace
Magnesium oxide	0.36	0.35	0.87	....
Manganese monoxide	0.30	0.30	1.90	1.84
Arsenical pyrites	....	....	....	0.68
Metallic iron + iron in the carbide FeC_3	22.84	23.06	28.55	3.37
Ferrous oxide	25.87	34.29	27.90	39.24
	100.00	100.00	100.00	100.00

On comparing the above results it is noticeable that IV. contains more silicon dioxide and less magnesium and calcium oxides than either I., II. or III. Moreover, it is not equally rich in sulphur trioxide. The thing that distinguishes IV. from the other samples more than anything else, and from the sample of cast iron is the fact that it contains arsenic. The mine water, which covered all four of the samples, contained 0.00005 gram of arsenic per liter. But, since samples I., II. and III. contained no arsenic the arsenic in IV. must have come from the cast iron, out of which IV. was produced, and not from the mine water. The cast iron, whose analysis has been given above, so far as all the analytical results obtained show, may have been the material out of which samples I. and II. have been produced, and, from the method of sampling, is the material out of which III. has been produced; but, for reasons already given, it could not have been the material out of which IV. has been produced. Consequently the analytical results from sample IV. are not strictly comparable with those from the sample of cast iron and I., II. and III. The percentage of carbon seems large in all the samples, with the possible exception of III., even when allowance has been made for the insolubility of carbon and the loss in weight which the original cast iron has sustained. It is not large enough, however, to warrant the conclusion that the percentages of carbon in I., II., and III. have been augmented by deposition of carbon in any of these samples. It will be seen that in the production of I., II., III. and IV., considerable iron must have passed out of the original cast iron, while oxygen and water have been added. A little silicon dioxide and sulphur complete the additions which the original cast iron has received. Therefore, it would appear, from the large amount of oxygen and the comparatively small amount of other substances added, that the transformation had been brought about chiefly by the addition of oxygen. However, since the oxides of iron are insoluble in water, this supposition does not account for the loss of iron which the original castings have sustained. The iron had to be changed into a soluble compound before it could pass out into the surrounding water. An analysis of the mine water ought, therefore, to reveal the nature of this soluble compound of iron and also the solvent of the iron. I am indebted to my assistant, Mr. John W. Edwards, for a partial analysis of the Hubb mine water. The results are below.

	Grams per liter.
Free and combined sulphuric acid	0.4551
Free sulphuric acid	0.0230
Calcium	0.0419
Silicon dioxide	0.0153
Magnesium	0.0222
Chlorine	0.0284
Arsenic	0.00005
Iron, aluminium, and manganese	0.0096

On account of the presence of sulphate of iron and free sulphuric acid in considerable quantities in the mine water, the former must have been the soluble compound of iron and the latter the solvent.

Going back to the formation of the sulphuric acid, the chemical changes in the original castings may be briefly summarized as follows: A part of the iron pyrites in the coal, acted upon by the moist air, has been converted by a well-known reaction into ferrous sulphate, free sulphuric acid, and sulphur. Once formed, the sulphuric acid has found its way into the mine water, which, after a time, has become strongly acidic enough to slowly attack the submerged cast iron. From this chemical action the sulphates of the strong metals in the castings have resulted, together with hydrogen and hydrocarbon. The soluble sulphates dissolved and passed out of the castings into the mine water, and the mixture of silicon, graphite, and the carbide of iron, FeC_3, described by Karsten, must, after a time, have resulted if the mine water had been more strongly acidic. But, instead of a strength of 10 per cent. sulphuric acid, the mine water attained only a strength of 0.0023 per cent. Consequently secondary chemical reaction set in, and the oxygen and carbon dioxide of the air, which the mine water held in solution attacked the cast iron and produced $FeO + H_2O$, $FeO_2 + FeO + H_2O$, and possibly at first a small quantity of $FeCO_3$, as described by Mallet. This reaction accounts for the existence of considerable oxide of iron in the transformed casting. The ferric iron in the compound, $Fe_2O_3 + FeO + H_2O$, could not, however, exist long in the presence of the hydrogen, produced by the action of the metallic iron on the sulphuric acid, as it would be changed to ferrous iron. The reducing action of hydrogen accounts for the almost complete absence of ferric oxide from the transformed cast iron. When taken from the mine the castings contained no carbonate. If any was ever formed, the sulphuric acid solution, after a time, became strong enough to dissolve it, with formation of ferrous sulphate, carbon dioxide and water. It is also very probable that a part of the ferrous oxide has dissolved in the sulphuric acid to form ferrous sulphate and water. Silicon and phosphorus have been gradually oxidized, while the carbon in the cast iron chemically has remained unchanged, except for a slight loss due to the formation of hydrocarbons. Sulphuric acid and atmospheric gases, dissolved in the mine water, are the principal chemical agents that have been instrumental in changing the original castings in the Hubb mine into masses having the appearance of graphite.

TUFTS COLLEGE

Contributions from the Chemical Laboratory of the Lehigh University.

III.—THE ACTION OF SULPHURIC ACID ON ANISOL.

BY W. B. SHOBER.

Various statements have been made by different investigators concerning the result of the action of sulphuric acid on anisol (methylphenyl ether). Kekulé[1] and Cahours[2] state that when anisol is treated with sulphuric acid, para- and orthoanisolmonosulphonic acids are formed.

Annaheim[3] obtained the para and ortho acids by heating methoxysulphobenzide with sulphuric acid.

Moody[4] treated 50 grams of anisol with an equal volume of sulphuric acid at ordinary temperature. He found that the ether dissolved readily with evolution of heat. On adding the reaction-mixture to water, a portion of the anisol was liberated. This was shaken with a further quantity of sulphuric acid at 80°. The acid solution was neutralized with calcium carbonate, and the calcium salt purified by fractional crystallization. He found but *one* calcium salt. This was converted into the amide (melting-point 108°).[5] The anisol used was obtained from Kahlbaum. Moody dried it over sodium and then carefully distilled it, rejecting the first and last portions. (boiling-point 153°). Franklin[6] treated anisol, obtained by decomposing diazobenzene sulphate with methyl alcohol (boiling-point 152°–154°), with three times its weight of ordinary concentrated sulphuric acid. In one case the mixture was heated on a water-bath for two hours, in another for one hour at 80°.

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[1] Ztschr. Chem., 1869, 201.

[2] Ann. Chem. (Liebig), **52**, 333.

[3] *Ibid.*, **172**, 47.

[4] Proc. Chem. Soc., 1892-93. 90.

[5] This melting-point is apparently too low. In this and a previous investigation, I have determined the melting-point of paramethoxybenzenesulphonamide repeatedly. Under all conditions it has melted at 112°-113°. Franklin gives the melting-point as 112°.

[6] Dissertation, 1894.

The acid mixture was poured into water and neutralized with barium carbonate. This was converted into the amide (melting-point 112°). Only *one* amide was found. Several years ago, with the object of comparing paramethoxybenzenesulphonamide obtained by decomposing paradiazobenzenesulphonic acid with methyl alcohol, and converting the resulting sulphonic acid into the amide, with the amide obtained from the sulphonic acid resulting from the action of sulphuric acid on anisol, I treated anisol with an excess of ordinary concentrated sulphuric acid.[1] The mixture was heated on the water-bath for a half hour, poured into water, neutralized with barium carbonate, and the barium salt converted into the chloride, which was found to melt at 86°. The following analysis showed the substance to be anisoldisulphon chloride :

Calculated for $C_6H_3.OCH_3.(SO_2Cl)_2$.			Found.	
			I.	II.
C_7	= 83.79	27.54	28.02	....
H_6	= 6.00	1.97	....	2.67
O_6	= 79.80	....	....	....
S_2	= 63.96	21.02	21.21	....
Cl_2	= 70.74	23.25	23.37	22.85

This result was unexpected, since Zervas[2], in order to make the disulphonic acid, treated anisol with fuming sulphuric acid.

The mother-liquor from which the disulphon chloride crystallized was not examined for other products. Recently I have attempted to repeat my former experiment, and, while the disulphonic acid is obtained as before, examination of the mother-liquor always shows the presence of a monosulphonic acid.

The present investigation was undertaken to determine, if possible, the conditions which influence the course of the reaction between sulphuric acid and anisol. The anisol used in the experiments described below was Kahlbaum's preparation. It was a clear, colorless liquid boiling constantly at 152°. The sulphuric acid was ordinary concentrated acid.

Experiment I.

Eighty-five grams of sulphuric acid was poured into 40

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[1] This JOURNAL, **15**, 388.

[2] Ann. Chem. (Liebig), **103**, 342.

grams of anisol. The temperature rose to 83°, and the liquid became a sherry red. The mixture was heated for 35 minutes on a rapidly boiling water-bath; a thermometer in the mixture indicated 92°.5 during the heating. After the heating the reaction-mixture, without being allowed to cool, was poured into 2 liters of water and neutralized with barium carbonate. The barium salt was converted into the sodium salt which, when dried, weighed 73 grams. This was converted into the chloride—a clear, faintly yellow oil which did not solidify on standing under water. On treatment with concentrated ammonium hydroxide it was converted into the amide, which, on crystallizing from a rather dilute solution, was obtained in the form of long, slender needles (melting-point 113°). On one occasion I obtained needles 7.5 cm. in length. The mother-liquor was carefully examined and two other amides were found. One of them melting at 169° is undoubtedly the amide of orthoanisolsulphonic acid; the other, melting at 239°, as shown by the analysis given below, is the amide of anisoldisulphonic acid. This result is not in accord with any results on record.

Weight of paramide (melting-point 113°) = 43.7 grams = 91.61 per cent.

Weight of orthoamide (melting-point 169°) = 3.7 grams = 7.76 per cent.

Weight of disulphonamide (melting-point 239°) = 0.3 grams = 0.63 per cent.

Experiment II.

This is a repetition of the experiment described by Moody.[1]

Equal volumes of the anisol and sulphuric acid (30 cc. of each; 54.6 grams acid; 29.6 grams anisol) were mixed and vigorously shaken for five minutes in a glass-stoppered cylinder. The liquid assumed a faintly pink color; the temperature rose to 52°. After standing several hours at the room temperature, the liquid was poured into a large volume of water; 1.5 cc. of anisol separated out. This was removed and the reaction-product neutralized with barium carbonate. The barium salt was converted into the sodium salt and this into the amide in

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[1] *Loc. cit.*

the usual way. The dried sodium salt weighed 43 grams. Two amides were found:

Weight of paramide 10.5 grams = 87.5 per cent.
Weight of orthoamide 1.5 grams = 12.5 per cent.

This experiment confirms Kekulé's result and is at variance with that of Moody. The variation is probably due to a difference in the temperatures at which the experiments were conducted.

Experiment III.

In this experiment 1 part by weight of anisol was treated with 2 parts of sulphuric acid (14 grams anisol, 28 grams sulphuric acid), the temperature of mixing being 53°. The mixture was heated thirty minutes on a rapidly boiling water-bath. The temperature of the mixture during the heating was 92°. As above, the reaction-product was converted into the sodium salt, and this into the amide.

The dried sodium salt weighed 26 grams. Three amides were found:

Weight of paramide = 13.5 grams = 90.60 per cent.
Weight of orthoamide = 0.2 grams = 1.34 per cent.
Weight of disulphonamide = 1.2 grams = 8.06 per cent.

Experiment IV.

To determine the effect of employing a larger excess of sulphuric acid than that used in the preceding experiment, 15 grams of anisol were mixed with 60 grams of sulphuric acid, the temperature of the mixing being 61°. The mixture was heated sixty minutes on a rapidly boiling water-bath, the temperature of the mixture during the heating being 92°. The product was converted into the amide. The sodium salt weighed 35 grams. Three amides were found:

Weight of paramide = 14.0 gram = 87.5 per cent.
Weight of orthoamide = 0.4 gram = 2.5 per cent.
Weight of disulphonamide = 1.6 grams = 10.0 per cent.

In Dr. Franklin's experiments he treated 1 part of anisol with 3 parts (by weight) of sulphuric acid and heated on the water-bath for one and two hours respectively. He found but *one* amide. In Experiment III, where the proportion of acid to anisol was 2 : 1, I found three amides, and in Experiment IV., the proportion of acid to anisol being 4 : 1, a similar result was obtained.

Experiment V.

In this experiment the proportion of acid to anisol was 6 : 1. 14 grams of anisol was treated with 84 grams sulphuric acid, the temperature of mixing being 60°. The mixture was heated thirty minutes on the water-bath, the temperature of the mixture during the heating being 92°. The reaction-product was converted into the amide. The dried sodium salt weighed 32 grams. *Two* amides were found :

Weight of paramide = 10.0 grams = 74.07 per cent.
Weight of disulphonamide = 3.5 grams = 25.93 per cent.

Experiment VI.

This is Experiment V repeated, the only difference being in the length of time of heating the mixture—sixty minutes. 14 grams of anisol and 84 grams sulphuric acid were mixed and treated as in the following experiment :

Temperature of mixing, 58°.
Time of heating, sixty minutes.
Temperature of mixture during heating, 92°.
Weight of the dry sodium salt, 33.3 grams.
Two amides were found :
Weight of paramide = 3.6 grams = 64.28 per cent.
Weight of disulphonamide = 2.0 grams = 35.72 per cent.

Experiment VII.

In this experiment the proportion of sulphuric acid to anisol was 10 : 1. 8 grams of anisol was mixed with 80 grams of sulphuric acid. The temperature of mixing was 44°. The mixture was heated thirty minutes on the water-bath, and the temperature of the mixture during the heating was 91°. As before, the reaction-product was converted into the amide. The weight of dried sodium salt obtained was 22 grams. Two amides were found :

Weight of paramide = 0.1 gram = 2.44 per cent.
Weight of disulphonamide = 4.0 grams = 97.56 per cent.

Experiment VIII.

This experiment was performed to determine the effect of a higher temperature upon the course of the reaction. 20 grams of anisol was treated with 44 grams of sulphuric acid. The mixture was heated for sixty minutes at a temperature of 120°–125°. The reaction-product was converted into the amide. The weight of dried potassium salt obtained was 40 grams. Only one amide was obtained—the paramide; the weight was 2.6 grams.

Experiment IX.

Twenty grams of anisol and 44 grams of sulphuric acid were mixed and heated for sixty minutes at a temperature of 150°–158°. The product was a thick, syrupy, reddish liquid. This was poured into water and treated as above. One amide was found, and that in very small quantity. Although the dried sodium salt weighed 49 grams, only 0.6 gram of the paramide was found.

An analysis of the amide, melting at 239°, gave the following results:

0.4429 gram substance gave 0.5242 gram of carbon dioxide and 0.1585 gram of water.

0.1681 gram substance gave 0.319 gram barium sulphate (Carius method).

1.087 gram substance gave 0.11519 gram nitrogen (Kjeldahl-Gunning method).

	Calculated for $C_6H_3.OCH_3(SO_2NH_2)_2$.		Found.
C_7	84	31.58	32.2
H_{10}	10	3.76	3.97
S_2	64	24.05	24.30
N	28	10.52	10.58
O_5	80	30.08	
	266	100.00	

The compound crystallizes in short columns of lustrous leaflets. It is difficultly soluble in cold water, soluble in hot water and in alcohol.

The anilide of paranisolmonosulphonic acid was prepared and analyzed with the following results:

0.2597 gram substance gave 0.5699 gram carbon dioxide and 0.115 gram water.

0.2144 gram substance gave 0.1886 gram barium sulphate (Carius method).

1.3685 gram substance gave 0.07166 gram nitrogen (Kjeldahl-Gunning method).

	Calculated for $C_6H_4.OCH_3.SO_2NH.C_6H_5$.		Found.
C_{13}	156	59.31	59.84
H_{13}	13	4.94	4.96
O_3	48	18.25	....
S	32	12.17	12.07
N	14	5.32	5.24
	263	99.99	

The compound crystallizes in long, fine, silky needles, melting at 109°. It is insoluble in cold water; very difficultly soluble in hot water; easily soluble in cold alcohol.

The results of the preceding experiments are herewith presented in tabular form:

Experiment.	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
Weight of sulphuric acid	85	54.6	28	60	84	84	80	44	44
Weight of anisol	40	28.1	14	15	14	14	10	20	20
Temperature of mixing	83°	52°	53°	61°	60°	58°	44°		
Time of heating	35		30	60	30	60	30	60	60
Temperature of heating	92.5°		92°	92°	92°	92°	91°	125°	158°
Weight of paramide	43.7	10.5	13.5	14	10	3.6	0.1	7.6	0.6
Weight of orthoamide	3.7	1.5	0.2	0.4					
Weight of disulphonamide	0.3		1.2	1.6	3.5	2.0	4.0		
Percentage of paramide	91.6	87.5	90.6	87.5	74.0	64.3	2.4	100	100
Percentage of orthoamide	7.76	12.5	1.34	2.5					
Percentage of disulphonamide	0.63		8.06	10.0	25.9	35.7	97.6		

The weights are given in grams; the time-figures in minutes.

Summary.

Anisoldisulphonic acid is formed in every case in which anisol and sulphuric acid were mixed and heated on the water-bath to 92°, the proportion of the acid increasing with the increase in the proportion of sulphuric acid, and with the increase in the time of heating.

It is not formed at a temperature of 125° or at higher temperatures.

Paranisolmonosulphonic acid was formed in every experiment, the amount decreasing with increase of temperature, time of heating, and excess of sulphuric acid.

Orthoanisolmonosulphonic acid was formed in greatest quantity relatively, when anisol and sulphuric acid were allowed to react at ordinary temperatures; the large amount obtained in Experiment I was probably due to the higher temperature of mixing—83°; and to the time of heating—thirty-five minutes. It is not formed when the proportion of sulphuric acid to anisol is greater than 4 : 1.

SOUTH BETHLEHEM, PA., May 13, 1896.

REVIEWS.

THE JOURNAL OF PHYSICAL CHEMISTRY.

American chemists must experience a feeling of gratification at the appearance in this country of a journal which is to be devoted exclusively to the interests of that important branch of Physics and of Chemistry known as Physical Chemistry. Professors Bancroft and Trevor, of Cornell University, are to edit the Journal, and they evidently have settled the financial part of the problem to their satisfaction, or else they would not put the price of subscription as low as it is ($2.50 a year), nor venture to clothe the Journal so well. The first two numbers have been received, and, if the character of these is a fair criterion, the Journal is to take a high place. The titles and authors of the original articles in No. 1 are: "On Irreversible Cells," by A. E. Taylor; "Chemistry and Its Laws," by F. Wald; "On Ternary Mixtures, II," by Wilder D. Bancroft. In No. 2 are the following: "Allotropy of Sucrose," by F. G. Wiechmann; "Nascent Hydrogen," by R. Franchot; "On Irreversible Cells (concluded)," by A. E. Taylor; and "Purification of Water by Distillation," by G. A. Hulett. Besides original articles, both numbers contain book reviews and abstracts of articles on topics in the field of physical chemistry. The editors are to be congratulated on their first two numbers, and it is to be hoped that they will be able to maintain the high standard they have set.

I. R.

JAHRBUCH DER ELEKTROCHEMIE. Berichte über die Fortschritte des Jahres 1895. Im wissenschaftlichen Theile bearbeitet von DR. W. NERNST, o. Professor an der Universität Göttingen. Im technischen Theile bearbeitet von DR. W. BORCHERS, Lehrer an der Kgl. Maschinenbau und Hüttenschule, zu Duisburg. II Jahrgang. Wilhelm Knapp. Halle, A. S. 1896. pp. 300.

Although the appearance of the first volume of the *Jahr-*

buch der Elektrochemie has already received notice in this Journal,[1] the second volume seems to call for special comment. The most striking feature of this work is the relative importance which technical electrochemistry has acquired. Of the three hundred pages contained in the book, only thirty-six are devoted to a review of the scientific development of electrochemistry during the year which the volume covers.

The reviews of technical operations and processes are in many cases fairly elaborate, and fortunately so, since many pieces of work in this line are published in places which are more or less inaccessible to the average reader, or are covered by patents, and would be overlooked by him.

Of especial interest are the chapters on accumulators, and the new devices for obtaining high temperatures by means of the current itself. The work of Moissan on the artificial preparation of the diamond is mentioned, but very briefly. His investigations which led to the liberation of several of the elements from their compounds, by means of the current, are considered at greater length.

We find here an account of the improvements in the metallurgical processes for separating sodium, potassium, magnesium, glucinum, aluminium, silver, gold, copper, zinc, tin, nickel, cobalt, chromium, molybdenum and iron. In the chapter on those interesting compounds, the carbides, it is stated that the cost of obtaining calcium carbide is about ninety-seven marks per thousand kilograms.

This has, of course, an important bearing upon the use of acetylene as an illuminant.

This volume, like the first, contains an unusual number of cuts of apparatus. Indeed one hundred and ninety-seven are employed to illustrate the text.

It is to be hoped that so commendable a work will receive the support which it deserves.

H. C. J.

FOODS; THEIR COMPOSITION AND ANALYSIS. BY ALEXANDER WYNTER BLYTH, M.R.C.S., F.I.C., F.C.S., etc. 7th Edition. London: Charles Griffin & Co. New York: D. Van Nostrand Co.

Part I. of this book is mainly historical. It treats of the practice and the punishment of adulteration in earlier times, more particularly in England, France, and Germany, and gives an account of English legislation with regard to the adulteration of food, and also of the development of the processes for its detection. Part II. deals with some of the forms of apparatus useful in food analysis, the application of the microscope, the spectroscope and photography to the chemis-

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[1] This JOURNAL, 18, 262.

try of foods, and the analysis of ash and estimation of nitrogen. The remaining parts, III.–IX., are special, treating of carbohydrates, including the cereals; products of the dairy; tea, coffee and cocoa; alcoholic liquors; vinegar; condiments; and water.

The work, though it lacks the exhaustive character of Koenig's *Nahrungs- und Genussmittel*, is one of great merit. It will be especially welcome to those who wish to obtain a correct and adequate view of the status, in England, of the problem of food adulteration and its suppression. H. N. M

THE ELEMENTS OF ELECTROCHEMISTRY. By MAX LE BLANC, Professor of Chemistry in the University of Leipsic. Translated by W. R. WHITNEY, Instructor of Chemistry in the Massachusetts Institute of Technology, of Boston, U. S. A. Macmillan & Co., London and New York. 1896. pp. 284.

The English translation of this excellent work by Le Blanc, the original of which has already been noticed in this JOURNAL,[1] will be welcomed by American and English students of electrochemistry. It is especially opportune, since it is the first book in English which deals with the modern developments of electrochemistry in a comprehensive manner. The reviewer is not unmindful of the volume on "Solutions and Electrolysis," by Whetham, which contains several valuable chapters on the electrical properties of solutions; but, as is implied in the title, only that side of electrochemistry is treated which has to do more directly with solutions.

The point is often made that it is better to read the original than a translation, and this is true, where the reader possesses sufficient knowledge of the foreign tongue. But the fact remains that a student of physical chemistry, who has not worked in Germany, will reach the stage at which he can read an advanced work on electrochemistry, intelligently, before he has acquired a knowledge of the German language which will enable him to use it unconsciously. Further, to grasp the subject of electrochemistry is not a simple task, and when the student must divide his energy between the contents of the book and the language in which it is written, the result is not likely to be entirely successful. For these and other reasons the translation of such a book as this meets a want, and the time of the translator has been well spent.

A comparison with the original will show that Dr. Whitney has furnished us with a satisfactory translation. This is further insured by the fact that the proof has been read by Dr. A. A. Noyes. H. C. J.

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[1] This JOURNAL, 18, 521.

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