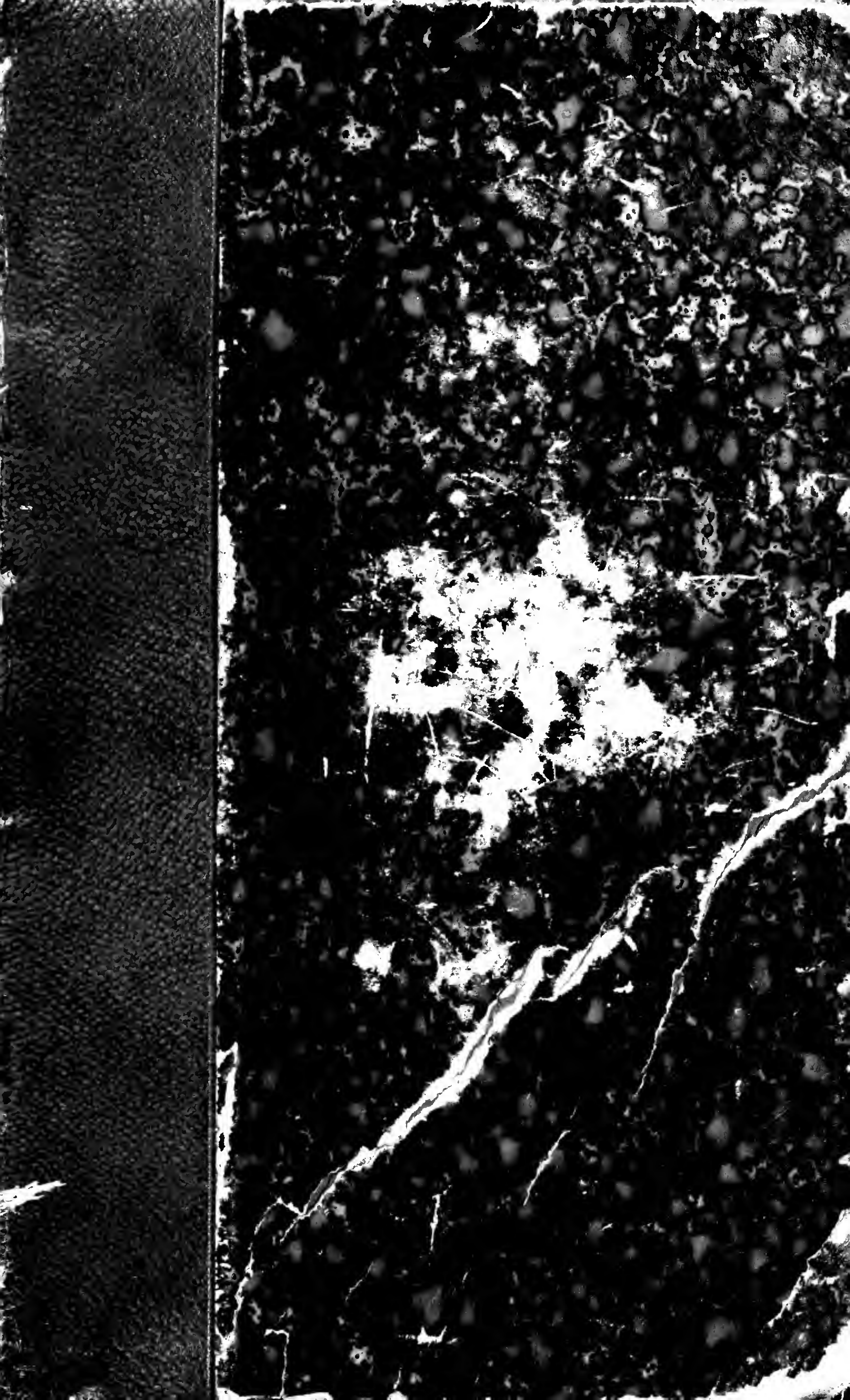

AMERICAN

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CONTENTS VOL. XXIII.

No. 1.

NOTE.

REVIEWS.

No. 2.

NOTE.

OBITUARY.

REVIEWS.

No. 3.

OBITUARY.

NOTES.

REVIEWS.

No. 4.

REVIEWS.

No. 5.

OBITUARY.

NOTES.

REVIEWS.

No. 6.

REPORT.

REVIEWS.

VOL. XXIII. JANUARY, 1900. NO. 1.

AMERICAN CHEMICAL JOURNAL

Contribution from the Kent Chemical Laboratory of the University of Chicago.

ON THE MOLECULAR REARRANGEMENT OF *o*-AMINOPHENYLETHYL CARBONATE TO *o*-OXYPHENYLURETHANE.[1]

BY JAMES H. RANSOM.

On reducing *o*-nitrophenylethyl carbonate,

$$O_2NC_6H_4OCOOC_2H_5,$$

with tin and hydrochloric acid in alcoholic solution, according to Bender,[2] a white crystalline compound (melting-point 95°, as given by Bender) separates out of the acid solution. Analysis gave figures agreeing with the composition of the expected reduction-product, aminophenylethyl carbonate, $H_2NC_6H_4OCOOC_2H_5$, and this constitution has been ascribed to the compound in spite of the striking absence of basic properties. The seeming contradiction between properties and constitution led Professor Stieglitz, who recently had occasion to use the substance in connection with an investigation with Dr. H. N. McCoy,[3] to suspect that after the reduction of the nitro compound to an amine base, a molecular rearrangement of the latter produces Bender's body. Such a

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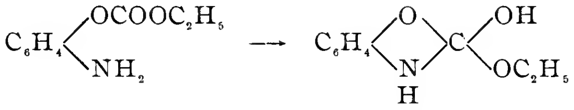
[1] See a preliminary report: Ber. d. chem. Ges., **31**, 1055.

[2] Ber. d. chem. Ges., **19**, 2268.

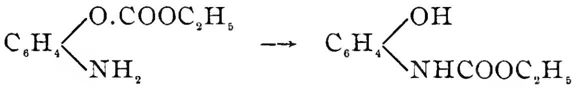
[3] This JOURNAL, **21**, 111.

molecular rearrangement could occur in one of the following ways :



$$C_6H_4{<}\genfrac{}{}{0pt}{}{OCOOC_2H_5}{NH_2} \longrightarrow C_6H_4{<}\genfrac{}{}{0pt}{}{O}{NH}{>}C{<}\genfrac{}{}{0pt}{}{OH}{OC_2H_5} \qquad (I)$$

or

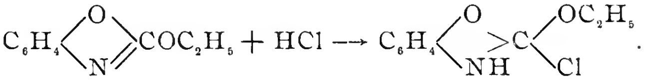


$$C_6H_4{<}\genfrac{}{}{0pt}{}{O.COOC_2H_5}{NH_2} \longrightarrow C_6H_4{<}\genfrac{}{}{0pt}{}{OH}{NHCOOC_2H_5} \qquad (II)$$

The well-known ease with which *o*-aminophenols give ring compounds suggested constitution (I). The possibility of isolating and identifying a substance of such a constitution seemed particularly important and worthy of close investigation for two reasons. In the first place, in the action of amines on acid esters, and *vice versa*, of alcohols on acid amides, an intermediate addition-product is quite generally assumed to be formed according to

$$RCOOR + H_2NR \rightleftarrows RC(NHR)(OH)OR \rightleftarrows RCONHR + HOR,$$

but the addition-product has not been isolated. Formula (I) represents such an addition-product of an amine to an ester, made stable, possibly, by the general tendency towards the formation of ortho rings. In the second place formula (I) represents the constitution of the hydroxide base corresponding to the hydrochloride of ethoxymethenylaminophenol (an imido ether) if the salts of imido ethers are formed by the addition of the acid to the double bond between the carbon and nitrogen atoms :[1]



$$C_6H_4{<}\genfrac{}{}{0pt}{}{O}{N}{\gg}COC_2H_5 + HCl \longrightarrow C_6H_4{<}\genfrac{}{}{0pt}{}{O}{NH}{>}C{<}\genfrac{}{}{0pt}{}{OC_2H_5}{Cl}.$$

A substance of constitution (I) would have to show the most intimate relationship to this hydrochloride ; and the existence or non-existence of such a relationship would go a great way towards settling the constitution of the hydrochlorides of imido ethers.

Constitution (II) would result from the migration of an acyl group from a negative phenol radical to the basic amido

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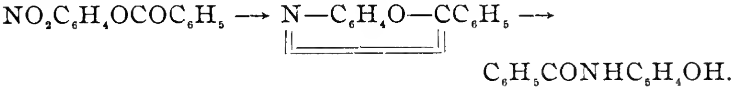
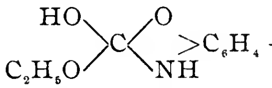
[1] *Vide* Stieglitz : This JOURNAL, **21**, 101.

group. Similar migrations have been observed, occasionally, before. Notably *o*-nitrophenyl benzoate, closely related to the nitro body under investigation, gives on reduction in hot alcoholic solution benzoyl-*o*-aminophenol. Böttcher[1] showed that the anhydro base, benzenylaminophenol, is formed by loss of water in the experiment, and under the same conditions goes over into benzoylaminophenol by the addition of water :



$$NO_2C_6H_4OCOC_6H_5 \longrightarrow N{-}C_6H_4O{-}CC_6H_5 \longrightarrow C_6H_5CONHC_6H_4OH.$$

He concluded, therefore, that benzenylaminophenol is an intermediate product in the rearrangement. But a substance of formula (II) could result, without the formation of an anhydro base, by further transformation of (I), according to



$\longrightarrow C_2H_5OCONHC_6H_4OH$,

a change entirely analogous to the conversion of an acid ester into an acid amide, as shown on page 10.

Such a rearrangement of an aminophenyl carbonate into an oxyphenylurethane (II), demonstrated to occur only in the ortho series, and to take place without the intermediate formation of an anhydro base, would prove the intermediate formation of compound (I), and thus incidentally strongly support the modern conception of ester and amide transformations. In such an event, also, the substance of constitution (I) would be shown to have an existence, however, transitory, and it might be possible to establish, even then, some connection between it and the hydrochloride of ethoxymethenylaminophenol, although the inability to isolate the hydroxide itself would, no doubt, render such a work not only more difficult but also far less decisive in determining the constitution of the hydrochlorides of the imido ethers.

With these objects in view, the present investigation was suggested by, and carried out under the direction of, Professor Stieglitz, to determine first, the true constitution of the reduc-

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[1] Ber. d. chem. Ges., **16**, 630.

tion-product of *o*-nitrophenylethyl carbonate (Bender's compound), that no opportunity might pass for isolating and investigating a possible hydroxide of constitution (I), and secondly, to study more closely than has been done by Böttcher and others the mechanism of the rearrangement after reduction.

The facts bearing on the question of the constitution of Bender's compound (m. p. 95°) known at the outset of this investigation were as follows: It crystallized out of strong acid solution and could not possibly have the constitution $H_2NC_6H_4OCOOC_2H_5$, which he assigned to it. Such a substance would have approximately the basicity of aniline and would dissolve readily in dilute hydrochloric acid (as has since been confirmed by isolating aminophenylethyl carbonate).

On the other hand, Bender prepared an acetyl derivative of his compound that on distilling gave acetylcarbonylaminophenol[1], $CH_3CO—\underline{N—C_6H_4—O—C}=O$, which evidently is in better accord with Bender's view of the constitution, $CH_3CONHC_6H_4OCOOC_2H_5$, than, for instance, with the isomeric constitution, $CH_3COOC_6H_4NHCOOC_2H_5$. Finally Groenvik[2] had already prepared an oxyphenylurethane (II), $HOC_6H_4NHCOOC_2H_5$ (soluble in alkalies, insoluble in dilute acids), from *o*-aminophenol and ethyl chlorformate, and found its melting-point to be 85°, which is 10° lower than that of Bender's compound. On comparing the two substances I found them to be identical. After one or more recrystallizations, of preparations made a number of times, the melting-point of both bodies was found to be 86°,[3] and this was not changed by mixing the two compounds even without recrystallizing. Both dissolve easily in alkalies and give in alkaline solution the same benzoate. In view of the solubility of the substance in alkali no doubt can remain that Bender's compound was not an aminophenylethyl carbonate but had suffered molecular rearrangement to (I) or (II).

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[1] Bender: Ber. d. chem. Ges., **19**, 2270.

[2] Bull. Soc. Chim., **25**, 177.

[3] The melting-point given by Bender is probably due to a typographical error or to an unreliable thermometer: *Vide*, Ber. d. chem. Ges., **19**, 2951.

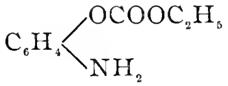
On reducing *o*-nitrophenylethyl carbonate, *o*-aminophenylethyl carbonate is undoubtedly first formed. The acid solution remains clear for some time, and the precipitation of Bender's compound is completed, in the cold, only after a day or two. By keeping the solution very cold while reducing and then rendering immediately alkaline, and extracting with ether, I was able to isolate *o*-aminophenylethyl carbonate—an oil soluble in dilute acids but insoluble in alkali—as the product of the first stage of the reaction. In the acid solution, therefore, a rearrangement of aminophenylethyl carbonate to oxyphenylurethane must occur according to

$$H_2NC_6H_4O(COOC_2H_5) \longrightarrow (COOC_2H_5)NHC_6H_4OH \text{ (II)},$$

if Groenvik's oxyphenylurethane really has the constitution one would be inclined to assign to it on the basis of its solubility in alkalies and of its preparation from *o*-aminophenol and ethyl chlorformate :

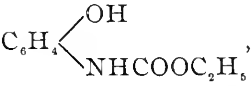
$$NH_2C_6H_4OH + ClCO_2C_2H_5 \longrightarrow (CO_2C_2H_5)NHC_6H_4OH.$$

It is obvious, however, that the attempt to prepare two compounds,



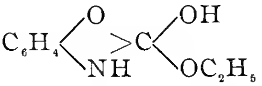
$$C_6H_4{<}\begin{matrix}OCOOC_2H_5\\NH_2\end{matrix}$$

and



$$C_6H_4{<}\begin{matrix}OH\\NHCOOC_2H_5\end{matrix},$$

could also lead to one and the same body, if in both cases the well-known tendency of the ortho series to form ring compounds was exhibited—both substances could yield the ring compound,



$$C_6H_4{<}\begin{matrix}O\\NH\end{matrix}{>}C{<}\begin{matrix}OH\\OC_2H_5\end{matrix} \quad \text{(I)},$$

as the stable form. It still remained, therefore, to determine whether *o*-oxyphenylurethane has the constitution (I) or (II).

The attempt to decide this question by alkylating with methyl iodide in alkaline solution was quite unsuccessful. Most of the substance was recovered unchanged. The substance also proved to be too sensitive to the oxidizing effects of silver oxide to prepare a silver salt for the purpose of methylation (blackening occurred under all conditions).

On the other hand, acyl derivatives were so easily made in the cold, by Baumann's method, with quantitative yields, that this method of investigation was pursued next. It led to most surprising results, the experimental data of which were carefully confirmed by me by two independent investigations with an interval of half a year. By benzoylating oxyphenylurethane, as Bender's and Groenvik's compound may be called, a benzoyl derivative is obtained melting at 75°.5. If oxyphenylurethane has the constitution its name expresses (II), the benzoate should be $C_6H_5COOC_6H_4NHCOOC_2H_5$. But exactly the same benzoyloxyphenylurethane (m. p. 75°.5) was obtained by me on treating benzoyl-*o*-aminophenol,

$$HOC_6H_4NHCOC_6H_5,$$

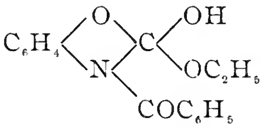
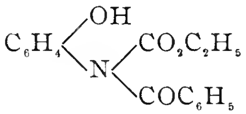
(from *o*-aminophenol and benzoyl chloride; soluble in alkalies, insoluble in acids), in alkaline solution with ethyl chlorformate. Both bodies melt at 75°.5 and there is no depression of the melting-point on mixing them. The two reactions,

$$HOC_6H_4NH\overset{*}{C}OOC_2H_5 + Cl\overset{**}{C}OC_6H_5$$

and

$$HOC_6H_4NH\overset{**}{C}OC_6H_5 + Cl\overset{*}{C}OOC_2H_5,$$

give the same product. The inevitable conclusion (excluding molecular rearrangements) is that both acyl carbon atoms, $\overset{*}{C}$ and $\overset{**}{C}$, must be attached to the nitrogen atom in benzoyloxyphenylurethane. The latter would then be


(I′) or

(II′).

The behavior of benzoyloxyphenylurethane towards heat would seem to show that, when oxyphenylurethane is benzoylated, the benzoyl group goes to the nitrogen atom. On heating it gives alcohol and benzoylcarbonylaminophenol,[1] in which the benzoyl group is found attached to nitrogen. The same substance was obtained by benzoylating carbonylaminophenol:

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[1] Bender's acetaminophenylethyl carbonate shows similar behavior.

$$H\underbracket{NC_6H_4O—CO} + ClCOC_6H_6 \longrightarrow$$
$$C_6H_5CO\underbracket{N.C_6H_4.O—CO} + HCl.$$

Benzoyloxyphenylurethane is insoluble in alkalies and shows none of the properties of a phenol. An acyl group entering the urethane molecule according to

$$HOC_6H_4NHCO_2C_2H_6 + ClCOC_6H_5 \longrightarrow$$
$$HOC_6H_4N(COC_6H_6)CO_2C_2H_6 + HCl,$$

would be without a parallel under the conditions observed. Phenylurethane, *o*-methoxyphenylurethane, etc., are not benzoylated under the same conditions. Consequently formula (II′) can be considered as completely disposed of as a possible constitution for benzoyloxyphenylurethane. If both acyl carbon atoms $\overset{*}{C}$ and $\overset{**}{C}$ are attached to nitrogen only formula (I′) would be left to represent the true constitution of benzoyloxyphenylurethane, and oxyphenylurethane itself would have the ring constitution

$$H\underbracket{NC_6H_4O—C}(OH)OC_2H_5 \text{ (I).}$$

Imide groups in similar ring complexes have frequently been found to give to compounds acid properties. For instance, ethenyl-*o*-phenylenediamine,[1]

$$H.\underbracket{NC_6H_4N=C}.CH_3,$$

and ethoxymethenyl-*o*-phenylenediamine,[2]

$$H.\underbracket{NC_6H_4N=C}OC_2H_6,$$

are soluble in alkalies, and this is undoubtedly due to the presence of the imide group (NH) in these substances. The solubility, in alkalies, of oxyphenylurethane as a ring derivative could then very well be due to the imide group, and, on benzoylating such a compound, the union of the benzoyl group with the nitrogen atom, as found above, would be expected in a normal case. The behavior of oxyphenylureth-

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[1] Bamberger: Ann. Chem. (Liebig), **273**, 274.

[2] Sandmeyer: Ber. d. chem. Ges., **19**, 2654.

ane towards acyl chlorides—exactly the same results were obtained on using *m*-nitrobenzoyl chloride in place of benzoyl chloride—agrees in every detail far better, therefore, with constitution (I), $H\underline{NC_6H_4OC}(OH)OC_2H_5$, than with constitution (II), $HOC_6H_4NHCO_2C_2H_5$.[1]

But in view of the fact that we were dealing with derivatives, for which one molecular rearrangement of the mother substance had already been positively proved, these conclusions were further tested as follows: Benzoyloxyphenylurethane, as $(C_6H_5CO)\underline{N.C_6H_4OC}(OH)OC_2H_5$, being insoluble in alkalies, the alcoholic hydroxyl group could have no marked acid properties. Now oxyphenylmethylurethane can be prepared from methylaminophenol and ethyl chlorformate according to the equation:

$$CH_3NHC_6H_4OH + ClCO_2C_2H_5 \longrightarrow C_2H_5O_2CN(CH_3)C_6H_4OH + HCl,$$

and being in every way analogous to oxyphenylurethane, it must have an analogous constitution, and would be, as a ring derivative, $CH_3\underline{NC_6H_4OC}(OH)OC_2H_5$. Such a compound, as explained in the case of benzoyloxyphenylurethane, having no acid imide group, should have no marked acid properties. On preparing oxyphenylmethylurethane it was found to dissolve quite readily in alkalies like an ordinary phenol. This result made the ring constitution for it, and consequently for oxyphenylurethane itself, again very doubtful, since the surprising nature of the acyl derivatives—verified experimentally in every point again—could very well be due to molecular rearrangements (see below) analogous to the proved rearrangement of aminophenylethyl carbonate. Recourse was had, therefore, in the final instance to methylation of oxyphenylurethane with diazomethane in neutral solution, following Von Pechmann's method for determining delicate questions of constitution. Von Pechmann[2] has shown that substances of an acid or a phenol character are easily methylated with this

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[1] See preliminary report, *loc. cit.*, p. 1059.

[2] Ber. d. chem. Ges., **28**, 855.

reagent in absolute ether solution, thus minimizing the probability of molecular rearrangements. Oxyphenylurethane gave with diazomethane, methoxyphenylurethane,

$$CH_3OC_6H_4NHCO_2C_2H_5,$$

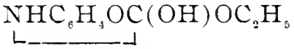
recognized by converting it into methoxyphenylurea,

$$CH_3OC_6H_4NHCONH_2,$$

which was in every particular identical with a preparation made synthetically from *o*-anisidine or from *o*-anisidineurethane. The constitution of *o*-oxyphenylurethane is consequently

$$HOC_6H_4NHCO_2C_2H_5 \text{ (II)},$$

and not



$$NHC_6H_4OC(OH)OC_2H_5 \text{ (I)}$$[1]

as decided in the preliminary report. The reaction with diazomethane is represented as follows :

$$HOC_6H_4NHCO_2C_2H_5 + CH_2N_2 \longrightarrow CH_3OC_6H_4NHCO_2C_2H_5 + N_2.$$

The second object of this investigation, *viz.*, the study of the process of rearrangement of *o*-aminophenylethyl carbonate to oxyphenylurethane, was also carried out to a considerable degree. It was possible to isolate aminophenylethyl carbonate as the first product of the reduction of *o*-nitrophenylethyl carbonate in acid solution and as the first undoubted *o*-aminophenol ester known. Its hydrochloride is quite stable in dry condition ; in aqueous solution it gradually goes over into oxyphenylurethane. But the free base, *o*-aminophenylethyl carbonate, is very much less stable—standing over night in a desiccator the oil is found to solidify to oxyphenylurethane—losing its basic properties and acquiring acid characteristics. This rearrangement of the free amine cannot possibly be due to the intermediate formation of the anhydro base, ethoxymethenylaminophenol, and its subsequent saponification, according to

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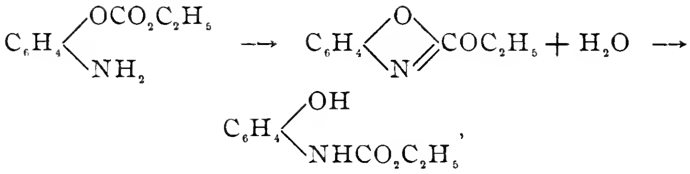
[1] *Vide*, preliminary report, *Loc. cit.*



since the anhydro base is quite a stable body, having been preserved for months without excluding traces of moisture, and even in contact with water no such rapid change was observed as in the case of aminophenyl carbonate. This conclusion is confirmed by the fact that diacylaminophenols, $Ac.NHC_6H_4OAc'$, as shown below, apparently suffer similar rearrangement, even more readily than aminophenylethyl carbonate itself, and, in their case, an anhydro base as intermediate product is plainly impossible. Aminophenylethyl carbonate, therefore, suffers rearrangement without the intermediate formation of an anhydro base, as Böttcher was led to assume in the analogous case of the reduction of *o*-nitrophenyl benzoate. Nevertheless, an intermediate ring derivative is most likely formed for the following reasons :

1. *p*-Aminophenyl carbonate was found to be a perfectly stable compound, not liable to rearrangement—the rearrangement is peculiar to the ortho series.

2. The rearrangement occurs as long as the nitrogen atom holds at least one hydrogen atom, and no longer.

Thus the fact that the two reactions,

$$HOC_6H_4NHCO_2C_2H_5 + ClCOC_6H_5,$$

and

$$HOC_6H_4NHCOC_6H_5 + ClCO_2C_2H_5.$$

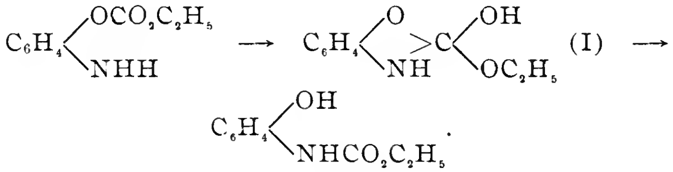
give one and the same substance, $C_6H_5COOC_6H_4NHCO_2C_2H_5$, (see below) is most likely due to similar rearrangements of the diacylaminophenols. But the analogous derivatives of methylaminophenol give two series of isomers ; *e. g.*,

$$C_6H_5COOC_6H_4N(CH_3)CO_2C_2H_5,$$

and

$$(C_2H_5O_2C)OC_6H_4N(CH_3)COC_6H_5,$$

both of which have been prepared, which are perfectly stable substances. There is, therefore, no direct exchange of acyls in the kind of rearrangement under discussion : its dependence on the hydrogen of the imide group points clearly to intermediate ring formations, which may be illustrated most simply in the rearrangement of aminophenylethyl carbonate itself:



$$C_6H_4\left\langle\begin{matrix}OCO_2C_2H_5\\ NHH\end{matrix}\right. \longrightarrow C_6H_4\left\langle\begin{matrix}O\\ NH\end{matrix}\right\rangle C\left\langle\begin{matrix}OH\\ OC_2H_5\end{matrix}\right. \quad (I) \longrightarrow C_6H_4\left\langle\begin{matrix}OH\\ NHCO_2C_2H_5\end{matrix}\right. .$$

It is obvious that at least one, but only one, reactive hydrogen atom of the amine group is essential to such rearrangements, and that the second one may be replaced by a second acyl group without interfering with the possibility of such ring transformations.

Thus, while oxyphenylurethane has not the ring constitution (I), there is every reason for believing that this ring compound has a transitory existence when aminophenylethyl carbonate goes over into oxyphenylurethane. No other rational explanation of the change seems possible on the basis of the experimental evidence presented. It follows then that derivatives, RC(OH)NH(OR), of the ortho acids are formed, but have no stable existence even under the favorable conditions caused by a ring formation.

The unusual results obtained in preparing diacylaminophenols, to which frequent reference has been made, require a few words of explanation. The same benzoyloxyphenylurethane (m. p. 75°.5, always giving by saponification with alkalies benzoic acid and oxyphenylurethane), was obtained by the following three reactions:

a. The action of benzoyl chloride on oxyphenylurethane,

$$HOC_6H_4NHCO_2C_2H_5 + ClCOC_6H_5.$$

b. The action of ethyl chlorformate on benzoylaminophenol in alkaline solution,

$$HOC_6H_4NHCOC_6H_5 + ClCO_2C_2H_5.$$

c. The action of benzoyl chloride on aminophenylethyl carbonate in aqueous alkaline, or in ether, solution,

$$(CO_2C_2H_5)OC_6H_4NH_2 + ClCOC_6H_5.$$

According to its behavior on saponification, and according to preparation *a* benzoyloxyphenylurethane seems to have the constitution $C_6H_5COOC_6H_4NHCO_2C_2H_5$ (A). According to preparations *b* and *c* and their behavior when heated (p. 6) benzoyloxyphenylurethane would be

$$(COOC_2H_5)OC_6H_4NHCOC_6H_5 \text{ (B)}.$$

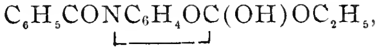
Since the same body is produced only one of these formulæ can be the correct one. When an attempt is made to prepare the second compound it is evidently converted by rearrangement into the stable modification. Formula (A) probably represents the true constitution of the stable substance, for the reason that when saponified it yields benzoic acid and oxyphenylurethane. This method gave perfectly reliable results in determining the position of the acyl groups in the case of bodies of undoubted constitution in the methylaminophenol series,

$$AcN(CH_3)C_6H_4OAc',$$

where both series of isomers have been prepared and found to be stable. With these compounds, the acyl group attached to oxygen is, without exception, removed first by saponification with alkalies. When the compound (B) is formed by methods *b* and *c* it at once goes over into the form (A) as follows:

$$(CO_2C_2H_5)OC_6H_4N\overset{*}{H}COC_6H_5 \longrightarrow C_6H_5COOC_6H_4NHCO_2C_2H_5.$$

As the hydrogen atom $\overset{*}{H}$ is essential for the rearrangement (when it is replaced by methyl there is no rearrangement), intermediate ring derivatives must be formed first similar to that given on page 2 as representing the rearrangement of aminophenylethyl carbonate. It is even possible that in the case of the diacyl compounds such a ring derivative represents the final form of the stable modification; for example, benzoyloxyphenylurethane may be

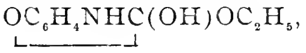


$$C_6H_5CONC_6H_4OC(OH)OC_2H_5,$$

which would agree, in part, somewhat better with its behavior than the constitution (A) assigned to it.

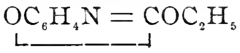
It is noteworthy that it has been possible to isolate the two isomers, aminophenylethyl carbonate and *o*-oxyphenylurethane, and to observe the change of the former into the latter, but that contrary to expectation all endeavors to isolate the corresponding second isomeric benzoyl derivative (and the second nitrobenzoyl isomer) have thus far been unsuccessful. In fact the two isomers in the series of *o*-diacylaminophenols, $AcOC_6H_4NHAc'$ and $Ac'OC_6H_4NHAc$, have in no instance been obtained with absolute certainty as yet. In the case of Ac being made benzoyl (C_6H_5CO), and Ac′ *m*-nitrobenzoyl ($NO_2C_6H_4CO$) substances were obtained, crystallizing persistently in different forms, but of practically the same melting-point, (152° and 153°) which was not depressed more than 4° (softening slightly at 146°, melting at 149°–153°) on mixing the two substances. The one crystal form was twice observed to change over into the other and remain so permanently,[1] and both compounds gave the same saponification products. It is somewhat uncertain, therefore, whether they really represent chemical isomers of the two series just mentioned, but it is probable that they do. Further investigation of the constitution of the stable compounds obtained will be carried out, and further attempts made to isolate isomers in this series and observe the conditions of their change to the stable forms.

The work involved in attaining the first two objects of this investigation—determining the constitution of oxyphenylurethane and studying the rearrangements in this group—left but little time for taking up the third object, a study of the connection between the ring derivative,



$$OC_6H_4NHC(OH)OC_2H_5,$$

and the hydrochloride of ethoxymethenylaminophenol,



$$OC_6H_4N = COC_2H_5$$

(see p. 2). As the ring derivative has only a transitory existence in the rearrangement of *o*-aminophenylethyl carbonate to *o*-oxyphenylurethane (p. 11) the basis for an experimental investigation seemed too slight for much work in this direc-

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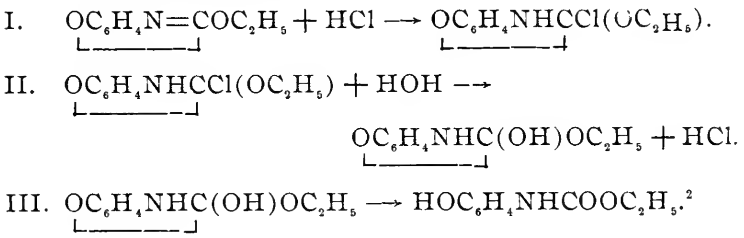
[1] *Vide*, experimental part.

tion at present. It was shown that the above hydrochloride gives, by hydrolysis, oxyphenylurethane under the same conditions that aminophenylethyl carbonate does. The reactions are exactly in accord with what was to be expected from hydrolysis[1] of the hydrochloride of an imido ether formed by the addition of hydrochloric acid to the double bond of ethoxymethenylaminophenol :[2]



$$\text{I.}\quad OC_6H_4N{=}COC_2H_5 + HCl \longrightarrow OC_6H_4NHCCl(OC_2H_5).$$

$$\text{II.}\quad OC_6H_4NHCCl(OC_2H_5) + HOH \longrightarrow OC_6H_4NHC(OH)OC_2H_5 + HCl.$$

$$\text{III.}\quad OC_6H_4NHC(OH)OC_2H_5 \longrightarrow HOC_6H_4NHCOOC_2H_5.^2$$

A more thorough investigation, for instance, of the reversibility of reaction II is necessary, to make the reactions of permanent value for the theory of the constitution of imidoether salts.

EXPERIMENTAL PART.

Reduction of o-Nitrophenylethyl Carbonate.

Oxyphenylurethane, $HOC_6H_4NHCOOC_2H_5$.—The reduction was carried out at first in alcoholic solution, according to Bender's directions: 27 grams of *o*-nitrophenyl carbonate were dissolved in alcohol, 65 cc. of concentrated hydrochloric acid added, and then slowly 40 grams of powdered tin. The whole was kept cool with ice-water. After three hours the solution was filtered and about an equal quantity of water added. Immediately an oil separated which slowly crystallized on being placed in ice-water. The melting-point of the crystals was 72°–83°. After crystallizing the substance three times from water and then precipitating it from a solution in benzene with ligroin, the melting-point remained constant at 86°. On heating the filtrate, from the oil which first separated, and then allowing it to cool slowly, more crystals sepa-

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[1] Stieglitz: This JOURNAL, **21**, 106.

[2] Stieglitz: *Ibid., Loc. cit.*

rated which had the melting-point 85°. If, however, the filtrate was allowed to stand without heating, crystals began to separate only after some hours, and then continued to form for some days. The melting-point was the same in both cases.

A quicker method of carrying out the reduction is to use a concentrated aqueous acid solution : 25 grams of the nitro carbonate are put in a flask with 60 cc. of concentrated hydrochloric acid and very little water, then 40 grams of tin slowly added, and the whole kept cold in ice-water during the first part of the action, it being allowed finally to reach the ordinary temperature. When the solution has become clear (in about forty-five minutes) it is filtered through glass-wool, after the addition of about an equal volume of water, and heated nearly to boiling for a few minutes. An oil separates which, on cooling, becomes a solid mass of crystals. On recrystallizing twice from water the melting-point is 86°.5. If the solution, during reduction, is allowed to become quite warm, mixtures result which melt between 70° and 130°, consisting of oxyphenylurethane (m. p. 86°) and carbonylaminophenol (m. p. 137°). This was proved by separating the mixture, by fractional precipitation, from a solution in benzene by carefully adding ligroin. Incidentally the presence of carbonylaminophenol was shown on treating a sample of oxyphenylurethane, which happened to contain some carbonylaminophenol, with diazomethane. Crystals separated in this case from the methoxyphenylurethane, which is an oil, and these were identified as carbonylmethylaminophenol (m. p. 86°), by comparison with the synthetic compound.

The oxyphenylurethane, prepared as described, crystallizes in rather short, thick needles or plates, varying somewhat with the medium from which it is crystallized. It is soluble in most of the organic solvents except ligroin, somewhat soluble in cold water, much more so in boiling water. It is soluble in cold, dilute, caustic alkalies, from which solution it is precipitated unchanged by acids. The crude crystals (m. p. 72°–83°) deposited from the acid solution invariably dissolved completely in dilute alkali. The change into oxyphenylurethane was, therefore, not effected by the process of purification but occurred in the original acid solution. From a concentrated solution in the alkalies the potassium and sodium salts crystallize in large needles.

Analyses of oxyphenylurethane, obtained by reduction of *o*-nitrophenylethyl carbonate, gave the following results :

I. 0.2485 gram substance gave 0.5410 gram CO_2, and 0.1371 gram H_2O.

II. 0.3244 gram substance gave 21.5 cc. N at 15.75° and 749.1 mm (corr.).[1]

	Calculated for $C_9H_{11}NO_3$.	Found.
C	59.66	59.35
H	6.07	6.12
N	7.73	7.76

For comparison with Bender's product, oxyphenylurethane was also prepared according to Groenvik's[2] method, by treating *o*-aminophenol (2 mols.) in ethereal solution with ethyl chlorformate (1 mol.). Transparent, thick needles separated out on partial evaporation, and these were recrystallized from hot water. The melting-point was then 86.°5, and in appearance the compound was similar to the substance obtained by reduction of nitrophenylethyl carbonate. Mixtures of the two had the same melting-point as either separately.

Benzoyloxyphenylurethane, $C_6H_5COOC_6H_4NHCO_2C_2H_5$.—In order more fully to establish the identity of the two substances as oxyphenylurethane, the benzoate was obtained from both preparations. Each of the substances was dissolved in a solution of potassium hydroxide (1 mol.). In each case an oil separated which, when shaken, hardened to a crystalline mass. This was recrystallized twice from alcohol, to which a little water had been added. The melting-point of each, as well as that of a mixture of the two, was 75°.5. Both were insoluble in alkalies and acids, very soluble in warm alcohol and most of the organic solvents. About 90 per cent of the theoretical yield was obtained.

I. 0.1696 gram substance gave 7.9 cc. N at 19°.2 C. and 744.7 mm. (corr.).

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[1] Corrected for vapor-tension over 30 per cent caustic potash.

[2] Bull. Soc. Chim., **25**, 177.

II. 0.3305 gram substance gave 15 cc. N at 23°.5 C. and 735.3 mm (corr.).

	Calculated for $C_{16}H_{15}NO_4$.	Found. I.	Found. II.
N	4.91	5.35	5.08

Benzoyloxyphenylurethane was also obtained by treating benzoyl-*o*-aminophenol with ethyl chlorformate.

Benzoyl-o-aminophenol, $C_6H_5CONHC_6H_4OH$. — This substance was first made by Hübner,[1] but the following method was found to give satisfactory results: 1 gram (2 mols.) of *o*-aminophenol was suspended in absolute ether, and 0.5 gram (1 mol.) of benzoyl chloride then slowly added to the mixture. A reaction began at once, the hydrochloride of 1 molecule of the base being precipitated, mixed with some of the benzoyl derivative which is not very soluble in ether. The hydrochloride was dissolved out with water, the ether solution washed with dilute hydrochloric acid and water, and the ether then evaporated. The benzoylaminophenol so prepared melted at 165°–167° (with decomposition), was soluble in alkalies, and had all the properties of Hübner's product.

Action of Ethyl Chlorformate on Benzoyl-o-aminophenol.

Three grams of benzoyl-*o*-aminophenol were dissolved in a little more than 1 molecule of potassium hydroxide and 1.5 grams (1 mol.) of ethyl chlorformate added. An oil separated out which solidified when shaken. The substance is very soluble in alcohol and ether, fairly soluble in ligroin (40°–60°), from which it crystallizes in white needles. After three recrystallizations the melting-point was constant at 76°.5.

0.2380 gram substance gave 0.5848 gram CO_2, and 0.1143 gram H_2O.

	Calculated for $C_{16}H_{15}NO_4$.	Found.
C	67.36	67.01
H	5.26	5.33

As the melting-point was so near that of its supposed isomer, obtained from oxyphenylurethane and benzoyl chloride in alkaline solution, and as the appearance of the two was so similar, more of that isomer was made and carefully purified

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[1] Ann. Chem. (Liebig), **210**, 387.

by recrystallizing it from ligroin. The melting-point now became 76°.5, and that of a mixture of the two was the same. Neither substance decomposed at the melting-point, which was unchanged after the substance solidified on cooling. The substances obtained from benzoyl chloride and oxyphenylurethane on the one hand, and from benzoylaminophenol and ethyl chlorformate on the other hand, are therefore identical. This unexpected conclusion was confirmed by a study of the saponification products of the two substances.

One gram of benzoyloxyphenylurethane (prepared from benzoylaminophenol) was shaken for an hour with a dilute aqueous solution of caustic potash (2 mols.), warming slightly toward the end. Nearly all went into solution. After acidifying, the mixture was extracted with ether, the ethereal solution shaken out with bicarbonate of soda, dried, and the ether evaporated. After recrystallizing from hot water the residue melted at 83°; mixed with *o*-oxyphenylurethane the melting-point was 84°, and it showed all the properties of this substance. The bicarbonate solution was acidified and extracted with ether, a substance being thus obtained whose odor and melting-point characterized it as benzoic acid.

Some of the benzoyloxyphenylurethane (p. 16) prepared from oxyphenylurethane and benzoyl chloride was saponified exactly as described above, and gave the same products—benzoic acid and oxyphenylurethane, thus confirming the identity of the two substances. Consequently some rearrangement in the molecule of one (or both) of them must have occurred. According to the saponification-products the stable substance is benzoyloxyphenylurethane,

$$C_6H_5COOC_6H_4NHCO_2C_2H_5.$$

The attempt to prepare the two possible isomers was repeated, the solutions being kept below 5°, in the hope that, at this temperature, real isomers might be isolated. The substances, however, were identical in every way with those described above, as proved both by appearance and melting-point as well as by saponification in alcoholic potash, which could be accomplished in one or two minutes. As seen under a microscope, no difference could be distinguished between the crystal forms. Both appeared as small, well-formed prisms with end faces perpendicular to the long axis. Finally, the two substances were prepared at —5°, at once washed with water, acid, and alcohol, and then immediately saponified by means of alcoholic potash. The same saponification-products were obtained, showing that one of the isomers did not change into the other stable modification in purifying it, but in preparing it.

Dry Distillation of Benzoyloxyphenylurethane.

Several grams of the dry substance were heated in an Anschütz distilling flask until the thermometer in the vapor had reached 100° C. The liquid collected in the receiver was then poured off and shown to be alcohol by the iodoform test. The flask was then heated again under somewhat reduced pressure, until crystals began to appear in the neck of the receiver. The liquid in the receiver was again poured off and, by its odor and boiling-point (213°), proved to be benzoic ether. A vacuum was again secured and most of the residue distilled at 200°–220°. A solid distillate collected in the receiver. This was digested some time with caustic soda, and filtered. The filtrate was acidified and extracted with ether. On evaporating the ether a small amount of a very impure substance was obtained, melting at 85°–105°. It was probably impure carbonylaminophenol, but was not further investigated. The larger part of the solid distillate was insoluble in alkali and was washed with acidified water, then with pure water, and finally recrystallized once from alcohol, in which it is soluble with difficulty. Crystals were obtained melting at 174° and possessing all the properties of benzoylcarbonylaminophenol, which will be described presently. When water was added to the mother-liquor from the first crystallization from alcohol, crystals were deposited which were very soluble in alcohol and melted at 97°–101°. Some of the substance, sublimed *in vacuo*, melted at 102°. The crystals were long needles soluble in cold ether and benzene, less soluble in ligroin, somewhat soluble in boiling water, slightly in dilute sulphuric acid, quite soluble also in concentrated hydrochloric acid, reprecipitated by alkalies. It was suspected that this substance was benzenylaminophenol (m. p. 101°–103°), and this was confirmed by preparing the latter synthetically according to the method described by Ladenburg.[1] The melting-point and properties of the substance were the same as those described above, and a mixture of the two had the same melting-point.

Benzoylcarbonyl-o-aminophenol, $C_6H_5Co\underline{NC_6H_4OC}O$. — By distilling oxyphenylurethane, alcohol is given off and carbonylaminophenol is formed. As in distilling benzoyloxyphenylurethane alcohol was formed in large quantities, it was concluded that the substance melting at 174° was the corresponding benzoylcarbonylaminophenol. This substance is not described in the literature, so that it became necessary to prepare it synthetically. This was done by treating carbonylaminophenol in alkaline solution with benzoyl chloride :

$$\underline{NHC_6H_4OCO} + C_6H_5COCl \longrightarrow C_6H_5CO\underline{NC_6H_4OCO} + HCl.$$

Recrystallized from alcohol the substance melts at 174°.

0.2851 gram substance gave 14.8 cc. of nitrogen at 18°, and 730.3 mm. (corr.).

	Calculated for $C_{14}H_9NO_3$.	Found.
N	5.85	5.88

By mixing equal portions of this substance with that formed by distillation (m. p. 174°) the melting-point was not lowered. The two are identical. The products of the dry distillation of benzoyloxyphenylurethane are therefore chiefly alcohol and benzoylcarbonylaminophenol, to a small extent ethyl benzoate and carbonylaminophenol, and finally some benzenylaminophenol. The formation of ethyl benzoate and carbonylaminophenol according to

$$C_6H_5COOC_6H_4NHCO_2C_2H_5\ (I) \longrightarrow \underline{HNC_6H_4OC}O + C_6H_5CO_2C_2H_5,$$

is perhaps in better accord with the constitution assigned to benzoyloxyphenylurethane than with the other possible open-chain form,

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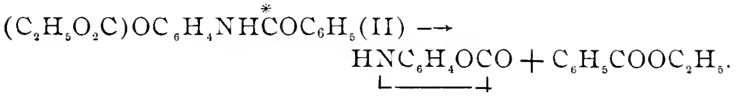
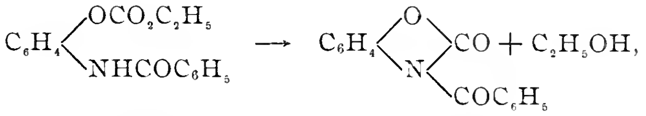
[1] Ber. d. chem. Ges., **9**, 1526.



$$(C_2H_5O_2C)OC_6H_4NH\overset{*}{C}OC_6H_5(II) \longrightarrow \underline{HNC_6H_4OCO} + C_6H_5COOC_2H_5.$$

The formation of these compounds would involve the separation of carbon atom $\overset{*}{C}$ from nitrogen, which does not occur as easily as from oxygen. But it is particularly worthy of note that the main products of the dry distillation of benzoyloxyphenylurethane are decidedly in better accord with this isomeric form[1] than with the one chosen on the basis of the saponification-products.



appears as a very simple and likely reaction, but the formation of the same products from

$$C_6H_5CO.O.C_6H_4NHCO_2C_2H_5$$

evidently would involve a much more complicated reaction since the benzoyl group is finally found attached to nitrogen. Much value was attached to this fact in my preliminary report—rightly it seems as long as molecular rearrangements of the diacyl compounds were not to be considered. But since these must take place under much simpler conditions below 0°, their occurrence in the process of dry distillation would not now be surprising. More work, however, has been planned for the study of these conditions. It may be mentioned, in this connection, that the dry distillation of the otherwise analogous *m*-nitrobenzoyloxyphenylurethane does not yield any *m*-nitrobenzoylcarbonylaminophenol. In this case the chief product is *m*-nitrobenzenylaminophenol, corresponding to the decomposition-product obtained from benzoyloxyphenylurethane in smallest quantity—the anhydro base, benzenylaminophenol. The formation of this substance acquires special interest therefrom. It was suspected that it is formed from benzoylcarbonylaminophenol as follows :

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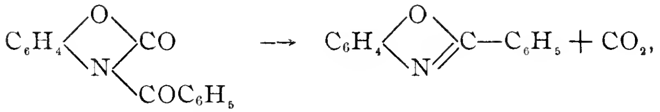
[1] Or with the ring form, see preliminary report, *loc. cit.*, p. 1063, and introduction, p. 6.



and it was shown that pure benzoylcarbonylaminophenol, when distilled, does decompose to some extent in the manner indicated. This may account for the fact that, in the case of *m*-nitrobenzoyloxyphenylurethane, as the *m*-nitrobenzoylcarbonylaminophenol disappears from the distilled product, the amount of anhydro base is proportionately increased. But it has also awakened the suspicion that the first action of heat may be to form alcohol and benzoyloxyphenyl isocyanate:[1]

$$C_6H_5COOC_6H_4NHCOOC_2H_5 \longrightarrow C_6H_5COOC_6H_4N{=}CO.$$

This could very well be converted into benzoylcarbonylaminophenol, or lose carbon dioxide, and give benzenylaminophenol. The preparation of this isocyanate will, therefore, be one of the first steps in the further study of these derivatives.

The result of the one case already given, in which the same substance is formed in whatever order the two acyl groups are introduced into the *o*-aminophenol molecule, was so unexpected that its correctness was tested by the use of other acyl radicals, in order to determine whether it holds, in general, for diacyl-*o*-aminophenols. *m*-Nitrobenzoyl chloride being easily available, it was first used in place of benzoyl chloride.

m-Nitrobenzoyloxyphenylurethane, $NO_2C_6H_4COOC_6H_4NHCO_2C_2H_5$, was prepared from oxyphenylurethane and *m*-nitrobenzoyl chloride in alkaline solution. Recrystallized from alcohol it melts at 86°.5.

I. 0.2425 gram substance gave 0.5147 gram CO_2, and 0.1032 gram H_2O.

II. 0.2541 gram substance gave 0.5388 gram CO_2, and 0.0992 gram H_2O.

III. 0.2698 gram substance gave 16.9 cc. N at 18°, and 730.4 mm. (corr.).

IV. 0.2523 gram substance gave 17.3 cc. N at 19°, and 734.9 mm. (corr.).

V. 0.2085 gram substance gave 16.2 cc. N at 20°, and 728.8 mm. (corr.).

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[1] *Vide* Hofmann: Ber. d. chem. Ges., **14**, 2727; Folin: This JOURNAL, **19**, 338.

	Calculated for $C_{16}H_{14}N_2O_6$.	Found. I.	II.	III.	IV.	V.
C	58.18	57.88	57.81	....	....	....
H	4.24	4.70	4.32	....	....	....
N	8.48	....	....	7.09	7.78	8.72

In the first two estimations of nitrogen, nitrite was found in the potash solution. Therefore the last analysis was made in a long furnace with the introduction of a spiral of reduced copper 12 to 15 inches in length.

The substance is soluble in alcohol, ether, and benzene, almost insoluble in ligroin, and insoluble in alkalies and acids. By dissolving in benzene and then adding ligroin, very fine prisms are formed.

Three grams of the substance (m. p. 86°.5) were saponified in the cold by alcoholic potash (2. mols.) and the products isolated in the usual manner. They were found to be oxyphenylurethane and *m*-nitrobenzoic acid, having all the properties of the synthetic products. A very small amount of ethyl *m*-nitrobenzoate (m. p. 40°–42°) was also recovered. The only products of the saponification of *m*-nitrobenzoyloxyphenylurethane are, therefore, *m*-nitrobenzoic acid and oxyphenylurethane. To a slight extent ethyl *m*-nitrobenzoate is split from the molecule, exactly as occurs on heating the substance. No *m*-nitrobenzoylaminophenol is formed.

Five grams of *m*-nitrobenzoyloxyphenylurethane (m. p. 86°.5) were heated in a metal bath to 250°–260°, an Anschütz flask being used. Alcohol was driven off, and also a small amount of a solid melting at 80°–123°. The flask was then exhausted and the contents distilled. Some decomposition occurred, giving a slight odor of aniline. About 2.5–2.75 grams of distillate were obtained. This was ground in a mortar with alkali, and filtered. On acidifying the filtrate a small amount of a white solid separated, which proved to be a mixture of *m*-nitrobenzoic acid and carbonylaminophenol. The neutral residue (chief part) was then boiled out with very little alcohol, to remove *m*-nitrobenzoic ether. On adding water to the filtrate a solid separated, which melted at 38°–41°, and proved to be this ether. The greater part was found to be almost insoluble in alcohol, ether, and acetone;

fairly soluble in chloroform and acetic acid, depositing a white solid melting at 203°–205°. Recrystallized from a large amount of absolute alcohol, the melting-point was raised to 207°, resolidifying at 200°. The compound is also soluble in concentrated hydrochloric acid, but is reprecipitated on adding water. Reasoning from the results of the work on the benzoyl derivative, it was thought to be either *m*-nitrobenzoylaminophenol or *m*-nitrobenzenylaminophenol, and was shown to be the latter by comparing it with synthetic preparations of these substances.

m-Nitrobenzoylcarbonylaminophenol, $NO_2C_6H_4CO—NC_6H_4OCO$.—Molecular quantities of carbonylaminophenol and *m*-nitrobenzoyl chloride in caustic soda solution gave this substance. On recrystallizing from alcohol, in which it is very difficultly soluble, it becomes pure white and melts at 199°.5–201°.5, but resolidifies at 180°, again melting at the same temperature as before. Mixed with the substance of melting-point 207°, obtained in the dry distillation of *m*-nitrobenzoyloxyphenylurethane, the melting-point was depressed to 175°–193°, showing that the substances are not identical. It is practically insoluble in ether, ligroin, alkalies, and concentrated hydrochloric acid, somewhat soluble in acetic acid, easily in chloroform. The purity of the substance was controlled by an analysis:

0.1986 gram substance gave 0.4289 gram CO_2, and 0.0545 gram H_2O.

	Calculated for $C_{14}H_8N_2O_5$.	Found.
C	59.15	58.89
H	2.81	3.04

m-Nitrobenzenyl-o-aminophenol, $C_6H_4(NO_2)C=NC_6H_4O$.—This anhydro base was prepared by heating molecular quantities of *o*-aminophenol and *m*-nitrobenzoyl chloride. The residue was difficultly soluble in alcohol, but recrystallized from this solvent in light grayish-yellow crystals of melting-point 207°, resolidifying at 200°. Mixed with the substance having the same melting-point, obtained by distilling *m*-nitrobenzoyloxyphenylurethane, no depression was observed. The two substances are therefore identical. Mixed with *m*-nitrobenzoylcarbonylaminophenol (m. p. 199°–201°) the melting-point was depressed 25°. The anhydro base is difficultly soluble in most organic solvents, except chloroform, but is soluble in concentrated hydrochloric acid, and is reprecipitated by adding water.

0.1052 gram substance gave 0.2498 gram CO_2, and 0.0346 gram H_2O.

	Calculated for $C_{13}H_8N_2O_3$.	Found.
C	65.00	64.76
H	3.33	3.61

The high-melting product of the dry distillation of nitrobenzoyloxyphenylurethane is, consequently, *m*-nitrobenzenyl-*o*-aminophenol. It is evident, therefore, that in distilling the molecule lost both alcohol and carbon dioxide. Several attempts were made to split off the first alone, by heating to different temperatures, but without success—both coming off at the same temperature, as was proved. The amount of the high-melting substance was always much less than the theoretical. On that account a roughly quantitative experiment was carried out as follows : 4.75 grams were slowly heated in a metal bath to 125°. The loss in weight, 0.2 gram, was apparently a little moisture. Pure, dry air was drawn through the flask into lime-water, but no trace of carbon dioxide was found ; nor had the melting-point of the substance changed. Heating was continued until the first indication of decomposition, 195°, and the temperature kept between this and 200° as long as action was visible. A very little oil had distilled, and the presence of alcohol and carbon dioxide was proved. The residue now weighed 4 grams. This was digested with cold alcohol and filtered into a tared beaker. When the alcohol had evaporated the residue weighed 2.63 grams. After boiling out the more insoluble part with a very little alcohol it weighed 0.8 gram, so that a large part was soluble in cold alcohol. The part soluble in cold alcohol was digested with caustic soda and filtered. On acidifying the filtrate a solid was deposited, which, after recrystallization from alcohol and water, was not quite pure, melting at 133°–135°, and proved to be carbonylaminophenol by the usual tests. The oily residue, insoluble in alkali, solidified on standing, melted at 38°–40°, and gave all the tests for *m*-nitrobenzoic ether. The most insoluble part, as well as that soluble in boiling alcohol, were mixtures melting from 150°–180°. No simple substance could be separated by recrystallization, but on heating them to 250° they were converted into *m*-nitrobenzenyl-*o*-aminophenol (m. p. 207°). It is evident that in the dry distillation of *m*-nitrobenzoyloxyphenylurethane the decomposition into ethyl nitrobenzoate and carbonylaminophenol occurs to a larger degree than in the case of benzoyloxyphenylurethane (page 6). The decomposition reactions, into nitrobenzoylcarbonylaminophenol, and of this into nitrobenzenylaminophenol, seem to occur at the same temperature, so that the anhydro base becomes one of the main products. The theoretical bearing of this has already been discussed (page 8).

As the substance by heat could not be made to lose alcohol alone, a little was dissolved in concentrated sulphuric acid and allowed to stand about five minutes. Then water was added slowly, when a solid separated which was recrystallized from much hot alcohol. The melting-point was 199°–201°, and mixed with *m*-nitrobenzoylcarbonylaminophenol, made synthetically and melting at this point, no depression of the melting-point was observed. We have here again the peculiar fact that the *m*-nitrobenzoyl group is found attached to nitrogen, while the above synthesis and saponification of *m*-nitrobenzoylurethane show it attached to oxygen, unless, indeed the diacyl-*o*-aminophenols have a ring constitution, which the monoacyl derivatives have been proved not to possess (page 9, introduction).

m-Nitrobenzoyl-o-aminophenol, $(m)\text{-}O_2NC_6H_4CONHC_6H_4OH$.—To 2 grams (2 mols.) of *o*-aminophenol, suspended in ether, an ether solution of 1.7 grams (1 mol.) of *m*-nitrobenzoyl chloride was added. The ethereal filtrate gave a small yield of a substance melting at 207°. The solid which was precipitated in the ether solution was washed with water to remove the hydrochloride of aminophenol. Recrystallized from alcohol, the substance was obtained in short, thick prisms of a light-yellow color, melting at 207°. Nitrobenzoylaminophenol dissolves in alkalies, forming a bright-yellow solution, and is reprecipitated unchanged on addition of dilute acids.

Action of Ethyl Chlorformate on m-Nitrobenzoyl-o-aminophenol.—3.35 grams of the nitrobenzoylaminophenol were dissolved in a little more than the calculated amount (1 mol.) of potassium hydroxide in solution, and 1.5 grams (1 mol.) of ethylchlorformate added. On shaking a solid separated in a somewhat oily condition. It was extracted with ether, but this solution immediately commenced to deposit crystals. The substance was purified by dissolving in benzene and carefully adding ligroin. The melting-point was found to be 86°.5. The yield was quantitative.

0.1335 gram substance gave 0.2845 gram CO_2, and 0.0536 gram H_2O.

	Calculated for $C_{16}H_{14}N_2O_6$.	Found.
C	58.18	58.12
H	4.24	4.42

The substance has the same appearance, crystalline form, and melting-point as its supposed isomer, *m*-nitrobenzoyloxyphenylurethane, and the melting-point of a mixture of the two is the same as that of either, proving the identity of the compounds. This was fully confirmed by the result of saponifying the substance whose preparation has just been described.

Two and three-tenths grams of the substance treated with alcoholic potash, as described for *m*-nitrobenzoyloxyphenylurethane, gave 0.93 gram *m*-nitrobenzoic acid (m. p. 139°–141°) and 1.18 grams oxyphenylurethane, which softened at 79° but melted at 84°. The melting-point was raised a little by mixing with pure oxyphenylurethane. These are the same saponification-products as *m*-nitrobenzoyloxyphenylurethane gives. Again the action of ethyl chlorformate on nitrobenzoyl-*o*-aminophenol,

$$HOC_6H_4NHCOC_6H_4NO_2 + ClCO_2C_2H_5,$$

and of nitrobenzoyl chloride on oxyphenylurethane,

$$HOC_6H_4NHCO_2C_2H_5 + ClCOC_6H_4NO_2,$$

give the same substance which, according to the saponification-products, is *m*-nitrobenzoyloxyphenylurethane,

$$NO_2C_6H_4COOC_6H_4NHCO_2C_2H_5.$$

A molecular rearrangement must then convert the isomer into this same compound.

Diacyl-*o*-aminophenols were also prepared, benzoyl and nitrobenzoyl being used as the two acyl radicals, without any carbethoxy group, particularly in order to determine whether their abnormal behavior—originally in excellent agreement with a ring formation, now considered to be due to rearrangements by means of ring formations—is dependent in any way on the reactivity of the carbethoxy group. The preliminary work indicated a difference of 15° in the melting-points of the two substances, benzoylaminophenol *m*-nitrobenzoate and *m*-nitrobenzoylaminophenol benzoate. By further purification, however, this difference was reduced to hardly 1°. The saponification-products of both substances were repeatedly found to be identical. However, the general appearance and crystalline forms remained persistently so different that I was led to a careful and exact reinvestigation of the reaction under different conditions. The results were the same, so that I shall describe only those conditions which seem to me to be the most favorable for the production and identification of isomeric bodies.

m-Nitrobenzoyl-o-aminophenol Benzoate, $NO_2C_6H_4CONHC_6H_4OCOC_6H_5$.—1.29 grams of *m*-nitrobenzoyl-*o*-aminophenol, freshly made and carefully purified, were dissolved in a solution of sodium hydroxide (1 mol.) at 0°, and 0.7 gram (1 mol.) of cold benzoyl chloride added, the whole being well shaken. The separated solid was filtered, washed with alkali, then thoroughly with water. A little was dried, and without being crystallized it melted at 148°–151°. The rest was washed with cold alcohol; a little dissolved which had the melting-point 151°–153°. Some was recrystallized twice from alcohol; it then melted at 153°.

0.2486 gram substance gave 17.4 cc. N at 22° C., and 726.9 mm. (corr.).

	Calculated for $C_{20}H_{14}N_2O_5$.	Found.
N	7.73	7.78

The crystals were long, white, hair-like needles, not very soluble in alcohol, insoluble in alkalies and acids. 3 grams of the substance, without crystallization, were treated with alcoholic potash in excess. In one minute all had dissolved, and this was not precipitated on adding water. The solution was acidified immediately, extracted with ether, the extracts washed with water, and a solution of sodium bicarbonate (*B*), dried with calcium chloride, and the ether evaporated. This residue (*A*) containing the monoacylaminophenols was dissolved in alkali and extracted with ether to remove any of the original substance, and again acidified. A solid separated which was recrystallized several times. The melting-point was about 160°, though not sharp. A little was dissolved in alkali and benzoyl chloride added. A solid formed, melting at 178°, 2° above that given for dibenzoyl-*o*-aminophenol. To remove any trace of *m*-nitrobenzoyl-*o*-aminophenol, the monoacylaminophenol was dissolved in alcohol, ammonia added, and hydrogen sulphide passed through the solution to reduce the nitro body. After evaporation the solid residue was washed with acid and water, then recrystallized from alcohol. It now softened at 164°, melting at 165°–167°. Mixed with benzoyl-*o*-aminophenol this was not depressed, showing that (*A*) consisted chiefly of this substance. The carbonate solution (*B*) was acidified and extracted with ether, yielding a substance melting at 139°–141°, and with all the properties of *m*-nitrobenzoic acid. The benzoate of *m*-nitrobenzoylaminophenol gives, therefore, as the chief products of saponification *m*-nitrobenzoic acid and benzoylaminophenol, in which the benzoyl group is attached to nitrogen, in the position originally held by the other acyl radical. Only traces of benzoic acid and *m*-nitrobenzoylaminophenol are formed. The substance was saponified also in warm hydrochloric acid, a little alcohol being used as solvent. The products were the same as those in alkaline solution.

Benzoyl-o-aminophenol-m-nitrobenzoate, $C_6H_5CONHC_6H_4OCOC_6H_4NO_2$.—4 grams of benzoyl-*o*-aminophenol were dissolved in caustic soda, 3.5 grams (1 mol.) of *m*-nitrobenzoyl chloride (in ether) added, and the whole shaken for some time. The separated solid was washed and then recrystallized from alcohol. After the first recrystallization the melting-point was constant at 152°. The crystals being colored, they were boiled with alcohol and bone-black, filtered, then allowed to crystallize. If heated very slowly the substance now melted at 151°. It was dried at 100° and analyzed.

0.1178 gram substance gave 0.2862 gram CO_2, and 0.0433 gram H_2O.

	Calculated for $C_{20}H_{14}N_2O_5$.	Found.
C	66.29	66.21
H	3.86	4.07

The substance crystallizes persistently in short, thick prisms, quite unlike the hair-like needles described above.

Two grams of the substance were shaken with a solution containing 2 molecules of caustic potash, heat being applied toward the end. Nearly all went into solution. After filtering and acidifying, the solution was extracted with ether, the ether solution washed with a solution of sodium bicarbonate (*B*), and the ether allowed to evaporate. The residue (*A*) containing monoacylaminophenol was boiled with water, then dissolved in alcohol, boiled with bone-black, and filtered. The crystals were then digested with a very little cold ether. Nearly all dissolved, leaving but a small amount of a substance melting at 204°–207°, which was recognized as *m*-nitrobenzoyl-*o*-aminophenol by the fact that a mixture of the two had the same melting-point. The chief part of (*A*), soluble in ether, on further purification softened at 158° and melted at 163°. It is evidently benzoyl-*o*-aminophenol mixed with a trace of the nitro body, but this was not removed as in the former case. The bicarbonate solution (*B*) when acidified and extracted with ether, left a substance melting at 136°–138° and having somewhat the odor of benzoic acid. It has all the properties of *m*-nitrobenzoic acid (m. p. 141°). The chief saponification-products of the *m*-nitrobenzoate of benzoylaminophenol are therefore *m*-nitrobenzoic acid and benzoylaminophenol, the same as those of the benzoate of *m*-nitrobenzoyl-*o*-aminophenol. But, exactly as in the case of the latter, very small quantities of benzoic acid and nitrobenzoylaminophenol are also formed—the latter containing the nitrobenzoyl group attached to nitrogen where the benzoyl group was originally held.

The melting-point of a mixture of benzoyl-*o*-aminophenol-*m*-nitrobenzoate,

$$C_6H_5CONHC_6H_4OCOC_6H_4NO_2$$

(m. p. 152°), and *m*-nitrobenzoyl-*o*-aminophenol benzoate,

$$NO_2C_6H_4CONHC_6H_4OCOC_6H_5$$

(m. p. 153°), was less exact than that of either separately, as it softened slightly at 146° and melted at 149°–153°. The saponification-products are the same but the crystal forms are persistently different. The solubility of the two forms, in alcohol, are 31.16 per cent and 27.5 per cent, respectively. Many attempts were made to change one form of crystals into the other, but under no conditions could more than a trace of the hair-like needles be changed into the prisms, and never any in the opposite direction. The closeness of the melting-points, the identity of the saponification-products,[1] and the fact that by mixing the two substances the depression of the melting-point is very slight, while, as a rule, in this series, such a mixture causes a depression of 15°–20°, raise some doubt as to the isomerism of the two substances. The persistent difference in crystal form and the like difference in solubility, make it very probable, on the other hand, that they are isomers. In that event, however, rearrangement must occur either just before or just after saponification, unless the substances are indeed ring derivatives.

One other attempt was made to obtain more sharply defined isomers of the two diacyl-*o*-aminophenol series by means of phenyl isocyanate. Leuckart has shown[2] that phenyl isocyanate, in the presence of aluminium chloride, unites with the amide group in *o*-amidophenol, but that in substituted *o*-amidophenols the isocyanate reacts with the hydroxyl group:

$$HOC_6H_4NH_2 + C_6H_5NCO \longrightarrow HOC_6H_4NHCONHC_6H_5;$$
$$HOC_6H_4NHCOR + C_6H_5NCO \longrightarrow C_6H_5NHCOOC_6H_4NHCOR.$$

Carbethoxyaminophenol Phenylcarbamate, $C_6H_5NHCOOC_6H_4NHCO_2C_2H_5$, or $C_6H_5NHCONHC_6H_4OCO_2C_2H_5$.—

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[1] See p. 36 as to the saponification-products of the two corresponding undoubtedly isomeric diacyl derivatives of methylaminophenol.

[2] J. prakt. Chem., **41**, 301.

Five grams of oxyphenylurethane and a little more than 1 molecule of phenyl isocyanate were mixed in solution in absolute ether, and a small amount of aluminium chloride slowly added. The solution became warm and the odor of hydrogen chloride was noticed. After standing some hours, and being shaken at intervals, an oil settled out. On evaporating the ether, and washing with water and hydrochloric acid, the oil solidified. On dissolving in alcohol a small amount of carbanilide was separated. After recrystallizing several times the melting-point was constant at 116°–118°.

0.1215 gram substance gave 10.5 cc. N at 20°.5 C. and 726.6 mm. (corr.).

	Calculated for $C_{16}H_{16}N_2O_4$.	Found.
N	9.33	9.65

The substance crystallizes in small, nearly white, prisms and is fairly soluble in most of the usual solvents, but is insoluble in alkalies and acids.

Action of Ethyl Chlorformate on Oxydiphenylurea.

Chemically pure oxydiphenylurea[1] (m. p. 167°) prepared according to Leuckart, was dissolved in sodium hydroxide, and ethyl chlorformate (1 mol.) added. An oil separated which was extracted with ether. The ether solution was washed with alkali, water, acid, then again with water until it gave no test for acid. The solution was dried for from fifteen to eighteen hours with fused sodium sulphate and the ether evaporated. It was then put in a vacuum over sulphuric acid for three days. It did not crystallize, nor would it crystallize on being cooled for a day to —10°–30° (cold winter night). It is insoluble in acid and alkalies, easily soluble in most of the organic solvents. As the oil could not be purified by distillation it was analyzed.

0.2867 gram substance gave 18.9 cc. N at 21° C. and 729 mm. (corr.).

	Calculated for $C_{16}H_{16}N_2O_4$.	Found.
N	9.33	7.37

The oil was apparently quite impure, but it is evidently not

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[1] Leuckart gives the melting-point at 163°-165°.

identical with the substance just described (m. p. 116°–118°), as it could not be made to crystallize by inoculation with a crystal of that substance. The small amount of the oil that remained was saponified, after standing a couple of months, with the result that, instead oxydiphenylurea, a few crystals of oxyphenylurethane were obtained. This result is as difficult to explain, on the assumption of an unchanged open chain, as those obtained with the other acyl derivatives, but, as with these, it is easily understood by assuming a ring constitution,

$$C_6H_5NHCO\underbrace{NC_6H_4OC}(OH)OC_2H_5,$$

or a rearrangement of some of the substances before or after saponification.

Acyl Derivatives of Methyl-o-aminophenol.

Of peculiar importance for the determination of the constitution of oxyphenylurethane and the interpretation of the nature of the diacyl derivatives of *o*-aminophenol, has been the study of the corresponding derivatives of *o*-methylaminophenol, $CH_3NHC_6H_4OH$. The replacement of one hydrogen atom by methyl made it possible to determine the seat of acidity in oxyphenylurethane and, preventing a rearrangement of the diacyl compounds, made a close study of the two isomeric series possible. The methylaminophenol necessary for the experiments, I found, can be prepared much more readily by means of carbonylmethylaminophenol than by way of the corresponding thiocarbonylmethylaminophenol.[1]

Carbonylmethylaminophenol,[2] $CH_3\underbrace{NC_6H_4OCO}$.—This is best prepared by dissolving carbonylaminophenol in methyl alcohol, in which is dissolved 1 molecule of potassium hydroxide, and heating for two hours with somewhat more than 1 molecule of methyl iodide. By this method 70 per cent of the theoretical yield was obtained and the remainder of the carbonyl body recovered. The best results were obtained by using not more than 5 grams of the carbonyl body for one experiment. It can be purified by repeated crystallization from

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[1] Jour. prakt. Chem. [2], **42**, 453.

[2] See Bender: Ber. d. chem. Ges., **19**, 2269; Carbonylethylaminophenol.

ligroin. It is very soluble in most organic solvents, but insoluble in acids and alkalies. It melts at 86°.

0.2347 gram substance gave 19.3 cc. N at 19° and 741 mm. (corr.).

	Calculated for $C_8H_7NO_2$.	Found.
N	9.39	9.42

Preparation of o-Methylaminophenol, $CH_3NHC_6H_4OH$.—Four to five grams of methylcarbonylaminophenol are sealed in a tube with 15–18 cc. of concentrated hydrochloric acid and heated to 180° for one and a half hours. The contents of the tube are then evaporated to dryness. By stopping the evaporation just at the right point, crystals of the hydrochloride can be obtained, but generally there remains a thick, sticky mass, which gradually hardens. By neutralizing this with a solution of sodium carbonate the free base, methyl-*o*-aminophenol, is liberated, as a white solid, in a fairly pure condition, and melts at 88°–90°.[1] The base turns brown on standing in the air, especially when moist.

Benzoylmethyl-o-aminophenol, $C_6H_5CO(NCH_3)C_6H_4OH$.—3.7 grams (2 mols.) of methyl-*o*-aminophenol are suspended in ether and 2.1 grams (1 mol.) of benzoyl chloride added. After shaking for some time, the ether solution is washed and partly evaporated. Crystals are deposited, which, after two recrystallizations from alcohol, melt at 160°–162°. The compound was dried at 105° and analyzed.

0.2845 gram substance gave 15.9 cc. N at 17°.5 C. and 727.5 mm. (corr.).

	Calculated for $C_{14}H_{13}NO_2$.	Found.
N	6.16	6.31

The substance is soluble in alkali and is reprecipitated by acids.

Benzoylmethyl-o-aminophenylethyl Carbonate, $C_6H_5CON(CH_3)C_6H_4OCO_2C_2H_5$. — 4.5 grams of benzoylmethyl-*o*-aminophenol were dissolved in 1 molecule of potassium hydroxide, and then a little more than 1 molecule of ethyl chlorformate added. A semisolid substance separated. This was extracted with ether, and the ether solution washed and

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[1] Seidel gives m. p. 80°. See J. prakt. Chem. [2], **42**, 453.

dried. On evaporating the ether an oily, crystalline mass was deposited, which was exceedingly soluble in alcohol, ether, and benzene, fairly soluble in ligroin (40°–60°). From the last solvent long, silky needles, free from oil and melting at 68°, were obtained.

0.3419 gram substance gave 14.4 cc. N at 18°.5 and 736.9 mm. (corr.).

	Calculated for $C_{17}H_{17}NO_4$.	Found.
N	4.68	4.80

One and nine-tenths grams of the substance (not quite c. p.) were shaken one and a half hours with 2 molecules of caustic soda. When nearly all had dissolved it was shaken with ether, to remove any unchanged material, then acidified and again extracted. The ether solution was washed with sodium bicarbonate. On evaporating the ether and recrystallizing the residue from alcohol it melted at 160°–162°, and was identical with benzoylmethyl-*o*-aminophenol. The solution in bicarbonate contained a very small amount of a solid which was not identified.

o-Oxyphenylmethylurethane (*ethyl-o-oxyphenylmethylcarbamate*), $HOC_6H_4N(CH_3)CO_2C_2H_5$.—2.72 grams (2 mols.) of methyl-*o*-aminophenol were suspended in absolute ether; to this was added 1.28 grams (1 mol.) of ethyl chlorformate, and then the mixture was shaken for some time. The ether solution was poured from the hydrochloride of the base, washed, dried, and the ether evaporated. The resulting oil was distilled at reduced pressure (18–20 mm.), nearly all passing over at 175°–180°. The oil did not crystallize in a freezing-mixture of ice and salt, nor on standing a week *in vacuo* in an ice chest. Some months later, when the temperature was –20° to —30°, it was kept for twenty-four hours at this temperature after adding a little ligroin, and thus it was crystallized. On recrystallization it tended to become oily, but I was able, by inoculation, to get a product sufficiently pure to determine the melting-point as 53°. The oil is soluble in alkalies and is reprecipitated by acids. It is separated from a little methylcarbonylaminophenol, formed in distilling, by dissolving in alkali, extracting with ether, acidifying, and again extracting. It was analyzed in the form of its benzoate.

Benzoyl-o-oxyphenylmethylurethane, $C_6H_5COOC_6H_4N(CH_3)CO_2C_2H_5$.—The purified oil was dissolved in sodium hydroxide, 1 molecule of benzoyl chloride added, and the whole shaken for some time. A solid separated, which was purified by recrystallization from alcohol. It melted at 88°–90°.

0.2623 gram substance gave 11.2 cc. N at 18°.5 C. and 725.6 mm. (corr.).

	Calculated for $C_{17}H_{17}NO_4$.	Found.
N	4.68	4.79

The substance crystallizes in nearly white needles, is fairly soluble in most organic solvents, but insoluble in alkalies and acids.

The benzoate, saponified and treated as usual, gave benzoic acid (m. p. 121°, not depressed by an admixture of the acid), and an oil which had all the properties of oxyphenylmethylurethane. The two reactions, between ethyl chlorformate and benzoylmethylaminophenol on the one hand, and between benzoyl chloride and oxyphenylmethylurethane on the other hand, led to two different substances—stable isomers:

$$HOC_6H_4N(CH_3)COC_6H_5 + ClCO_2C_2H_5 \longrightarrow (CO_2C_2H_5)OC_6H_4N(CH_3)COC_6H_5 + HCl,$$

and $HOC_6H_4N(CH_3)CO_2C_2H_5 + ClCOC_6H_5 \longrightarrow$

$$C_6H_5COOC_6H_4N(CH_3)CO_2C_2H_5 + HCl.$$

By saponification each compound loses first the acyl bound to oxygen. A mixture of the two isomers (melting respectively at 68° and 88°–90°) had, of course, no constant melting-point, but it melted partly at 58°, and from this slowly to 80°. The former was much the more soluble in alcohol, and the general appearance of the two was quite different.

m-Nitrobenzoylmethyl-o-aminophenol, $HOC_6H_4N(CH_3)COC_6H_4NO_2$, was prepared from methyl-*o*-aminophenol (2 mols.) and *m*-nitrobenzoyl chloride (1 mol.). The substance is not very soluble in ether. On crystallizing from alcohol beautiful, large, nearly white crystals separated. They melted at 105°, and decomposed at 110°–115°. The substance is soluble in alkalies. It was analyzed in the form of its benzoate.

m-Nitrobenzoylmethyl-*o*-aminophenol, $HOC_6H_4N(CH_3)$-$COC_6H_4NO_2$ (1.5 grams), was dissolved in sodium hydroxide and somewhat more than 1 molecule of benzoyl chloride added. An oil separated, which solidified with difficulty. On recrystallizing it from alcohol, the crystals were pure white and exceptionally perfect, melting at 141°.

0.3231 gram substance gave 0.7908 gram CO_2, and 0.1227 gram H_2O.

	Calculated for $C_{21}H_{16}N_2O_5$.	Found.
C	67.00	66.76
H	4.25	4.21

One gram of the substance was saponified exactly as in the former cases. The acid part melted at 117°–120°, and, mixed with benzoic acid, this melting-point was not depressed. It also had the odor and other properties of benzoic acid. The other portion, crystallized from ether, melted at 105° and decomposed at 110°. It had all the properties of *m*-nitrobenzoylmethyl-*o*-aminophenol.

m-Nitrobenzoate of Benzoylmethyl-o-aminophenol, $NO_2C_6H_4COOC_6H_4N(CH_3)COC_6H_5$.--Benzoylmethyl-*o*-aminophenol, $HOC_6H_4N(CH_3)COC_6H_5$ (1.75 grams), was dissolved in sodium hydroxide (1 mol.) and *m*-nitrobenzoyl chloride (1 mol.) added. An oil separated which slowly solidified. On recrystallizing it from alcohol, it separated in large, stout crystals melting at 123°.5.

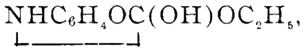
0.2109 gram substance gave 14.5 cc. N at 20°.5 C. and 735 mm.

	Calculated for $C_{21}H_{16}N_2O_5$.	Found.
N	7.45	7.78

The substance is quite soluble in alcohol, ether, and benzene; insoluble in acids and alkalies.

One gram of the substance was saponified, two to three times the calculated amount of alcoholic potash being used. All dissolved in a few minutes, and nothing was precipitated on adding water. The solution was then acidified and treated as in other cases, when it yielded benzoylmethyl-*o*-aminophenol, melting at 159°–161°, and *m*-nitrobenzoic acid, melting at 139°–141°. A mixture of the two isomers, melting respectively at 123°.5 and 141°, melted at 115°. In the diacyl derivatives of methyl*o*-aminophenol, therefore, there is no molecular rearrangement. Both isomers are stable, and by saponification the acyl attached to oxygen is always split off first.

Methylation of Oxyphenylurethane, $HOC_6H_4NHCOOC_2H_5$.—The behavior of the diacyl derivatives of *o*-aminophenol, and particularly of the acylated *o*-oxyphenylurethanes, showed plainly that we were dealing with derivatives of the ring form,



$$NHC_6H_4OC(OH)OC_2H_5,$$

or with substances possessing a most remarkable tendency to rearrangement. The study of the acyl derivatives of *o*-methylaminophenol, particularly of *o*-oxyphenylmethylurethane, on the other hand, made the ring constitution again improbable, and the probability of molecular rearrangements correspondingly greater. As no definite conclusion as to the constitution of oxyphenylurethane was reached by this line of experiment, recourse was had again to the surer process of methylation. It had failed early in the course of this study, before the investigation of the acyl derivatives had been taken up. The failure of the earlier attempts at methylating oxyphenylurethane seemed to be due to the fact that methyl iodide, in boiling alkaline solution, reacted much too slowly to be of value in the determination of such a delicate question of constitution, and that no silver salt could be prepared on account of the sensitiveness of the substance toward silver oxide. By using Von Pechmann's method of methylating by means of diazomethane, perfectly definite results were obtained, oxyphenylurethane giving *o*-methoxyphenylurethane (anisidineurethane), $CH_3OC_6H_4NHCOOC_2H_5$, and having, therefore, the constitution $HOC_6H_4NHCOOC_2H_5$.

Since it seemed possible that *o*-anisidineurethane would be obtained, it was thought best to prepare this substance first, synthetically, from *o*-anisidine to determine the best means of identifying it. These derivatives of anisidine will be described first.

o-Methoxyphenylurethane (*o-Anisidineurethane*), $CH_3OC_6H_4NHCO_2C_2H_5$.—Anisidine was suspended in water, an excess of alkali added, and then one molecule of ethyl chlorformate. An oil was formed, insoluble in acids. It was washed with dilute acid, extracted with ether, and this solution dried. After evaporating the ether the oil was distilled at 25–30 mm. pressure. This distillate was fractionated, when a nearly colorless oil, boiling at 180°–182° under 26 mm. pressure, was obtained.

0.3146 gram substance gave 20.4 cc. N at 18°.5 C. and 733.1 mm. (corr.).

	Calculated for $C_{10}H_{13}NO_3$.	Found.
N	7.18	7.36

o-Methoxybromphenylethylurethane, $CH_3OC_6H_3BrNHCO_2C_2H_5$.—An attempt to brominate the urethane, so as to get a solid derivative, showed that mixtures of two products were formed, one melting at 252°, the other at 102°.5, which it was very hard to purify. The last substance gave figures which corresponded very well with a monobrom derivative of anisidineurethane, but the mixtures were so difficult of separation that it was not thought practical to attempt an identification of anisidineurethane by this method. The substance, melting at 102°.5, was dried over sulphuric acid *in vacuo* and analyzed.

I. 0.2302 gram substance gave 0.3796 gram CO_2, and 0.0997 gram H_2O.

II. 0.3181 gram substance gave 0.5211 gram CO_2, and 0.1298 gram H_2O.

III. 0.1588 gram substance gave 0.2626 gram CO_2, and 0.0652 gram H_2O.

IV. 0.2740 gram substance gave 12.9 cc. N at 18°.5 and 745.4 mm. (corr.).

	Calculated for $C_{10}H_{12}BrNO_3$.	Found.			
		I.	II.	III.	IV.
C	43.79	44.96	44.67	45.08	....
H	4.37	4.82	4.52	4.53	....
N	5.10	....	....	....	5.43

A much more satisfactory identification was based on the change of the urethane into the corresponding urea chloride by means of phosphorus pentachloride, according to the method of Lengfeld and Stieglitz,[1] as modified by Folin and Stieglitz. The urea chloride was converted into anisidineurea and anisidinephenylurea, which were easily purified and identified. The reactions are represented thus:

$$\text{I. } CH_3OC_6H_4NHCOOC_2H_5 + PCl_5 \longrightarrow CH_3OC_6H_4NHCOCl + C_2H_5Cl + POCl_3;$$

$$\text{II. } CH_3OC_6H_4NHCOCl + 2NH_3 \longrightarrow CH_3OC_6H_4NHCONH_2 + NH_4Cl.$$

Two and two-tenths grams of anisidineurethane were placed in a distilling flask, and after adding some chloroform and 2.33 grams (1 mol.) of phosphorus pentachloride the mixture was warmed on a water-bath to 50°–55° as long as a gas (ethyl chloride) was evolved. Then the contents of the flask were cooled and dry hydrogen chloride passed through the solution until the chloroform and most of the phosphorus oxychloride were evaporated. More chloroform was added and again evaporated. Without attempting to purify the urea chloride it was converted into the urea by pouring it into a concentrated solution of ammonia. Immediately an amorphous solid, which was very soluble in alcohol, separated, but on adding water to the alcoholic solution a crystalline substance, which melted at 130°–140°, separated. On boiling it with ligroin, in which it was insoluble, then recrystallizing it from water again, and finally from chloroform and ligroin, the melting-point became constant at 143°–145° (Beilstein gives m. p. 146°.5). It was identical with the urea made from anisidine hydrochloride and potassium isocyanate.

o-Anisidinephenylurea, $(CH_3O)C_6H_4NHCONHC_6H_5$.—0.61 gram of anisidine and 0.59 gram of phenyl isocyanate were mixed in a small beaker, cooled with water. On stirring the mass a thick, heavy oil formed. When the reaction was ended dilute hydrochloric acid was added, which caused the oil to solidify. The urea is soluble in alcohol, ether, and chloroform, almost insoluble in ligroin (40°–60°). Recrystallized from alcohol, it melts at 144°. Dissolved in chloro-

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[1] This JOURNAL, **16**, 70.

form and precipitated with ligroin, it crystallized in thick prisms with the same melting-point.

0.2709 gram substance gave 28 cc. N at 22° and 736.8 mm. (corr.).

	Calculated for $C_{14}H_{14}N_2O_2$.	Found.
N	11.66	11.65

On heating a little on platinum foil a strong odor of isocyanate was noticed.

The urea chloride of anisidine was again made, as before described, from the urethane, and then poured into an excess of pure aniline. A heavy, thick oil formed, mixed with a solid. It was washed with dilute acid and water, the oil extracted with ether, and the ether evaporated. The thick oil which remained refused to crystallize even when scratched with a glass rod, and allowed to stand *in vacuo* for several days. But on rubbing into the oil, moistened with alcohol, a crystal of the synthetic urea, it became crystalline immediately. It was recrystallized from alcohol, then from chloroform and ligroin. The crystals now softened at 141° and melted at 142°–144°. Mixed with the synthetic urea the point of fusion was raised slightly. When heated on platinum foil the isocyanate odor became distinctly perceptible.

Methylation of o-Oxyphenylurethane with Diazomethane.—The diazomethane was prepared from nitrosomethylurethane according to the method of Von Pechmann.[1] The methylamine was prepared from acetamide[2] according to Hofmann's method. Nitrosomethylurethane was prepared by following the description of Von Pechmann,[3] the ethereal solution of the urethane being placed in the separating-funnel in which it was to be washed and dried. In this way I avoided entirely the disagreeable effects experienced by this experimenter.

One and eight-tenths grams of oxyphenylurethane were

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[1] Ber. d. chem. Ges., **28**, 855.

[2] As no details could be found of the methods employed for making acetamide from ammonia and acetic ether, experiments were carried out to determine the conditions for obtaining the best yield. By mixing 100 grams of the ether with 200 cc. of concentrated ammonia (sp. gr. 0.90), and allowing the mixture to stand until it had become homogeneous (two days), and then distilling, 75-80 per cent of the theoretical amount was obtained.

[3] *Loc. cit.*

dissolved in a small amount of ether, and to this solution was added diazomethane dissolved in ether. The whole was then warmed on the water-bath for an hour, a reflux condenser being used. The yellow color of the solution nearly disappeared and a gas (nitrogen) was evolved. More diazomethane was added and it was again warmed. When the color of the solution remained light-yellow, which showed a slight excess of diazomethane, the ether solution was washed with sodium hydroxide, then with hydrochloric acid and water. On drying and evaporating the ether an oil remained, insoluble in acids and alkalies. It is somewhat viscous, possesses a pleasant, ethereal odor, and is soluble in most of the organic solvents. It could not be made to crystallize in the cold, but was identified as *o*-methoxyphenylethylurethane,

$$CH_3OC_6H_4NHCO_2C_2H_5,$$

by converting it into methoxyphenylurea and methoxycarbanilide by treatment with phosphorus pentachloride, followed by ammonia or aniline, as described above for the synthetic urethane. 0.7 gram of the urethane was thus converted into the urea. A little oil separated, which soon solidified. After filtering it off the solution was evaporated to dryness. The solid residue was dissolved in chloroform, and ligroin carefully added. Transparent crystals formed which, after several recrystallizations, were of a light-brown color, and melted at 145°, softening a little at 140°–142°. Mixed with the urea (m. p. 143°–145°) made from anisidine urethane, the melting-point was not depressed. The crystal forms, as seen under the microscope, were the same, proving conclusively that the two substances are identical.

More of the urea chloride of the methylated urethane was made as already described, and poured into an excess of aniline. A thick oil was formed, which was washed with dilute acids and water. On rubbing the oil with a crystal of the synthetic urea it became a solid mass of crystals. These were purified by recrystallizing from chloroform and ligroin. The substance melted at 144°, and, mixed with the synthetic phenylurea, the melting-point was not depressed. On heating some of the substance on platinum foil, the isocyanate odor was easily perceptible. The methylated oxyphenylurethane is undoubtedly an anisidine derivative, and therefore *o*-oxyphenylurethane must contain a phenol hydroxyl group.

o-Aminophenylethyl Carbonate, $H_2NC_6H_4OCO_2C_2H_5$.—Having established the fact that a rearrangement occurs when *o*-nitrophenyl carbonate is reduced with tin and hydrochloric acid, and that oxyphenylurethane was the only product thus far liberated, it seemed of interest to isolate the free aminophenyl carbonate, which must be the first product of the reduction, as that might throw some light on the mechanism of the rearrangement. After some unsuccessful attempts, the following method was found to give satisfactory results:

Four grams of *o*-nitrophenyl carbonate are put in a flask with 15 cc. of concentrated hydrochloric acid and cooled in ice-water. To this is added powdered tin in small portions and the whole shaken, the temperature being kept near 0°. If the solution is kept sufficiently cold, almost immediately after becoming clear a fine, white, crystalline solid begins to appear. This contains both organic and inorganic material and is probably a double salt. When no more crystals form, the contents of the flask are poured slowly into a well-cooled solution of 50 grams of potassium hydroxide in 50 cc. of water. If too much heat is allowed to develop at this stage the results are negative. The alkaline solution is immediately extracted six times with ether, a sufficient amount of water being added during the last extractions to dissolve the potassium chloride. The ether solution is washed with water and then dried with solid potassium hydroxide. When dry, the ether is poured off and dry hydrogen chloride passed into it. A copious, white precipitate of the hydrochloride of *o*-aminophenylethyl carbonate is formed which can be filtered and dried on a clay plate. It is stable at the ordinary temperature, and remains perfectly white. From 60–70 per cent of the theoretical yield is obtained. It melts at 150°–152° with evolution of much gas. It is very soluble in cold water and in alcohol. Sodium carbonate decomposes it, forming aminophenylethyl carbonate, an oil which is soluble in dilute acids. On heating an aqueous solution of the salt it becomes cloudy before the boiling-point is reached, and an oil separates which gradually solidifies on cooling. On recrystallizing this solid from somewhat diluted alcohol, crystals are formed which melt at 85°–86°.5, and resemble oxyphenylurethane. When these crystals are mixed with oxyphenylurethane the melting-point is not depressed. It is also soluble in alkalies and is reprecipitated by acids. A nearly saturated solution of the hydrochloride of *o*-aminophenylethyl carbonate was made, and to this a concentrated solution of platinic chloride was added. After a few minutes, yellow crystals formed. They were somewhat soluble in water and alcohol, insoluble in ether. They were washed with ether in which was some alcohol, dried and analyzed.

0.0446 gram chlorplatinate gave 0.01125 gram of platinum.

	Calculated for $C_{18}H_{24}N_2O_6PtCl_6$.	Found.
Pt	25.16	25.22

0.1664 gram of the hydrochloride was titrated with tenth-normal silver nitrate, potassium chromate being used as indicator. 7.7 cc. of the solution were required.

	Calculated for $C_9H_{12}NClO_3$.	Found.
Cl	16.32	16.42

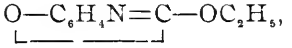
Some of the salt was put into a separating-funnel with ether and a solution of sodium carbonate added to alkaline reaction. The ether solution was then washed, dried with fused potassium sulphate, and the ether evaporated *in vacuo*. Aminophenylethyl carbonate remained as a basic oil, which was easily soluble in dilute acids and could be converted back into the hydrochloride and the chlorplatinate of *o*-aminophenylethyl carbonate. It was kept over sulphuric acid. After twelve hours it had changed to a crystalline solid which melted at 86°, and it was now soluble in alkalies and was reprecipitated by acids. All the properties of this solid, as well as the melting-point of a mixture with oxyphenylurethane, proved it to be this substance.

In an attempt to convert the hydrochloride of aminophenylethyl carbonate into the corresponding urea, 0.3 gram of the hydrochloride was dissolved in water and a solution of potassium isocyanate added. An oil separated which was dissolved in water, and, on standing some hours, crystals melting at 86° separated, which proved to be oxyphenylurethane. Another attempt was made, an alcoholic solution of the salt being used, but it was converted into the urethane, as in the former experiment. Evidently the rearrangement takes place rather than the usual addition to isocyanic acid.

One gram of the hydrochloride was treated with an ice-cold solution of 2 molecules of sodium hydroxide and a little more than 1 molecule of benzoyl chloride added. The solution was then extracted with ether several times. The residue, left on evaporating the ether, was again digested with very little ether, which dissolved all but a little, and this, recrystallized from alcohol, melted at 180°, and, mixed with dibenzoylaminophenol, did not melt lower.[1] The ether solution deposited crystals which, after one recrystallization from ligroin, melted at 76° and in its crystal form as in its other properties, was identical with the benzoyl derivative of oxyphenylurethane. A mixture of the two had the same melting-point.

In a second attempt to prepare the isomer of the latter compound a little more than 1 gram of the hydrochloride, corresponding to 0.9 gram (2 mols.) of the free base, was put in a separating-funnel with ether and then treated with an excess of sodium carbonate. The ether solution of the free base was washed, dried with solid potassium hydroxide, and then 1 molecule of benzoyl chloride added. After a minute the hydrochloride of 1 molecule of the base separated. This was filtered out, the ether washed with alkali, then with dilute acid, finally with water, and dried with calcium chloride. On distilling the ether a solid remained which melted at 76°. Mixed with the benzoyl derivative of oxyphenylurethane, the melting-point was not depressed.

In order to compare the behavior of aminophenylethyl carbonate towards dilute acid, with that of ethoxymethenylaminophenol,



$$O-C_6H_4N=C-OC_2H_5,$$

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[1] Hübner gives 176° as the melting-point of this derivative.

1 gram of the hydrochloride was allowed to stand twenty-four hours with less dilute hydrochloric acid than was sufficient to dissolve all of it. Then it was completely dissolved in this reagent. After standing some days longer, the solution was divided into two portions and one was extracted with ether. On evaporating the ether a solid remained, which, after one recrystallization from water, melted at 70°–119°. The other portion, on standing longer, deposited crystals which melted at 70°–80°, but when mixed with oxyphenylurethane, the melting-point was raised a little. Decomposing this by distilling some of it into the upper part of a test-tube the melting-point was raised to 135°–137°, which proved the sublimate to be carbonylaminophenol. It is quite certain that the original product is a mixture of oxyphenylurethane and carbonylaminophenol, as I have found that mixtures of these, in different proportions, have melting-points anywhere between 70° and 120°. By distillation they give pure carbonylaminophenol.

Action of Hydrochloric Acid on Ethoxymethenyl-o-aminophenol. —In the reduction of the *o*-nitrophenyl carbonate it was thought possible that the hydrochloride of the anhydro base, ethoxymethenylaminophenol, might be formed[1] instead of the amino base. A comparison of this base with aminophenylethyl carbonate was, therefore, undertaken. Some of the anhydro base, obtained through the kindness of Dr. H. N. McCoy, was dissolved in absolute ether and dry hydrogen chloride passed into the solution. The first bubbles produced a crystalline deposit, but this immediately disappeared, and, on evaporating the ether, only carbonylaminophenol remained. The experiment was repeated in dry ligroin solution at —11°. A solid separated which was stable at that temperature, but when put on a clay plate in a cold room the crystals began to decompose, giving off a gas (ethyl chloride) which burned with a green flame. On the clay plate there remained pure carbonylaminophenol (m. p. 136°–138°).[2] The behavior of this

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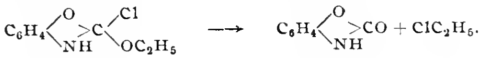
[1] As in Böttcher's experiments with *o*-nitrophenylbenzoate.

[2] This is the typical behavior of the hydrochloride of an imido ether which ethoxymethenylaminophenol hydrochloride represents:



$$C_6H_4\begin{matrix}O\\NH\end{matrix}>C\begin{matrix}Cl\\OC_2H_5\end{matrix} \longrightarrow C_6H_4\begin{matrix}O\\NH\end{matrix}>CO + ClC_2H_5.$$

Attention may be called to the unusually low temperature at which the salt decombase is therefore different from that of the amino base formed by reducing *o*-nitrophenyl carbonate. And this fact, coupled with the observation already given, that the amino base on standing is converted into the urethane while the anhydro base is stable in ordinary moist air, proves conclusively that the latter is not an intermediate product in the intramolecular rearrangement.

For reasons stated in the introduction (p. 9), it was thought desirable to compare the behavior of the anhydro base toward dilute hydrochloric acid with that of aminophenylethyl carbonate (see above). The anhydro base was allowed to stand several days in contact with dilute hydrochloric acid. The oil gradually disappeared and was replaced by white crystals. When all the oil had disappeared the crystals were filtered off, recrystallized from water, and dried. They melted at 70°–80°, were soluble in alkali, and reprecipitated by acids. On distilling into the upper part of a test-tube and then recrystallizing from water, in which was a little alcohol, a substance melting at 136°–138° was obtained, which proved to be carbonylaminophenol. The low-melting substance is certainly a mixture of oxyphenylurethane, and carbonylaminophenol. The products formed are identical with those obtained by allowing the hydrochloride of aminophenyl carbonate to stand in an acid solution.

p-Nitrophenyl Carbonate, $NO_2C_6H_4OCOOC_2H_5$.—The peculiar rearrangement observed on reducing *o*-nitrophenyl carbonate in the usual way, by which *o*-oxyphenylurethane results, suggests a comparison of corresponding derivatives in the meta or para series, preferably the para series, as that is the more susceptible to molecular rearrangement, and usually resembles the ortho series more than the meta series does.

Ten grams of *p*-nitrophenol were treated with excess of potassium hydroxide, and somewhat more than 1 molecule of

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poses. It recalls the behavior of the hydrochloride of ethylphenylimidochlorformate, $ClC(NC_6H_5)OC_2H_5$, which, decomposing below —15° into ethyl chloride and chlorformanilide, could not be isolated by Lengfeld and Stieglitz,[1] although its formation was clearly indicated and formed an important link in their arguments. The properties of the solid hydrochloride of ethoxymethenylaminophenol fully support their assumption of such an intermediate hydrochloride.

[1] This JOURNAL, 16, 73.

ethyl chlorformate was added in small portions, while the contents were vigorously shaken. A quantitative yield of a nearly white solid melting at 68° was obtained.

0.2533 gram substance gave 14.8 cc. N at 17° and 736.8 mm.

	Calculated for $C_9H_9NO_5$.	Found.
N	6.63	6.71

The carbonate is soluble in ligroin, ether, alcohol, and somewhat in boiling water, from all of which it crystallizes in long, white needles.

Synthesis of p-Nitrophenylethyl Carbonate.

In order fully to establish that in *p*-nitrophenyl carbonate the carbethoxy group is attached to phenol oxygen and not to the nitro group, a synthesis from phenylethyl carbonate was carried out. The phenyl carbonate was cooled to 0° in ice-water and then poured slowly into ice-cold, fuming nitric acid. On pouring the mixture into water a nearly white, crystalline solid separated immediately. If allowed to stand for some time in the strong nitric acid the product is much more impure. On recrystallizing from alcohol it crystallizes well and melts at 68°. A mixture of this with the carbonate made from *p*-nitrophenol has the same melting-point as either, and the two are identical in all their properties.

p-Aminophenylethyl Carbonate, $H_2NC_6H_4OCO_2C_2H_5$.—Several attempts were made to reduce the carbonate with tin and hydrochloric acid, in aqueous and in alcoholic solution, but the yields in each case were small owing to the fact, afterwards discovered, that the base is somewhat soluble in water and is not extracted with ether completely. The best results are secured by proceeding as follows :

Two grams of the nitrocarbonate were dissolved in warm alcohol, concentrated hydrochloric acid added, and then slowly, and in small portions, 11 grams (6 mols.) of stannous chloride. The solution became light-yellow. After fifteen minutes a drop gave no precipitate with water. The whole was then diluted and hydrogen sulphide passed into the solution, until all the tin was thrown down. After filtering, the solution was concentrated *in vacuo* at 50°–55°. On standing, white crystals of the hydrochloride of *p*-aminophenylethyl carbonate were deposited. The yield was 70 per cent. The crystals are very soluble in water. From dilute solutions caustic alkalies do not precipitate the base. From fairly concentrated solutions sodium hydroxide or sodium carbonate precipitates an oil which solidifies on standing and then melts at 36°. On recrystallizing it an oil, which solidifies only on standing some days, is formed at first. Both crystals and oil dissolve in acid. The base is somewhat soluble in water, gives no purple color with ferric chloride, and does not become colored in the air. On heating the hydrochloride it darkens at 160° and melts at 197° with violent decomposition.

0.2005 gram of the hydrochloride dissolved in water and titrated with tenth-normal silver nitrate, potassium chromate being used as indicator, required 9.3 cc. of the nitrate solution.

	Calculated for $C_9H_{12}NO_3Cl$.	Found.
Cl	16.32	16.46

The platinum salt was made in aqueous solution by precipitating with chlorplatinic acid, washing the precipitate with alcohol and ether, and then drying *in vacuo* over sulphuric acid.

0.2869 gram substance gave 0.0722 gram Pt.

	Calculated for $(C_9H_{12}NO_3)_2PtCl_6$.	Found.
Pt	25.16	25.16

It is a bright-yellow, crystalline solid melting at 237°, blackening at 208°.

p-Ureidophenylethyl Carbonate, $NH_2CONHC_6H_4OCOOC_2H_5$.—The paraminophenylethyl carbonate can also be identified easily by converting it into its urea. 0.3 gram of the hydrochloride was dissolved in a little water and the calculated amount of potassium cyanate added. An oil separated which soon became crystalline. On crystallizing once from hot water it was nearly white and melted at 147°–150°. It is insoluble in alkalies.

All attempts to cause a rearrangement of *p*-aminophenylethyl carbonate to *p*-oxyphenylurethane were unsuccessful. One gram of the hydrochloride was dissolved in water, and, after the addition of some hydrochloric acid, the solution was allowed to stand two days. No change having taken place, apparently, the solution was boiled two and a half hours under a reflex condenser. It was then allowed to stand a week. The solution was then evaporated at 50°–60° *in vacuo* in an atmosphere of hydrogen sulphide. The residue was washed with a little water, filtered, and tested as follows:

Ferric chloride produced a deep-purple color, due to *p*-aminophenol. Sodium carbonate produced a solid which gradually turned brown on standing. A urea, made as in the former experiment, melted at 167°, blackening at 162° (*p*-oxyphenylurea melts at 167°). It was quite soluble in alkalies. Mixed with the urea of *p*-aminophenyl carbonate (m. p. 147°–150°), the melting-point became 130°–150°. Evidently the acid had caused a saponification of the hydrochloride of *p*-aminophenylethyl carbonate to that of *p*-aminophenol.

Another gram of the hydrochloride of *p*-aminophenylethyl carbonate was dissolved in water and allowed to stand at the temperature of the room for a week. The solution was then evaporated as was the first portion. Ferric chloride gave a very light-purple color. Sodium carbonate precipitated an oil which became solid on inoculating it with a crystal of *p*-aminophenyl carbonate. The oil dissolved in hydrochloric acid. The urea was made as in the former case. It softened slightly at 142°, melting at 146°–148°. Mixed with a synthetic *p*-ureidophenylethyl carbonate, the melting-point was not lowered. It was insoluble in alkalies. No change had occurred. A third portion of the hydrochloride was dissolved in water and alcohol, allowed to stand a week, and then treated as in the former case.

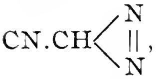
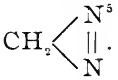
Ferric chloride gave a reddish-purple color. Sodium carbonate separated an oil which gave tests corresponding to *p*-aminophenyl carbonate and formed the same urea. It is evident from these tests that *p*-aminophenylethyl carbonate exhibits no tendency to change into a urethane corresponding to *p*-oxyphenylurethane.

I wish here to express my thanks to Professor Stieglitz for valuable suggestions and for the careful attention he has given to each step of this work.

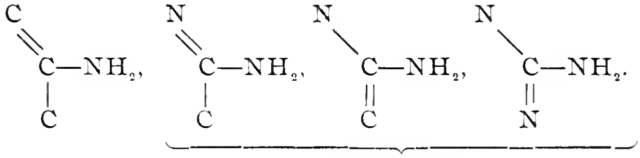
DIAZOCAFFEINE.

By M. Gomberg.

Such few of the aliphatic amines as yield diazo derivatives at all have the amido group linked to a primary or secondary carbon atom. As a consequence the tendency towards the formation of a closed ring is easily satisfied. Curtius' historical diazoacetic ester[1] has the constitution

A similar constitution is ascribed to the esters of diazopropionic[2] and diazosuccinic[3] acids, diazoacetonitril,[4] , as well as to the diazomethane itself, .

There is, therefore, a wide difference between these diazo compounds and those of the aromatic series. The first cannot combine with phenols and amines to form azo dyes, while the latter always do so. No diazo derivatives have been prepared of aliphatic amines in which the amido group is linked to a tertiary carbon atom whose three valencies are taken up by three radicals. Some heterocyclic amines, however, with a tertiary carbon atom, have been diazotized, and the derivatives so obtained closely resemble those of the purely aromatic series in their capacity for coupling with phenols and amines. In all such heterocyclic amines the carbon atom carrying the amido group has a linking similar to that in the aromatic amines:



Aromatic. Heterocyclic.

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[1] Curtius: J. prakt. Chem. [2], **38**, 396.

[2] Curtius and Koch: *Ibid.*, 487.

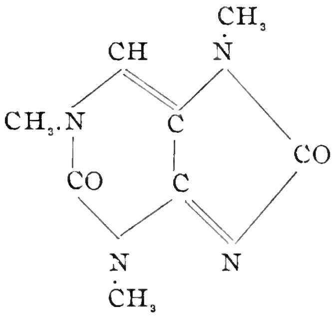
[3] Curtius and Koch: *Ibid.*, 474.

[4] Curtius: Ber. d. chem. Ges., **31**, 2489.

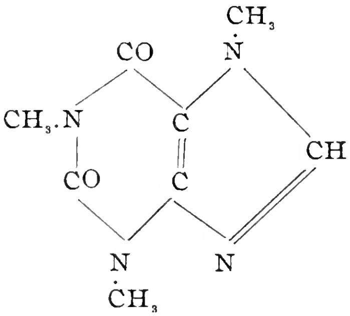
[5] Von Pechmann: *Ibid.*, **27**, 1888.

Not all heterocyclic amines of the above constitution can, however, be diazotized. Only very few have yielded such derivatives, and in some cases the diazo salts were not isolated in the dry state, but could exist only in solution. Amidotetrazol,[1] diamidophenylosotriazol,[2] amidotriazol,[3] as well as its methyl and carboxy derivatives, are the most important examples of heterocylic amines that have been successfully diazotized.

Caffeine, although usually looked upon as an aliphatic compound, behaves in many of its reactions more like an aromatic body. Its halogen substitution derivatives part with the halogen with great difficulty; ammonia acts upon them only at a comparatively high temperature and pressure, while zinc ethyl[4] does not act at all at a temperature of 120°–130° C. Caffeine, like all other ureides, can be looked upon as a heterocyclic compound. Its constitution from this standpoint is that of a naphthalene-like combination of a methylated pyrimidine and glyoxaline rings:



Old formula.



Recent formula.[5]

It is therefore not strange that amidocaffeine, with the amido group linked to the tertiary carbon atom, should give a diazo compound on treatment with nitrous acid, even if the amine itself is a very weak base.

Diazocaffeine is a very unstable substance, and so far has been obtained only in solution; even in that form it could be

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[1] Thiele and Marais: Ann. Chem. (Liebig), **273**, 144; **287**, 244.

[2] Thiele and Schleusner: *Ibid.*, **295**, 150.

[3] Thiele and Manchot: *Ibid.*, **303**, 40, 50, 54.

[4] Gomberg: This JOURNAL, **14**, 616.

[5] E. Fischer: Ber. d. chem. Ges., **30**, 553.

kept without decomposition at a comparatively low temperature only. It possesses a very great tendency to combine with aromatic phenols and amines. The beautiful azo dyes so formed are quite stable, and are of intense dyeing power. The following few typical examples are described in this paper: Caffeineazophenol, caffeineazodimethylaniline, caffeineazophenylenediamine, and caffeineazo-β-naphthol.

That the caffeine molecule is not broken up by the action of nitrous acid, but that a true diazo salt of caffeine is formed, has been proved in two ways. First, if caffeine instead of its amido derivative is subjected to the same treatment with nitrous acid, it remains entirely unchanged. Second, the azo dyes (the dimethylaniline compound, for instance) on treatment with stannous chloride, furnish almost quantitatively amidocaffeine and the corresponding aromatic body:

$$C_8H_9N_4O_2.N:N.C_6H_4N(CH_3)_2 + 4H = C_8H_9N_4O_2.NH_2 + H_2N.C_6H_4.N(CH_3)_2.$$

Diazocaffeine couples readily not only with a large number of aromatic compounds but with aliphatic as well. It combines with acetoacetic ester and the free acid, with their homologues, with nitroethane, nitropropane, etc.

Ever since V. Meyer's[1] discovery of the action of diazobenzene upon acetoacetic ester, this same question has been repeatedly the subject of investigations. The derivatives obtained by this reaction are no longer looked upon as azo bodies,—a view originally entertained by the discoverer,—but rather as hydrazones. This change of view as to the constitution of these and all analogous bodies is due especially to the work of R. Meyer,[2] of Japp and Klingemann,[3] and to the more recent investigations of Bamberger and of Von Pechmann upon the constitution of the formazyl derivatives. It has been established that whenever a diazo salt combines with an aliphatic compound containing a methylene or a methine group, made negative by carbonyl or nitro groups, the derivatives so obtained do not possess the expected azo constitu-

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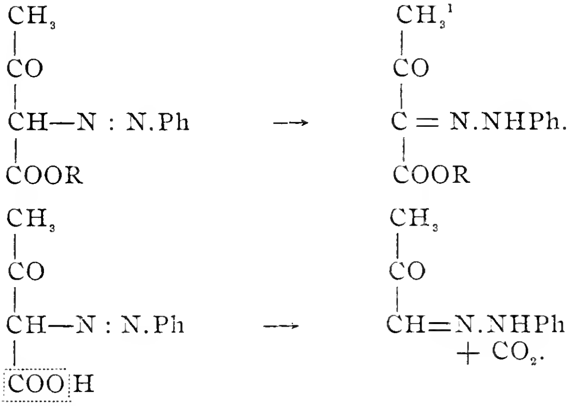
[1] Ber. d. chem. Ges., **10**, 2075.

[2] *Ibid.*, **21**, 118; **24**, 1241.

[3] Ann. Chem. (Liebig), **247**, 190.

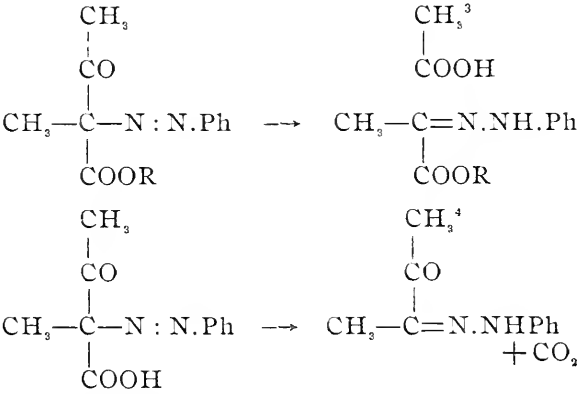
tion, but suffer an intramolecular change to the hydrazones:



$$\begin{array}{l} CH_3 \\ | \\ CO \\ | \\ CH—N:N.Ph \\ | \\ COOR \end{array} \longrightarrow \begin{array}{l} CH_3{}^{1} \\ | \\ CO \\ | \\ C=N.NHPh. \\ | \\ COOR \end{array}$$

$$\begin{array}{l} CH_3 \\ | \\ CO \\ | \\ CH—N:N.Ph \\ | \\ \boxed{COO}H \end{array} \longrightarrow \begin{array}{l} CH_3 \\ | \\ CO \\ | \\ CH=N.NHPh \\ \qquad + CO_2. \end{array}$$

So great is this tendency to change into hydrazones, that if an *alkyl* acetoacetic ester is employed in this reaction then one of the two negative groups—the acetyl or the carboxyl, depending upon the conditions of the experiment—is entirely split off in order to allow the formation of such a hydrazone:[2]



$$\begin{array}{rl} & CH_3 \\ & | \\ & CO \\ & | \\ CH_3— & C—N:N.Ph \\ & | \\ & COOR \end{array} \longrightarrow \begin{array}{rl} & CH_3{}^{3} \\ & | \\ & COOH \\ & \\ CH_3— & C=N.NH.Ph \\ & | \\ & COOR \end{array}$$

$$\begin{array}{rl} & CH_3 \\ & | \\ & CO \\ & | \\ CH_3— & C—N:N.Ph \\ & | \\ & COOH \end{array} \longrightarrow \begin{array}{rl} & CH_3{}^{4} \\ & | \\ & CO \\ & | \\ CH_3— & C=N.NHPh \\ & \qquad + CO_2 \end{array}$$

The recent investigations of Bamberger,[5] Von Pechmann,[6]

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[1] Bülow, in a recent article (Ber. d. chem. Ges., **32**, 197) still maintains that in case of acetoacetic ester and some diazo salts true azo bodies result. A similar constitution is ascribed by him to benzoylacetone. *Ibid.*, 2637.

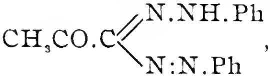
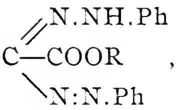
[2] Bülow's diacetylsuccinic ester seems to form an exception to this rule. Ber. d. chem. Ges. **32**, 2880.

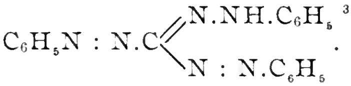
[3] Japp and Klingemann: Ann. Chem. (Liebig), **247**, 208.

[4] *Ibid.*, **247**, 218. Also, for instance, in the action of diazobenzene upon camphoric acid (Betti: Ber. d. chem. Ges., **32**, 1995).

[5] Bamberger and Wheelright: Ber. d. chem. Ges., **25**, 3201; Bamberger: *Ibid.*, 3547.

[6] *Ibid.*, **25**, 3175.

Claisen,[1] and Wislicenus[2] show, however, that under certain conditions a second diazo molecule can be introduced into these and similar compounds, and a class of bodies—the formazyl derivatives—is obtained which contain both the hydrazone and the azo constitution. In case of acetoacetic ester we get either acetylformazyl,  $CH_3CO.C\begin{array}{l}\diagup N.NH.Ph\\ \diagdown N{:}N.Ph\end{array}$, or formazylformic ester,  $C\begin{array}{l}\diagup N.NH.Ph\\ -COOR\\ \diagdown N{:}N.Ph\end{array}$, the nature of the product being governed by the conditions of the experiment. In presence of a large excess of alkali, even a third molecule of the diazo compound can be introduced, and thus only one carbon atom is left of the whole chain of the acetoacetic ester:



$$C_6H_5N:N.C\begin{array}{l}\diagup N.NH.C_6H_5\\ \diagdown N:N.C_6H_5\end{array}.$$[3]

It is unnecessary to enter here in detail upon the behavior of the formazyl derivatives, so thoroughly studied by Bamberger, Von Pechmann, and especially by Wedekind.

The body which I have obtained by the action of diazocaffeine upon acetoacetic acid resembles in appearance so strongly the formazyl compounds, that at first thought it was taken for such. It was considered rather unusual that a formazyl-like body should be formed to such a large extent in an acid solution, especially when the acetoacetic acid was always in excess. Instead of a pale to an orange-yellow hydrazone a body of dark-blue to violet color was obtained in every instance, with a beautiful metallic luster and having the appearance either of fuchsin or of methyl-violet. It possesses intense coloring properties and shows characteristic color reactions in cold and hot water, not unlike those peculiar to cobalt salts. The results of elementary analysis of several samples point, however, to a formula different from what a

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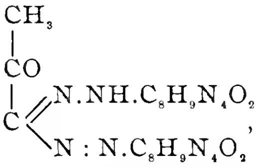
[1] Ber. d. chem. Ges., **25**, 746.

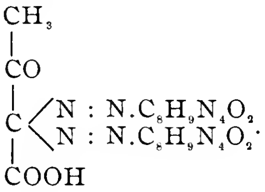
[2] *Ibid.*, **25**, 3453.

[3] This benzeneazoformazyl is the end-product of the action of diazobenzene upon a large number of compounds containing either the $CH_3.CO$ group, or the CH_2 group linked to two negative radicals which can be split off more or less readily by hydrolysis.

caffezyl body would require. Instead of the caffezylmethylketone,

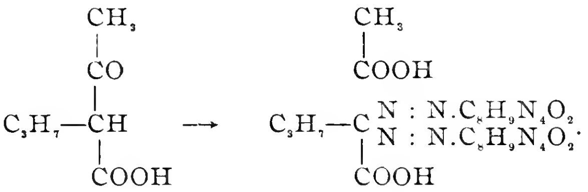


the analytical results point rather to a disazo body.

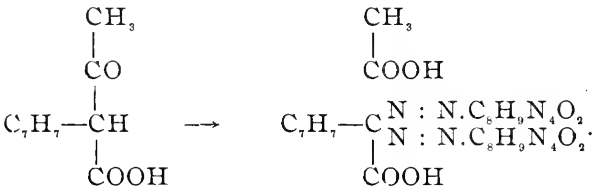


Such a reaction has, to my knowledge, been observed only once.[1]

Propyl and benzylacetoacetic acids were next taken for this reaction, with the expectation that in this case monoazo bodies would result. But here, too, judging from the results of analysis, disazo compounds were formed, at the expense of the acetyl group:



$$\begin{array}{c} CH_3 \\ | \\ CO \\ | \\ C_3H_7\text{—}CH \\ | \\ COOH \end{array} \longrightarrow \begin{array}{c} CH_3 \\ | \\ COOH \end{array} \quad C_3H_7\text{—}\begin{array}{c} C \\ | \\ COOH \end{array}\!\!\begin{array}{l} N : N.C_8H_9N_4O_2 \\ N : N.C_8H_9N_4O_2. \end{array}$$

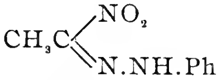


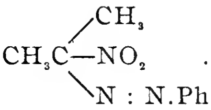
$$\begin{array}{c} CH_3 \\ | \\ CO \\ | \\ C_7H_7\text{—}CH \\ | \\ COOH \end{array} \longrightarrow \begin{array}{c} CH_3 \\ | \\ COOH \end{array} \quad C_7H_7\text{—}\begin{array}{c} C \\ | \\ COOH \end{array}\!\!\begin{array}{l} N : N.C_8H_9N_4O_2 \\ N : N.C_8H_9N_4O_2. \end{array}$$

All these dyes, while not at all, or only slightly, soluble in water, dissolve in dilute alkalies, even in solutions of sodium carbonate, a fact which points to the presence of a carboxyl

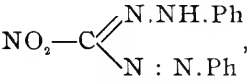
[1] Unfortunately, the exact reference has escaped me for the present.

group. While they dissolve in concentrated sulphuric acid, some with reddish, and some with yellowish-green color, none, however, gives on the addition of ferric chloride or of potassium dichromate the blue or violet of Bülow's reaction, so characteristic of all the hydrazones and consequently of the formazyl derivatives. And yet, notwithstanding all these facts, I should still be of the opinion that we have here to deal with formazyl-like bodies had it not been for the following consideration :

Bamberger[1] has shown that the constitution assigned by V. Meyer to the so-called mixed nitroazoparaffins is correct only in cases in which the diazo molecule is linked to a tertiary carbon atom. In all other cases they, too, must be considered as hydrazones.[2] Thus, nitroethane forms  $CH_3C\begin{matrix}\diagup NO_2\\ \diagdown N.NH.Ph\end{matrix}$, while *i*-nitropropane gives, under similar conditions,



$$CH_3C\begin{matrix}\diagup CH_3\\ -NO_2\\ \diagdown N:N.Ph\end{matrix}\quad .$$

And as the NO₂ group, unlike the acetyl or the carboxyl, cannot be split off under the conditions of the experiment,[3] it follows that of all the nitroparaffins nitromethane alone can give rise to formazyl derivatives. In fact, nitroformazyl,  $NO_2-C\begin{matrix}\diagup N.NH.Ph\\ \diagdown N:N.Ph\end{matrix}$, is the principal product of the interaction of diazobenzene and nitromethane. The yellow hydrazone can be obtained only by observing special precautions.

Diazocaffeine, however, gives in alkaline solutions with nitroethane and nitropropane, compounds which resemble in appearance and in the characteristic color reactions so closely the body obtained from acetoacetic acid as to leave no doubt that the nature of the reaction must be the same in both cases.

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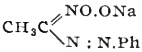
[1] Ber. d. chem. Ges., **27**, 155.

[2] The salts have a true azo constitution, as  $CH_3C\begin{matrix}\diagup NO.ONa\\ \diagdown N:N.Ph\end{matrix}$. Bamberger: Ber. d. chem. Ges., **31**, 2626.

[3] The NO_2 group in the azoparaffins can be removed by hydrolysis by means of alkali when heated. Bamberger: *Ibid.*, 2630.

But, as neither nitroethane or nitropropane can, according to Bamberger, give rise to formazyl derivatives—caffezyl compounds in this case—it must be concluded that the dyes from acetoacetic acid also, which resemble so markedly the above nitro compounds, are not caffezyl compounds. It must, however, be remembered that the elementary analysis of the nitro bodies, while pointing to a disazo formula, did not give satisfactory results in the case of carbon and hydrogen. Whether this was due to insufficient purification of the small amount of material at hand, or as in Bamberger's experience,[1] to the marked tendency of these bodies to form oxides of nitrogen during combustion has not yet been determined.

It is hoped that further study of the action of diazocaffeine upon aliphatic compounds will help to clear up the nature of the reaction.

Diazocaffeine Hydrochloride.

After many trials it was found that amidocaffeine can best be diazotized when dissolved in concentrated hydrochloric acid, because the base is only very slightly soluble in dilute acids, and even when in very fine suspension, is only slowly attacked by nitrous acid. Amidocaffeine[2] is dissolved in five times its weight of hydrochloric acid (sp. gr. 1.20) and the solution is well cooled in a freezing-mixture to about —18° C. The calculated quantity of sodium nitrite, dissolved in about four to five times its weight of water, is very slowly run into the bottom of the dish containing the amine, the solution being vigorously stirred by means of a turbine. The temperature is best kept down to —10° C. The foam on the surface of the solution can be broken up by the occasional addition of a few drops of alcohol. The strongly yellow solution, decanted from the solid sodium chloride which separates during the reaction will remain clear for over an hour, if kept in a freezing-mixture. But if the temperature is allowed to rise, a

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[1] Ber. d. chem. Ges., **27**, 157.

[2] The amido compound was prepared according to E. Fischer's method [Ann. Chem. (Liebig), **215**, 265]. The heating under pressure was done in autoclaves, by placing in it a large test-tube containing the chlorocaffeine and alcoholic ammonia. Ordinary packing, such as asbestos, rubber, graphite, etc., would not stand. Strips of sheet-lead gave very good satisfaction. In this manner 20 grams of the halogen compound could be used in one operation, and the yield was 17–18 grams of pure amidocaffeine. The temperature of the oil-bath was kept at 150°-160°.

gas, probably nitrogen, is evolved, and a small quantity of very bulky amorphous decomposition-product separates out. The clear solution shows all the reactions of a diazo compound. All the efforts to obtain it in the form of some insoluble salt—as chromate, picrate, or cyanide[1]—proved fruitless. Attempts to reduce it by stannous chloride to a hydrazine were equally unsuccessful. The solution of the diazo salt stains the skin dark-red, quickly changing to brown, which remains permanent for some days.

Apparently the same diazo compound is produced by the action of nitric acid upon amidocaffeine in the cold. This is probably due to a partial reduction of the nitric to nitrous acid.

Caffeine-p-azophenol, $C_8H_9N_4O_2.N:N.C_6H_4(OH)(p)$.—Diazocaffeine couples with phenol in both acid and alkaline solutions, in water or in alcohol. The solution of the diazo salt in hydrochloric acid can at once be added to an ice-cold solution of phenol in water. The azo compound separates immediately as a dark-yellow to an orange mass, resembling in its appearance freshly precipitated ferric hydroxide. The mixture is allowed to stand about an hour, filtered, washed, and dried on a porous plate. The almost black powder is best recrystallized from a large quantity of glacial acetic acid, from which it can be obtained, on slow cooling, in beautiful red needles reflecting light strongly. For analysis it must be recrystallized several times from the same solvent in order to free it entirely from some of the disazophenol, which, as could be judged from the high percentage of nitrogen, was also formed to some extent in the same reaction.

I. 0.1862 gram substance gave 0.3650 gram CO_2, and 0.0778 gram H_2O.

0.1744 gram substance gave 40.4 cc. N at 21°.5 C. and 743.5 mm.

II. 0.1409 gram substance gave 34.7 cc. N at 26° C. and 731.7 mm.

	Calculated for $C_8H_9N_4O_2.N_2.C_6H_4OH$.	Found.	
		I.	II.
C	53.50	53.52	....
H	4.46	4.64	....
N	26.75	26.52	27.26

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[1] Ann. Chem. (Liebig), **305**, 64.

The dye is insoluble in cold water and only slightly when heated. It dissolves in dilute alkali hydroxides and carbonates with a deep-red color. Alcohol, even on boiling, takes up only traces of the dye forming yellow solutions. The same is true of chloroform. It is insoluble in ether and benzene. Glacial acetic acid and nitrobenzene are the best solvents for this substance. Concentrated sulphuric acid dissolves the dye with a deep-red color, which instantly changes to an intense violet-blue; this color is changed to a pale-yellow by a drop of potassium dichromate solution, but ferric chloride imparts to it a greenish tint. A slightly alkaline solution of the azo body dyes unmordanted cotton pink, which is discharged by acids, but is brought back by soap solutions.

Caffeine-p-azodimethylaniline, $C_8H_9N_4O_2.N : N.C_6H_4N(CH_3)_2(p)$.—Diazocaffeine combines with dimethylaniline even in the presence of hydrochloric acid. A better yield of the dye is, however, obtained when a solution of the diazo salt in concentrated hydrochloric acid is slowly added to a cold solution of the calculated quantity of dimethylaniline, to which sufficient sodium acetate has been added to take up all the hydrochloric acid. The solution of the dimethylaniline is best cooled by introducing ice directly into it. After standing for from one to two hours the mixture is gently heated on the water-bath until the apparently amorphous precipitate assumes a decidedly crystalline appearance. Ten grams of amidocaffeine gave in this way 9 grams of the azo body. For further purification the dye is recrystallized from boiling chloroform, from which it comes down almost completely on the addition of a very small quantity of ether. The long, dark-red needles, of a beautiful greenish iridescence, were again redissolved in chloroform, and the concentrated solution, while hot, was slowly poured into boiling toluene. The dye is at once precipitated in the form of dark steel-blue needles. A portion of this was then recrystallized from a large quantity of toluene.

I. From toluene: 0.1550 gram substance gave 0.3204 gram CO_2, and 0.0828 gram H_2O.

0.1698 gram substance gave 43.9 cc. N at 25° C. and 745.5 mm.

II. From chloroform and toluene: 0.1865 gram substance gave 0.3885 gram CO_2, and 0.1001 gram H_2O.

0.1916 gram substance gave 49.4 cc. N at 24° C. and 745.5 mm.

III. From chloroform alone: 0.1650 gram substance gave 42 cc. N. at 25° C. and 739 mm.

	Calculated for $C_8H_9N_4O_2\ N_2.C_6H_4N(CH_3)_2$.	Found. I.	 II.	 III.
C	56.30	56.37	56.80	....
H	5.57	5.93	5.96	....
N	28.73	29.18	29.19	28.48

This azo compound can be obtained, as mentioned above, either in cherry-red crystals with a green reflection or in the form of steel-blue needles, or as bluish-red, shining crystals. It is hardly at all soluble in water, dissolves only slightly in dilute, but fairly readily in glacial acetic acid. It is only sparingly soluble in alcohol (red solution), or benzene, not at all in ether. It dissolves in dilute mineral acids forming a deep-red solution. Concentrated sulphuric acid dissolves it with a yellowish-green color, while concentrated hydrochloric acid forms a deep-green solution. The hydrochloride of the base was prepared by dissolving the body in chloroform and passing gaseous hydrochloric acid into the solution. It is a fairly stable salt when dry, but easily decomposed by water.

It dissolves in pure chloroform with a clear red color. But when the chloroform is contaminated with certain impurities then it dissolves the dye with a distinct violet color. Several samples of chloroform on the market responded to this test, giving violet solutions, but on purification gave the red solutions. I was unable to find out just what impurities cause this change in color. Experiments have shown that it is not due to traces of hydrochloric acid, alcohol, or carbonyl chloride.

Reduction with Stannous Chloride.

Two grams of the dimethylaniline dye were dissolved in concentrated hydrochloric acid, and to this solution, while hot, a solution of stannous chloride (10 grams in 20 cc. of concentrated hydrochloric acid) was added drop by drop until the green color was completely discharged. The solution was then diluted with water to about 300 cc. and the acid partially neutralized. In about an hour the amidocaffeine separated in the form of a white granular powder. It was washed with dilute acid (in which it is almost insoluble), alcohol, and ether. The yield was nearly 1 gram. For analysis it was recrystallized from glacial acetic acid.

0.1643 gram substance gave 50.2 cc. (moist) N at 19°.5 C. and 742 mm.

	Calculated for $C_8H_9N_4O_2NH_2$.	Found.
N	33.50	33.82

The filtrate from amidocaffeine was shaken out with ether, and the residue obtained on evaporating the latter was tested in the usual way for *p*-amidodimethylaniline by means of hydrogen sulphide and ferric chloride. The characteristic methylene blue was thus obtained.

The reaction with stannous chloride is therefore to be represented by the equation:

$$C_8H_9N_4O_2.N:N.C_6H_4N(CH_3)_2 + 4H = C_8H_9N_4O_2NH_2 + NH_2.C_6H_4.N(CH_3)_2.$$

Caffeineazo-2,4-diamidobenzene,

$$C_8H_9N_4O_2.N:N.C_6H_3\left\langle\begin{matrix}NH_2\ (o)\\ NH_2\ (p)\end{matrix}\right.$$

.—The diazo salt couples very readily with metaphenylenediamine. The reaction was carried out in presence of sodium acetate. The bulky chocolate-brown precipitate becomes almost black on drying. It was recrystallized from glacial acetic acid and analyzed with the following results:

0.1620 gram gave 48.9 cc. N at 26°.5 C. and 736.5 mm.

	Calculated for $C_8H_9N_4O_2.N_2.C_6H_3(NH_2)_2$.	Found.
N	34.15	33.54

It is of a brown color. It is only slightly soluble in the usual organic solvents. Hot glacial acetic acid is the best solvent for it. It does not melt at 285° C. It dissolves in dilute mineral acids with an intense reddish-brown color.

Caffeineazo-β-naphthol, $C_8H_9N_4O_2.N : N.C_{10}H_6OH$. — Five grams of amidocaffeine were diazotized in the usual manner and added to the theoretical amount of β-naphthol in 500 cc. of a 4 per cent solution of potassium hydroxide. The separation of the azo body begins at once, and is greatly hastened and increased by saturating the solution with salt. It was filtered and washed with a solution of salt. On the addition of dilute mineral acid to a warm solution of the alkali salt of the naphthol compound, the free azonaphthol separates in the form of brown flakes mixed with an oil, which on further warming and stirring changes all to a granular precipitate. It was then filtered, washed, first with water then with alcohol and ether, to remove any free β-naphthol, and finally dried on a porous plate. The yield was 6 grams. For analysis the substance was recrystallized from glacial acetic acid; the crystals were collected in two separate crops, the first consisting of minute ponceau-red needles, the second crop being of a somewhat lighter color.

I. 0.2324 gram substance gave 0.5007 gram CO_2, and 0.0976 gram H_2O.

0.2071 gram substance gave 41.4 cc. N at 24° C. and 735.5 mm.

II. 0.1589 gram substance gave 33.9 cc. N at 25°.5 C. and 733 mm.

	Calculated for $C_8H_9N_4O_2.N_2.C_{10}H_6OH$.	Found.	
		I.	II.
C	59.34	48.82	....
H	4.40	4.66	....
N	23.08	22.56	23.63

The dye, insoluble in water, dissolves slowly in a cold solution of sodium carbonate, more rapidly when heated; is soluble in dilute hot alkali hydroxide, forming a deep-red solution. Alcohol dissolves it only slightly, with a violet-blue color; it is insoluble in ether, but dissolves in hot benzene and chloroform with a deep-red color. It dissolves in concentrated sulphuric acid, giving a deep-blue solution, which is intensified by a drop of a solution of ferric chloride, but is discharged by potassium dichromate. This reaction with ferric chloride reminds one in its play of colors of Bülow's reaction for hydrazones—a structure sometimes ascribed to oxyazo compounds.

Reaction with Acetoacetic Acid.

Diazocaffeine couples with acetoacetic ester and the free acid, in alkaline solutions, as well as in presence of acetic acid, and even in hydrochloric acid solutions.

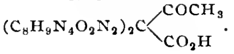
After many trials the following method was adopted: 6.5 grams (1 molecule) of the ester are dissolved in about 100 cc. of dilute potassium hydroxide containing 3 grams (1 molecule) of the alkali, and allowed to stand twenty-four hours for complete saponification. 10.5 grams (1 molecule) of amidocaffeine are diazotized in the manner above described, and slowly added to the well-cooled, slightly acidulated solution of the acetoacetic acid, to which about 100 grams of sodium acetate and 300 cc. of water has been previously added. On the first addition of the diazo solution a noticeable evolution of gas takes place, but this soon stops. The azo compound separates at once as a bulky, dark-brown precipitate, which completely fills the beaker. The mixture is allowed to stand in ice about two hours. Salt is then added to saturation, and the solution is gently warmed on the water-bath, whereby the precipitate becomes granular and is easily filtered. On washing, however, with distilled water it swells up again, and can then be filtered only with difficulty. The precipitate, dried on a porous plate, presents a green to blue iridescence, and not infrequently possesses the metallic copper luster of malachite-green. The yield is about 5 grams. It can be recrystallized either from glacial acetic acid or from chloroform. When to the warm solution of the dye in glacial acetic acid a few drops of alcohol or ether are added, it begins to come down at once in the form of a gelatinous, stringy mass, which very soon changes to lumps of dark-blue crystals with a decided green reflection. Alcohol also helps in the crystallization of the substance from chloroform.

I. From glacial acetic acid: 0.2968 gram substance gave 0.4869 gram CO_2, and 0.1214 gram H_2O.

0.1987 gram substance gave 55.5 cc. N at 24° C. and 734.7 mm.

II. From chloroform: 0.2765 gram substance gave 0.4472 gram CO_2, and 0.1105 gram H_2O.

0.1627 gram substance gave 48 cc. (moist) N at 27° C. and 737 mm.

	Calculated for  $(C_8H_9N_4O_2N_2)_2C\begin{cases}COCH_3\\CO_2H\end{cases}$.	Found.	
		I.	II.
C	44.28	44.73	44.15
H	4.06	4.55	4.44
N	31.00	31.12	31.55

The acetoacetic acid compound possesses, as mentioned above, a beautiful dark-green, cantharidine-like luster. It is somewhat soluble in water, dissolving slowly, and forming a reddish-violet solution. On boiling the solution turns deep-blue, of almost the same shade as Fehling's reagent. On cooling the original color comes back. The same changes of color are more marked in dilute solutions of sodium carbonate or hydroxide, in which the dye dissolves, forming intensely colored solutions. It is only slightly soluble in alcohol and benzene, with a pure blue color in the first and a violet-blue in the second. It is fairly soluble in chloroform, and here again the color of the solution is violet-blue. The phenomena of change of color in hot and cold solutions are much more marked in the case of nitroethane and nitropropane compounds. The azo compound shows slight signs of melting at about 200° C., but no further melting is noticeable even at 285° C.

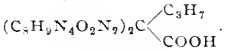
As regards Bülow's reactions, the substance dissolves in concentrated sulphuric acid with a red color, which is not changed either by ferric chloride or potassium dichromate.

Reaction with Propylacetoacetic Acid.

Eight and six-tenths grams (1 molecule) of propylacetoacetic ester mixed with 3 grams (1 molecule) of potassium hydroxide in 100 cc. were allowed to stand twenty-four hours for complete saponification. To this dilution, diluted to about 500 cc. and well cooled, the hydrochloric acid solution of 10.5 grams (1 molecule) of diazotized amidocaffeine was slowly added. Considerable foaming took place at the beginning. The separation of the azo compound greatly increased on the addition of about 100 grams of sodium acetate to the dark-red solution. The mixture, after standing for some time, was saturated with salt and warmed for a short time on the water-bath. The precipitate became granular and was easily filtered. It was washed with a little water and dried on a porous plate. An attempt to remove all the inorganic salts by suspending the well-dried dye in cold water (a treatment successfully employed with other dyes in this work) gave a gelatinous thick mass which proved almost impossible to filter. The yield of the dry substance, well washed with ether, was about 2.8 grams. The substance was dissolved in hot chloroform and to the filtered concentrated solution one-half its volume of ether was added. The crop of crystals which separated in a few hours was recrystallized from glacial acetic acid with the addition of a little alcohol.

0.2493 gram substance gave 0.4217 gram CO_2, and 0.1205 gram H_2O.

0.2054 gram substance gave 55.4 cc. N at 21°.5 C. and 738 mm.

	Calculated for  $(C_8H_9N_4O_2N_2)_2C{<}^{C_3H_7}_{COOH}$.	Found.
C	46.49	46.17
H	4.80	5.37
N	30.09	30.91

It is a dark-brown crystalline powder with a bluish tint, but lacks the metallic luster of the acetoacetic acid compound. It is very slightly soluble in water, but readily in alkali carbonates and hydroxides—in all cases with a yellow-green color which does not change on boiling. Dilute mineral acids take up small quantities of this azo compound forming a red, cobalt-like solution. The dye is only slightly soluble in benzene, giving a bluish-red solution, while to chloroform, in which it is fairly soluble, it imparts a reddish-violet color. It does not melt at 285° C.

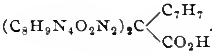
It dissolves in concentrated sulphuric acid, forming a red solution which is not affected by ferric chloride, but is discharged by potassium dichromate.

Reaction with Benzylacetoacetic Acid.

The reaction proceeds as with the propylacetoacetic acid but less smoothly. As this ester is not saponified readily, the alkaline solution, after standing twenty-four hours, was gently warmed for a short time to about 50° C., acidulated and filtered from the unsaponified ester. The coupling was done in presence of sodium acetate. There was considerable foaming on the addition of the diazo salt. There was some flocculent precipitate mixed with a considerable amount of a black oil. It was filtered, thoroughly washed with water, dried on a porous plate, and washed directly on the plate with ether. The dull-black powder was recrystallized twice from chloroform with the addition of ether. The precipitate, at first amorphous, becomes crystalline on standing. The yield of the pure substance was 0.5 gram from 10 grams of amidocaffeine.

0.1802 gram substance gave 0.3320 gram CO_2, and 0.0792 gram H_2O.

0.1872 gram substance gave 49.6 cc. (moist) N at 22° C. and 737 mm.

	Calculated for  $(C_8H_9N_4O_2N_2)_2C\begin{matrix}\diagup C_7H_7 \\ \diagdown CO_2H\end{matrix}$.	Found.
C	50.84	50.30
H	4.40	4.88
N	28.47	29.07

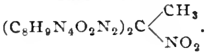
This body resembles in its solubility very much the propyl derivative, giving yellow to yellow-green solutions. In Bülow's reaction it is almost identical with the propyl compound. It does not melt at 285° C.

Reaction with Nitroethane.

The diazo salt was added to a well-cooled solution of an excess (1.5 molecule) of nitroethane in about 700 cc. of water containing enough potassium hydroxide to neutralize all the hydrochloric acid of the diazo solution. After standing for some hours the precipitate was filtered off from the dark cherry-red solution, and was well washed with water. The dry substance was dissolved in hot chloroform and the filtered solution concentrated. The crystals, consisting of deep-blue flakes, were filtered, washed with a mixture of chloroform and ether, and recrystallized once more in the same way. The melting-point remained constant, 218°–219° C. Seven grams of amidocaffeine gave about 0.5 gram of the purified dye. The results of analysis are given below, although the carbon and hydrogen are considerably higher than theory for a disazo body requires. I hope to obtain larger amounts of this body, and establish its composition more exactly.

I. 0.1241 gram substance gave 0.2023 gram CO_2, and 0.0604 gram H_2O.
0.1442 gram substance gave 45.8 cc. N at 22° C. and 739 mm.

II. 0.1224 gram substance gave 38.9 cc. N at 23° C. and 739 mm.

	Calculated for  $(C_8H_9N_4O_2N_2)_2C\genfrac{}{}{0pt}{}{CH_3}{NO_2}$.	Found.	
		I.	II.
C	41.94	44.50	....
H	4.08	5.41	(?)....
N	35.34	35.90	35.80

The nitroethane derivative presents some very peculiar color reactions, similar in nature to those of the acetoacetic acid derivative but more pronounced in character. While insoluble in cold water it dissolves on boiling, giving a deep-blue solution, not unlike that of an ammoniacal copper solution. On cooling, the solution first becomes violet and finally almost entirely red. On reheating, the same phenomena can be observed. This change of color from red to blue and conversely is even more pronounced in dilute alkali solutious, in which the dye is only slightly more soluble than in water. The substance is insoluble in ether, very slightly in benzene (blue solution), readily soluble in chloroform with an intense blue color, and dissolves also in glacial acetic acid, forming a red solution.

Dissolved in concentrated sulphuric acid it gives, like formazyl derivatives,[1] a red solution, which, however, does not change, on standing, into a violet of Bülow's reaction, as

[1] Wedekind: Ber. d. chem. Ges., 30, 2995.

nitrohydrazones do through intramolecular oxidation;[1] nor does ferric chloride or potassium dichromate bring about this change into the blue or violet.

Reaction with Nitropropane.

The reaction was carried on under the same conditions as with nitroethane. The brown precipitate, after washing and drying, was recrystallized twice from chloroform with the addition of ether and obtained in the form of very light, deep-blue flakes with a slight metallic luster, and melting with decomposition at 237°–238° C. The yield was again small. Ten grams of amidocaffeine furnished about 0.7–0.8 gram of the purified product. The carbon and hydrogen are considerably higher than the theory for a disazopropane requires. What was said under nitroethane applies equally well in this case.

0.2488 gram substance gave 0.4189 gram CO_2, and 0.1186 gram H_2O.

0.1415 gram substance gave 44 cc. N at 21° C. and 739 mm.

	Calculated for $(C_8H_9N_4O_2N_2)_2C{<}^{C_2H_5}_{NO_2}$.	Found.
C	43.29	45.95
H	4.35	5.29
N	34.40	35.26

This body is somewhat more soluble in all the solvents than the corresponding nitroethane derivatives. It shows the same peculiar color reactions when its solution in water or dilute alkalies is heated, giving, when hot, a deep-blue solution, which, on cooling, assumes a lavender color.

Towards concentrated sulphuric acid and oxidizing agents it behaves exactly like the nitroethane compound.

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July, 1899.

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[1] Bamberger: Ber. d. chem. Ges., **31**, 2631.

THE ACTION OF ETHYL IODIDE ON TARTARIC ESTER AND SODIUM ETHYLATE.

BY JOHN E. BUCHER.

INTRODUCTION.

By the action of the ethylate of sodium or of potassium on symmetrical dibromsuccinic ester (m. p. 58°), a number of investigators have obtained diethoxysuccinic ester. The symmetrical constitution for this compound seems to have been generally accepted. Michael and Bucher,[1] however, showed that it consists mainly of the unsymmetrical diethoxysuccinic ester. They also obtained the same ester by the addition of sodium ethylate to several unsaturated compounds. In no case did they prove the presence of the corresponding symmetrical ester. The following investigation was undertaken with the object of preparing the symmetrical ester and acid so that their properties might be studied.

One of the most obvious methods seemed to be the action of ethyl iodide on disodium tartaric ester. The literature on the subject was not found to be favorable to this method. Meyer and Jacobson,[2] in speaking of the esters of tartaric acid, make the following statement: "Die Wasserstoffatome der alkoholischen Hydroxylgruppen können in diesen Estern durch Natrium und Kalium ersetzt werden; die so entstehenden Alkoholate, wie $C_2H_2(OK)_2(CO_2C_2H_5)_2$, sind zu doppelten Umsetzungen indessen nicht brauchbar." Reference is made to the work of Perkin, Lassar-Cohn, and Mulder. As the original articles, except that of Lassar-Cohn,[3] were not accessible, it was necessary to rely on abstracts in the Chemisches Central-Blatt. In these abstracts no mention is made of the fact that Perkin[4] has studied the action of ethyl iodide and bromide on the above sodium or potassium derivatives. Lassar-Cohn, however, states that Perkin supposed he had probably replaced the sodium in sodium tartaric ester by this

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[1] Preliminary articles: Ber. d. chem. Ges., **28**, 2511; **29**, 1792.

[2] Lehrbuch d. organischen Chemie, p. 805.

[3] Ber. d. chem. Ges., **20**, 2003.

[4] Chem. Centrbl., 1867, p. 593.

method. Lassar-Cohn found that no reaction took place on treating the monosodium derivative with methyl iodide or ethyl bromide. The disodium derivative proved to be equally inactive. From these observations he concluded that Perkin probably mistook tartaric ester, regenerated by the action of moisture, for the expected ethoxy derivative. More recently Mulder[1] has published a number of long papers on the action of ethyl chloride on disodium tartaric ester. From the abstracts it appears that he was entirely unsuccessful in preparing diethoxysuccinic ester but that a ketone ester was obtained.

Apparently, the above investigators used the dry sodium or potassium derivatives. It was thought that the reaction might take place in alcoholic solution. A preliminary experiment showed this to be the case, an oil being obtained which was not soluble in alkalies and which gave no color reaction with ferric chloride. After having prepared diethoxysuccinic ester and obtained several salts from it, the abstract of an article by Purdie and Pitkeathly[2] appeared. They had obtained the symmetrical diethoxysuccinic ester by the action of ethyl iodide on tartaric ester and silver oxide. In view of their work, it has seemed desirable to publish the results thus far obtained, although the work is still in progress.

EXPERIMENTAL PART.

One experiment will be described in detail, so that only the variations need be mentioned in the others. To a cooled solution of 27 grams of sodium (25 grams = 2 atoms) in 340 cc. of absolute alcohol 112.5 (2 mols.) grams of tartaric ester and 245 grams of ethyl iodide were added. The solution was boiled with a reflux condenser for twelve hours. The clear solution soon became colored yellow and later red. The red color was not due to the separation of iodine. Carbon dioxide was now passed into the solution, which was very faintly alkaline. The alcohol and excess of ethyl iodide were then distilled off on the water-bath. The residue, after the addition of water, was extracted with ether. This extract was

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[1] Chem. Centrbl., **61**, 467; **62**$_2$, 442: **63**, 587; **64**$_2$, 529, 644; **66**, 531; **67**$_1$, 797; **67**$_2$, 345.

[2] *Ibid.*, **70**, 779.

then shaken violently for one-half minute with a solution of caustic alkali to remove any tartaric and ketone esters. The extract was dried with calcium chloride and the ether distilled off on the water-bath. In this way 60 grams of crude product were obtained as a slightly yellowish-red oil.

A part of the aqueous solution, which had been extracted with ether, was acidified and again extracted. So much hydriodic acid was dissolved by the ether that it turned red rapidly from the separation of iodine. This interfered so much that the viscous oil thus obtained was not examined. A solution of calcium chloride was added to the remainder of the aqueous solution. A large quantity of a white precipitate was obtained which was shown to be mainly calcium tartrate (or racemate). The above 60 grams of crude ester were distilled under diminished pressure with a column of beads, using the method described by Michael.[1] About 0.9 of the product came over between 134°–140° at 11.5 mm. The first few cc., being colored by free iodine, were rejected. There was some decomposition at the end of the distillation, about 1 gram of residue remaining in the flask. On redistillation the greater part boiled at 131°.5–136°.5 at 10.5 mm. It was found to contain 53.86 per cent of carbon and 8.10 per cent of hydrogen.

The experiment was repeated many times, varying the conditions and the quantities of the reacting substances. Usually about 2.2 molecules of ethyl iodide were used to each molecule of tartaric ester. In some cases the excess of absolute alcohol was driven from the sodium ethylate by drying *in vacuo* at 230°, and the tartaric ester and ethyl iodide were added to the dry solid. In a few experiments the solution of sodium ethylate was allowed to flow into the boiling mixture of tartaric ester and ethyl iodide. In a few of the earlier experiments the ether extract was not shaken out with caustic alkali, but this was not neglected after finding much tartaric (or racemic) ester in the product, when using one atom of sodium per molecule of tartaric ester. The shaking was not continued more than one-half minute, using a 5 per cent solution of caustic alkali. In one experiment no heat was ap-

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[1] J. prakt. Chem., N. F., 46 Nachtrag.

plied, the substances being allowed to stand at the room temperature for two weeks. The quantity of sodium varied from 1 to 2.2 atoms per molecule of tartaric ester. The yield of crude product varied between 50 and 60 per cent of the weight of the tartaric ester used. Evidently other reactions interfere, so that only about one-half of the calculated yield of crude ester is obtained. The products distilled under diminished pressure, with a column of beads, did not have a constant boiling-point, the range being from 4° to 10°. Analyses of the above products showed that, although the yield was fairly constant, the composition varied very much, the percentage of carbon in the various fractions varying from 51.8 to 54.9 per cent.

	Calculated for $C_2H_2(OC_2H_5)_2(CO_2C_2H_5)_2$.	Calculated for $C_2H_2(OH)(OC_2H_5)(CO_2C_2H_5)_2$.	Calculated for $C_2H_2(OH)_2(CO_2C_2H_5)_2$.
C	54.89	50.75	46.60
H	8.40	7.60	6.80

When from 1 to 1.1 atoms of sodium per molecule of tartaric ester were used, the average composition of the fractions was 52.4 per cent of carbon, and when from 2 to 2.2 atoms were used, the average was 54.3 per cent of carbon. As the fractions analyzed did not represent the entire yield, the following additional experiments were made. The entire product was collected in one fraction, only about 5 per cent being lost at each end of the distillation.

Experiment a.—To 5 grams (1 atom) of sodium dissolved in 60 cc. absolute alcohol, 45 grams (1 mol.) of tartaric ester and 130 grams of ethyl iodide were added. After boiling five hours with a reflux condenser the alcohol and excess of ethyl iodide were distilled off on the water-bath. Water was added to the residue and the mixture extracted with ether. The ether extract was shaken out with caustic alkali for one-half minute. The yield of crude product was 23 grams, boiling at 146°–150° at 17 mm. $[\alpha]_D$ was $+ 31°$ at 20°.

Experiment b.—Proceeded exactly as in Experiment *a*, except that the quantities were as follows: 8 grams (1.07 atoms) of sodium, 100 cc. of absolute alcohol, 67.5 grams (1 mol.) of tartaric ester, 150 grams of ethyl iodide, crude product 36 grams (=53 per cent of the weight of tartaric ester). The time of boiling was seven hours, and the ester distilled at 145°–150° at 16 mm. $[\alpha]_D$ was +24° at 20°.

Experiment c.—Proceeded as in Experiment *a*, except that the quantities were as follows: 15 grams (3 atoms) of sodium, 180 grams of absolute alcohol, 45 grams (1 mol.) of tartaric ester, and 150 grams of ethyl iodide. The yield of crude product was 20 grams, or 44 per cent of the weight of the tartaric ester. It boiled at 144°–147° at 17 mm. $[\alpha]_D$ was +1.1° at 20°.

Analyses of these three preparations gave the following results:

a,I. 0.2269 gram substance gave 0.4379 gram CO_2, and 0.1637 gram H_2O.

b,I. 0.2042 gram substance gave 0.3954 gram CO_2, and 0.1486 gram H_2O.

b,II. 0.2170 gram substance gave 0.4199 gram CO_2, and 0.1574 gram H_2O.

c,I. 0.2379 gram substance gave 0.4750 gram CO_2, and 0.1788 gram H_2O.

c,II. 0.2056 gram substance gave 0.4085 gram CO_2, and 0.1515 gram H_2O.

	a,I.	*b*,I.	*b*, II.	*c*,I.	*c*,II.
C	52.63	52.81	52.77	54.34	54.19
H	8.02	8.09	8.06	8.36	8.19

From these five analyses and the preceding ones to which reference has already been made, it is evident that when about 1 atom of sodium is used per molecule of tartaric ester the resulting product contains about 52.6 per cent of carbon, and when 2 to 3 atoms of sodium are used the percentage of carbon is increased to about 54.3. These results show that, as might be expected, when only 1 atom of sodium is used, much diethoxysuccinic ester is formed. Also, that when 2 or 3 atoms are used the product consists mainly of this ester. It was possible, in some cases, to obtain a product having the composition of pure diethoxysuccinic ester by fractional distillation under diminished pressure. As these products did not have a constant boiling-point it was evident that fractional distillation did not offer a practical method of obtaining the pure ester or acid.

Accordingly, a specimen of ester having the composition of diethoxysuccinic ester and boiling at 127°.5 to 130° at 9 mm., was saponified by warming with a solution of caustic soda in dilute alcohol. After driving off the alcohol and neutralizing the excess of caustic alkali, a white crystalline precipitate was obtained on the addition of barium chloride.

The results of two analyses of this salt were:

I. 0.5035 gram air-dried salt lost 0.0272 gram at 100°.

II. 0.5762 gram air-dried salt lost 0.0313 gram at 100°, and gave 0.3747 gram $BaSO_4$.

	Calculated for $C_2H_2(OC_2H_5)_2(CO_2)_2Ba.H_2O$.	Found.		
		I.	II.	III.
H_2O	5.01	5.40	5.44	5.11
Ba	38.22	...	38.27	38.44

The results tabulated under III. were obtained from another portion of the same sample of ester. In this case, after saponifying, the solution was acidified and extracted with ether. The acid, which was a very viscous oil, was dissolved in water, neutralized with ammonia, and precipitated with barium chloride.

III. 0.3773 gram air-dried salt lost 0.0193 gram at 100°, and gave 0.2464 gram $BaSO_4$.

The free acid was prepared from the latter specimen of barium salt by adding dilute sulphuric acid and extracting with ether. The ether was removed from the extract at the room temperature, leaving a very viscous colorless oil. The oil was soluble in water and gave no color reaction with ferric chloride solution. On heating a drop of the oil on a watch-glass over the water-bath, bubbles were given off and it turned into a white solid. The white solid was very soluble in water, and gave an intense red color with ferric chloride solution. It was oxalacetic acid. This reaction and the composition of the barium salt led to the conclusion that the oil was not the symmetrical compound, but that it was identical with the unsymmetrical diethoxysuccinic acid studied by Michael and Bucher. This was confirmed by dissolving the oil in water, neutralizing with ammonia, and making the salts of silver, calcium, and lead by precipitation.

The silver salt, which was a white crystalline precipitate, was dried in the air to constant weight and analyzed with the following result:

0.6499 gram salt gave 0.4428 gram AgCl.

	Calculated for $C_2H_2(OC_2H_5)_2(CO_2Ag)_2$.	Found.
Ag	51.40	51.29

The calcium salt separated as a white crystalline precipitate. These microscopic crystals were six-sided plates, many having four sides curved, so that they had the same appearance as sections cut from a barrel parallel to its axis. The salt also showed great creeping power when freshly precipitated. These properties are very characteristic of the calcium salt of unsymmetrical diethoxysuccinic acid. An analysis of the air-dried calcium salt gave the following result:

0.4963 gram salt gave 0.2553 gram $CaSO_4$.

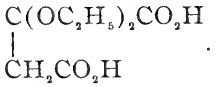
	Calculated for $CH_2(OC_2H_5)_2(CO_2)_2Ca.H_2O$.	Found.
Ca	15.28	15.14

The lead salt also was a white crystalline precipitate. The analysis of the air-dried salt gave the following result:

I. 0.5018 gram salt gave 0.3553 gram $PbSO_4$.
II. 0.5262 gram salt gave 0.3729 gram $PbSO_4$.

	Calculated for $C_2H_2(OC_2H_5)_2(CO_2)_2Pb.H_2O$.	Found.	
		I.	II.
Pb	48.23	48.35	48.40

The properties of the free acid and the composition of these four salts leave no doubt that the acid has the constitution



$$\begin{array}{l} C(OC_2H_5)_2CO_2H \\ | \\ CH_2CO_2H \end{array} .$$

This complicated the matter somewhat, and in order to obtain a large quantity of ester all the remaining specimens of the older preparations were united. The 90 grams thus obtained were subjected to fractional distillation. The main lot boiled at 138°–143° at 13 mm., about 16 cc. being rejected at the beginning and 6 cc. at the end of the distillation. This fraction was again distilled at 133°–137° at 11 mm., about 3 cc. being rejected at each end. This was redistilled, and the first two-thirds, boiling at 133°–135°.5 at 11 mm., was collected as fraction *k*. $[\alpha]_D$ at 23° was $+1°.4$ for this fraction. All the other fractions were reunited and found to boil at 133°–139° at 11 mm. This will be called fraction *n*. $[\alpha]_D$ at 23° was $+2°.5$ for this fraction.

The average of three analyses of fraction *k* and four of fraction *n* gave the following result :

	Calculated for $C_2H_2(OC_2H_5)_2(CO_2C_2H_5)_2$.	Found. *k*	*n*
C	54.89	54.72	53.92
H	8.40	8.22	8.07

Fraction *k* had the composition of a nearly pure diethoxysuccinic ester. Exactly 5 grams were saponified by caustic soda dissolved in dilute alcohol. After the alcohol had been driven off on the water-bath the excess of alkali was neutralized and an aqueous solution of 5.5 grams of calcium chloride added. The volume of the solution was 150 cc., and, after filtering, the precipitate was washed with 150 cc. of water. The yield of air-dried salt was 2.51 grams, but on concentrating the filtrate and washings an additional 0.2 gram was obtained. This total of 2.71 grams of calcium salt corresponds to 54 per cent of unsymmetrical ester in fraction *k*. The salt was not quite pure, however, as it contained 15.98 per cent of calcium. Probably 45 per cent of the unsymmetrical ester is near the truth. This calcium salt, combined with that obtained by saponifying the remainder of fraction *k*, was acidified with dilute acid and extracted with ether. The colorless viscous oil thus obtained yielded the pure calcium salt, an analysis giving 15.33 per cent of calcium.

Fraction *n* was treated exactly as fraction *k* had been. From 5 grams of ester 1.77 grams of air-dried calcium salt, corresponding to 35 per cent of unsymmetrical ester, were obtained. This calcium salt seemed not to be quite as pure as that from fraction *k*, and probably 25 per cent is about the quantity of unsymmetrical ester present. The remainder of fraction *n* was saponified and treated with calcium chloride as before. After filtering off the insoluble calcium salts the filtrate was acidified and extracted with ether. On evaporation, a very viscous colorless oil was obtained, which did not give any color with ferric chloride solution, before or after it had been heated to 100°. It did not solidify on standing over sulphuric acid in the ice-chest for a week. After neutralizing, it did not give a precipitate with barium, calcium, or lead salts. Both the neutral and acid potassium salts are very soluble in water. $[\alpha]_D$ for this crude acid in aqueous solution at 18° was $+2°$. The oil was neutralized with caustic potash and the solution evaporated to a doughy mass on the water-bath. Absolute alcohol was then added slowly. In this way it was possible to separate out a nice crystalline precipitate. This salt, dried at 150°, gave the following result on analysis:

I. 0.3244 gram salt gave 0.2010 gram K_2SO_4.

Another specimen was prepared in the same way, dried at 150°, and analyzed with the following result:

II. 0.4172 gram salt gave 0.2573 gram K_2SO_4.

	Calculated for $C_2H_2(OC_2H_5)_2(CO_2K)_2$.	Found. I.	Found. II.
K	27.71	27.81	27.68

An aqueous solution of this salt had no action on polarized light. The pure acid was prepared from this potassium salt by acidifying and extracting with ether. On evaporating the ether *in vacuo* the acid separated as an oil, which quickly solidified at the temperature of the room. Without further purification it was dried over sulphuric acid in a partial vacuum for a week. It melted at 97°–99°. The results of an analysis were as follows:

0.2273 gram substance gave 0.3890 gram CO_2, and 0.1416 gram H_2O.

	Calculated for $C_2H_2(OC_2H_5)_2(CO_2H)_2$.	Found.
C	46.67	46.58
H	6.92	6.87

The aqueous solution of the acid had no effect on polarized light. When neutralized with ammonia, it did not give precipitates with solutions of lead, calcium, or barium salts of the ordinary strength. It was not changed on heating to 100°. A portion was boiled with 10 per cent sulphuric acid with reflux condenser, and on adding a solution of phenylhydrazin sulphate, no precipitate was formed. This shows that no pyruvic acid was formed. These two experiments show how the above acid differs from the unsymmetrical one, and it evidently has the constitution represented by the formula

$$\begin{matrix} CH(OC_2H_5)CO_2H \\ | \\ CH(OC_2H_5)CO_2H \end{matrix} .$$

The remainder of this acid was boiled with water and barium carbonate. The solution was filtered and evaporated on the water-bath. The salt which crystallized out was air-dried, and, on analysis, gave the following result :

0.5025 gram salt lost on heating one hour and a half, finally at 190°–215°, 0.0872 gram, and gave 0.2836 gram $BaSO_4$.

	Calculated for $C_2H_2(OC_2H_5)_2(CO_2)_2Ba.4H_2O$.	Found.
Ba	33.23	33.22
H_2O	17.48	17.35

This salt was soluble in about 12 parts of water at the room temperature and had no effect on polarized light. Nothing else was separated in the pure form from these 90 grams of ester, although there must have been a number of other compounds present. It was at this point that the preparations already referred to as *a*, *b*, and *c* were made.

Fifteen grams of preparation *b* were saponified with caustic soda in dilute alcoholic solution. After driving off the alcohol on the water-bath, and neutralizing the excess of alkali, calcium chloride solution was added. Only 50 milligrams of precipitate were obtained, and this was not the calcium salt of unsymmetrical diethoxysuccinic acid. Hence, very little, if any, of the unsymmetrical ester is formed when 1 atom of sodium is used per molecule of tartaric ester. This result is confirmed below under the saponification of fraction *a*. The filtrate from the above calcium salt was acidified with sulphuric acid and extracted ten times with ether. The first four of these extracts were united and yielded 5.4 grams of a very viscous oil, and the remaining six yielded 2.6 grams more. Neither specimen gave, before or after heating to 100°, a color reaction with ferric chloride, nor did they solidify in the ice-chest.

The specimen weighing 5.4 grams was converted into the barium salt by means of barium carbonate. The solution was filtered and evaporated to 14 cc. The salt which crystallized out on cooling was air-dried. The following results were obtained on analysis:

I. 0.4767 gram salt lost, on heating to 110°–130° for one hour, 0.0840 gram, and gave 0.2694 gram $BaSO_4$.

II. 0.4026 gram salt lost, on heating to 155° for one hour, 0.0725 gram, and gave 0.2277 gram $BaSO_4$.

	Calculated for $C_2H_2(OC_2H_5)_2(CO_2)_2Ba.4H_2O$.	Found. I.	Found. II.
Ba	33.23	33.26	33.29
H_2O	17.48	17.62	18.01

$[\alpha]_D$ for this sample in aqueous solution was +14°. The salt was recrystallized from water by evaporating *in vacuo* over sulphuric acid. The crystals which first separated were short and compact, looking exactly like those which were prepared by Purdie and Pitkeathly's method for comparison. Later, however, the substance crystallizing out had a different appearance. $[\alpha]_D$ for the recrystallized salt was now +18°. This is lower than the value given by Purdie and Pitkeathly, showing the difficulty in separating the active from the inactive salt. There is no doubt that the part first separating out is the barium salt of *d*-diethoxysuccinic acid. The salts, which remained in the mother-liquor from the first crystallization of the barium salt, were much more soluble and less active than the latter. The efforts to isolate them were entirely unsuccessful.

The 2.6 grams of acid from the last six extractions were dissolved in a very small quantity of water, and a concentrated solution of lead acetate added. The white precipitate thus prepared was dried at 100° and gave the following result on analysis:

0.4828 gram salt gave 0.3823 gram $PbSO_4$.

	Calculated for $C_2H_2OH(OC_2H_5)(CO_2)_2Pb$.	Found.
Pb	54.03	54.07

The salt does not separate out unless the solution is rather concentrated, and it was not examined in polarized light.

The existence of the hydroxyethoxysuccinic ester and acid was confirmed by the next experiment.

Preparation *a* was saponified in the same manner as the above. As in the former case, there was little or no precipitate of insoluble calcium salt, proving the absence of the unsymmetrical ester. The acid was converted into the barium salt in the usual manner. The solution was then evaporated on the water-bath until a scum began to form. Absolute alcohol was added to the hot mass and the pasty precipitate rejected. The filtrate was treated in the same manner. This last filtrate was concentrated, acidified, and extracted with ether. The acid thus obtained was added to a strong solution of lead acetate, and the white precipitate thus obtained, after being dried to a constant weight in the air-bath, contained 53.9 per cent of lead. This corresponds to the percentage of lead in the lead salt of hydroxyethoxysuccinic acid.

Preparation *c* (from 3 atoms of sodium per molecule of tartaric ester) was lost, but not before it was shown to contain much unsymmetrical diethoxysuccinic ester. One gram was saponified in the usual manner. From this an insoluble calcium salt separated in abundance. The acid prepared from this showed the characteristic conduct of the unsymmetrical acid on heating to 100°, and toward ferric chloride solution before and after heating.

It is evident from the fact that the unsymmetrical diethoxy ester was formed from tartaric ester, a compound having the symmetrical constitution, that the reaction must be more complicated than the simple replacement of hydrogen by ethyl. The following preliminary experiment may throw some light on the subject: When 1 molecule of tartaric ester is boiled with 2 atoms of sodium, dissolved in absolute alcohol, a yellowish-brown salt begins to separate in about fifteen minutes, and the reaction seems to be complete within an hour. The salt can be filtered off, and on evaporating the filtrate there seems to be nothing left except a small quantity of the same substance.

The salt can be acidified and extracted with ether. The very viscous oil is apparently a ketone ester, as it gives a deep-red color with ferric chloride and reacts with phenylhydrazine. On neutralizing the aqueous solution which had been extracted with ether, and adding calcium chloride solution, a small quantity of a white precipitate was obtained. It was the calcium salt of tartaric acid or its isomers.

The yellowish-brown salt, when boiled with caustic soda and evaporated to a small bulk, yields sodium oxalate very abundantly. Also, when it is dissolved in dilute sulphuric acid, and a solution of phenylhydrazine sulphate added, a large quantity of oily product is formed immediately. This turns to a sticky solid mass in the ice-chest. When this substance is boiled with caustic alkali it passes into solution. From this highly colored solution acids precipitate a substance which it is difficult to obtain pure. By alternately boiling with bone-black and crystallizing from dilute alcohol it was obtained nearly colorless. With ferric chloride it gave the violet color-test for 1-phenyl-5-pyrazolon-3-carboxylic acid. The melting-point also corresponded to that of this compound, but the crystals had a different appearance from those prepared by other methods. The percentage of carbon was about 0.5 higher than the calculated amount. It was probably impure 1-phenyl-5-pyrazolon-3-carboxylic acid, but this conclusion can only be regarded as tentative. If oxalacetic ester is formed, this might possibly form an ethoxy ester by the action of ethyl iodide on its sodium salt, and this, by the addition of sodium ethylate, form an unsymmetrical product. W. Wislicenus got a carbon homologue from the sodium salt of oxalacetic acid, but he did not follow the reaction very far.

One experiment has been made, using ethyl bromide instead of ethyl iodide with the sodium ethylate and tartaric ester. The yield of ester was fully as good as with ethyl iodide, and it has the great advantage of not forming halogen by-products.

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NOTE.

Improvements in the Manufacture of Sulphuric Acid.

In a recent number of the Journal of the Society of Chemical Industry, there is an interesting address by Professor G. Lunge from which the following is taken :

"We naturally begin with *sulphuric acid*, and here we are at once confronted with the greatest revolution which has taken place since that acid became a commercial product in the days of Ward and Roebuck ; a revolution beside which the invention of the Gay-Lussac and Glover tower, let alone that of plate-columns and the like, sinks into insignificance. I mean, of course, the total abolition of the vitriol chamber, and even of the use of nitrous fumes as oxygen carriers, by the use of the catalytic power of platinum, perhaps also by that of ferric oxide and other substances, a reaction of which the first literary landmark is the British patent of Phillips taken out in 1831, but which has been mainly worked out by German chemists, Döbereiner, Magnus, Wöhler, Plattner, Clemens Winkler, and others, not to forget my originally German countryman, Messel. All of these had been content to apply that reaction to the preparation of sulphur trioxide, in the shape of Nordhausen fuming acid. Some years ago it was whispered that the Badische Anilin and Soda Fabrik had perfected and cheapened that process to such a degree that they were manufacturing ordinary sulphuric acid in this way cheaper than by the old process, and that they were gradually pulling down their vitriol chambers. This was hardly believed to be possible, and was taken as an exaggeration of the truth. But last year the Badische applied for patents in all countries, some of which are now published. Other firms have proceeded on the same lines partly with other contact substances, among them oxide of iron in the shape of pyrites cinders, with which I myself experimented many years ago as a means for combining SO_2 with oxygen."

"We now know the Badische invention. The principal feature of it is their discovery that it is necessary to get rid of the heat of the reaction in order to obtain a quantitative union of sulphur dioxide and oxygen to sulphur trioxide, and that under such circumstances a *complete* union is obtained, even when using ordinary dilute technical gases, such as result from pyrites burners. As a measure of the progress made, I may remind you that, as I wrote at the end of the year 1897 in 'The Mineral Industry of the United States and Other Countries,' p. 130 :—

"'Probably 67 per cent must be considered very good work, and the remaining 33 per cent. of sulphurous acid must be sent into lead chambers, together with better gas from other burners.'

"In lieu of 67 per cent. we must *now* speak of 98 per cent.

"The said removal of the heat of reaction can be effected in such a way as to heat the entering gases to the temperature necessary for the reaction, so that the contact stoves when once started work automatically.

"A further important feature of the Badische invention consists in the discovery of the reason why the contact-substance (platinized asbestos) as hitherto used, in a short time wholly or partly loses its activity, and of means for preventing this. The cause of this loss of activity has been traced to certain constituents in the technical gases, the deleterious action of which was hitherto unknown. To remove these, a special washing process has been invented, which, in a certain direction, goes far beyond any attempt at purification published up to this time.

"Of course there is still a wide step from knowing those principles, to carrying them out as paying concerns; although former employees have offered their knowledge of the principles referred to for sale for several years, it is not known that anyone has successfully manufactured from their information. But it is absolutely certain that at Ludwigshafen itself that step has been made, and that in more than one large works the lead chambers are either entirely abolished or at least moribund.

"This is a sad outlook for those whose capital is, to a great extent, sunk in the old vitriol process! But as yet very many of them need not despair. It would appear that in the case of less concentrated acids, up to the point of chamber acid, or even Glover tower acid, the chamber process can still compete with the catalytic process, and for acid of such strength there would be no need whatever to incur the expense of introducing the catalytic system. Indeed the Badische patents state :—

"'Acids weaker than up to 50° Bé. (that is, containing about 63 per cent H_2SO_4) can, according to this invention, be prepared at least as cheaply as by means of the chamber process, and all stronger acids are produced by this invention more cheaply, the advantages being greater the stronger the acid.'

"In cases, however, where the purity of the acid is an important point, the Badische process is advantageous even for dilute acids, for all the acids made by this process are exceptionally pure and especially free from arsenic. It is worth mentioning also that the cost of plant for the new process is considerably less than that of the old one and requires less space. Thus, in the Badische works, I am told that the capital outlay for a plant which is used for making all grades of acid from anhydride down to weak acid costs about two-thirds as much as a plant calculated to yield a corresponding quantity of concentrated oil of vitriol of 66° Bé.

"Since in the case of less concentrated acids, say up to about 80 per cent. H_2SO_4, the chamber process can still compete for cheapness with the catalytic process, the enormous capital sunk in vitriol chambers for the manufacture of superphosphates, of salt-cake and all analogous cases would still remain operative; but certainly vitriol makers are now put upon their mettle to look out for the best means for improving the efficiency of their plant and of their method of working. For various reasons I shall abstain from going into reasons on that point; but I may be excused for indulging in some "music of the future," in mentioning the advantages to be derived from using oxygen in a more concentrated form than that of atmospheric air. The proposal of Messel for employing electrolytic oxygen, or that of myself for Brin's oxygen, came undoubtedly too early even for the manufacture of SO_3 at its former prices, but since we can make a gaseous mixture rich in oxygen, very cheaply by liquefying air, the possibility of employing that mixture in the manufacture of sulphuric acid is decidedly less removed from the sphere of actuality. In Germany 'Linde-Luft,' as it is there called, is already an article of commerce; it is actually used for the preparation of an explosive, and it is at least thought of even for such uses as the working of gas-producers. In America they are going ahead with it much faster, if we may credit even a portion of the sensational accounts which reach us. Do not let us forget that in this case the advantage will again lie with those nations who possess cheap force in the shape of water-power, in order to produce liquid air.

"Coming back from the aërial regions to the solid ground of present facts, there seems to be no doubt that the catalytic processes have a decided advantage over the chamber process where acid of a higher concentration than Glover acid or of special purity is required.

"Proof of this is the fact that one after the other the great German colour works, where mainly strong acid is used, have introduced the new processes, or are making preparations for doing so. But even here some comfort remains to the owners of lead chambers, and glass or platinum retorts and the like. Where the initial cost of plant has been written off to a great extent during former better years, and especially in small-sized works they will, in the face of the cost of new plant and of the royalties to be paid for the processes, be able to hold on to their existing plant for a number of years. The first to change will be probably those works where much waste acid is to be disposed of and reconcentrated, as for instance in the manufacture of explosives. But I must content myself with these general allusions."

REVIEWS.

THE SOLUBLE FERMENTS AND FERMENTATION. BY J. REYNOLDS GREEN, Sc.D., F.R.S., Trinity College, Cambridge; Professor of Botany to the Pharmaceutical Society of Great Britain; Formerly Senior Demonstrator in Physiology in the University of Cambridge. Cambridge University Press. 1899. 480 pp.

This book, which is one of the Cambridge Natural Science Manuals, Biological Series, aims to give a full and concise account of the present state of our knowledge concerning the so-called soluble ferments. The subject is treated historically so that we have, in addition, a more or less complete account of the lines along which development has taken place up to the present time. This gives the volume added value as a book of reference, a value which is increased by the very full bibliography at the end of the volume.

The first chapter deals with the nature of fermentation and its relation to enzymes, followed by a classification of enzymes, in which the latter are grouped according to the materials on which they work. While the list is not wholly complete, mention is made of *urease* which forms ammonium carbonate from urea, and the new *zymase* of Buchner, *i.e.*, the alcohol-producing enzyme. Four chapters are devoted to a discussion of vegetable and animal diastase, while inulase, cytase and other cellulose-dissolving enzymes, urease, pectase, oxidases or oxidizing enzymes, are each given a chapter descriptive of their chemico-physiological properties. To proteolytic enzymes and proteolysis three chapters are devoted. The clotting enzymes are likewise given due consideration, while fat-splitting enzymes and sugar-splitting enzymes are duly considered, as are also alcoholic fermentation, the fermentative power of protoplasm, the secretion of enzymes, the constitution of enzymes, while a brief account of the theories of fermentation closes the volume.

We have in this book by Dr. Green, a very readable statement of existing knowledge regarding enzymes, but we fail to find in it much that is original. This, perhaps, is hardly to be expected, since the book aims primarily, as stated in the preface, "to put together as far as possible, the results reached up to the present time." The book is especially opportune at the present moment, since we have now reached a point in our knowledge where we are practically compelled to drop the old distinction between organized and unorganized ferments, and the more thoroughly knowledge is disseminated regarding the part which enzymes play in intracellular, metabolism, so much the sooner will the chemical and physiological world acquire a true appreciation of the many points of similarity between the metabolic processes of higher and lower organisms. Enzymes are unquestionably intimately associated with the living substance of protoplasm, and consequently we may look for an intimate relationship between fermentation and the ordinary processes of metabolism. For furthering the spread of knowledge regarding these points, the present volume is especially well adapted, and the book is to be welcomed as a valuable addition to the store-house of knowledge.

Careful scrutiny of the subject-matter composing some of the chapters of the book must lead to criticism of the thoroughness with which the work of compilation and selection has been done. Thus, on pages 264–267, dealing with the myosin ferment and the proteids of muscle, we look in vain for any reference to the very important work of Von Furth on this subject, which appeared in volumes 36 and 37 of the *Archiv für experimentelle Pathologie und Pharmakologie*, 1895–1896. Further, in chapter XVI, dealing with thrombase, the fibrin-ferment, we find among the various facts and theories of blood-coagulation discussed, no mention of the widely quoted work of Lilienfeld on this subject, which appeared in 1894, and which is now incorporated in all recent text-books of physiological chemistry. Again, on page 188, where the characteristic products of trypsin-proteolysis are discussed, we look in vain for any mention of the very important work of Kossel and his coworkers on the hexone bases, arginin, lysin, and histidin, which are now recognized as among the characteristic end-products of trypsin-proteolysis. Among these bases, lysin was first emphasized as a product of trypsin-proteolysis in 1891 by Drechsel and Hedin. These are a type of criticisms, however, which apply to nearly all books. Perfection is not of this world. It may be, however, that these omissions simply represent the author's opinion of the relative value of the omitted facts as contrasted with those presented. If this is the case, the reviewer cannot agree with the author in his estimate of their relative value in any discussion of soluble ferments and fermentation.

R. H. CHITTENDEN.

EINFÜHRUNG IN DIE CHEMIE IN LEICHTFASSLICHER FORM. VON PROF. DR. LASSAR-COHN. Königsberg, Hamburg und Leipzig; Verlag von Leopold Voss.

In this volume Prof. Lassar-Cohn offers a text-book of chemistry for university-extension work. He acknowledges in his preface that the problem of how to write a book for this purpose is difficult, and that the task first seemed to him impossible. The present volume is a natural sequence of his popular lectures published under the title "Die Chemie im täglichen Leben,"[1] and every reader of those admirable lectures will feel that Lassar-Cohn was well qualified to attempt a text-book simpler in form and matter than those used in colleges, yet addressed to thinking men and women.

The descriptive part of the book treats of the more important elements and inorganic compounds, omitting all reference to less important substances; the theoretical part covers the same field as an ordinary text-book of inorganic chemistry. In the chapter on carbon, the commonest organic compounds and their relations to the simpler hydrocarbons are briefly discussed, while the fundamental theories of organic chemistry including substitution, valence, Kekulé's benzene theory, isomerism, ortho, meta, and para compounds, are explained clearly and simply.

The impression left on the reviewer is that the author has succeeded in his task; that he has written a book simple enough to enable an intelligent working man to master it with the help of experimental lectures, and scientific enough to give the learner a solid basis for further work, should opportunity offer. The book should interest us all in view of the spread of the university-extension movement in this country.

E. R.

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[1] The English translation of this book by M. M. Pattison Muir, "Chemistry in Daily Life" was reviewed in This JOURNAL, 19, page 81.

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ON SOME ABNORMAL FREEZING-POINT LOWERINGS PRODUCED BY CHLORIDES AND BROMIDES OF THE ALKALINE EARTHS.

By HARRY C. JONES AND VICTOR J. CHAMBERS.

Jones and Mackay,[1] in their work on solutions of double sulphates, used both the conductivity and freezing-point methods to determine the condition of these substances in solution. Jones and Ota,[2] in their work on the double chlorides, attempted to follow the same plan. They succeeded in applying the conductivity method to the solutions of double chlorides and their constituents, but were not able to get satisfactory results with the freezing-point method. The results were irregular in the case of the double salts, and did not point to any definite conclusion. Jones and Knight[3] extended the work of Jones and Ota to a number of double chlorides and bromides, and again attempted to apply the freezing-point method in the same connection. They also obtained unsatisfactory results in the cases of a number of double salts, and found, for some of the constituents, that the molecular lower-

[1] This JOURNAL, **19**, 83.
[2] *Ibid.*, **22**, 5.
[3] *Ibid.*, **22**, 110.

ing increased with increase in concentration from a certain dilution, and then increased again from this point with the dilution, as would be expected. The increase in the molecular lowering became very marked at great concentrations, indeed, so pronounced that the molecular lowering of a normal solution was as great as, or greater than, the theoretical molecular lowering when all of the salt was completely dissociated.

This was evidently a phenomenon worthy of careful study, and we undertook the investigation which will now be described. Before beginning experimental work we examined the literature to ascertain what had been done bearing upon this point.

Arrhenius,[1] in applying the freezing-point method to the then newly proposed theory of electrolytic dissociation, found the following freezing-point lowerings for a few solutions of calcium, strontium and magnesium chloride, and cadmium iodide :

$CaCl_2$.		$SrCl_2$.		$MgCl_2$.		CdI_2.	
Concentration.	Molec. low.	Concentration.	Molec. low.	Concentration.	Molec. low.	Concentration.	Molec. low.
0.0476	5.17	0.043	5.37	0.0532	5.13	0.0544	2.96
0.119	4.95	0.107	4.89	0.133	5.02	0.136	2.35
0.199	5.01	0.214	4.92	0.322	5.33	0.342	2.09
0.331	5.16	0.356	5.03	0.537	5.70	0.684	2.19

In each of these cases the molecular lowering increases with the concentration, from a certain point, and then increases from this same point with the dilution. The data are, however, too meager to warrant conclusions to be drawn from them. Further, when this work was done the freezing-point method was so imperfectly developed, that errors of considerable magnitude are necessarily present in the results.

From the work of Arrhenius, it seems probable that a minimum in the freezing-point lowering exists in a few other salts.

An increase in the molecular lowering with increase in concentration was also observed by Arrhenius[2] in the cases of four organic compounds, glycerin, mannite, dextrose, and cane-sugar. This has been subsequently[3] verified by one of us[1] for cane-sugar and dextrose.

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[1] Ztschr. phys. Chem., **2**, 496.

[2] *Ibid.*, **2**, 495.

[3] Jones : *Ibid.*, **12**, 642.

A possible explanation of the increase in molecular lowering, from a certain point, with increase in concentration, has been offered by Arrhenius[1] for the non-electrolytes.

In the formula for osmotic pressure:

$$\pi = AK + BK^2.$$

π is the osmotic pressure, A is the product of the gas constant R into the absolute temperature, B is a new constant, which gives the difference between the following attractive forces: That between the solvent and dissolved substance, and that of dissolved substance for itself. K is the concentration.

If the concentration K is small, BK^2 with respect to AK is small, and we have the law for an ideal gas. But if K increases, the osmotic pressure would, relatively, increase or decrease as B is positive or negative. But with water as a solvent, B is, in general, positive. Therefore, as solutions which fulfil the above conditions increase in concentration, the osmotic pressure would increase more rapidly than the concentration, and $\frac{\pi}{K}$ would increase.

He showed later, in the same communication, that proportionality exists between osmotic pressure and freezing-point lowering. Since freezing-point lowering is proportional to osmotic pressure, $\frac{E}{K}$ would increase ($E =$ lowering), and this agrees with experimental facts.

An increase in the molecular lowering of the freezing-point, with increase in concentration, has been observed by Loomis[2] for hydrochloric acid and magnesium chloride. He obtained the following results:

Hydrochloric acid.		Magnesium chloride.	
Concentration.	Molec. low.	Concentration.	Molec. low.
0.01	3.61	0.01	5.14
0.02	3.60	0.02	5.07
0.05	3.59	0.05	4.98
0.10	3.546	0.10	4.948
0.20	3.565	0.15	4.965
0.30	3.612	0.20	5.019
		0.25	5.079
		0.30	5.186

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[1] Ztschr. phys. Chem., **10**, 51.

[2] Wied., Ann., **57**, 503.

Loomis did not obtain any evidence of a minimum of molecular lowering with barium chloride. He concluded from his extensive work on freezing-point lowerings, that "the molecular lowering continually increases with the dilution. The only exceptions are $MgCl_2$ and HCl in the region of stronger concentration. Both show a minimum value of the molecular lowering at $m = 0.10$ (m = concentration normal). This minimum is pronounced with $MgCl_2$, it is much less striking with HCl but is just as certain. To avoid any possible doubt in reference to the minimum with hydrochloric acid, the value of the molecular lowering for 0.3 normal was determined. This shows with certainty the position of the minimum at approximately 0.1 normal."

The work which has been done hitherto is thus evidently fragmentary, and shows that for a few substances there is a minimum of molecular lowering. But no generalization whatever can be made from what has thus far been done. Are these abnormal results peculiar to a substance here and there, regardless of its chemical nature, or are they confined to some group of compounds? Do substances which are chemically allied show this peculiarity, or is it due to some physical property or properties of the compounds? It is with the hope of answering such questions as these that we have taken up a systematic study of the problem.

It is well known that the alkaline halides give normal freezing-point lowerings, *i. e.*, the molecular lowering increases with the dilution from the greatest concentrations which have been studied. It is also very probable from what has already been done, that cadmium chloride gives normal lowerings of the freezing-point. Since abnormal values had already been observed by Jones and Knight for one or two members of the calcium group (the alkaline earths), we determined to study this group more thoroughly. We have therefore measured the lowering of the freezing-point of water produced by calcium chloride, barium chloride, strontium chloride, and magnesium chloride. In order to see whether the same abnormal values were obtained with cadmium, we also measured the freezing-point lowerings of fairly concentrated solutions of cadmium chloride.

In measuring the freezing-point lowerings produced by the above compounds, care was taken to keep the temperature of the freezing-bath only a little below the temperature at which the solution froze. Indeed, the bath was always kept at the highest temperature at which it was possible to freeze the solution. The difference between the temperature of the bath and that of the solution when it froze was always less than 2°.

A number of experiments were made to determine the effect of the temperature of the bath on the freezing-point of the solution. While the molecular lowering of dilute solutions changed very appreciably with change in the temperature of the bath, this was not observed with the more concentrated solutions. A change of 5° or 6° in the temperature of the bath, changed the molecular lowering of the most concentrated solutions to only a slight extent. This is what we might expect, since the magnitude of the quantity measured is so much smaller for the more dilute solutions. The apparatus used was essentially that described by Beckmann, with some slight changes.

The results which we obtained for the chlorides named above, are given in the following tables. The most concentrated solution of each chloride was standardized gravimetrically by determining one of the constituents. From this, all of the remaining dilutions were prepared. Column I gives the concentration of the solution in terms of normal, column II the observed lowering of the freezing-point, column III the correction for ice separation, column IV the correct lowering of the freezing-point, and column V the molecular lowering.

Calcium Chloride (110.9).

I.	II.	III.	IV.	V.
0.102	0.519°	0.011°	0.508°	4.98
0.153	0.770	0.018	0.752	4.91
0.204	1.045	0.033	1.012	4.96
0.255	1.294	0.027	1.267	4.97
0.306	1.577	0.040	1.537	5.02
0.408	2.124	0.020	2.104	5.16
0.510	2.724	0.043	2.681	5.26
0.612	3.397	0.049	3.348	5.47

Strontium Chloride (158.6).

I.	II.	III.	IV.	V.
0.05	0.265°	0.007°	0.258°	5.16
0.10	0.501	0.013	0.488	4.88
0.135	0.673	0.021	0.652	4.82
0.20	1.002	0.029	0.973	4.87
0.30	1.498	0.027	1.471	4.90
0.40	2.007	0.029	1.978	4.95
0.50	2.597	0.053	2.544	5.09
0.75	4.166	0.095	4.071	5.42

Barium Chloride (208.3).

I.	II.	III.	IV.	V.
0.0976	0.480°	0.007°	0.473°	4.85
0.1953	0.959	0.027	0.932	4.77
0.2929	1.448	0.035	1.413	4.82
0.4882	2.485	0.067	2.418	4.95
0.5858	3.005	0.060	2.945	5.03

Magnesium Chloride (95.26).

I.	II.	III.	IV.	V.
0.0508	0.287°	0.007°	0.280°	5.51
0.1016	0.550	0.013	0.537	5.28
0.1525	0.798	0.027	0.771	5.06
0.2033	1.088	0.030	1.058	5.20
0.2541	1.372	0.037	1.335	5.25
0.3801	2.055	0.040	2.015	5.30
0.5082	2.837	0.075	2.762	5.43
0.6099	3.510	0.038	3.472	5.69

Cadmium Chloride (182.9).

I.	II.	III.	IV.	V.
0.214	0.743°	0.016°	0.727°	3.39
0.322	1.051	0.029	1.022	3.18
0.429	1.342	0.044	1.298	3.03
0.643	1.862	0.030	1.832	2.85
0.858	2.369	0.040	2.329	2.72
1.072	2.908	0.023	2.947	2.65

It will be seen from the above results that the chlorides of calcium, barium, strontium, and magnesium, all have a minimum lowering which lies between 0.1 and 0.2 normal. The results for cadmium chloride show that the molecular lowering increases from the most concentrated to the most dilute solution used, there being nothing to indicate the presence of a minimum in the molecular lowering.

The relations between the molecular lowerings for the above substances will be seen most readily in the following curves (Fig. I). The molecular lowerings are plotted as ordinates, the concentrations as abscissae.

The dotted portions of the curves, and the entire curve for sodium chloride introduced for the sake of comparison, are plotted from data previously obtained by one of us.[1]

Having found this minimum in the molecular lowering for the chlorides of the alkaline earths, we next turned our attention to the bromides of this group. These compounds, like the corresponding chlorides, were carefully purified, and a standard solution prepared in each case. From this solution all the remaining dilutions were made. The bromides of calcium, barium, strontium, and magnesium were studied to ascertain whether there is a minimum in the molecular lowering, and if so, at what concentration it exist. The bromide of cadmium was examined to see whether it is normal, like cadmium chloride. It is well known that the bromides of the alkalies behave normally, *i. e.*, the molecular lowering increases throughout with increase in dilution. The results which were obtained for the bromides are given in the following tables, the several columns representing the same quantities as with the corresponding chlorides :

Calcium Bromide (199.92).

I.	II.	III.	IV.	V.
0.04355	0.233°	0.005°	0.228°	5.24
0.08710	0.462	0.017	0.445	5.11
0.13065	0.686	0.022	0.664	5.07
0.17422	0.936	0.032	0.904	5.18
0.2613	1.403	0.035	1.368	5.23
0.3484	1.893	0.046	1.847	5.30
0.4355	2.421	0.024	2.397	5.50
0.5226	3.007	0.058	2.949	5.64

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[1] Jones : Ztschr. phys. Chem., **11**, 113, 529.

Fig. I

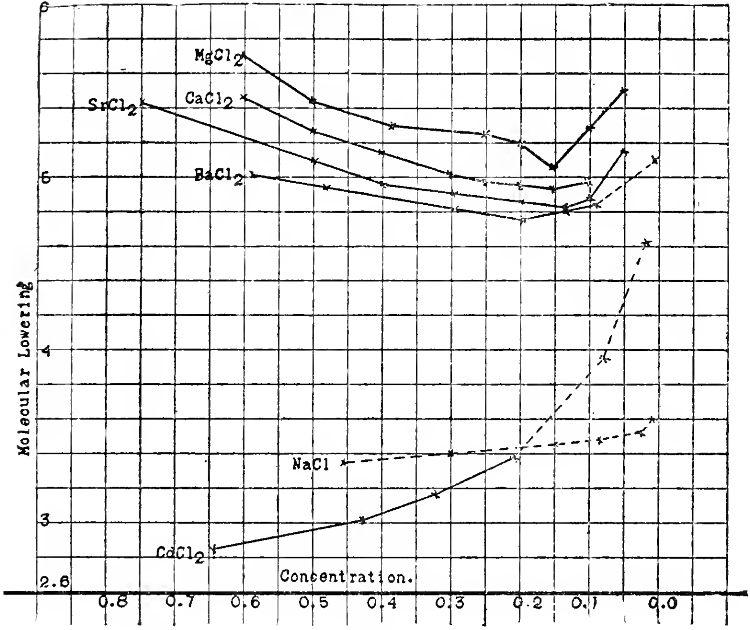
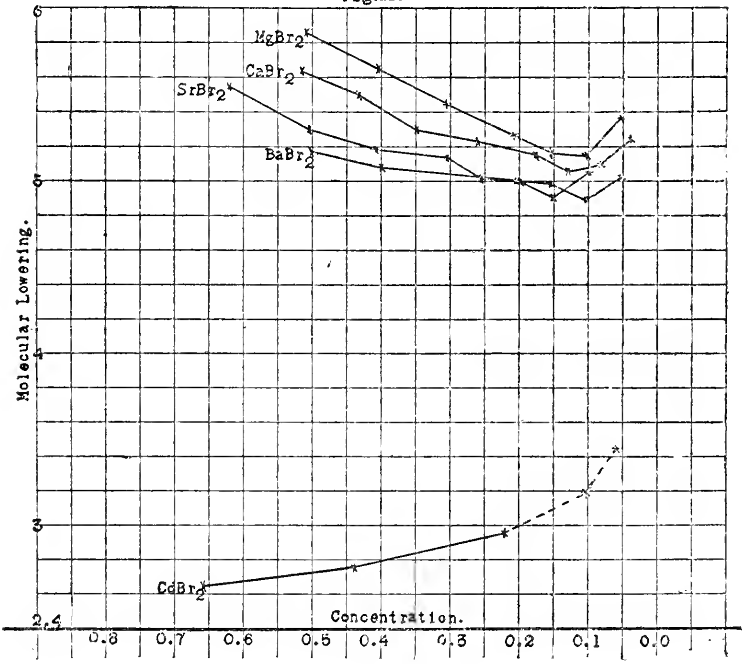

MgCl$_2$
CaCl$_2$
SrCl$_2$
BaCl$_2$
NaCl
CdCl$_2$
Molecular Lowering
Concentration.
6
5
4
3
2.6
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0

Fig. II.


MgBr$_2$
CaBr$_2$
SrBr$_2$
BaBr$_2$
CdBr$_2$
Molecular Lowering.
Concentration.
6
5
4
3
2.4
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0

Strontium Bromide (247.59).

I.	II.	III.	IV.	V.
0.052	0.270°	0.008°	0.262°	5.04
0.103	0.521	0.018	0.503	4.88
0.155	0.795	0.022	0.773	4.98
0.207	1.062	0.027	1.035	5.00
0.259	1.327	0.019	1.308	5.05
0.310	1.615	0.023	1.592	5.13
0.414	2.203	0.056	2.147	5.19
0.517	2.781	0.040	2.741	5.30
0.621	3.516	0.069	3.447	5.55

Barium Bromide (297.34).

I.	II.	III.	IV.	V.
0.10	0.518°	0.012°	0.506°	5.06
0.15	0.759	0.022	0.737	4.91
0.20	1.026	0.025	1.001	5.00
0.40	2.084	0.045	2.039	5.09
0.50	2.633	0.042	2.591	5.18

Magnesium Bromide (184.27).

I.	II.	III.	IV.	V.
0.0517	0.283°	0.006°	0.277°	5.36
0.103	0.557	0.026	0.531	5.14
0.155	0.824	0.023	0.801	5.17
0.207	1.093	0.005	1.088	5.26
0.310	1.710	0.020	1.690	5.45
0.414	2.413	0.066	2.347	5.67
0.517	3.097	0.075	3.022	5.84

Cadmium Bromide (272.2).

I.	II.	III.	IV.	V.
0.22	0.665°	0.013°	0.652°	2.959
0.44	1.220	0.007	1.213	2.757
0.66	1.768	0.030	1.738	2.633
0.88	2.314	0.037	2.277	2.587

The results obtained for the bromides are plotted in curves (Fig. II), the same units being used as ordinates and abscissae as in Fig. I. The dotted portion of the curve for cadmium bromide was plotted from results previously obtained by one of us.[1]

The curves for the bromides as for the chlorides show a

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[1] Jones: Ztschr. phys. Chem., 11, 529.

distinct minimum, and all of them at about the same dilution, from 0.1 to 0.15 normal. This is almost exactly the same concentration as that at which the corresponding chlorides showed a minimum of molecular lowering. The curves of the chlorides were extended, in a number of cases, beyond the dilution used in this work, on the basis of work previously done, to show that the minimum of molecular lowering had unquestionably been reached. The results for sodium chloride were plotted on the same scale, for the sake of comparison.

The general conclusion which can be drawn from the freezing-point lowerings is that all the chlorides and bromides of the alkaline earths have a minimum of molecular lowering of the freezing-point, this minimum lying between 0.1 and 0.2 normal. Further, in very concentrated solutions these substances give a lowering of the freezing-point as great as, or greater than, the theoretical lowering, if the compounds were completely broken down into ions. These apparently abnormal results are shown neither by the alkaline halides nor by the halogen compounds of the magnesium-zinc group.

It is a little difficult to see at first sight how these results can be brought into accord with the theory of electrolytic dissociation, or interpreted in terms of it. Before attempting any explanation of these results, we determined to measure the conductivity of the same solutions whose freezing-point lowerings we had studied. The conductivities of a number of these solutions had already been measured by Jones and Knight,[1] in connection with their work on the condition of double chlorides and bromides in solution. We measured the conductivities of the more concentrated solutions of calcium and barium chlorides, and calcium, strontium, and magnesium bromides. For the conductivities of the more dilute solutions of these substances we are indebted to Mr. Caldwell, who kindly made the measurements which we desired. The conductivities of the remaining compounds had, as already stated, been measured by Jones and Knight.

We give below the molecular conductivities of the compounds which showed abnormal freezing-point lowerings, and state in each case by whom the measurements were made :

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[1] This JOURNAL, **22**, 110.

Calcium Chloride.

(Chambers.)

v.	μ_{v} 25°.
1.961	134.3
3.912	152.06
4.902	156.62
6.536	164.75
9.804	174.05
12.256	179.35
19.610	185.75
33.333	197.50
(Caldwell.)	
32.66	198.15
65.33	210.8
130.66	222.55
261.33	234.97
522.66	244.94
1045.33	246.59
2090.66	253.44
4181.33	265.73

Strontium Chloride.

(Knight.)

v.	μ_{v} 25°.
1	108.5
2	130.0
4	146.6
8	162.6
16	179.5
40	196.1
80	207.4
160	219.0
320	229.3
640	237.6
1600	246.4
3200	252.5
6400	260.0
12800	270.0

Barium Chloride.

(Chambers.)

v.	μ_{v} 25°.
2.013	131.45
4.026	148.37
5.033	158.44
6.711	161.14
10.063	170.62
12.580	184.85
20.130	191.16
33.558	200.88
(Caldwell.)	
33.547	203.06
67.094	213.78
134.188	224.77
268.37	237.0
536.75	248.2
1073.5	260.8
2147.0	270.3
4294.0	276.3

Magnesium Chloride.

(Knight.)

v.	μ_{v} 25°.
1.76	126.3
3.52	143.3
7.04	159.8
14.08	175.1
35.2	190.3
70.4	201.1
140.8	211.3
281.6	221.1
563.2	227.4
1408.0	234.5
2816.0	243.2
5632.0	253.3

Calcium Bromide.

(Chambers.)

v.	$\mu_{v\ 25^\circ}$.
2.193	151.2
4.596	170.88
5.74	174.37
11.48	189.8
14.34	191.9
22.96	201.3
38.27	210.1

(Caldwell.)

38.27	208.2
76.54	219.8
153.08	230.3
306.2	241.2
612.3	248.8
1224.7	256.0
2449.0	262.5
4898.0	270.2

Strontium Bromide.

(Chambers.)

v.	$\mu_{v\ 25^\circ}$.
1.932	141.33
3.864	159.46
4.831	165.7
6.439	171.6
9.661	181.5
12.08	183.9
19.32	194.1
32.20	207.7

(Caldwell.)

32.19	208.6
64.38	221.6
128.8	231.6
257.5	244.6
515.0	254.2
1030.1	261.8
2060.2	272.5
4120.3	282.4

Barium Bromide.

(Knight.)

v.	$\mu_{v\ 25^\circ}$.
2	147.7
4	162.4
8	176.5
16	190.9
32	202.0
80	218.5
160	228.8
320	241.5
640	249.2
1280	257.1
3200	270.8
6400	280.8

Magnesium Bromide.

(Chambers.)

v.	$\mu_{v\ 25^\circ}$.
3.868	141.9
4.812	159.3
6.447	163.8
9.671	173.5
12.09	176.2
19.34	187.5
32.26	190.3

(Caldwell.)

32.24	191.7
64.48	206.1
128.9	216.7
257.9	226.8
515.8	234.8
1031.6	245.0
2063.2	253.9
4126.3	257.8

For the sake of comparison, the conductivities of cadmium chloride and cadmium bromide, as measured by Knight, are also given.

Cadmium Chloride.

(Knight.)

v.	$\mu_{v\ 25°}$.
0.932	28.0
1.864	44.9
3.728	62.8
7.456	82.5
14.91	101.5
37.37	129.6
74.75	150.3
149.5	171.7
299.0	192.3
598.0	206.5
1495.0	227.6
2990.0	242.0
5980.0	255.3
11960.0	269.5

Cadmium Bromide.

(Knight.)

v.	$\mu_{v\ 25°}$.
2.60	41.3
5.20	57.4
10.40	75.7
20.80	95.1
41.60	115.3
104.0	144.2
208.0	166.0
416.0	188.8
832.0	209.3
1664.0	228.2
3328.0	242.4
6656.0	256.1

The conductivity measurements given in the above tables are plotted in curves (Figs. III and IV), that they may be compared directly with the freezing-point lowerings. The conductivities of the dilute solutions are not included in the curves, since these are far less interesting from our present point of view. The conductivity results, from the most concentrated solutions used to about 0.025 normal, are included in the curves. The part of the conductivity curve which is of special interest is that for the concentration at which the freezing-point curve shows a minimum. We wish especially to see whether there is any irregularity in the conductivity curve in this region. The molecular conductivities are plotted as ordinates, the concentrations as abscissae. The concentrations are expressed in "volumes," or the number of liters which contain a gram-molecular weight of the substance. An examination of the conductivity curves shows no irregularity in the region where the molecular lowering of freezing-point becomes a minimum. The conductivity curves are just such as would be expected for any strongly dissociated electrolyte in water. The conductivity increases regularly from the most concentrated to the most dilute solution investigated, and shows a continually increasing dissociation with increase in dilution.

Fig. III.

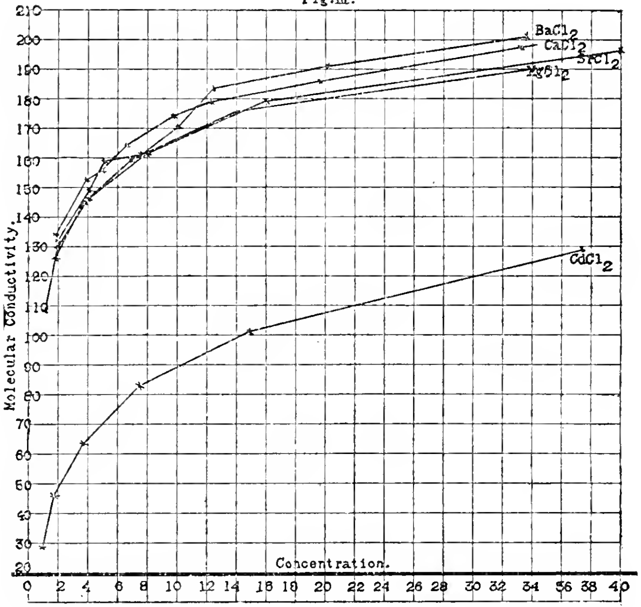
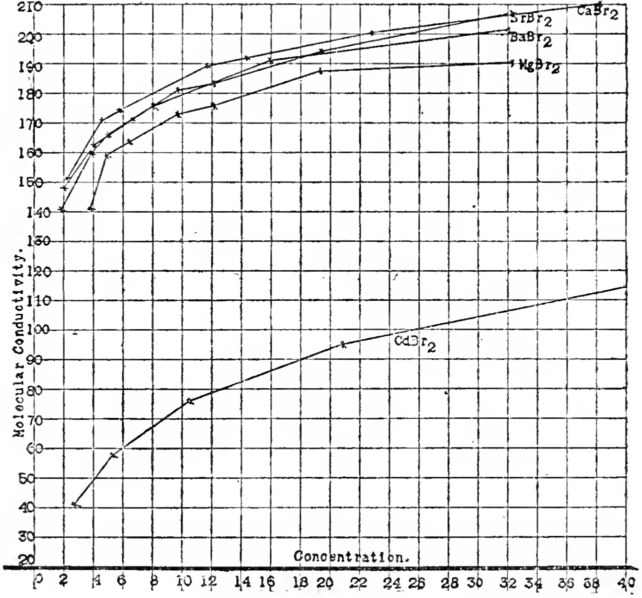


Fig. IV.



A Possible Explanation of the Abnormal Results.

The facts which have to be taken into account are these: The molecular lowering of the freezing-point increases from about 0.1 normal with increase in concentration and also with increase in dilution, there being a minimum of molecular lowering for the chlorides and bromides of the alkaline earths at about this concentration. The increase in molecular lowering with increase in dilution is normal, but the increase in the molecular lowering with increase in concentration is abnormal, and apparently at variance with the theory of electrolytic dissociation.

The conductivities of solutions of these chlorides and bromides increase, as would be expected, from the most concentrated to the most dilute solution employed.

These facts mean that the freezing-point lowering produced by concentrated solutions of these chlorides and bromides are much greater than we should expect from a consideration of the theory, especially when we take into account the fact that the dissociation of the most concentrated solutions is hardly more than 50–60 per cent, as is shown by the conductivity measurements.

How is it then possible to account for these abnormally great depressions of the freezing-point? There appears to us to be only one way. In concentrated solutions these chlorides and bromides must take up a part of the water forming complex compounds with it, and thus removing it from the field of action as far as freezing-point lowering is concerned. The compound, which is probably very unstable, formed by the union of a molecule of the chloride or bromide with a large number of molecules of water, acts as a unit, or as one molecule in lowering the freezing-point of the remaining water. But the total amount of water present, which is now acting as solvent, is diminished by the amount taken up by the chloride or bromide molecules. The lowering of the freezing-point is thus abnormally great, because a part of the water is no longer present as solvent, but is in combination with the chloride or bromide molecules. By assuming that a molecule of the halide is in combination with a large number of molecules of water, it is possible to explain all of the freezing-point results obtained.

But the conductivity results must also be taken into account. These show, unmistakably, a marked degree of dissociation even in the most concentrated solutions employed. There must, therefore, be a certain number of the molecules broken down into ions, either by the water acting as solvent, or by the water in combination with the molecules, just as salts are probably dissociated in their water of crystallization.

We know of cases where there is direct experimental proof that molecules combine with water in the more concentrated solutions, and are then dissociated with increase in dilution.

The case of sulphuric acid is especially interesting in this connection. It was shown by one of us,[1] while working in the laboratory of Arrhenius, that sulphuric acid first forms the definite hydrates, $H_2SO_4.H_2O$ and $H_2SO_4.2H_2O$, and then, on further addition of large volumes of water, it is known from the conductivity measurements that sulphuric acid breaks down completely into ions.

The existence of the hydrates was shown by the freezing-point method. Acetic acid was used as the solvent, and the lowering of its freezing-point produced by sulphuric acid alone was determined. Then the lowering of the freezing-point of acetic acid by water alone was determined, and, finally, the lowering produced by sulphuric acid and water when brought together into the acetic acid. This was never equal to the sum of the separate lowerings, and from the amount of the difference the amount of water in combination with the sulphuric acid was calculated.

It should be observed in connection with the explanation we have offered of these abnormal results, that the chlorides and bromides of the alkaline earths are, generally, very hygroscopic substances, resembling sulphuric acid in their power of attracting water. Some of them are, it is true, far more hygroscopic than others, yet, when dehydrated, they all combine readily with water. It may be due to this property that they combine with water to such an extent in concentrated solutions. It is true that the chlorides of zinc and cad-

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[1] Jones: Ztschr. phys. Chem., **13**, 419; This JOURNAL, **16**, I.

mium are also hygroscopic, but the halides of zinc, and especially of cadmium and mercury, behave, in general, abnormally with respect to their dissociation in water.

It should also be noted that the compound, in addition to magnesium chloride, with which Loomis found a minimum of molecular lowering—hydrochloric acid—is also very hygroscopic, attracting water with great energy.

We do not put forward the above suggestion to account for our results as a final statement of a theory, but only as tentative, and subject to modification as new facts are brought to light. It does, however, seem to account qualitatively for the experimental facts which have been brought to light.

We propose to extend this investigation to a much larger number of hygroscopic substances, to ascertain whether there is any relation between this property and abnormal freezing-point lowerings such as those recorded in this paper.

CHEMICAL LABORATORY,
JOHNS HOPKINS UNIVERSITY,
MAY, 1899.

Contributions from the Chemical Laboratories of the Massachusetts Institute of Technology.

XXIII.—THE PREPARATION OF PURE TELLURIUM.

BY JAMES F. NORRIS, HENRY FAY, AND D. W. EDGERLY.

In testing a volumetric method[1] for the estimation of tellurium which we proposed some time ago, we were led to study the methods which had been used for the purification of tellurium. As it appeared that a substance of undoubted purity could be obtained only by a very long series of operations, which involved fusion with potassium cyanide, precipitation, and subsequent distillation in hydrogen, a new method was sought. It seemed probable that the basic nitrate of tellurium might be used for this purpose, as it is a well-crystallized compound, very easily obtained. We accordingly prepared it, and having found that the sample did not agree in some of its properties with those which had been assigned to it in the literature, a careful study of it was made. Klein and Morel[2]

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[1] This JOURNAL, **20**, 278.

[2] Bull. Soc. Chim. [2], **43**, 198.

prepared the compound by dissolving tellurium in nitric acid (1.25 sp. gr.) and evaporating the solution. To the crystals which formed they assigned the formula $4TeO_2.N_2O_5.1\frac{1}{2}H_2O$. Only very small crystals were formed and these were hygroscopic. The nitrate prepared by us by the method of Klein and Morel was obtained in crystals sometimes a centimeter in length and were not hygroscopic. An analysis was accordingly made, which showed that the compound has the formula $4TeO_2.N_2O_6.H_2O$, or better $Te_2O_3(OH)NO_3$, since the water is not present as water of crystallization.

In the preparation of the nitrate it is crystallized from nitric acid, and as the impurities present in the tellurium do not form crystalline compounds under these conditions, it was thought that the salt could be obtained quite pure. The tellurium obtained from it would, as a result, be free from those substances with which it is invariably mixed when precipitated from solution by sulphur dioxide or other reducing agents. A sample of basic nitrate was recrystallized three times and then subjected to a careful study, with the result that no impurity was discovered.

On account of the fact that the most trustworthy atomic weight determinations of tellurium have given results which place it in the eighth group in the periodic system of the elements, notwithstanding its striking similarity to sulphur and selenium, the hypothesis has been put forward that tellurium is a mixture of true tellurium with an atomic weight of about 125, and another element with a higher atomic weight. Brauner,[1] who spent a number of years studying tellurium, has expressed this as his opinion.

As no known substance was found in the tellurium obtained from the pure nitrate, the element was subjected to a fractionation to determine whether it could be broken down into two or more substances by this means, which proved so effective in the case of didymium. The double bromide of tellurium and potassium, made from tellurium dioxide, hydrobromic acid, and potassium bromide prepared with the greatest care, was carried through a fractionation which involved over 200 crystallizations. In order to determine whether this fraction-

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[1] J. Chem. Soc., **55**, 382; and **67**, 549.

ation had accomplished any decomposition, the tellurium from the end fractions was converted into the nitrate, and the loss in weight of the latter compound on ignition determined. Any change in atomic weight could be determined in this way. The results obtained with the two fractions were identical within the limits of accuracy of the method. The differences obtained, 0.4 of a unit in the atomic weight, was probably due to inaccuracies in the method. The conversion of the nitrate into the oxide, as at present carried out, does not appear to give results from which the atomic weight of tellurium can be determined with great accuracy.

Preparation of Basic Tellurium Nitrate.

The tellurium used was obtained from a residue obtained in the electrolytic refining of copper. This residue was a solution which consisted principally of the sodium salts of tellurous, selenous, and silicic acids, with the last-named acid in great excess. Whitehead[1] has described the process by which the copper is refined and how the liquid is obtained. Tellurium was obtained from this liquid in two ways. At first the solution was diluted with water and neutralized with sulphuric acid, which threw out a heavy white precipitate of tellurous acid and silica. This mixture was evaporated to dryness twice with hydrochloric acid to render the silica insoluble, and the residue extracted several times with strong hydrochloric acid. From the solution of the chloride so formed, the tellurium was obtained by precipitation with acid sodium sulphite. In later experiments the tellurium was precipitated from the hot alkaline solution with commercial glucose. The tellurium obtained by both methods contained silica and other impurities. The crude metal was added to warm dilute nitric acid (sp. gr. 1.25), and the resulting solution evaporated to dryness in order to insure complete removal of silica. The mixture of basic nitrate and oxide was ignited till free from nitric acid, and was then extracted a number of times with strong hydrochloric acid. The solution in hydrochloric acid was filtered through asbestos and precipitated with acid sodium sulphite. The sulphite was added slowly until the precipitate

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[1] J. Am. Chem. Soc., **17**, 849.

formed was black, thus showing that most of the selenium was precipitated. After the mixed precipitates of selenium and tellurium had settled, the solution was decanted, filtered, and the precipitation continued. The tellurium which had been freed from a large share of its impurities by this second precipitation was again dissolved in nitric acid (sp. gr. 1.25), and the basic nitrate obtained from the solution by crystallization. The nitrate was twice recrystallized. This was best done as follows: The salt was stirred with a large amount of nitric acid (sp. gr. 1.25) heated to about 70° C. At a higher temperature the nitrate was decomposed into a mixture of amorphous and crystalline oxide, which was not readily dissolved by the acid. The solution was filtered through asbestos and evaporated at a temperature of about 80°. In some cases the solution was allowed to cool after crystals appeared. In other cases the evaporation was continued while the crystals were separating from the liquid. By the latter method larger crystals were obtained, which were at times 0.5 cm. in length. The nitrate crystallizes in orthorhombic prisms, terminated by macrodomes and truncated by well-developed macropinacoids and small brachypinacoids. The salt is not hygroscopic, some crystals having stood in the open air for over a month without losing their bright luster.

Purity of the Basic Nitrate of Tellurium.

The purity of the basic nitrate of tellurium, which had been twice recrystallized, was studied. It was again recrystallized from nitric acid and a qualitative analysis of the crystals was made. The mother-liquor was evaporated to dryness and also analyzed. The presence of no foreign element was detected in either case. Whitehead[1] and Keller[2] have determined what substances are present in the crude copper from which the tellurium used in this work was obtained. These are silver, gold, bismuth, arsenic, antimony, and selenium. As none of these elements forms a crystalline compound which is difficultly soluble in nitric acid, it is seen that the basic nitrate of tellurium was readily obtained in pure condition. Brauner has shown that pure tellurium cannot be obtained

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[1] J. Am. Chem. Soc., **17**, 849.

[2] *Ibid.*, **19**, 778.

by precipitation, and that repeated distillation of the metal is necessary to free it from the heavy metals.

In order to test for minute traces of selenium, a common impurity in tellurium, the following method was devised, based on the difference in behavior of the oxides of selenium and tellurium with hydriodic acid. The former oxide is reduced and iodine set free, while the latter is converted into the tetraiodide. The test is made in this way: About 0.15 to 0.2 gram of the oxide to be tested is dissolved in 2 cc. of a 10 per cent solution of sodium hydroxide, and 3 cc. of hydrochloric acid (sp. gr. 1.12) is added. The solution is then cooled to the room temperature, carbon bisulphide and 2 drops of a dilute solution of potassium iodide (2 grams in 100 cc. water) are added, and the tube is shaken. Under the above conditions, if selenium is present, the carbon bisulphide will be colored by the iodine liberated, and the small amount of tellurium tetraiodide formed will remain in solution. It is necessary to avoid a large amount of potassium iodide in order to prevent the formation of much tellurium tetraiodide, which would dissolve in the carbon bisulphide and so obscure the color of the iodine. Any doubt whether the color is due to liberated iodine or to tellurium tetraiodide can be decided definitely by shaking the carbon bisulphide with water. The color produced by the iodine is not altered while the tellurium tetraiodide is decomposed and the carbon bisulphide again becomes colorless. The accuracy of the method was tested by mixing known amounts of selenium dioxide with the tellurium to be tested. Using the amounts given above, 0.0012 mg. selenium can be detected in the presence of 0.160 gram of tellurium dioxide, that is about 1 part in 150,000. No selenium could be detected in the oxide obtained from the pure nitrate when this very delicate test was applied.

It is of interest to note here that a strong solution of potassium iodide acidified with hydrochloric acid, is a very delicate test for tellurium. The dark color produced is quite characteristic, resembling somewhat in strong solution the color of platinum solutions containing iodides. The difference is readily shown, however, by dilution, when the color produced by platinum persists as a pink, while the color produced by the tellurium disappears on account of the decomposition of the iodide.

No foreign substance was found in the tellurium from the nitrate by careful qualitative analysis, yet it was subjected to additional tests. Brauner and Wills found that the purest tellurium obtained by precipitation invariably left a residue when distilled in hydrogen. A sample of the oxide prepared from the nitrate was dissolved in pure hydrochloric acid and the tellurium precipitated with sulphur dioxide and washed until free from hydrochloric acid. The tellurium was then distilled in a stream of hydrogen, which was prepared by the action of sulphuric acid on zinc. The gas was purified by the method used by Wills[1] in preparing pure tellurium for a determination of its atomic weight. After the distillation a bright stain was left on the porcelain boat. The tellurium was redistilled a number of times with the same result. The gray, shiny spot on the boat was not affected by hot sodium hydroxide, hydrochloric, or nitric acid, and was not volatilized by the heat of a blast-lamp.

From the following experiments it was shown that this residue was due to the union of a small amount of tellurium with the porcelain of the boat at the high temperature required for the distillation. Some tellurium prepared from the nitrate was next distilled in a vacuum. After the first distillation a light gray substance was left in the boat. This was flocculent, dissolved completely in dilute hydrochloric acid and sodium hydroxide, and evidently was tellurium dioxide, which is always present in precipitated tellurium. The tellurium, when redistilled in vacuum, left no residue, but when distilled in hydrogen a stain was left on the boat as before. Some pure tellurium, obtained by distillation in a vacuum, was heated on porcelain in a blast-lamp flame. A stain was left which was caused by the combination of a small amount of the tellurium with the porcelain. This does not take place when the metal is distilled in a vacuum as the temperature of distillation is lower.

The oxide prepared from the nitrate was also completely volatile without leaving a residue. It was heated to redness

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[1] J. Chem. Soc., 35, 704.

on a platinum foil placed inside of a porcelain crucible. The above experiments show that a careful examination of the tellurium obtained by recrystallization of the basic nitrate did not show the presence of any known substance.

Analysis of Basic Tellurium Nitrate.

As the basic nitrate obtained by crystallization from nitric acid is a stable substance, and is not hygroscopic as Klein and Morel have reported, a careful analysis of it was considered necessary. The water was determined by igniting the substance, which had been previously dried at 120°, in a current of oxygen for two hours. In the front part of the tube was placed metallic copper to reduce the oxides of nitrogen. The nitrogen was estimated by a method which was essentially that of Dumas. The tellurium dioxide was determined by heating the nitrate slowly until all of the oxides of nitrogen were given off, and then fusing quickly the oxide left. The decomposition of the nitrate was accomplished most conveniently by placing the platinum crucible inside of a larger porcelain crucible, which was heated by a Bunsen burner. After an hour's heating the oxide was in the form of a loose white powder. The results of the analyses follow:

I. 0.7975 gram substance gave 23.25 cc. N at 0° and 760 mm. pressure.

II. 1.2222 gram substance gave 37.20 cc. N at 0° and 760 mm. pressure.

I. 2.0530 gram substance gave 0.0538 gram H_2O.
II. 2.2981 gram substance gave 0.0590 gram H_2O.
I. 0.9491 gram substance gave 0.7925 gram TeO_2.
II. 0.9920 gram substance gave 0.8282 gram TeO_2.

	Calculated for $4TeO_2.N_2O_5.1\frac{1}{2}H_2O$.	Calculated for $4TeO_2.N_2O_5.H_2O$.	Found. I.	Found. II.
N	3.62	3.66	3.64	3.84
H_2O	3.49	2.36	2.62	2.57
TeO_2	82.54	83.52	83.49	83.36

The atomic weight of tellurium has been taken as 127.6 in calculating the above results. Klein and Morel,[1] using 129 as the atomic weight of tellurium, obtained these results:

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[1] Bull. Soc. Chim. [2], 43, 198.

	Calculated for $4TeO_2.N_2O_5.1\frac{1}{2}H_2O$.	Found. I.	II.
N	3.59	3.70	....
H_2O	3.47	2.90	3.80
TeO_2	82.66	82.20	83.30
Te	65.57	66.10	66.50

Experiments described below show that there is no water of crystallization in the compound. The formula therefore is best written $Te_2O_3(OH)NO_3$.

Decomposition of Basic Tellurium Nitrate by Heat.

Two samples of the nitrate were heated at gradually increasing temperatures in order to determine whether the hydrogen in the compound is present as water of crystallization. The substance was heated for two or more hours at intervals of 10°, beginning at 110°. If at the end of that time the weight had changed, the heating was continued without changing the temperature until constant weight was obtained. The results follow :

Number of hours heated.	Temperature.	Percentage loss. I.	II.
12	110°–170°	0.00	0.00
2	170°–180°	0.07	0.03
4	180°–190°	0.42	0.26
11	190°–200°	2.47	3.36
9	200°–210°	3.71	4.15
9	210°–220°	4.02	5.85
6	220°–230°	8.00	9.67
9	230°–250°	8.60	10.30
1	About 350°	16.51	16.50

From the above results it will be seen that there is no loss of weight up to 170°, when a slight decomposition begins. At 190° oxides of nitrogen begin to be evolved. There was no distinct point at which the water was given off. The decomposition was gradual, both water and nitric acid being given off at the same time. The figures in the last line of the table give the results of heating two portions of the nitrate in covered platinum crucibles protected by porcelain crucibles. The results are practically the same as those obtained in the very accurate determinations described later; *viz.*, 16.47. The oxide which was left was tested for nitric acid by phenol-sulphonic acid, and only a trace was found. It is therefore unnecessary to fuse the oxide in making a gravimetric estimation of tellurium, if it is heated in the manner described. The loss which accompanies fusion can be done away with and more accurate results obtained. The experiments recorded above are not in accord with the statement of Klein and Morel that the nitrate begins to decompose at the fusing-point of lead.

Action of Nitric Acid on the Nitrate.

In recrystallizing the nitrate it was observed that at times a residue was left which dissolved with difficulty in nitric acid. This residue examined under the microscope showed well-developed crystals in the form of octahedra, and, when ignited, it did not lose in weight. The nitrate was changed into a mixture of amorphous and crystalline tellurium dioxide. It was therefore important to study the conditions of formation of the oxide in order to be able to get crystals of the nitrate in perfectly pure condition.

Some nitrate was heated with not enough nitric acid (sp. gr. 1.20) to dissolve it. After the acid had boiled twenty-five minutes the residue was examined and found to contain no nitrate. From the hot solution a small amount of white amorphous powder separated. On evaporation of the nitric acid solution well-defined crystals of the nitrate were formed. These were shown by analysis to be free of oxide. The loss in weight on ignition was 16.51 per cent. Theory requires a loss of 16.48 per cent. The same results were obtained when nitric acid of specific gravity 1.25 was used. It will be seen, therefore, that, while the dilute acids decompose the nitrate, any crystals which are formed from it by concentration are pure nitrate. The reasons for the directions given above for the recrystallization of the nitrate, are now evident. The nitrate is stirred with the acid (sp. gr. 1.25) at about 70° in order to avoid decomposition into the oxide, and saturation of the solvent. Crystals of the nitrate increase markedly in size when heated with concentrated boiling nitric acid, and a large amount crystallizes from the oxide on cooling.

Electrolytic Deposition of Tellurium.

Schucht[1] and Whitehead[2] have shown that tellurium is deposited by the electric current from an acid or alkaline solution. Numerous attempts were made to get the conditions under which the deposit would be made in such a form that it could be weighed. It was deposited from hydrochloric and nitric acid solutions and from solutions of the alkali tellurites. As tellurium is nearest to antimony in the electrolytic scale, the conditions under which antimony is deposited were applied to tellurium. The precipitate was always in an amorphous, flocculent condition. Some tellurium which had been deposited by electrolysis was converted into the nitrate and the loss in weight on ignition determined. This was done to determine whether the electrolysis had effected any decomposition of the element. As the loss in weight was 16.55 per cent, it was concluded that no decomposition had taken place.

Fractional Crystallization of Potassium Bromtellurate.

Owing to the uncertainty of the homogeneity of tellurium it was subjected to a careful fractionation. Wills[3] fused tellurium with potassium cyanide and precipitated the element in two fractions from the aqueous solution of the telluride by a current of air. Brauner used this same process but separated the tellurium into four fractions. He also precipitated tellurous acid in eight portions from a solution of tellurium tetrachloride, and subjected tellurium tetrabromide to fractional sublimation in a vacuum. The details of the latter method are not given.

Staudenmaier[4] crystallized telluric acid and collected the compound in four portions. In all cases atomic weight determinations of the fractions gave no evidence of a breaking down of the tellurium.

The importance of testing the hypothesis of the compound nature of tellurium led us to undertake a more careful fractionation than had been accomplished heretofore. The results of Wills, Brauner, and Staudenmaier are not conclusive, since the fractionation was not carried far enough in any case

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[1] Jahresbericht, 1883, 222, 1514.

[2] J. Am. Chem. Soc., **17**, 849.

[3] J. Chem. Soc., **35**, 704.

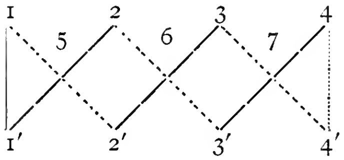
[4] Ztschr. anorg. Chem., **10**, 189.

to warrant definite conclusions. Crystallization was selected as the means of fractionation, as it appears to be much more efficient than precipitation. A number of compounds were studied with the view of using them for this purpose. The organic compounds formed by tellurium tetrachloride with anisol and phenetol, $TeCl_2(C_6H_4.OCH_3)_2$, $TeCl_2(C_6H_4OC_2H_5)_2$, were prepared. They are described as crystallizing well. The progress of the crystallization could be easily watched as the compounds have distinct melting-points. It was found extremely difficult, however, to prepare these compounds in large quantities and to recrystallize them.

The salt finally selected was the double bromide of tellurium and potassium. This salt is readily prepared and crystallizes well from water. In order to have the results of the fractionation as conclusive as possible all the reagents used were prepared with the greatest care.

Potassium bromide was prepared by heating chemically pure potassium bromate of commerce which had been recrystallized four times. Hydrobromic acid was made by Squibb's method, and purified by four redistillations from potassium bromide. The tellurium dioxide was made from basic nitrate which had been recrystallized three times from nitric acid. The nitrate was decomposed at about 350° and then fused in portions of 6 to 10 grams in a platinum crucible protected by a larger porcelain crucible. Theoretical quantities of tellurium dioxide and potassium bromide were dissolved in hydrobromic acid and the salt obtained by crystallization. Throughout the work porcelain dishes alone were used. Eight hundred grams of this compound were then subjected to fractional crystallization.

The following diagram may help to make the scheme of fractionation clear. Crystals are represented by solid lines and mother-liquors by dotted lines:



Four portions of 200 grams each were dissolved in water, usually containing a small amount of hydrobromic acid, and the solutions evaporated to such a point that about 100 grams of salt separated on cooling. The salt from fraction 1 was set aside; the salt from fraction 2 was added to the mother-liquor of fraction 1, making number 5; the salt from number 3 was added to the mother-liquor from number 2; and the salt from 4 was added to mother-liquor number 3. The mother-liquor from fraction 4 was set aside during the intermediate crystallization of fractions 5, 6, and 7. These solutions were evaporated as before. The salt from fractions 1 and 5 were united, making the first portion of the second series. The mother-liquor of number 5 and the crystals from 6 made number 2 of the second series. The mother-liquor of 6 and the crystals from 7 made number 3, and finally the mother-liquors of 4 and 7 made number 4 of the second series. It will be seen that a complete series involves seven crystallizations. This procedure of adding the crystals of one fraction to the mother-liquor of another tends to make the most soluble and the least soluble portions collect in the end fractions. The fractionation was repeated thirty times, which involved 215 crystallizations.

There were no indications during the work of any change in the salts, so an atomic weight determination of the tellurium from the end fractions had to be made. More than fifteen different methods have been studied in attempting to determine the atomic weight of tellurium, and of these but one method, the determination of bromine in the tetrabromide, was found to give concordant results. As the use of this method is not free from objections, and involves a large amount of work, a simpler method was sought. Very concordant results were obtained in the analysis of the basic nitrate when it was changed to the oxide by ignition, and it seemed possible that trustworthy results, which would show any variations in the atomic weight, might be obtained, if the ratio between the nitrate and oxide was determined with great care.

As Klein and Morel have stated that the nitrate is hygroscopic, experiments were made with a pure sample to test this point. Two portions of the salt were heated for eight hours at 120° in platinum crucibles, transferred to a desiccator, and after cooling were weighed immediately, a platinum crucible being used as a tare. After standing half an hour and fifteen hours in the balance case, the crucibles were weighed again, with the following results :

Hours.	A.	B.
0	1.96242	2.19839
0.5	1.96275	2.19860
15.0	1.96274	2.19855

It will be seen that the weights remained perfectly constant after the crucibles had stood long enough to be in equilibrium with the atmosphere of the balance case, which shows conclusively that the salt is not hygroscopic. It was then heated at 120° for varying periods of time to determine whether it could be brought to constant weight.

Hours heated.	A.	B.
2.5	2.28692	2.12905
14.0	2.28667	2.12897
7.5	2.28676	2.12896
7.0	2.28672	2.12905

The above results show that this could be done very satisfactorily.

The preliminary experiments on the decomposition of the nitrate showed that the oxides of nitrogen evolved during heating carried off a small amount of tellurium dioxide mechanically. In order to avoid this loss the following device was used : A platinum crucible was provided with two removble platinum disks which fitted the crucible at distances of about one-half and one inch from the bottom. In the center of the lower disk a hole was cut about one-eighth inch in diameter. The salt was placed in the crucible, the disks adjusted, and the cover put on. There were three surfaces over which the issuing gases had to pass, and on these the oxide carried along was deposited. In the experiments a slight dullness was visible on the upper disk, but the cover was bright, thus showing that no oxide had reached it.

The nitrate was decomposed slowly in order to avoid a rush of gas. It was heated for two hours at 200°, 250°, and 300° ;

three hours at 350°, 400°, 450°, 500°, and 550°; and was finally fused quickly in the oxidizing flame of a Bunsen burner.

The tellurium from the two end fractions of the fractional crystallization was converted into nitrate. The salt was moistened with concentrated nitric acid when being ground in order to prevent decomposition from atmospheric moisture. The finely divided nitrate was heated to constant weight and converted into the oxide in the manner described above.

The results of the analysis of the nitrate prepared from the tellurium from the fraction which would contain the most soluble portion, follow:

	$Te_2O_3(OH)NO_3$.	TeO_2.	Percentage TeO_2.
I.	2.84426	2.37354	83.45
II.	2.55736	2.13397	83.44

The analysis of the nitrate from the fraction which would contain the least soluble portion, was made under the same conditions as before.

	$Te_2O_3(OH)NO_3$.	TeO_2.	Percentage TeO_2.
III.	1.39948	1.16824	83.48
IV.	1.85244	1.54649	83.49

The difference between the average of determinations I and II and the average of III and IV corresponds to a difference of 0.4 in the atomic weight. When a sample weighing 2 grams is used an error of 0.3 mg. in the weight of the nitrate would affect the atomic weight to this extent. Although the weights of the nitrate in the above experiments appear to be accurate to 0.1 mg., nevertheless the difference found is probably more apparent than real.

The basic nitrate is a crystalline compound and may have held mother-liquor within the crystals, although the salt was ground to a fine powder and did not lose weight when heated for ten hours at 120°. On account of this uncertainty, we do not consider the results as data which can be used for calculating the atomic weight of tellurium. The results are of value, however. The analyses of the nitrate prepared from the fractionated tellurium were made under exactly the same conditions, and any error in the method would have affected the two determinations equally. We can, therefore, safely conclude that the fractionation of potassium bromtellurate did not effect any decomposition of the tellurium, which could be detected by a method capable of giving results accurate to 0.4 of a unit in the atomic weight.

The work described above is preliminary to an atomic weight determination which is now in progress. When a method has been devised which will give accurate results, the atomic weight from the end fractions will be determined, in order to decide whether the difference of 0.4 of a unit indicated by the experiments given above is a real one or not. We hope also to offer more conclusive evidence in regard to the elementary nature of tellurium. The fractional sublimation of tellurium dioxide, which is now in progress, seems to offer a more efficient means of deciding this point than fractional crystallization.

This paper has been published in this unfinished form, as the departure of one of us from the Institute prevents us from continuing the work in common.

BOSTON, Dec. 1, 1899.

XXIV.—THE REDUCTION OF SELENIUM DIOXIDE BY SODIUM THIOSULPHATE.

BY JAMES F. NORRIS AND HENRY FAY.

Some time ago we proposed a volumetric method for the estimation of selenous acid[1] based on the reaction between it and sodium thiosulphate in the presence of hydrochloric acid. The procedure, in brief, is as follows: The solution in which the selenous acid is to be determined is diluted with ice-water, acidified with dilute hydrochloric acid, and an excess of a tenth-normal solution of sodium thiosulphate added. The excess of thiosulphate is determined by titration with a solution of iodine. It was shown that 1 molecule of selenous acid reacted with 4 molecules of sodium thiosulphate, and that the reaction afforded a means for the accurate determination of selenium.

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[1] This JOURNAL, **18**, 703.

At the time this method was proposed we were not able to state the exact nature of the reaction, but we have studied further the reduction and are now able to write the complete reaction. The most probable reaction between the two substances may be represented by the following equation :

$$SeO_2 + 4Na_2S_2O_3 = 2Na_2S_4O_6 + Se + 2Na_2O.$$

If strong solutions of selenium dioxide and sodium thiosulphate are mixed, selenium is precipitated, and the solution shows an alkaline reaction. In dilute solutions, on the other hand, no selenium is precipitated, and the reaction is not complete according to the above equation, since the sodium hydroxide formed neutralizes a part of the selenous acid which, accordingly, does not enter into the reaction. If, however, acid is present, 4 molecules of sodium thiosulphate react with 1 molecule of selenium dioxide. The amount of acid required to complete the reaction was determined. This was found to vary with the dilution, the excess of thiosulphate, and the time of reaction. The following table gives the results obtained. In each case 10 cc. of a solution of selenium dioxide, which was equivalent to 26.40 cc. of sodium thiosulphate, according to the ratio $SeO_2 : 4Na_2S_2O_3$, were used :

	Molecules HCl.	$Na_2S_2O_3$ taken. cc.	$Na_2S_2O_3$ used. cc.	Water added. cc.
I.	3	50	17.90	...
II.	4	27	22.02	300
III.	4	27	24.96	300
IV.	4	50	25.40	300
V.	5	30	26.38	300
VI.	4	50	26.40	...

In experiment I., 3 molecules of acid were used and only 17.90 cc. of thiosulphate entered into the reaction. Using 4 molecules in II, 22.02 cc. of thiosulphate reacted. In the third experiment the same proportions were used, but the solutions stood forty minutes before the excess was determined. This had a marked effect on the result, as about 3 cc. more of the thiosulphate reacted. A large excess of thiosulphate hastened the reaction, as is shown in experiment

IV. Experiment V shows that 5 molecules of acid are sufficient at a dilution of 300 cc., and with a slight excess of sodium thiosulphate to complete the reaction. In experiment VI no water was added to the solutions used and the reaction was complete when the proportion of the reagents were $SeO_2 : 4Na_2S_2O_3 : 4HCl$. These are, therefore, the amounts of reagents which enter into the reaction.

In order to determine the products of the reaction, a solution of the constituents in the above proportions was prepared. The study of this solution led to the following equation, which expresses the reaction :

$$SeO_2 + 4Na_2S_2O_3 + 4HCl = Na_2S_4SeO_6 + Na_2S_4O_6 + 4NaCl + 2H_2O.$$

The formation of sodium selenopentathionate, similar to potassium pentathionate, seemed probable, since no selenium was precipitated as a result of the reduction. Debus,[1] in an exhaustive study of Wackenroder's solution, which is prepared by the action of hydrogen sulphide on an aqueous solution of sulphur dioxide, isolated some salts of pentathionic acid in a pure condition, and carefully studied their properties. He gives the following characteristic reactions :

"I. An ammoniacal solution of silver nitrate causes, in a solution of potassic, ammonic, or baric pentathionates, a brown coloration which rapidly becomes darker, and by degrees a black precipitate is thrown down from the mixture. This reaction is not produced in a solution of tri- or tetrathionates, potassic thiosulphate, or ammonic sulphite. An ammoniacal solution of silver nitrate also seems to have no effect on them. Consequently a pentathionate, even if present in very small quantity, can be detected by means of this reaction in a mixture containing potassic tri- and tetrathionates, and sodic, potassic, or ammonic thiosulphates.

"II. Potassic hydroxide, in solutions of pentathionates, immediately produces a separation of sulphur. As tri- and tetrathionates and thiosulphates are not changed by this reagent, a proportionally small quantity of a pentathionate can be detected in a mixture of the four salts by addition of potassic hydroxide.

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[1] J. Chem. Soc., **53**, 278.

"III. Ammonia added to a solution of potassic pentathionate causes, after about one or two minutes, a precipitation of sulphur.

"IV. Hydric chloride does not change solutions of tetra- and pentathionates."

A solution prepared by mixing the constituents in the proportions represented in the equation, was subjected to the above tests. A precipitate was formed with ammoniacal silver nitrate, as described above under I, and potassium hydroxide caused an immediate precipitation of selenium. Ammonia acted more slowly, and the solution was stable toward strong hydrochloric acid. The solution showed, therefore, the characteristic reactions of a pentathionate, selenium, however, being precipitated instead of sulphur. This is in accord with the formula proposed, $Na_2S_4SeO_6$. An effort was made to isolate the selenopentathionate, but without success, as selenium was always precipitated when the solutions were concentrated by heat or in a vacuum. From the solution, however, we were able to isolate sodium tetrathionate, which was proved to be such by qualitative and quantitative analysis.

A dilute solution containing the new salt could be boiled some time without change. A number of neutral salts were found to decompose the compound. Stannous chloride caused a precipitation of selenium after a few minutes. A dilute solution of sodium thiosulphate produced the same effect only much more slowly, whereas a number of hours' standing was necessary before potassium iodide caused any decomposition.

An acid solution of tellurium dioxide is reduced by sodium thiosulphate, giving a bright yellow solution, from which sodium hydroxide precipitates tellurium. Tellurium, therefore, probably forms a compound analogous to a selenopentathionate. This is remarkable, since no compounds containing tellurium, analogous to the thionates, are known. Crane[1] attempted to prepare substances similar to the thiosulphates, by boiling sodium tellurite with sulphur, selenium, and tellurium, but there was apparently no reaction.

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[1] Dissertation, Johns Hopkins University.

By misunderstanding a statement made in our former paper, Mr. J. T. Norton, Jr.,[1] has been led to study the influence of hydrochcloric acid on titrations with sodium thiosulphate, and to repeat our work on the estimation of selenium. He says, referring to the method, "the explicit statement of the authors that the amount of hydrochloric acid present does not influence the result provided the titration is made at the temperature of melting ice, is so extraordinary in view of generally accepted ideas in regard to the interaction of hydrochloric acid and sodium thiosulphate as to suggest the necessity of a careful investigation of this point." In the paper referred to we made this statement: "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." Mr. Norton evidently confuses *excess* with *amount*. We used in all of our experiments 10 cc. hydrochloric acid (1.12 sp. gr.), which is seven to eight times the amount required according to the above statement, and obtained excellent results. The statement is, therefore, not so extraordinary as might appear.

As the action of hydrochloric acid on sodium thiosulphate was known to us when we were making a study of the method, we took the precautions to have the solutions containing the acid dilute, and used ice to keep the temperature as low as possible. The necessity for these precautions was stated in the directions given. Mr. Norton further points out that it is advisable to use not more than 20 cc. excess of sodium thiosulphate in order to prevent decomposition by the acid. We have made some new determinations of selenium in order to test the directions given in the original paper under the most unfavorable conditions. The results follow:

	SeO_2 taken. Gram.	$Na_2S_2O_3$ taken. cc.	$Na_2S_2O_3$ used in reaction. cc.	SeO_2 found. Gram.	Dilution. cc.
I	0.0995	43	39.62	0.0995	300
II	0.0336	15	13.39	0.0336	300
III	0.0336	50	13.13	0.0331	300
IV	0.0336	50	13.24	0.0333	300
V	0.0435	50	17.20	0.0432	400
VI	0.0430	50	16.41	0.0412	200

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[1] Am. J. Sci., **157**, 287.

In Experiments I. and II. the directions as given in our paper were followed, and a small excess of sodium thiosulphate was used. In order to have a large excess of thiosulphate present in the other experiments, small amounts of selenium dioxide and 50 cc. of thiosulphate were used. In III. and IV. the excess, 36.87 cc., was nearly three times the amount necessary for the reaction—13.13 cc. Since a bare excess only is necessary, a careful analysis would hardly be based on such a procedure. Experiment VI. shows the necessity of working in dilute solutions. In all of the above determinations 10 cc. hydrochloric acid (1.12 sp. gr.) were used, but since 5 cc. is quite sufficient to bring about the reaction, the modification which Mr. Norton suggests as the result of his work, namely the use of the latter amount of acid, can readily be accepted.

Mr. Norton points out also that his results always come high. We had not observed this in our work and accordingly we sought the cause. As we had standardized the sodium thiosulphate by titration against known weights of iodine, under the conditions which were to be used in the subsequent analyses, that is, titration in the cold in the presence of acid, a standardization was made under ordinary conditions. The factor found was higher by about 0.2 per cent than the one previously obtained. This discrepancy was shown to be due to the fact that the iodine-starch reaction is more sensitive at 3° in presence of dilute acids than under the conditions which are ordinarily used in the titration of iodine and thiosulphate. The following table gives the number of cubic centimeters of one-hundredth normal iodine solution required to produce a color with starch under different conditions of temperature and with varying amounts of dilute hydrochloric acid (sp. gr. 1.12). The starch solution was made by grinding 2 grams of soluble starch with 5 cc. of cold water, and pouring the mixture into 500 cc. boiling water. In all tests 5 cc. of this solution were used and diluted to 300 cc. with water.

No.	Acid. cc.	Temperature.	Iodine. cc.
1	....	20°	0.61
2	1.00	20°	0.32
3	10.00	20°	0.26
4	50.00	20°	0.27
5	....	3°	0.30
6	....	15°	0.50
7	....	20°	0.57
8	....	25°	0.85
9	....	30°	1.17
10	10.00	3°	0.15

Experiments 1–4 show the effect of acids and 5–9 the effect of temperature. In Experiment 10 the most favorable conditions for the reaction were combined and 0.15 cc. of the iodine solution gave a distinct color, whereas in the absence of acid, at 25°, 0.85 cc. was necessary. It has long been known that temperature has an effect on the blue compound formed by the action of iodine on starch but, as far as we can find, it has never been shown that this effect is appreciable at the temperatures used in the course of an analysis. Although the error arising is small when the facts brought out by the above experiments are overlooked, nevertheless, when very accurate results are desired, they should be taken into consideration.

BOSTON, Dec. 1, 1899.

ACTION OF PICRYL CHLORIDE ON PYROCATECHIN IN PRESENCE OF ALKALIES.

BY H. W. HILLYER.

Being engaged in a study of some derivatives of diphenyl ether, $C_6H_5OC_6H_5$, made by the general method of Willgerodt,[1] the attention of the writer was called to the reaction discovered by G. S. Turpin,[2] and used by him in the preparation of dinitrophenoxazine and to the reaction used by F. Kehrmann,[3] in preparing dinitrophenthiazine. Turpin brought together in alcoholic solution one molecular proportion of picryl chloride, one of orthoamidophenol, and two of an alkali. He readily obtained dinitrophenoxazine with the elimination of chlorine, and one nitro group from the picryl chloride as follows:

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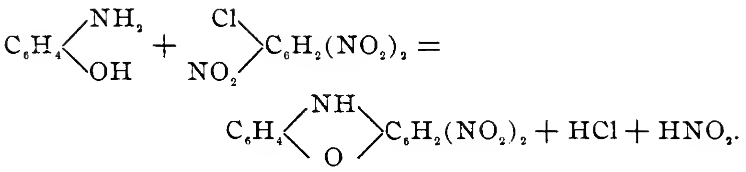
[1] Ber. d. chem. Ges., **12**, 1278; and **13**, 887.

[2] J. Chem. Soc. (London), 1891, 714.

[3] Ber. d. chem. Ges., **32**, 2605.



$$C_6H_4\left\langle\begin{matrix}NH_2\\OH\end{matrix}\right. + \left.\begin{matrix}Cl\\NO_2\end{matrix}\right\rangle C_6H_2(NO_2)_2 = C_6H_4\left\langle\begin{matrix}NH\\O\end{matrix}\right\rangle C_6H_2(NO_2)_2 + HCl + HNO_2.$$

In this connection the idea came to the writer to ascertain whether a similar reaction would take place on bringing to-together picryl chloride and pyrocatechin in equimolecular proportions and adding a double molecular proportion of sodium hydroxide, thus forming a double aromatic ether.

Fifteen grams picryl chloride and 6.6 grams pyrocatechin were dissolved in 500 cc. common alcohol and a solution of sodium in alcohol, equivalent to 4.8 grams of sodium hydroxide, were added. The solution turned dark-brown, and after some time deposited a brown precipitate soluble in water. The mixture was heated to 60°–70° for six hours. The brown precipitate gradually disappeared, and was replaced by a dense, yellow, granular precipitate, which, after five hours, did not seem to increase in amount. It was filtered from the solution and washed with alcohol and water, and after drying weighed 13.75 grams, or 85 per cent of the theoretical. The solution filtered from the yellow precipitate contained large quantities of chloride and nitrite.

The crude yellow product melts at 191°–192°.5. It dissolves quite readily in hot benzene, and crystallizes from it on cooling in yellow spherulites. It is best purified by crystallization from hot glacial acetic acid, from which it also separates in lemon-yellow spherulites. By this purification its melting-point is changed but little, the melting-point of the twice crystallized substance being 192°–192°.5. When rapidly heated it decomposes almost explosively, but when carefully heated it may be sublimed in the form of beautiful lemon-yellow leaflets of the same melting-point. It will not dissolve in hydrochloric acid. It dissolves in concentrated sulphuric acid, but apparently separates unchanged on adding water. It will not dissolve except perhaps slightly in dilute alkalies, showing that it is not a phenol. Heated with strong alkalies it dissolves, forming a brown solution, and from this solution a new substance not yet studied is thrown down on adding an acid.

A portion of the yellow substance twice crystallized from glacial acetic acid, washed with alcohol, and dried for one hour at 130°–140° was analyzed, and gave the following results:

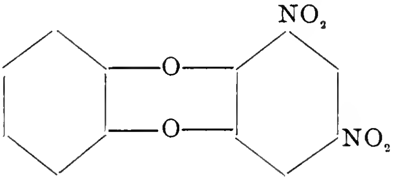
I. 0.2211 gram substance gave 0.4283 gram CO_2, and 0.0486 gram H_2O.

II. 0.2093 gram substance gave 0.4005 gram CO_2, and 0.0431 gram H_2O.

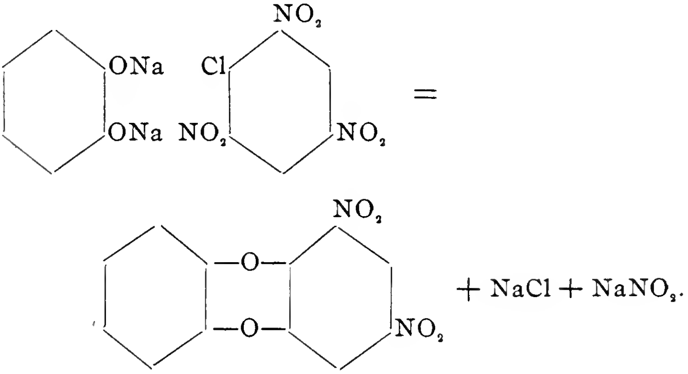
III. 0.2477 gram substance gave 23.2 cc. N at 21° and 748 mm. pressure.

	Calculated for $C_6H_4O_2C_6H_4(NO_2)_2$.	Found.	
		I.	II.
C	52.55	52.83	52.18
H	2.19	2.44	2.29
N	10.22	....	10.49

In view of these analytical results and of the formation of chloride and nitrite in making it, and also from its not being a phenol, the substance may be represented by the formula



and is produced by the reaction



It is a 1,3-dinitroorthodiphenylene dioxide. In view of the stability of the phenyl ethers, it seems probable that the mother-substance of which this is a dinitro derivative may yield other interesting derivatives. For the mother-substance, to indicate its analogy with phenoxazine and phenthiazine, and to point out the presence of the two oxygen atoms connecting the two phenylene groups, the name *phenoxozone* is proposed.

The action by which the new substance, dinitrophenoxozone, is prepared presents one more case of which there are now several in which a nitro group may be split off with formation of a closed chain. The cases published are cases in which the nitro group is in the ortho position to a side chain, usually nitrogenous, and of such a character that it can form either a five-membered or six-membered ring. In the present case there is a formation of a six-membered ring of four carbon atoms and two oxygen atoms.

It is desired to reserve, for study in this laboratory, the action of orthonitrohalogen benzene derivatives on di- and poly-acid phenols of the ortho series, and the character and reactions of the derivatives of diphenylene dioxide or phenoxozone.

Laboratory of Organic Chemistry,
University of Wisconsin,
December 20, 1899.

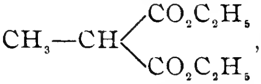
Contributions from the Chemical Laboratory of the Rose Polytechnic Institute.

XVII.—CAMPHORIC ACID.

[EIGHTH PAPER.]

By William A. Noyes.

An account of the preliminary work toward the synthesis of 2.33-trimethylcyclopentanone has already been given.[1] The synthesis has now been brought to a successful completion.

Ten grams of sodium were dissolved in 130 cc. of absolute alcohol and 92 grams (calculated 76.5 grams) of methyl malonic ester,  $CH_3—CH<\begin{matrix}CO_2C_2H_5\\CO_2C_2H_5\end{matrix}$, were added, and then 97 grams of the ethyl ester of γ-bromisocaproic acid,

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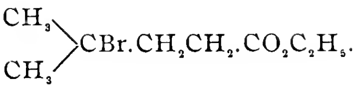
[1] This Journal, **22**, 258.

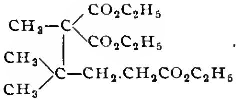


$$\begin{matrix} CH_3 \\ CH_3 \end{matrix} > CBr.CH_2CH_2.CO_2C_2H_5.$$

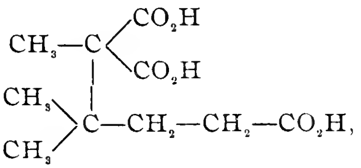
The mixture was boiled for two hours, filtered from sodium bromide, the alcohol distilled over a free flame, the residue filtered again, and then distilled under diminished pressure. After two distillations there were obtained 5 grams of an ester boiling at 180°–187° under a pressure of 20 mm. A second preparation with the use of 121 grams of the brom ester gave 8.1 grams, boiling at 170°–180° under a pressure of 13–15 mm. The portion boiling at 178°–180° was analyzed.

I. 0.1930 gram substance gave 0.4244 gram CO_2, and 0.1404 gram H_2O.

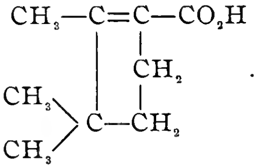
II. 0.2010 gram substance gave 0.4425 gram CO_2, and 0.1473 gram H_2O.

	Calculated for 	Found. I.	 II.
C_{16}	60.76	59.97	60.04
H_{28}	8.86	8.08	8.12
O_6	30.38	....	....

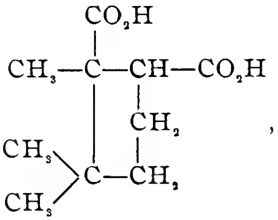
The ester was evidently contaminated with some compound or compounds containing less carbon and hydrogen, but, owing to the difficulty of preparation, it could not be further purified. The ester of the first preparation was saponified by boiling for one hour with alcoholic potash. The solution was diluted, evaporated to remove alcohol, acidified, and extracted several times with ether. The impure 2.33-tetramethylhexoic 1,2^1,6-acid,



was heated in an oil-bath to 200° for a few minutes till the evolution of carbon dioxide ceased. The resulting $\alpha\beta\beta$-trimethyladipic acid was mixed with twice its weight of lime and the mixture distilled from a small distilling-bulb. The distillate was distilled and 0.35 gram, which passed over at 160°–180°, was mixed with alcohol and a solution containing 0.6 gram of hydroxylamine chloride and 0.5 gram of sodium hydroxide. After several hours the solution was poured into a crystallizing dish, and allowed to evaporate spontaneously. The oxime which separated was recrystallized from ligroin. It crystallized in needles which melted at 104°. When a small portion was mixed with an equal amount of the oxime prepared from α-hydroxydihydrociscampholytic acid,[1] the mixture melted at exactly the same temperature, and after solidification the melting-point still remained the same. The identity of the two substances is, therefore, established, and the ketone from camphor is 2.33-trimethylcyclopentanone. From this it follows that ciscampholytic acid is the Δ^1-2.33,-trimethylcyclopentenoic acid,



There also remains no reasonable doubt that Perkins'[2] older formula for camphoric acid,



and Bouveault's[3] formula for camphor,

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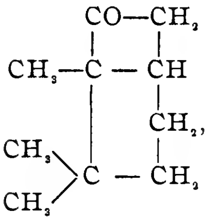
[1] This JOURNAL, **22**, 265.

[2] Proc. Chem. Soc., 1896, 191.

[3] Chem. Ztg., **21**, 762.



are correct.

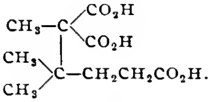
Owing to the small quantity of the oxime available, the analysis was not satisfactory.

0.0353 gram substance gave 0.0387 gram of nitrogen.

	Calculated for $C_8H_{14}NOH$.	Found.
N	9.93	10.96

The ester from the second preparation above was saponified by longer boiling with alcoholic potash, and there was obtained from it an acid which partly solidified. By treatment with a small amount of ether the pure 2.33-tetramethylhexanoic 1,2^1,6-acid was obtained. The acid crystallizes from ether in needles. When heated it begins to decompose at about 175°, but does not melt to a clear liquid till a somewhat higher temperature is reached. When heated to 190°–200° for a few minutes it is decomposed quantitatively into carbon dioxide and *αββ*-trimethyladipic acid. The ammoniacal solution of the acid gives no precipitate with calcium chloride in the cold, but, on warming, a precipitate is formed, which redissolves on cooling.

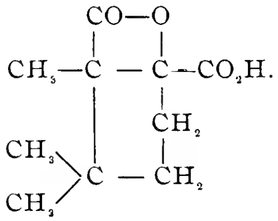
0.1226 gram of the acid gave 0.2319 gram CO_2, and 0.0780 gram H_2O.

	Calculated for 	Found.
C_{10}	51.72	51.59
H_{16}	6.90	7.07
O_6	....	....

0.65 gram of the pure trimethyladipic acid obtained by heating a portion of the acid last mentioned to 200° was mixed with 2 grams of lime and the mixture distilled from a small distilling-bulb. The decomposition took place with very little blackening and a light-yellow oil passed over. This had the peculiar peppermint, musty odor, characteristic of the 2.33-trimethylcyclopentanone from camphor. It was partly purified by distilling with steam, and an attempt was made to prepare the condensation-product[1] with benzaldehyde. The condensation took place easily, but a viscous oil was formed from which no crystals could be obtained. Unfortunately, none of the condensation-product from the preparation from camphor remained with which to start the crystallization. While the failure to secure the crystallized condensation-product is disappointing, it cannot be considered that it throws any doubt on the positive result obtained with the oxime.

The demonstration of the correctness of Perkins' older formula for camphoric acid and of Bouveault's formula for camphor, which has been furnished above, renders it possible to discuss, with some degree of certainty, the transformations which these bodies undergo. Only a few points will be taken up for consideration in the present paper.

Blanc has recently[2] expressed the opinion that camphanic acid is a β-lactone having the structure,



The formation of this acid from bromcamphoric anhydride appears to furnish a strong basis for this view. In the opinion of the writer, however, it appears more probable that the acid in question is a normal γ-lactone, and for the following reasons:

Neither of the β-hydroxy acids formulated below gives a lactone directly.

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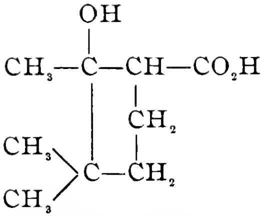
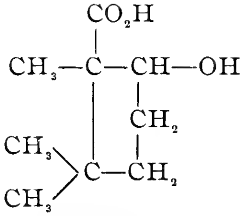
[1] This JOURNAL, **22**, 265.

[2] Bull. Soc. Chim., **19**, 353.



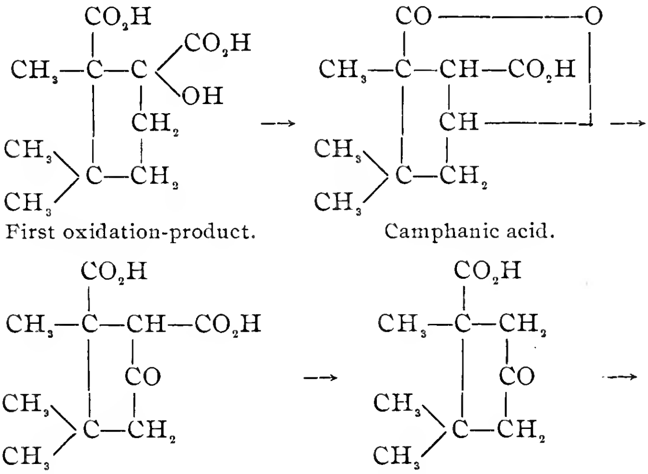
β-Hydroxydihydrocampholytic acid.[1]



β-Hydroxylauronic acid.[2]

Further, camphanic acid loses carbon dioxide and gives campholactone and lauronolic acid[3] on distillation. Campholactone is also formed on warming γ-lauronolic acid with dilute sulphuric acid.[4] γ-Lauronolic acid must be a $\beta\gamma$-unsaturated acid (see below) and the formation of a β-lactone from it is highly improbable.

The consideration of camphanic acid as a γ-lactone also furnishes a much more satisfactory explanation of the formation of camphoronic acid from camphoric and camphanic acids than if we consider it a β-lactone. The steps appear to be as follows: the transformation of the first oxidation-product to camphanic acid being accomplished by the elimination, addition, and a second elimination of water. Such transformations take place with peculiar ease in this series :



First oxidation-product. Camphanic acid.

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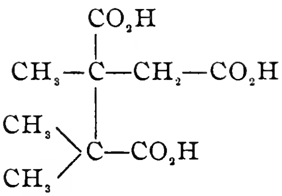
[1] This Journal, **17**, 424.

[2] *Ibid.*, **18**, 687.

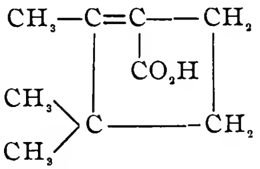
[3] Ann. Chem. (Liebig), **227**, 10.

[4] This Journal, **17**, 433.

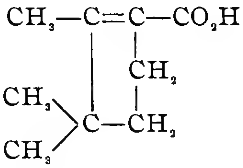


Camphoronic acid.

In a previous paper[1] the opinion has been expressed that the "cistrans"-campholytic acid and ciscampholytic acid are stereomeric. In the light of our present knowledge the two acids would be formulated thus:



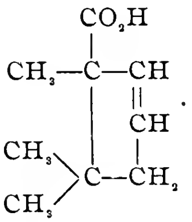
Cistranscampholytic acid.



Ciscampholytic acid.

While the formula for cistranscampholytic acid here given is not considered as established, it appears to be more in accordance with the facts now known than that given by Blanc,[2] who considers the acid to be a $\beta\gamma$-unsaturated acid.

Lauronolic and γ-lauronolic acids, apparently, have each the formula



Such an acid is optically active, and it is possible that γ-lauronolic acid is one of the optical isomers, and that lauronolic acid is the racemic form. It is my purpose to undertake, as soon as possible, a systematic study of these four acids with the hope of clearing up their relationships.

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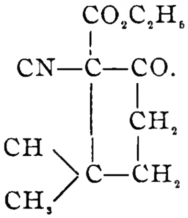
[1] This JOURNAL, 17, 423.

[2] Private communication.

It has been found that when the sodium derivative of the methyl ester of cyanacetic acid acts on the ethyl ester of γ-bromisocaproic acid the same dimethylcyancarboxethylcyclopentanone described in my last paper,[1] is formed. The melting-point of the product is the same, and the analysis gave 6.79 per cent of nitrogen. Calculated 6.70 per cent. The structure of the substance is, therefore,



It is hoped that the synthesis of camphoric acid, itself, may be effected with the aid of this compound.

TERRE HAUTE, Dec. 19, 1899.

Contributions from the Sheffield Laboratory of Yale University.

LXXIII.—ON THE REARRANGEMENT OF IMIDO-ESTERS.

[SECOND PAPER.]

BY HENRY L. WHEELER.

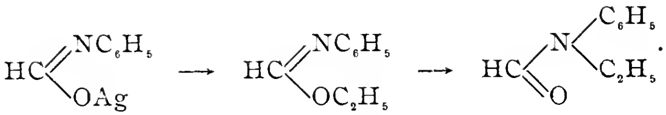
As described in our[2] first paper on this subject, we had occasion to prepare phenylformimidoethyl ester, and, instead of following the usual method[3] of treating silver formanilide with ethyl iodide at low temperatures, we heated the materials in a closed tube to 100°. We thereupon unexpectedly obtained a rearrangement of phenylformimidoethyl ester into the isomeric ethyl anilide :[4]

[1] This JOURNAL, **22**, 260.

[2] Wheeler and Johnson : This JOURNAL, **21**, 185.

[3] Comstock : This JOURNAL, **13**, 514.

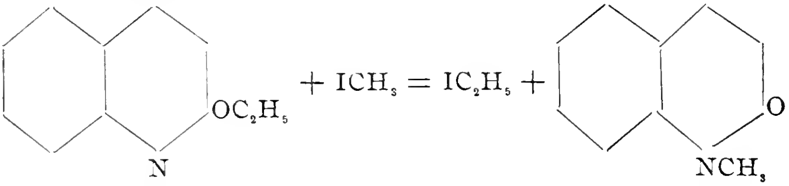
[4] The prediction of Freer and Sherman in regard to this salt is now completely fulfilled, *i. e.*, "With suitable alkyl or acyl halides and alteration of conditions, it will probably be possible to procure both oxy and nitrogen derivatives from the silver salt" (This JOURNAL, **18**, 571). In This JOURNAL, **18**, 381, Wheeler and Boltwood showed that this salt gives in fact benzoylformanilide, a nitrogen derivative, with benzoyl chloride.



$$\mathrm{HC}\begin{array}{l}{/\!\!/}\,\mathrm{NC_6H_5}\\ \backslash\,\mathrm{OAg}\end{array} \longrightarrow \mathrm{HC}\begin{array}{l}{/\!\!/}\,\mathrm{NC_6H_5}\\ \backslash\,\mathrm{OC_2H_5}\end{array} \longrightarrow \mathrm{HC}\begin{array}{l}/\,\mathrm{N}\begin{array}{l}/\,\mathrm{C_6H_5}\\ \backslash\,\mathrm{C_2H_5}\end{array}\\ \backslash\!\!\backslash\,\mathrm{O}\end{array}.$$

This was confirmed by the fact that benzimidoethyl ester gave ethylbenzamide when heated with ethyl iodide. We stated that we hoped to reserve the further examination of this rearrangement for this laboratory.

On the publication of these results Professor Knorr called our attention to his work along similar lines in the case of the cycloimido esters. He had previously shown that the oxygen esters of the α-quinolones[4] are converted by methyl iodide "langsam schon in der Kälte, rasch und vollständig in der Wärme, in die Stickstoff-Methylester." Thus, ethoxyquinoline is converted into methylquinolone :



He also found that the oxygen methyl and ethyl esters of oxy-γ-lepidine behaved in a similar manner. He showed that this reaction in the case of γ-methoxyquinaldine[2] takes place first by addition ; and that this intermediate product then when heated to 200° gives the nitrogen derivative. Again, along with E. Fertig,[3] he found that α-phenyl-γ-methoxyquinoline was converted directly into the isomeric derivative with methyl iodide, and finally he stated : "Ich hoffe bald weitere Mittheilung machen zu können, ob sich ganz allgemein die Imidoäther $R'N : CR''OR'''$ durch Jodmethyl in Amide secundärer Basen, $CH_3R'NCR''O$ überführen lassen."

In view, however, of the work already done in this laboratory, and, since I informed Professor Knorr of my desire to publish the work of my students, which was finished at the time our first publication appeared, Professor Knorr kindly gave over the entire field to me.

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[1] Ber. d. chem. Ges., **30**, 929.

[2] *Ibid.*, **30**, 924, 926.

[3] *Ibid.*, **30**, 937.

I wish to take advantage of this occasion to thank him for his kindness and also to refer to other work bearing on the rearrangement of the imido esters.

In the year 1885 Ponomarew[1] found that by treating silver cyanurate with alkyl iodides, at low temperatures, the oxygen esters result, while at higher temperatures the nitrogen esters are the chief products.

In 1886 Hofmann[2] showed that the oxygen methyl ester of cyanuric acid is transformed into the nitrogen ester simply by heating.

In 1891 Andreocci[3] found that when phenylpyrodiazolon or phenylmethylpyrodiazolon is methylated, and then treated with methyl iodide, similar results are obtained, and that the oxygen methyl compounds, when heated to 200°, are also transformed into the nitrogen compounds.

All the above are examples of the rearrangement of cycloimido esters. The transformation of benzimidochlorethyl ester into β-chlorethylbenzamide, under the influence of heat alone, as described by Gabriel and Neumann,[4] is especially interesting, and, outside of our work, this appears to be the only known example of a rearrangement taking place in the acyclic series.[5]

In the cycloimido ester series N-alkyl derivatives have frequently been obtained from silver salts, but particularly at higher temperatures. This has notably been the case in the uric acid group in Fischer's investigations.[6] Since, however, the silver salt of hydroxycaffeïn gives with ethyl iodide chiefly ethoxycaffeïn, he concludes that the former substance does not have the grouping —CO—NH, but —COH=N—. In this case he also noticed the formation of some tetramethyluric acid.

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[1] Ber. d. chem. Ges., **18**, 3271.

[2] *Ibid.*, **19**, 2061.

[3] *Ibid.*, **24**, R, 203.

[4] *Ibid.*, **25**, 2383.

[5] I wish to express my thanks to Professor Gabriel for calling my attention to this work. In a private communication from Dr. Stieglitz the following was mentioned : "I intended calling your attention to Knorr's paper in the Berichte, 1897, pp. 929–933. At the time when this came out I was heating ethyl imidobenzoate in a sealed tube at 100° with ethyl iodide, but did not go on with the action on account of Knorr's reservation."

[6] Ber. d. chem. Ges., **30**, 550.

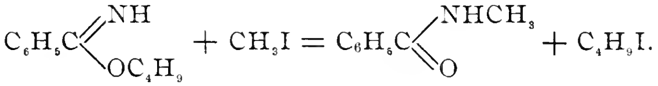
We find that the imidoesters of Pinner react slowly, even at ordinary temperatures with methyl and ethyl iodides giving alkyl amides. In the case of the benzimido esters benzamide and benzonitril invariably accompany the alkyl amide. In the lower-boiling portions of the reaction-product the presence, in small amount, of a substance that gave off an amine odor on distilling was also observed.

With isobutyl iodide the chief products were benzamide and isobutylene:

$$C_4H_9I = C_4H_8 + HI,$$

and $C_6H_5C(NH)OC_4H_9 + HI = C_6H_5CO.NH_2 + C_4H_9I.$

In general, however, the chief reaction of methyl and ethyl iodides is as follows:



$$C_6H_5C\left\langle\begin{matrix}NH\\OC_4H_9\end{matrix}\right. + CH_3I = C_6H_5C\left\langle\begin{matrix}NHCH_3\\O\end{matrix}\right. + C_4H_9I.$$

In the case of the action of ethyl iodide on benzimidoethyl ester, diethylbenzamide was sought for, but no evidence of its presence was observed.

Besides others there are, therefore, three principal reactions that take place when the acyclic imidoesters are treated with the lower alkyl iodides:

a. A transference of alkyl group from oxygen to nitrogen.

b. The formation of hydrogen iodide which with unaltered imidoester gives a primary amide (benzamide).

c. A decomposition of the imidoester into nitril and alcohol.

Experiments with Benzimidoesters.[1]

Benzimidomethylester and methyl iodide readily react at ordinary temperature. Thirty grams of the imidoester were allowed to stand for a month with 16 grams of methyl iodide (0.5 molecule); in a short time crystals separated, which finally developed into well-crystallized, flattened prisms. This material proved to be benzamide containing a small amount of cyanphenin and it weighed 3.5 grams. The oil filtered from this was distilled at 13-12 mm. pressure (*A* below).

For comparison, 20 grams of the ester were heated to about

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[1] The imidoesters in the following experiments were all freshly distilled. Under diminished pressure they boil unaltered without exception.

100° for five and a half hours with 1 gram of methyl iodide. On cooling, crystals separated but were not filtered off, the whole being distilled at 9–12 mm. pressure when the following fractions were obtained (*B*):

A.		Grams.	*B.*		Grams.
(1) below	159°	3.4	(1) below	155°	2.9
(2)	159°–169°	9.8	(2)	155°–165°	7.9
(3)	169°–174°	11.5	(3)	165°–168°	7.7

The first portions, in both cases, consisted chiefly of benzonitril.

The second portions did not solidify on standing or when cooled in a freezing-mixture. When distilled at 760 mm. pressure, 2–*B*, for example, began to boil at 276°, and a strong odor of amine and benzonitril was given off. The material had no constant boiling-point, but distilled steadily up to 291°, when the distillation was stopped and the residue (the greater portion) was cooled. It then solidified and, when crystallized from a small amount of alcohol, gave colorless flattened prisms melting at 82°. This material had all the properties of methylbenzamide (see below).

The third fractions in both cases readily solidified and were crystallized from water. 3-*A* gave square tables of methylbenzamide, while 3-*B*, from which benzamide was not removed by filtration, gave a mass of plates melting at 128°, *i. e.*, benzamide.[1]

The products identified in these reactions are, therefore, methylbenzamide, benzamide, benzonitril, and a trace of cyanphenin.

From the above it appears that the action of methyl iodide on benzimidomethyl ester is the same at 100° as at ordinary temperatures, and that a small amount of methyl iodide produces practically the same result in this reaction as a large amount.

[1] In describing benzimidomethyl ester (This JOURNAL, **17**, 398), the author stated that this ester, on standing, deposits benzamide. It is now known that this result was due to the presence of methyl iodide since the pure ester prepared by Pinner's method does not deposit benzamide on standing. Dains (J. Am. Chem. Soc., **21**, 166), in his work on the isoureas, quotes this supposed behavior in his comparisons. Benzimidomethyl ester, when pure, is quite stable.

Benzimidoethyl Ester and Ethyl Iodide.—In the previous paper the ester was heated with ethyl iodide, while the following is a description of the action at ordinary temperatures: 49 grams of the ester were mixed with 52 grams of ethyl iodide and allowed to stand for a month. At the end of this time 5.2 grams of beautifully crystallized cyanphenin separated. It melted sharply from 230°–231°. The filtrate from this was distilled at 773 mm. pressure, when 51.7 grams of crude ethyl iodide were recovered (below 185°). After the ethyl iodide was over, the material began to distil at 185° when, up to 278°, 2 grams of fishy-smelling oil were obtained, mostly benzonitril. From 278°–293° 10.8 grams of oil were collected, while from 293°–300° the remainder practically all came over. This weighed 23.5 grams, and when crystallized once from dilute alcohol it separated in small flattened prisms and melted from 69°–70°, this material being pure ethylbenzamide.

A search was made for diethylbenzamide in the portion boiling from 278°–293°, it having been found that this substance boils at 282°. For this purpose the fraction was cooled in a freezing-mixture, and considerable ethylbenzamide was then removed by filtering. The filtrate, when distilled at 763 mm. pressure, gave a few drops of fishy-smelling oil below 200°; then up to 290° no definite boiling-point was observed, the mercury in the thermometer not stopping an instant at the boiling-point of diethylbenzamide. From the lower-boiling portion of this fraction benzonitril was obtained; the higher consisted mostly of benzamide.

The chief products of this reaction are, therefore, ethylbenzamide, benzamide, benzonitril, and cyanphenin.

Diethylbenzamide was prepared from 5 grams of diethylamine by means of the Baumann-Schotten reaction. It was obtained as a clear, colorless oil that became thick, but did not solidify at —25°. It boiled from 282°–283° at 763 mm. pressure, and agreed in properties with the products obtained by Hallmann[1] and by Romburgh.[2] It is less soluble in warm water than in cold.

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[1] Ber. d. chem. Ges., **9**, 846.

[2] Recueil d. Travaux chim. d. Pays-Bas., **4**, 387.

An experiment to determine whether benzonitril, ethyl iodide, and ethyl alcohol react under the above conditions was performed as follows: 10.5 grams of benzonitril were mixed with alcohol and ethyl iodide in molecular proportions and the mixture heated from 100°–115° for nine hours. On opening the tube there was no pressure, and, on distilling at about 10 mm. pressure, the entire material boiled from 71°–72° (benzonitril), except a few drops of black tar which remained in the residue. No benzamide or ethylbenzamide was formed.

Benzimidoisobutyl Ester and Methyl Iodide.—Thirty grams of the ester were heated with a little over one molecular proportion of methyl iodide from 80°–115° for four hours. On cooling, an oil was obtained containing some crystals in suspension. They were filtered and consisted of cyanphenin and benzamide (separated by boiling water). The oil was distilled at 765 mm. pressure, when the portion boiling below 160° was collected. It weighed 24 grams, while the calculated yield of isobutyl iodide is 31 grams. On redistilling, it boiled mostly from 121°–121°.5, and proved to be pure isobutyl iodide.

The residue boiling above 160° was then distilled at 18–19 mm. pressure, when three fractions were obtained: (1) 98°–172° (benzonitril); (2) 172°–177°; (3) 177°–187°. The last portion readily solidified; the second deposited crystals on standing. On crystallizing the material from alcohol prisms were obtained melting at 82°. Romburgh gives 78° as the melting-point of methylbenzamide. That the material is methylbenzamide is shown by its properties and the following nitrogen determination:

	Calculated for C_8H_9NO.	Found.
N	10.37	10.40

The most striking property of the alkylbenzamides is the behavior of their saturated aqueous solutions. When these are warmed they become turbid in consequence of the separation of the amides in the form of oils. This turbidity disappears again on warming to boiling, and on again cooling, this behavior is reversed.

Benzimidoisobutyl Ester and Isobutyl Iodide.—Thirty grams of the former were heated from 165°–185° for several hours. On cooling and opening the tube considerable inflammable gas escaped. It was concluded from its odor that this was isobutylene. On distilling, 21 grams of isobutyl iodide were recovered. The remaining material was distilled at 13 mm. pressure, when benzonitril and benzamide were the chief products. The higher-boiling portion was crystallized from water, when it melted from 126°–127°, and a nitrogen determination gave :

	Calculated for $C_6H_5CO.NH_2$.	Found.
N	11.57	11.22

Isobutylbenzamide.—This was prepared from 6 grams of isobutylamine by the Baumann-Schotten method. The material thus prepared boiled from 173°–178° at 13 mm. pressure, and at 308°–313°, with slight decomposition, at 760 mm. pressure. The oil thus obtained solidified to a beautiful crystalline mass, which was crystallized from alcohol with the aid of a freezing-mixture. It then melted at from 57°–58°. A nitrogen determination gave :

	Calculated for $C_{11}H_{15}NO$.	Found.
N	7.91	8.19

Isobutylbenzamide forms chisel-shaped prisms and is difficultly soluble in water and petroleum ether, readily in ether, chloroform, and alcohol.

Benzimidoethyl ester and isobutyl iodide did not act smoothly. The products obtained were benzamide, benzonitril, cyanphenin, ethyl and isobutyl benzamides, and a substance, in too small amount for identification, which, after crystallization from alcohol separated in colorless, stout crystals, which melted at 192° with effervescence.

EXPERIMENTS WITH PHENYLACETIMIDOESTERS.

By Treat B. Johnson.

Phenylacetimidomethyl Ester and Methyl Iodide.—(1) Twenty grams of phenylacetimidomethyl ester were heated with 9.5 grams of methyl iodide (1 molecule of ester to 0.5 molecule of iodide) for an hour from 95°–105°. The product was then diluted with ether and the precipitated material filtered off. This proved to be phenylacetamide, and weighed 2.2 grams. The ether solution was evaporated and the oil distilled at 25–28 mm. pressure. The first fraction was collected from 115°–to 187°. This weighed 4.2 grams and consisted mostly of phenylacetonitril. The second fraction was collected from 187°–197°. This weighed 6 grams and was crude methylphenylacetamide containing phenylacetamide. On crystallizing it from benzene and ligroin it melted at 147°, and on recrystallizing it from water it melted from 154°–155° (the melting-point of phenylacetamide). If, however, the higher-boiling fractions are crystallized from alcohol by means of a freezing-mixture methylphenylacetamide is obtained.

(2) For comparison, 20 grams of phenylacetimidomethyl ester were again heated, this time with only 0.6 gram of methyl iodide for six hours to the same temperature as before. The residue left by ether (phenylacetamide) weighed 2.7 grams. On distilling the remainder at 27 mm. pressure the first fraction, boiling between 110°–187°, weighed 4.8 grams; the second fraction, 187°–197°, weighed 5.5 grams.

(3) In another experiment 30 grams of the ester were heated with 14.2 grams of methyl iodide, for six hours, from 100°–110°. In this case the phenylacetamide weighed 3.6 grams. The first fraction of the oil distilled at about 20 mm. pressure, boiled at from 110°–180° (mostly 110°–130°), and weighed 8.4 grams; the second fraction (184°–190° at 18 mm. pressure) weighed 10.5 grams. This latter was combined with the second fraction obtained in our second experiment and redistilled at 19 mm. pressure, when the greater portion boiled from 179°–184°, leaving little or no residue. This distillate readily solidified and, when crystallized from alcohol, finally melted from 54°–57° (the melting-point of methylphenylacetamide is given by Taverne[1] as 58°).

A nitrogen determination in this material gave:

	Calculated for $C_6H_5CH_2CONHCH_3$.	Found.
N	9.39	9.14

The substance formed in chief amount in these reactions is, therefore, methylphenylacetamide.

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[1] Recueil d. Travaux chim. d. Pays-Bas., **16**, 35.

In order to simplify the comparison, the above results are given in the following table:

	Grams of ester taken.	Weight of iodide.	Time.	Weight of phenylacetamide. (*b*)	Weight of first fractions. Crude nitril. (*c*)	Weight of second fractions. Crude methyl amide. (*a*)
(1)	20	9.5	1 hr.	2.2	4.2	6.0
(2)	20	0.6	6 hrs.	2.7	4.8	5.5
(3)	30	14.2	6 hrs.	3.6	8.4	10.5

From this it is evident that, in this rearrangement the same result is obtained whether a little (0.6 gram) or a large amount (9.5 grams) of alkyl iodide is used. The close agreement of experiments (1) and (2) under widely different conditions suggest that there is some definite relation between the three principal reactions mentioned in the introduction. The columns (*a*, *b*, *c*) show roughly to what extent these three reactions take place. In estimating this, however, it must be remembered that the total weight of phenylacetamide is low according to column (*b*); that the weight of nitril includes some phenyl- and some methylphenylacetamide; and that column (*a*) represents a mixture of the latter two substances.

Phenylacetimidoethyl Ester and Ethyl Iodide.—Twenty grams of the ester were heated from 100°–106° with 19.1 grams of iodide for six hours. On cooling, the tube contained a thick, red oil, together with some plates. The contents of the tube were extracted with ether, and the insoluble residue, after being crystallized from water, melted from 153°–154°; this was pure phenylacetamide. The ether was then evaporated and the remaining oil was distilled at 13 mm. pressure. The first fraction, collected below 178°, proved to be chiefly phenylacetonitril. The second fraction, collected from 188°–198° at 17 mm. pressure, was obtained as a thick oil which soon solidified in a freezing-mixture. This, when crystallized twice from water, separated in the form of colorless plates melting from 73°–74°. A nitrogen determination shows that this material is ethylphenylacetamide:

	Calculated for $C_6H_5CH_2CONHC_2H_5$.	Found.
N	8.58	8.45

In this rearrangement, in certain cases, some high-boiling material was formed, but this decomposition-product was not examined.

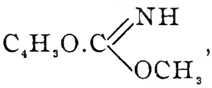
(2) 34.8 grams of phenylacetimidoethyl ester were heated with 33.3 grams of ethyl iodide (1 molecule of ester to 1 molecule of iodide) for six hours from 95°–106°. The amount of phenylacetamide then obtained, on proceeding as above, weighed 2.5 grams, and the amount of crude ethylphenylacetamide weighed 10.9 grams, the remainder being phenylacetonitril and some high-boiling residue.

(3) In another experiment 20 grams of the ester were heated to 100°–110° for six hours with 19.1 grams of ethyl iodide, when the amount of amide isolated weighed 1.3 grams, and the amount of crude ethylamide weighed 5.2 grams.

In all of the above experiments the first fractions were tested for unaltered imidoester by mixing a portion with benzene, and passing in dry hydrogen chloride, when no precipitate was produced; hence in each case the imidoester had entered into reaction completely.

EXPERIMENTS WITH FURIMIDOMETHYL ESTER, *p*-TOLENYLIMIDOMETHYL ESTER, AND *β*-NAPHTHYLIMIDOETHYL ESTER.

By Munson D. Atwater.



Furimidomethyl ester, $C_4H_3O.C\begin{cases}=NH\\ -OCH_3\end{cases}$, was easily obtained from furyl cyanide by following the directions of Pinner[1] for the preparation of the corresponding ethyl ester. It was obtained as a clear, colorless oil of peculiar odor. When distilled at 8 mm. pressure it boiled from 52°-57°. Redistilled at 762 mm. pressure it boiled from 169°–172°; and a nitrogen determination gave the following result:

	Calculated for $C_6H_7NO_2$.	Found.
N	11.2	11.4

Furimidomethyl Ester and Methyl Iodide.—(1) Nineteen grams of the ester were heated for six hours at 100° with a little over 10 grams of methyl iodide. The product, a light-yellow oil,

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[1] Die Imidoäther, p. 50.

was distilled at 21 mm. pressure, when 12 grams of material, boiling from 137°–147°, was obtained. This was redistilled at ordinary pressure and collected between 250°–253°. This portion, on standing several days in a desiccator, deposited a considerable crop of colorless, stout crystals, which, when crystallized from ligroin, melted at 64°. A nitrogen determination gave :

	Calculated for $C_6H_7NO_2$.	Found.
N	11.2	11.4

This material is, therefore, methylpyromucamide. The corresponding ethylpyromucamide was found by Wallach[1] to be an oil boiling at 258°.

(2) In another experiment 30 grams of the imidoester were mixed with 17 grams of methyl iodide and allowed to stand nineteen days. At the end of this time 1 gram of pyromucamide had separated, melting at 140°. The oil filtered from this was distilled at 20 mm. pressure. The oil collected below 143° had the odor of the unaltered material, while the remaining portion, between 143°–148°, solidified and proved to be a mixture of pyromucamide and methylpyromucamide.

The behavior of this ester with methyl iodide is therefore closely similar to that of the preceding.

p-Tolenylimidomethyl Ester.—This ester was prepared from *p*-tolunitril by Pinner's directions. It was obtained as a clear, colorless oil, with an odor entirely different from that of the nitril. It boiled at 105°.5 at 10.5 mm. pressure. A nitrogen determination gave :

	Calculated for $C_9H_{11}NO$.	Found.
N	9.39	9.48

p-Tolenylimidomethyl Ester and Methyl Iodide.—Twenty grams of the ester were heated to 100° for four hours. A little pressure was found on opening the tube, which was filled with a yellow crystalline mass of material. On crystallizing twice from water(?) this melted from 144°–145° (the melting-point of *p*-toluic methylamide is given by Gattermann and Schmidt[2] as 143°). A nitrogen determination gave :

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[1] Ann. Chem. (Liebig), **214**, 229.

[2] *Ibid.*, **244**, 51.

	Calculated for $C_9H_{11}NO$.	Found.
N	9.39	9.36

p-Tolenylimidomethyl Ester and Methyl Alcohol.—Fifteen grams of the ester were heated with one molecular proportion of methyl alcohol for six hours at from 100°–110°. As there appeared to be no reaction, the mixture was heated at from 100°–140° for six hours more, and finally at from 150°–175° for some time. The material then had the odor of nitril, and it was distilled at 13 mm. pressure, when, after the alcohol escaped, it all boiled from 95°–97° (the boiling-point of *p*-tolunitril), except a very slight residue. This, crystallized from water, melted at 159°, and was therefore *p*-toluic amide. Under these conditions no rearrangement took place.

β-Naphthylimidoethyl Ester and Ethyl Iodide.—The ester was prepared from *β*-naphthonitril, Pinner's directions being followed. It was found that it could be distilled under diminished pressure, but the record of its boiling-point is not at present available to the writer. That it did not suffer decomposition in this treatment is shown by the following nitrogen determination:

	Calculated for $C_{13}H_{13}NO$.	Found.
N	7.0	7.4

The material thus prepared is a clear, colorless oil, and quite stable. Twenty-four grams of this ester were heated with 9.4 grams of ethyl iodide for six hours at 100°. On cooling, the tube was found to contain a solid mass of yellow material. It was treated with alcohol, which left behind a small amount of white crystals which melted above 280°. The soluble part, when crystallized from alcohol, melted constantly at 129°–131°, and is undoubtedly ethyl-*β*-naphthamide, but a nitrogen determination gave 8.1 per cent of nitrogen. (Calculated for amide 8.2 per cent, for ethyl amide 7.0 per cent.) The lack of sufficient pure material prevented a duplicate analysis.

EXPERIMENTS WITH SILVER SUCCINIMIDE AND BENZOYLBENZIMIDOETHYL ESTER.

By Bayard Barnes.

Silver Succinimide and Methyl Iodide.—It was shown by Comstock and Wheeler[1] that if perfectly dry silver succinimide is treated with alkyl iodides at ordinary temperatures, and especial care is taken to avoid moisture, oxygen esters can be isolated. The formation of a small amount of the nitrogen ester under these conditions was also observed, and it was remarked that "If the nitrogen ether is formed by molecular rearrangement from the oxygen ether that rearrangement must take place in this case at ordinary temperature." This we now know to be the case, since this rearrangement is the chief reaction at high temperatures. For example: 27 grams of the silver salt were heated with 22.8 grams of methyl iodide for six hours at 100°. The material was then extracted with ether and distilled at 20 mm. pressure, when it boiled from 140°–155°. This readily solidified and, on crystallizing from alcohol, it melted from 68°–70°. A nitrogen determination gave:

	Calculated for $C_5H_7NO_2$.	Found.
N	12.38	12.45

The material is therefore *N*-methylsuccinimide. On extracting the silver residue with alcohol, and crystallizing the extract from benzene, succinimide was obtained.

Silver Succinimide and Ethyl Iodide.—(1) Twenty-four grams of the silver salt and 22.5 grams of ethyl iodide were heated for twelve hours at 100°. As unaltered silver salt still remained, 13.8 grams more iodide were added, and the whole reheated six hours longer. The material was then extracted with benzene and distilled at 20 mm. pressure. The first fraction was collected between 122°–132°; the second from 132°–142°; while above 142° the material solidified in the delivery tube.

The first portion was a pale-yellow oil at ordinary temperature, but it solidified on cooling, and, on freezing out of ether,

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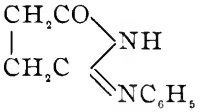
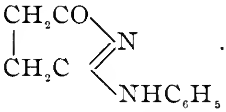
[1] This Journal, 13, ~~519.~~ 520

it was obtained in colorless crystals melting at 26° (the melting-point of *N*-ethylsuccinimide). The second fraction was mixed with a little aniline, and the presence of the oxygen ethyl ester established by the formation of crystals, which, after purification by dissolving in hydrochloric acid and precipitating with ammonia, melted at 216°, this substance being the "base" described by Comstock and Wheeler, which perhaps may be called α-ketopyrrolidine-α-phenylimide or α-anilidopyrrolon according to whether it has the structure :



or



The third fraction or residue was found to consist of succinimide.

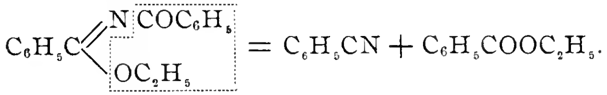
(2) In another experiment 30 grams of the silver salt were heated with 45 grams of ethyl iodide for ten hours at from 150°–155°. The material was then extracted with dry chloroform and the extract distilled at about 20 mm. (?) pressure. The portion boiling below 134° was redistilled at ordinary pressure, when it nearly all came over at from 233°–235° (*N*-ethylsuccinimide boils from 234°–235°). A nitrogen determination in this material gave :

	Calculated for $C_6H_9NO_2$.	Found.
N	11.02	10.70

It follows from the above that the oxygen ethers of succinimide undergo rearrangement at high temperatures with methyl and ethyl iodides giving the isomeric nitrogen compounds.

Benzoylbenzimido Ester and Ethyl Iodide.—As an example of the behavior of the acylimido esters with ethyl iodide, we describe the following experiment. We were unable to discover any evidence of a rearrangement taking place in this case. This is probably due to the negative character of the acyl ester rather than to a stereochemical interference depending on the molecular magnitude of the =NR grouping. This subject will be investigated later.

Twenty grams of benzoylbenzimidoethyl ester and 6 grams of ethyl iodide were heated for eight hours at from 110°–120°, when the material was found to be unaltered. It was reheated for seven hours at from 120°–150° with the same result. Finally, when heated to 200° for six hours, it decomposed. On opening the tube there was considerable pressure and a strong odor of benzonitril. The material was shaken with sodium carbonate and extracted with ether. The solution of sodium carbonate extracted benzoic acid, and the ether took up benzonitril and ethyl benzoate. The amount of benzonitril obtained weighed 5.6 grams, while the calculated yield of benzonitril for the following decomposition is 8 grams:



$$C_6H_5C\left\langle\begin{matrix}N\,\boxed{COC_6H_5}\\ \boxed{OC_2H_5}\end{matrix}\right. = C_6H_5CN + C_6H_5COOC_2H_5.$$

It is our intention to continue the study of these rearrangements in other series.

NEW HAVEN, CONN., June 27, 1899.

THE DOUBLE HALIDES OF ANTIMONY WITH ANILINE AND THE TOLUIDINES.

BY HOWARD H. HIGBEE.[1]

This investigation, like others in the series, was undertaken for the purpose of testing the truth of the laws governing the composition of double halides first pointed out by Professor Remsen.[2]

The method of preparing the salts was to bring the halide of the base together with the corresponding halide of antimony, each constituent being previously dissolved in the corresponding halogen acid.

The results were found to be most satisfactory when each solution was heated before mixing; the base was then added to the metallic chloride.

[1] From the author's dissertation submitted to the Board of University Studies of the Johns Hopkins University, June, 1896, for the degree of Doctor of Philosophy. The investigation was undertaken at the suggestion of Professor Remsen and was carried on under his guidance.

[2] This JOURNAL, **11**, 291; and **14**, 87.

The plan adopted in making the mixtures was to add the halide of the metal in gradually increasing molecular proportions to 1 molecule of the halide of the base.

Since in no case the analyses of any of the mixtures indicated that more than 1 molecule of the halide of the metal had combined with 1 molecule of the halide of the base, mixtures were not made containing more than 3 molecules of the halide of the metal to one molecule of the halide of the base.

Similar trials were then made in the other direction, *i. e.*, 1 molecule of the metallic halide was mixed with a gradually increasing number of molecules of the halide of the organic base in the ratios of 1 : 2, 1 : 3, 1 : 4, and 1 : 6, respectively. The limit of double salt formation in this direction was considered reached, since in many cases the halide of the base crystallized out even in mixtures of 1 : 3, and in no case was a salt found which contained more than 4 molecules of the halide of the base to one of the antimony.

Every mixture made produced a double salt of some kind. When the solutions were of a proper consistency the formation of the crystals was of a uniform character, and they were easily obtained, as a rule, in that condition. The compounds formed differed markedly in their powers of crystallization, but as the formation of crystals with well-defined angles and faces would require days and often weeks, no special attempt was made to gather and study the substances crystallographically. Such investigation was further interfered with by the fact that many of the substances rapidly underwent changes which rendered them unfit for that kind of study.

A few notes, however, of a crystallographic character, kindly furnished by Mr. A. C. Spencer, of the Geological Department of this University, will give an idea of the nature of some of the substances in this respect.

As a rule, if the first crop of crystals was found to be uniform in appearance, they was subjected to chemical analysis, the determination of the halogen and the antimony being considered sufficient for the identification of the substance.

The results of the analyses of the compound formed from each mixture are placed in a table at the end of the description of these compounds.

Under each mixture is placed the results of the analysis of the compound obtained from that mixture, and in the smaller table is found the summary of the results of the analyses grouped under the formula of those compounds which the analyses seem to indicate have been formed.

The estimation of antimony was effected as follows: About 0.3 gram of the dried salt was weighed off, and after dissolving in a few cc. of a strong solution of tartaric acid, the whole was considerably diluted with water and heated to boiling. The solution was then acidified with sulphuric acid and a current of washed hydrogen sulphide passed into the solution for some time. When the antimony had been completely precipitated the liquid was heated for some time to drive off the hydrogen sulphide. The precipitate was then collected in a porcelain Gooch filter and washed successively with water, alcohol, ether, and carbon disulphide. The crucible was then dried in a hot-air bath, filled with carbon dioxide, gradually heated to 250°, and kept at that temperature for about an hour.

Experiments with Aniline Hydrochloride and Antimony Trichloride.

The account of the experiments with aniline hydrochloride and antimony trichloride will now be taken up in detail.

From mixture No. 1 (one part of the base to one of the metallic chloride), there crystallized out a colorless salt in thick irregular prisms, which on analysis gave results for chlorine and antimony, as recorded in Column 1 of Table I.

On comparing these results with the theoretical values which ought to be obtained if a compound called for by the one at the head of Column 1 had been formed, no agreement between these values was found, but as these experimental results did compare with the theoretical percentages of the compound heading Column 5, it was concluded that a compound was formed, having the composition expressed by the formula $(C_6H_5.NH_2.HCl)_3.SbCl_3.H_2O$, which may be called trianiline chlorantimonite.

Properties of the Compound.

This substance crystallizes in thick, colorless, monoclinic prisms, having the appearance shown in Fig. 1.

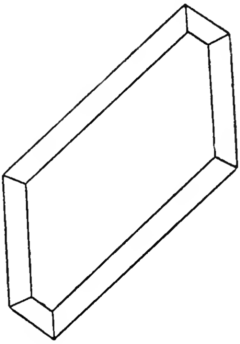


Fig. 1.

The action of a number of solvents was tried, and it was found to dissolve quite readily even in all the dilute mineral acids as well as in a number of organic acids in concentrated form; *e.g.*, tartaric and acetic acids. It required rather strong ethyl and methyl alcohol to effect solution.

Water or dilute alcohol precipitated a white antimonyl compound.

On boiling a solution of the salt the odor of nitrophenol was given off.

On gently heating the dry substance in an open tube it was rapidly decomposed, hydrochloric acid being given off.

After exposure to the air for several days the substance acquired an opaque greenish appearance. On keeping specimens for several months no further change in appearance seemed to occur.

The results of an analysis of mixture No. 2, in which the constituents were combined in the proportion of 1 molecule of aniline hydrochloride to 2 molecules of antimony trichloride, pointed to a compound of the formula

$$C_6H_5.NH_2.HCl.SbCl_3.H_2O.$$

Monaniline chlorantimonite crystallized out in long, thin, colorless plates. In general it was found to be similar to the first salt described.

Analyses of mixture No. 3 showed that monaniline chlorantimonite was again formed.

Mixtures 4, 5, and 7, each in turn, produced one and the same compound; *viz.*, trianiline chlorantimonite, the one first described above.

The results recorded include the analyses of both first and second crops, but in no case were the second crops found different from the first.

Table I.—Salts of Aniline Hydrochloride and Antimony Trichloride.

	I.		II.		III.		IV.		V.	
	$C_6H_5.NH_2.HCl.SbCl_3$.	$C_6H_5.NH_2.HCl.SbCl_3.H_2O$.	$C_6H_5.NH_2.HCl(SbCl_3)_2$.	$C_6H_5.NH_2.HCl(SbCl_3)_2.H_2O$.	$C_6H_5.NH_2.HCl(SbCl_3)_3$.	$C_6H_5.NH_2.HCl(SbCl_3)_3.H_2O$.	$(C_6H_5.NH_2.HCl)_2SbCl_3$.	$(C_6H_5.NH_2.HCl)_2SbCl_3.H_2O$.	$(C_6H_5.NH_2.HCl)_3.SbCl_3$.	$(C_6H_5.NH_2.HCl)_3SbCl_3.H_2O$.
Theor.										
Sb	33.70	32.08	41.20	39.96	44.49	4.53	24.70	23.83	19.51	18.95
Cl	39.88	37.97	42.66	41.38	43.88	42.92	36.56	35.25	34.63	33.65
Exp.										
Sb	19.18	...	....	....	32.71	....	19.01	....	....	19.05
Cl	....	33.31	....	....	37.54	....	....	....	....	33.54
Sb	19.93	19.74	34.11	34.65	32.62	32.66	19.50	19.28	....	19.18
Cl	....	33.69	37.36	37.47	38.08	38.13	33.63	33.77	....	33.50
Sb	....	...	33.90	....	....	....	....	....	....	19.10
Cl	....	....	37.46	....	....	....	....	....	....	33.24
Sb	....	....	....	....	....	....	....	....	....	19.08
Cl	....	....	....	....	....	....	....	....	....	33.29

Summary of Aniline Hydrochloride and Antimony Trichloride Salts.

	I.		V.	
	$[C_6H_5.NH_2.HCl.SbCl_3.H_2O.]$		$[(C_6H_5.NH_2.HCl)_3SbCl_3.H_2O.]$	
	Sb.	Cl.	Sb.	Cl.
Theor.	32.08	37.97	18.95	33.65
Exp.	32.71	38.08	19.05	33.54
	32.62	38.13	19.18	33.50
	32.66	37.54	19.10	33.24
	33.51	37.36	19.08	33.29
	33.90	37.47	19.01	33.63
	....	37.38	19.50	33.77
	....	37.46	19.28	33.31
	....	....	19.18	33.23
	....	....	19.74	33.69
	....	....	19.93	33.33
	....	....	18.88	....

Experiments with o-Toluidine Hydrochloride and Antimony Trichloride.

Experiments were next undertaken in the *o*-toluidine series, the line of work being carried out in a manner similar to that followed in the experiments with aniline.

The analyses of the compounds resulting from the several mixtures in this series point to the existence of only one compound, *viz.*, di-*o*-toluidine chlorantimonite, having the composition expressed by the formula $(C_6H_4.CH_3.NH_2.HCl)_2.SbCl_3$.

A large quantity of colorless crystals separated out from mixture No. 5, which, when dissolved and treated with hydrogen sulphide, gave no reaction for antimony.

The substance was the halide of the base. On pouring off the mother-liquor from these crystals, a compound of a different form at once separated out, which proved to be the double salt above mentioned. This substance, as usually formed, did not differ much in appearance from the aniline salts already described.

When allowed to form rapidly the tendency of both the aniline and all the toluidine chlorantimony salts is to crystallize out in beautiful sheaf-like masses with a satin luster.

The analytical results of the study of this series are placed in Table II :

Table II.—Salts of o-Toluidine Hydrochloride and Antimony Trichloride.

	I.		II.		III.		IV.		V.		VI.
	$C_6H_4.CH_3.NH_2.HCl.SbCl_3.$	$C_6H_4.CH_3.NH_2.HCl.SbCl_3.H_2O.$	$C_6H_4.CH_3.NH_2.HCl(SbCl_3)_2.$	$C_6H_4.CH_3.NH_2.HCl(SbCl_3)_2.H_2O.$	$C_6H_4.CH_3.NH_2.HCl(SbCl_3)_3.$	$C_6H_4.CH_3.NH_2.HCl(SbCl_3)_3.H_2O.$	$(C_6H_4.CH_3.NH_2.HCl)_2SbCl_3.$	$(C_6H_4.CH_3.NH_2.HCl)_2SbCl_3.H_2O.$	$(C_6H_4.CH_3.NH_2.HCl)_3SbCl_3.$	$(C_6H_4.CH_3.NH_2.HCl)_3.SbCl_3.H_2O.$	$(C_6H_4.CH_3.NH_2.HCl)_6.SbCl_3.$
Theor.											
Sb	32.43	..	40.23	..	....	..	23.36	22.57	18.26	..	....
Cl	38.38	..	....	..	....	..	34.56	33.39	32.42	..	....
Exp.											
Sb	23.96	..	25.03	..	25.60	..	23.65	....	24.06	..	....
Cl	34.48	..	34.83	..	34.97	..	34.24	....	34.40	..	25.6
Sb	23.92	..	24.99	..	25.23	..	23.73	....	24.14	..	....
Cl	34.52	..	34.84	..	34.85	..	34.41	....	34.87	..	....

Summary of o-Toluidine and Antimony Trichloride Salts.

IV.

$(C_6H_4.CH_3NH_2.HCl)_2SbCl_3.)$

	Sb.		Cl.	
Theor.	23.36		34.56	
Exp.	23.65	23.96	34.24	34.87
	23.73	23.92	34.41	34.83
	....	....	34.48	34.84
	....	....	34.52	34.97
	....	....	34.40	34.85

Experiments with m-Toluidine Hydrochloride and Antimony Trichloride.

As in the case of experiments with *o*-toluidine, the hydrochloride of the *m*-base was mixed in various proportions with the chloride of antimony. On an examination of the compounds obtained from each of the seven mixtures made, only two substances were found which proved to be different from each other. Each of the seven mixtures, except the third, gave a compound having the formula

$$(C_6H_4.CH_3.NH_2HCl)_3.SbCl_3,$$

which should be named tri-*m*-toluidine chlorantimonite.

This substance always crystallized in thin orthorhombic tablets in the form of radiating groups, and perfectly transparent and colorless.

Following is a brief crystallographic account of one of the crystals examined :

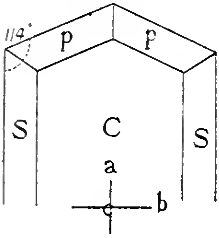


Fig. 2.

Orthorhombic.

C = basal plane.
p = brachypinacoids.
S = macrodomes.
C = $\mathfrak{C}$.

Mixture No. 3 gave a compound which on analysis pointed to a substance whose composition should be expressed by the formula

$$(C_6H_4.CH_3.NH_2.HCl)_2.SbCl_3.H_2O,$$

di-*m*-toluidine chlorantimonite.

An analysis of one sample of the substance pointed to the previous substance without water of crystallization. The only form in which this compound was obtained was in fine granular crystals.

The results of experiments with *m*-toluidine compounds are recorded in Table III.

Table III.—Salts of m-Toluidine Hydrochloride and Antimony Trichloride.

	I.		II.		III.			IV.		V.		VI.	VII.
	$C_6H_4.CH_3.NH_2.HCl.SbCl_3$.	$C_6H_4.CH_3.NH_2.HCl.SbCl_3.H_2O$.	$C_6H_4.CH_3.NH_2.HCl(SbCl_3)_2$.	$C_6H_4.CH_3.NH_2HCl(SbCl_3)_2.H_2O$.	$C_6H_4.CH_3.NH_2.HCl(SbCl_3)_3$.	$C_6H_4.CH_3.NH_2.HCl(SbCl_3)_3.H_2O$.		$(C_6H_4.CH_3.NH_2.HCl)_2SbCl_3$.	$(C_6H_4.CH_3.NH_2.HCl)_2SbCl_3.H_2O$.	$(C_6H_4.CH_3.NH_2.HCl)_3.SbCl_3$.	$(C_6H_4.CH_3.NH_2.HCl)_3SbCl_3.H_2O$.	$(C_6H_4.CH_3.NH_2.HCl)_4SbCl_3$.	$(C_6H_4.CH_3.NH_2.HCl)_6SbCl_3$.
Theor.													
Sb	32.43	..	40.23	..	....	....	....	23.36	22.57	18.26	..	....	....
Cl	38.38	..	....	..	....	....	....	34.56	33.39	32.42	..	....	....
Exp.													
Sb	19.87	..	18.69	..	20.65	23.11	22.56	....	18.76	18.82	..	18.65	17.97
Cl	32.51	..	32.58	..	33.19	34.08	33.14	....	32.35	32.25	..	32.65	31.97
Sb	19.73	..	18.66	..	20.71	....	22.51	....	18.78	18.79	..	18.61	....
Cl	32.41	..	32.43	..	33.28	....	33.43	....	22.19	32.69	..	32.29	....

Summary of m-Toluidine Hydrochloride and Antimony Trichloride Salts.

	V.				VI.	
	$[(C_6H_4.CH_3.NH_2.HCl)_3SbCl_3.]$				$[(C_6H_4.CH_3.NH_2.HCl)_2SbCl_3.H_2O.]$	
	Sb.		Cl.		Sb.	Cl.
Theor.	18.61		32.42		22.57	33.39
Exp.	18.61	18.78	32.29	32.41	22.56	33.14
	18.65	18.69	32.35	32.58	22.51	33.43
	18.82	18.66	32.25	32.43	23.11	34.08
	18.79	17.97	32.69	32.51	....	33.19
	18.76	19.03	32.35	31.97	....	33.28
	....	....	32.19	32.31	....	....

Experiments with p-Toluidine Hydrochloride and Antimony Trichloride.

The compounds obtained in this group are di-*p*-toluidine chlorantimonite, $(C_6H_4.CH_3.NH_2.HCl)_2SbCl_3.\frac{1}{2}H_2O$, and tri-*p*-toluidine chlorantimonite, $(C_6H_4.CH_3.NH_2.HCl)_3SbCl_3.H_2O$.

Mixtures 1, 2, 3, and 4 produced the second of the above compounds, while the first was formed only by mixture 5. The tri-compound forms in colorless granular crystals, while the di-compound is formed in long, colorless, silky needles. Neither of these compounds seems to undergo any change on being kept for months.

The analytical results are recorded in the following table and summary :

Table IV.—Salts of p-Toluidine Hydrochloride and Antimony Trichloride.

	I.		II.		III.		IV.		V.	
	$C_6H_4.CH_3.NH_2.HCl.SbCl_3$.	$C_6H_4.CH_3.NH_2.HCl.SbCl_3.H_2O$.	$C_6H_4.CH_3.NH_2.HCl(SbCl_3)_2$.	$C_6H_4.CH_3.NH_2.HCl(SbCl_3)_2.H_2O$.	$C_6H_4.CH_3.NH_2.HCl(SbCl_3)_3$.	$C_6H_4.CH_3.NH_2.HCl(SbCl_3)_3.H_2O$.	$(C_6H_4.CH_3.NH_2.HCl)_2.SbCl_3$.	$(C_6H_4.CH_3.NH_2.HCl)_2.SbCl_3.\frac{1}{2}H_2O$.	$(C_6H_4.CH_3.NH_2.HCl)_3.SbCl_3$.	$(C_6H_4.CH_3.NH_2.HCl)_3.SbCl_3.H_2O$.
Theor.										
Sb	32.43	..	40.23	..	....	..	23.36	22.97	18.26	17.77
Cl	38.38	..	....	..	....	..	34.56	33.95	32.42	31.55
Exp.										
Sb	23.68	..	23.40	..	23.68	..	....	22.09	18.27	....
Cl	33.52	..	33.66	..	33.16	..	....	33.13	31.54	....
Sb	23.58	..	23.50	..	24.03	..	....	22.61	18.21	....
Cl	33.49	..	33.38	..	33.08	..	....	33.10	28.14	....
Sb	....	..	....	..	....	..	....	....	18.27	....
Cl	33.10	..	....	..	....	..	....	....	31.46	....
Sb	....	..	....	..	....	..	....	....	18.11	....
Cl	....	..	....	..	....	..	....	....	31.55	....

Summary of p-Toluidine Hydrochloride and Antimony Trichloride Salts.

	IV. $(C_6H_4.CH_3.NH_2.HCl)_2.SbCl_3.\frac{1}{2}H_2O$.				V. $(C_6H_4.CH_3.NH_2.HCl)_3.SbCl.H_2O$.			
	Sb.		Cl.		Sb.		Cl.	
Theor.	22.97		33.95		17.77		31.55	
Exp.	23.68	23.50	33.52	33.66	18.27	18.27	31.54	31.55
	23.58	23.68	33.49	33.38	18.21	18.11	....	31.46
	23.40	24.03	....	....	....	....	....	....

Experiments with Aniline Hydrobromide and Antimony Tribromide.

The following series of mixtures of the above substances were made in hydrobromic acid solution: 1 : 1, 1 : 2, 1 : 3, 2 : 1, 3 : 1, 4 : 1, and 6 : 1.

In beaker No. 1 there was formed a copious crop of fine, light-yellow needles. In No. 2 there was a scant crop of two kinds of crystals, one kind being thin, flat, rectangular plates; the other yellow, granular crystals. Mixture 3 gave yellow needles, similar in appearance to those in No 1. In beaker 4 was formed a small crop of yellow needles along with larger yellow, granular crystals. A copious crop of light-yellow, scaly crystals was found in beaker 5. In No. 6 appeared a copious crop of yellow, granular crystals. A copious crop of irregular, flat, thick, whitish-yellow plates formed in beaker 7.

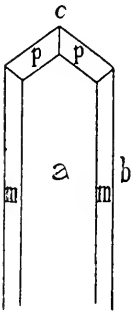


Fig. 3.

As in each case, the crystals had formed too quickly to be well defined and uniform, all the crops were redissolved, the solutions somewhat diluted, and again set aside to crystallize out.

The next series of crystals were generally of better form. Salts from beakers 1, 2, 3, 4, and 5 crystallized out in centimeter-long, canary-yellow, lath-shaped crystals of the orthorhombic system and of the form shown in the accompanying figure.

The cleavage is parallel to *a*. The crystals also showed parallel extinction in polarized light.

A chemical analysis of each of these five crops resulted in pointing to only one chemical compound, which is represented by the formula $(C_6H_5.NH_2.HBr)_2SbBr_3$, and receives the name dianiline bromantimonite.

It is of a canary-yellow color and translucent, stable in the air, undergoing no perceptible change on being kept for several months. The analyses showing its composition are given in the following table :

Mixtures 6 and 7 produced substances, which though of the same yellow color, differed markedly in their crystal habit. This will be best indicated by the figure. Cleavage is parallel to *a* and perfect. Habit tabular and perpendicular to *a*. Orthorhombic system.

a = brachypinacoid.
c = basal plane.
p = macropinacoids.
m = macroprisms.

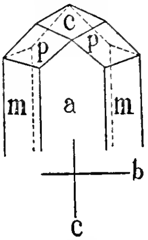


Fig. 4.

An analysis of this salt showed it to have an unusual composition, there being 4 molecules of the halide of the base combined with 1 molecule of the halide of antimony.

Its composition is expressed by the formula $(C_6H_5.NH_2.HBr)_4SbBr_3.H_2O$, and the compound receives the name tetraniline bromantimonite.

It was found impossible to determine the water of crystallization by exposure of the substance over sulphuric acid, as after a short treatment of this kind dense fumes of hydrobromic acid were given off.

On preserving crystals of the substance for some time they gradually became opaque.

The results of the above experiments are recorded in Table V :

Table V.—Salts of Aniline Hydrobromide and Antimony Tribromide.

	I.		II.		III.		IV.		V.		VI.		VII.	
	$C_6H_5.NH_2.HBr.SbBr_3$.	$C_6H_5.NH_2.HBr.SbBr_3.H_2O$.	$C_6H_5.NH_2.HBr(SbBr_3)_2$.	$C_6H_5.NH_2.HBr(SbBr_3)_2.H_2O$.	$C_6H_5.NH_2.HBr(SbBr_3)_3$.	$C_6H_5.NH_2.HBr(SbBr_3)_3.H_2O$.	$(C_6H_5.NH_2.HBr)_2SbBr_3$.	$(C_6H_5.NH_2.HBr)_2SbBr_3.H_2O$.	$(C_6H_5.NH_2.HBr)_3SbBr_3$.	$(C_6H_5.NH_2.HBr)_3SbBr_3.H_2O$.	$(C_6H_5.NH_2.HBr)_4SbBr_3$.	$(C_6H_5.NH_2.HBr)_4SbBr_3.H_2O$.	$(C_6H_5.NH_2.HBr)_6.SbBr_3$.	$(C_6H_5.NH_2.HBr)_6SbBr_3.H_2O$.
Theor.														
Sb	22.47	..	26.85	..	28.71	..	16.95	16.53	13.60	..	11.36	11.17	8.55	..
Br	59.93	..	62.64	..	63.79	..	56.49	55.10	54.42	..	53.03	52.14	51.28	..
Exp.														
Sb	16.74	..	17.45	..	16.53	..	16.77	....	16.40	..	....	11.26	11.06	..
Br	56.75	..	57.05	..	56.02	..	56.56	....	56.39	..	....	52.26	52.16	..
Sb	....	..	11.59	..	16.34	..	....	....	....	..	....	...	11.24	..
Br	....	..	54.80	..	58.82	..	....	....	....	..	....	....	51.97	..
Sb	....	..	....	..	....	..	....	....	....	..	....	....	11.07	..
Br	....	..	....	..	....	..	....	....	....	..	....	....	52.22	..

Summary of Aniline Hydrobromide and Antimony Tribromide Salts.

	IV.		VI.	
	$(C_6H_5.NH_2.HBr)_2SbBr_3$.		$(C_6H_5.NH_2.HBr)_4SbBr_3.H_2O$.	
	Sb.	Br.	Sb.	Br.
Theor.	16.95	56.49	11.17	52.14
Exp.	16.74	56.75	11.06	52.16
	16.45	57.05	11.24	51.97
	16.53	56.02	11.07	52.12
	16.34	55.82	11.26	52.26
	16.77	56.56	....	....
	16.40	56.39	....	....

Experiments with o-Toluidine Hydrobromide and Antimony Tribromide.

From the seven mixtures which were made, judging by the appearance of the crystals formed, only one kind of compound seemed to be produced. The crystals of this substance had the same general appearance in each beaker, being of a light-yellow color. The crystallizing force of the substance seemed to be weaker than that of any of the compounds previously analyzed.

Small, short, blunt prisms crystallized out, both as first and second crops, from the same mixture.

Determinations of antimony and bromine led to the conclusion that tri-*o*-toluidine bromantimonite $(C_6H_4.CH_3.NH_2.HBr)_3SbBr_3$, was the only compound formed from the constituents employed.

Table VI.—Salts of o-Toluidine Hydrobromide and Antimony Tribromide.

	I.		II.		III.		IV.		V.		VI.		VII.	
	$C_6H_4.CH_3.NH_2.HBr.SbBr_3$.	$C_6H_4.CH_3.NH_2.HBr.SbBr_3.H_2O$.	$C_6H_4.CH_3.NH_2.HBr(SbBr_3)_2$.	$C_6H_4.CH_3.NH_2.HBr(SbBr_3)_2.H_2O$.	$C_6H_4.CH_3.NH_2.HBr(SbBr_3)_3$.	$C_6H_4.CH_3.NH_2.HBr(SbBr_3)_3.H_2O$.	$(C_6H_4.CH_3.NH_2.HBr)_2SbBr_3$.	$(C_6H_4.CH_3.NH_2.HBr)_2SbBr_3.H_2O$.	$(C_6H_4.CH_3.NH_2.HBr)_3SbBr_3$.	$(C_6H_4.CH_3.NH_2.HBr)_3SbBr_3.H_2O$.	$(C_6H_4.CH_3.NH_2.HBr)_4SbBr_3$.	$(C_6H_4.CH_3.NH_2.HBr)_4SbBr_3.H_2O$.	$(C_6H_4.CH_3.NH_2.HBr)_6SbBr_3$.	$(C_6H_4.CH_3.NH_2.HBr)_6SbBr_3.H_2O$.
Theor.														
Sb	21.89	21.20	26.43	25.92	28.39	27.99	16.30	15.91	12.98	12.74	10.80	10.62	8.06	7.97
Br	58.39	....	61.56	....	63.09	....	54.35	53.05	51.95	50.95	50.36	49.56	....	...
Exp.														
Sb	....	....	13.37	....	12.80	....	12.67	....	12.87	....	12.78	....	12.86	...
Br	50.63	....	51.70	....	50.62	....	50.76	....	51.71	....	51.26	....	51.41	...
Sb	....	....	....	....	....	....	....	....	....	....	....	....	....	...
Br	50.57	....	....	....	51.84	....	51.57	....	....	....	....	....	51.51	...
Sb	13.17	....	....	....	....	....	....	....	....	....	....	....	....	...
Br	51.07	....	....	....	....	....	....	....	....	....	....	....	....	...

Summary of o-Toluidine Hydrobromide and Antimony Tribromide Salts.

V.

$(C_6H_4.CH_3.NH_2.HBr)_3SbBr_3$.

	Sb.		Br.	
Theor.	12.98		51.95	
Exp.	13.17	12.87	51.70	51.70
	13.37	12.78	51.84	51.26
	12.80	12.86	51.07	51.51
	12.67	....	51.57	51.41

Experiments with m-Toluidine Hydrobromide and Antimony Tribromide.

Out of the seven combinations made only one compound was found. This substance crystallized out in each beaker in long, very pale-yellow, silky needles. The air-dried salt was more opaque and yellower than when seen in the mother-liquor. An analysis of the result of each mixture pointed to one compound only, and this has the composition expressed by the formula $(C_6H_4.CH_3.NH_2.HBr)_2SbBr_3$, and called di-*m*-toluidine bromantimonite.

Table VII.—Salts of m-Toluidine Hydrobromide and Antimony Tribromide.

	I.		II.		III.		IV.		V.		VI.		VII.	
	$C_6H_4.CH_3.NH_2.HBr.SbBr_3$.	$C_6H_4.CH_3.NH_2.HBr.SbBr_3.H_2O$.	$C_6H_4.CH_3.NH_2.HBr(SbBr_3)_2$.	$C_6H_4.CH_3.NH_2.HBr(SbBr_3)_2.H_2O$.	$C_6H_4.CH_3.NH_2.HBr(SbBr_3)_3$.	$C_6H_4.CH_3.NH_2.HBr(SbBr_3)_3.H_2O$.	$(C_6H_4.CH_3.NH_2.HBr)_2SbBr_3$.	$(C_6H_4.CH_3.NH_2.HBr)_2Sb_3Br_3H_2O$.	$(C_6H_4.CH_3.NH_2.HBr)_3SbBr_3$.	$(C_6H_4.CH_3.NH_2.HBr)_3.SbBr_3.H_2O$.	$(C_6H_4.CH_3.NH_2.HBr)_4.SbBr_3$.	$(C_6H_4.CH_3.NH_2.HBr)_4SbBr_3.H_2O$.		$(C_6H_4.CH_3NH_2HBr)_6SbBr_3$.
Theor.														
Sb	21.89	21.20	..	26.43	..	28.39	..	16.30	..	12.98	..	10.80	..	8.06
Br	58.39	56.53	..	61.56	..	63.09	..	54.35	..	51.95	..	50.36	..	...
Exp.														
Sb	15.89	....	..	....	..	15.65	..	16.66	..	....	..	16.45	..	15.96
Br	54.27	....	..	54.49	..	54.27	..	54.38	..	54.03	..	54.93	..	54.20
Sb	....	....	..	....	..	....	..	16.31	..	....	..	....	..	....
Br	....	....	..	54.86	..	....	..	54.49	..	53.93	..	....	..	54.25

Summary of m-Toluidine Hydrobromide and Antimony Tribromide Salts.

IV.

$(C_6H_4.CH_3.NH_2.HBr)_2SbBr_3$.

	Sb.		Br.	
Theor.	16.30		54.35	
Exp.	16.31	15.96	54.49	54.20
	16.66	15.89	54.86	54.25
	16.45	15.65	54.38	54.27
	....	....	54.03	54.27
	....	....	53.93	54.93
	....	....	54.49	....

Experiments with p-Toluidine Hydrobromide and Antimony Tribromide.

The mixtures of the constituents were made in the usual way in hydrobromic acid solution. Mixtures 1, 2, 4, 5, and 7 all gave crops of silver-white needles.

Repeated attempts were made to get a salt from mixture No. 6, but it was possible only to obtain the *p*-toluidine hydrobromide from the solution.

Mixture No. 3 gave a crop of very small lemon-yellow plates.

Owing to the ease with which the white salts give up or take up water of crystallization it was difficult to get sharp analytical data. The analyses of all the salts obtained seem to point to the existence of three different compounds, and one of them also with water of crystallization. They were as follows: Di-*p*-toluidine bromantimonite $(C_6H_4.CH_3.NH_2.HBr)_2.SbBr_3$; the same compound with 1 molecule of water of crystallization $(C_6H_4.CH_3.NH_2.HBr)_2.SbBr_4.HO$; tri-*p*-toluidine bromantimonite, $(C_6H_4.CH_3.NH_2.HBr)_3.SbBr_3$; and tetra-*p*-toluidine bromantimonite, $(C_6H_4.CH_3.NH_2.HBr)_4.SbBr_3$. In dry air these compounds are canary-yellow, but if exposed to the air on a damp day they change to snow-white. The compound which crystallized out from mixture 3, in the form of small plates, seems to be quite stable as to its color—it remains yellow constantly.

The yellow color can be restored in all three compounds by gently heating a portion on a piece of platinum foil.

The analyses of the compounds are tabulated in the usual manner in Table VIII.

Table VIII.—Salts of p-Toluidine Hydrobromide and Antimony Tribromide.

	I.		II.		III.		IV.		V.		VI.		VII.	
	$C_6H_4.CH_3.NH_2.HBr.SbBr_3$.	$C_6H_4.CH_3.NH_2.HBr.SbBr_3.H_2O$.	$(C_6H_4.CH_3.NH_2.HBr)(SbBr_3)_2$.	$(C_6H_4.CH_3.NH_2.HBr)(SbBr_3)_2.H_2O$.	$C_6H_4.CH_3.NH_2.HBr(SbBr_3)_3$.	$C_6H_4.CH_3.NH_2.HBr(SbBr_3)_3.H_2O$.	$(C_6H_4.CH_3.NH_2.HBr)_2SbBr_3$.	$(C_6H_4.CH_3.NH_2.HBr(_2SbBr_3.H_2O$.	$(C_6H_4.CH_3.NH_2.HBr)_3SbBr_3$.	$(C_6H_4.CH_3.NH_2.HBr)_3SbBr_3.H_2O$.	$(C_6H_4.CH_3.NH_2.HBr)_4SbBr_3$.	$(C_6H_4.CH_3.NH_2.HBr)_4SbBr_3.H_2O$.	$(C_6H_4.CH_3.NH_2.HBr)_6SbBr_3$.	$(C_6H_5.CH_3.NH_2.HBr)_6SbBr_3.H_2O$.
Theor.														
Sb	21.89	21.20	26.43	25.92	28.39	27.99	16.30	15.91	12.98	12.74	10.80	10.62	8.06	7.97
Br	58.39	....	61.56	....	63.09	....	54.35	53.05	51.95	50.95	50.36	49.56	....	....
Exp.														
Sb	....	....	16.04	....	....	....	....	....	12.59	....	....	....	15.09	....
Br	....	....	52.73	....	54.78	....	....	...	51.45	....	....	....	52.90	....
Sb	....	....	15.73	....	....	....	10.85	....	....	....	....	....	....	....
Br	53.55	....	....	....	54.72	....	....	....	51.49	....	....	....	52.58	....
Sb	....	....	....	....	....	....	10.65	....	....	....	....	....	....	....
Br	53.94	....	....	....	54.54	...	49.83	....	....	....	....	....	....	....
Sb	....	....	....	....	....	....	....	....	....	....	....	....	....	....
Br	54.15	....	....	....	....	....	50.00	....	....	....	....	....	....	....
Sb	....	....	....	....	....	....	....	....	....	....	....	....	....	....
Br	53.70	....	....	....	....	....	....	....	....	....	....	....	....	....

Summary of p-Toluidine Hydrobromide and Antimony Tribromide Salts.

	IV.				V.		VI.	
	Sb.	Br.	Sb.	Br.	Sb.	Br.	Sb.	Br.
Theor.	16.30	54.35	15.91	53.05	12.98	51.95	10.80	50.36
Exp.	....	53.94	16.04	52.73	12.59	51.45	10.85	50.00
	....	53.55	15.73	52.52	....	51.49	10.65	49.83
	....	54.15	....	52.48	....	....	....	....
	....	53.70	....	52.90	....	....	....	....
	....	54.78	....	52.58	....	....	....	....
	....	54.72	....	....	....	....	....	....
	....	54.54	....	....	....	....	....	....

On exposing the compound (which on analysis showed the presence of water of crystallization) in the desiccator over concentrated sulphuric acid, there was a constant loss of weight, due to the evolution of hydrobromic acid, presumably.

Experiments with Aniline Hydriodide and Antimony Triiodide.

Study in this series was begun with the aniline salt. Some difficulty was experienced here, since it was necessary to prepare hydriodic acid only in such quantities as would be immediately needed, owing to its rapid decomposition. It was also difficult to avoid the separation of free iodine when heating the mixtures.

The mixtures of the aniline and antimony halides were made up in the usual proportions hitherto employed.

A crop of finely divided, granular, scarlet crystals separated from mixture No. 1. On drying, these seemed to undergo no change. A determination of antimony and iodine clearly pointed to the existence of a compound whose composition is expressed by the formula $C_6H_5.NH_2.HI.SbI_3$, monaniline iodantimonite.

Out of mixture No. 2 small, almost microscopic, scarlet octahedra with modified edges crystallized out. An analysis of these revealed no new compound.

Crystals from mixture 3, again in the form of modified and twinned octahedra, proved on analysis to be identical with the first compound discovered in this series.

Mixtures 4 and 6 yielded nothing new in the way of double salts. Mixture No. 5, on the other hand, yielded a beautiful crop of fine carmine needles, which on analysis proved to be a combination not yet met with in the present investigation. The compound is composed of 3 molecules of aniline hydriodide and 2 molecules of antimony triiodide, expressed by the formula $(C_6H_5.NH_2HI)_3(SbI_3)_2$, trianiline diiodantimonite.

The last mixture examined was that in which the ratio of the constituents was 6 : 1. A new compound seemed to be formed here. The mixture from which the compound was finally obtained yielded at first only a large crop of the halide of the base. On evaporating the mother-liquor, a crop of uniform golden-yellow plates was obtained. These were dried and tested for antimony. It was found to be present in considerable quantity. As soon as the crystals were drained off they began to undergo change in color from golden-yellow to orange-red. When dry they were analyzed and gave results pointing to the formula $(C_6H_5.NH_2.HI)_4SbI_3$, tetraniline iodantimonite.

The analytical results of the study of this series are given in Table IX.

Table IX.—Aniline Hydriodide and Antimony Triiodide.

		I.	II.	III.	IV.	V.	Va.	VI.	VII.
		$C_6H_5.NH_2.HI.SbI_3$.	$C_6H_5.NH_2.HI(SbI_3)_2$.	$C_6H_5.NH_2.HI(SbI_3)_3$.	$(C_6H_5.NH_2.HI)_2SbI_3$.	$(C_6H_5.NH_2.HI)_3SbI_3$.	$(C_6H_5.NH_2.HI)_3(SbI_3)_2$.	$(C_6H_5.NH_2.HI)_4SbI_3$.	$(C_6H_5.NH_2HI)_6SbI_3$.
Theor.									
Sb	16.62	16.21	19.62	....	....	10.31	14.41	8.66	....
I	70.36	68.64	72.69	73.08	67.34	65.46	68.64	64.19	62.56
Exp.									
Sb	16.78	....	....	....	....	14.52	....	....	8.71
I	70.15	....	70.30	70.14	70.84	68.23	....	70.29	64.32
Sb	16.80	....	....	....	....	14.48	....	....	8.24
I	70.44	....	70.39	70.10	70.08	68.31	....	69.99	64.31
Sb	....	....	....	....	....	14.14	....	....	....
I	....	....	....	....	....	68.35	....	....	64.47
Sb	....	....	....	....	....	14.34	....	....	....
I	....	....	....	....	....	68.75	....	....	....

Summary of Aniline Hydriodide and Antimony Triiodide Salts.

	I.			Va.		VI.	
	Sb.	I.		Sb.	I.	Sb.	I.
Theor.	16.62	70.36		14.41	68.64	8.66	64.19
Exp.	16.78	70.15	70.10	14.52	68.23	8.71	64.32
	16.80	70.44	70.84	14.48	68.31	8.24	64.31
	....	70.31	70.08	14.14	68.35	...	64.47
	....	70.39	69.99	14.34	68.75	...	....
	....	70.14	70.29	....	....	...	....

Experiments with o-Toluidine Hydriodide and Antimony Triiodide.

The usual experiments were made with the above ingredients and no difficulty was experienced in obtaining well-characterized products in each experiment. The double salts which crystallized out from each of the first three mixtures had the same general appearance, consisting of short blunt needles of a brick-red color. Analyses of the three sets of crystals pointed to one and the same compound, containing 1 molecule of each of the original ingredients. The formula expressing the composition is shown by the following: $C_6H_4.CH_3NH_2.HI.SbI_3$, mon-*o*-toluidine iodantimonite.

An examination of the double salts formed from mixtures 4, 5, 6, and 7 indicated that a new variety had been formed. The appearance of the crystals in the above cases was quite different from that of the first compound described. They consisted of irregular-shaped, bronze-covered leaves. Analyses of a sample of each set indicated that only one individual had been formed, *viz.*, tri-*o*-toluidine diiodantimonite,

$$(C_6H_4.CH_3.NH_2.HI)_3.(SbI_3)_2.$$

Table X.—Salts of o-Toluidine Hydriodide and Antimony Triiodide.

	I.	II.		III.	IV.	V.	Va.	VI.	VII.
	$C_6H_4.CH_3.NH_2.HI.SbI_3.$	$C_6H_4.CH_3.NH_2.HI(SbI_3)_2.$	$C_6H_4.CH_3.NH_2.HI(SbI_3)_2.H_2O.$	$C_6H_4.CH_3.NH_2.HI(SbI_3)_3.$	$(C_6H_4.CH_3.NH_2.HI)_2SbI_3.$	$(C_6H_4.CH_3.NH_2.HI)_3SbI_3.$	$(C_6H_4.CH_3.NH_2.HI)_3(SbI_3)_2.$	$(C_6H_4.CH_3.NH_2.HI)_4SbI_3.$	$(C_6H_4.CH_3.NH_2HI)_6SbI_3.$
Theor.									
Sb	16.30	19.40	....	....	12.35	9.95	14.06	8.32	6.28
I	69.02	71.06	70.83	....	65.40	63.18	66.96	61.69	59.81
Exp.									
Sb	16.19	....	....	....	13.89	....	....	....	....
I	68.44	68.63	....	68.89	66.71	66.67	....	66.33	66.43
Sb	15.88	....	....	....	....	....	....	....	....
I	68.36	68.70	....	69.00	66.78	66.37	....	....	66.25

Summary of o-Toluidine Hydriodide and Antimony Triiodide Salts.

	I.			Va.		
	$C_6H_4CH_3NH_2.HI.SbI_3$.			$(C_6H_4CH_3NH_2.HI)_3(SbI_3)_2$.		
	Sb.	I.		Sb.	I.	
Theor.	16.30	69.02		14.06	66.99	
Exp.	16.19	68.44	68.70	13.89	66.71	66.25
	15.88	68.36	68.89	....	66.78	66.37
	....	68.63	69.00	....	66.33	66.67
	....	....	....	....	66.43	....

Experiments with m-Toluidine Hydriodide and Antimony Triiodide.

Mixtures of the above ingredients were made up in the usual way and well-defined crystals began to appear in each beaker as soon as the solutions were cool. On examination of the various sets of crystals, by means of the lens, they appeared to be all of the same general character. After removal from the solutions, and drying, the crystals were in the form of glistening, brick-red prisms.

Analysis pointed, in the case of each of the deposits, to the formation of only one chemical compound. This proved to be tri-*m*-toluidine diiodantimonite, having the formula

$$(C_6H_4.CH_3.NH_2.HI)_3.(SbI_3)_2.$$

This substance, like the corresponding ortho compound, seems to possess a strong crystallizing force. A statement of the analytical results leading to the above formula will be found in the following tables :

Table XI.—Salts of m-Toluidine Hydriodide and Antimony Triiodide.

	I.	II.	III.	IV.	V. Va.	VI.	VII.
	$C_6H_4.CH_3.NH_2.HI.SbI_3$.	$C_6H_4.CH_3.NH_2.HI(SbI_3)_2$.	$C_6H_4.CH_3.NH_2.HI(SbI_3)_3$.	$(C_6H_4.CH_3.NH_2.HI)_2SbI_3$.	$(C_6H_4.CH_3.NH_2.HI)_3SbI_3$. $(C_6H_4.CH_3.NH_2.HI)_3(SbI_3)_2$.	$(C_6H_4.CH_3.NH_2.HI)_4SbI_3$.	$(C_6H_4.CH_3.NH_2.HI)_6SbI_3$.
Theor.							
Sb	....	....	....	....	14.06	....	....
I	....	....	....	....	66.96	....	....
Exp.							
Sb	....	....	....	13.74	....	....	....
I	66.67	66.93	66.86	66.53	66.95	66.89	66.68
Sb	....	....	....	....	....	....	....
I	67.00	66.78	67.08	67.03	66.74	66.26	66.76

Summary of m-Toluidine Hydriodide and Antimony Triiodide Salts.

Va.
$(C_6H_4.CH_3.NH_2.HI)_3(SbI_3)_2$.

	Sb.	I.	
Theor.	14.06	66.96	
Exp.	13.74	66.77	67.03
	....	67.00	66.95
	....	66.93	66.74
	....	66.78	66.89
	....	66.86	66.26
	....	67.08	66.68
	....	66.53	66.76

Experiments with p-Toluidine Hydriodide and Antimony Triiodide.

In working with this series some difficulty was met with in obtaining well-characterized and uniform crystals in the same beaker. From nearly every mixture worked with there crystallized out side by side light, orange-colored, blunt, prismatic crystals and darker, orange-colored needles. The prismatic forms seemed to be the more soluble of the two, and by regulating the concentration of the solution it was possible to obtain a uniform crop of the needle variety. Specimens of the light prismatic type were gotten out, but on being transformed to a porous earthenware plate, began to turn orange-red in a very short time.

Analyses of both kinds of crystals, after being dried in the air, showed that there was no difference in their composition. The composition of this compound, mono-*p*-toluidine iodantimonite, is expressed by the formula

$$C_6H_4.CH_3.NH_2.HI.SbI_3.$$

Table XII.—Salts of p-Toluidine Hydriodide and Antimony Triiodide.

	I.		II.		III.		IV.		V.		VI.		VII.	
	$C_6H_4.CH_3.NH_2.HI.SbI_3.$	$C_6H_4.CH_3.NH_2.HI.SbI_3.H_2O$	$(C_6H_4.CH_3.NH_2.HI)(SbI_3)_2.$	$(C_6H_4.CH_3.NH_2.HI)(SbI_3)_2.H_2O.$	$C_6H_4.CH_3.NH_2.HI(SbI_3)_3.$	$C_6H_4.CH_3.NH_2.HI(SbI_3)_3.H_2O.$	$(C_6H_4.CH_3.NH_2.HI)_2SbI_3.$	$(C_6H_4.CH_3.NH_2.HI)_2SbI_3.H_2O.$	$(C_6H_4.CH_3.NH_2.HI)_3SbI_3.$	$(C_6H_4.CH_3.NH_2.HI)_3SbI_3.H_2O.$	$(C_6H_4.CH_3.NH_2.HI)_4SbI_3.$	$(C_6H_4.CH_3.NH_2.HI)_4SbI_3.H_2O.$	$(C_6H_4.CH_3.NH_2.HI)_6SbI_3.$	$(C_6H_4.CH_3.NH_2.HI)_6SbI_3.H_2O.$
Theor.														
Sb	16.30	....	19.40	19.12	....	..	12.35	..	9.95	..	8.32	..	6.28	..
I	69.02	67.37	71.06	70.83	....	..	65.40	..	63.18	..	61.69	..	59.81	..
Exp.														
Sb	....	....	16.58	....	16.88	..	16.08	..	....	..	....	..	....	..
I	69.12	....	68.86	....	....	..	....	..	68.51	..	68.56	..	68.42	..
Sb	....	....	16.27	....	....	..	16.75	..	....	..	....	..	....	..
I	69.30	....	68.67	....	....	..	....	..	68.43	..	....	..	68.37	..
Sb	....	....	....	....	....	..	16.34	..	....	..	....	..	....	..

Summary of p-Toluidine Hydriodide and Antimony Triiodide Salts.

I.

$C_6H_4.CH_3.NH_2.HI.SbI_3$.

	Sb.		I.	
Theor.	16.30		69.02	
Exp.	16.58	16.08	69.12	68.43
	16.27	16.75	69.30	68.56
	16.88	16.34	68.86	68.42
	....	....	68.67	68.37
	....	....	68.51	....

ON THE RANCIDITY OF FATS.

By Iskar Nagel.

Under the direction of the late Prof. Benedikt, in Vienna, I carried on an investigation on the rancidity of fats and the refining of rancid oils and fats, and stated that these contain the following substances in variable quantities :

1. Free fatty acids, saturated as well as unsaturated.
2. Hydroxy acids of the fatty acid series.
3. Lactones and anhydrides of fatty acids.
4. Alcohols, as butyl, amyl, caproyl, and capryl alcohol.
5. Esters of saturated, of unsaturated, and of hydroxy acids of the fatty acid series with higher and sometimes also polybasic alcohols as butyl, caproyl, capryl alcohol, etc. ; glycol, etc.
6. Aldehydes, saturated, as butyric, caproic, caprylic aldehyde, etc., and unsaturated, as acrolein an oenanthic aldehyde.
7. Acetals, which are ether-like compounds of the above-mentioned aldehydes and alcohols.
8. Terpenes.

There may also be other substances present, but they could not be identified.

To remove these substances from a crude or rancid fat or oil, I proceeded as follows :

I. The free saturated and unsaturated acids, as well as the hydroxy acids, are easily removed by means of an aqueous solution of soluble glass. If the neutralization is effected with sodium carbonate or with caustic soda, emulsions are obtained, and it is possible only by a long and tedious method to separate the oil from these emulsions, free from water and alkali. Emulsions are entirely avoided if, instead of the alkalies, an aqueous solution of glass is used. If such a solution is added to an oil or melted fat containing free acid, the acid unites with the bases of the silicates, and silicic acid is set free. The free silicic acid draws the alkali salts mechanically to the bottom, when it is impossible for them to be dissolved in the oil and to form an emulsion.

II. The lactones contained in the fats are more or less volatile with water vapor. Some of them, however, are insoluble in water and not volatile with water vapor. The volatile lactones are removed by the method described under VI. The non-volatile compounds must be converted into salts of hydroxy acids of the fatty acid series. This is accomplished by boiling for several hours the oil, which contains no free acid, with concentrated solutions of alkalies, as for instance, with a small quantity of a solution of sodium carbonate or of caustic soda. These then become visible in the oil, forming difficultly soluble flakes which fall to the bottom and are easily filtered off. These are the salts of the hydroxy acids.

III. The alcohols and esters of fatty acids and of hydroxy acids contained in fats and oils can be removed by the method described under VI, provided they are volatile with water vapor.

IV. Some of the aldehydes are volatile with water vapor and can be removed according to VI, while others are not, and these must be removed as follows: Four volumes of oil are heated for several hours with one volume of a concentrated solution of sodium bisulphite, and, after cooling, the aqueous solution is separated from the oil. It is known that the compounds of aldehydes with sodium bisulphite are usually solid, crystalline bodies, which are always slightly soluble in the solution of bisulphite. If the aldehydes are present only in small quantity no crystals are formed, and only a cloudy layer appears between the aqueous solution and the oil, or the solution, at first clear, becomes cloudy and contains the compounds of the aldehydes with the sodium bisulphite in solution. These are removed together with the solution.

V. To remove the acetals, if they are not volatile with water vapor, I have found it best to heat the oil or fat for some time with dilute sulphuric acid. The higher acetals are decomposed by the sulphuric acid into alcohols and aldehydes, which are either volatile with water vapor and are removed according to VI or removed according to IV, if volatile. The acetals which are volatile with water vapor are removed according to VI.

VI. The terpenes are all volatile with water vapor and are removed by distillation with steam. It must be remembered that it is not always sufficient to conduct ordinary steam through the oil for the purpose of removing the volatile substances mentioned under 3–7, since it sometimes has a bad effect on the oil.

There are some substances which are not volatile or only very difficultly volatile with steam at 100° C., but which are more easily volatile with steam at a higher temperature. Hence, the distillation with steam at 100° C. would take a very long time, and even then would not entirely purify the oil. On the other hand, it is stated that the continuous contact of heated oils with steam or atmospheric air, while decomposing the fat, favors the formation of the substances named under 1–8.

These difficulties may be avoided in three ways:

a. By conducting steam together with some indifferent gas as hydrogen or carbon dioxide through the oil.

b. By conducting steam under diminished pressure through the oil.

c. By conducting steam heated gradually from 100°–170° C., together with an indifferent gas through the oil.

If this fractioning with superheated steam is made use of, those substances which are easily volatile are carried over first, before the more highly heated steam, which would decompose them, becomes necessary. It is well to let the oil cool *in vacuo* or in an atmosphere of some indifferent gas.

The method above described for purifying fats and oils is carried out in practice as follows: The fat or oil, freshly pressed, extracted or already purified with sulphuric acid, is heated and thoroughly mixed with a concentrated solution of soluble glass, the quantity depending on the amount of free acid present, and is then filtered from the heavy precipitate which has settled to the bottom. The oil is now boiled with dilute sulphuric acid for about six hours. After cooling, the sulphuric acid is separated from the oil, which is washed again with a solution of soluble glass. The oil is then thoroughly mixed and heated with a fourth of its weight of a mixture of a concentrated solution of sodium carbonate and milk of lime (1 : 1) for several hours. In this process a very small quantity of the oil is saponified, and the soap thus formed sinks to the bottom. After cooling, the filtered oil is heated with a fourth of its weight of a concentrated solution of sodium bisulphite. The mixture is now allowed to cool, and the aqueous solution is separated from the oil, which is transferred to a distilling apparatus and subjected to distillation with steam, the temperature of which is gradually raised. Finally, the oil is allowed to cool in a current of carbon dioxide.

If the oil, before being subjected to the above method of purification, is carefully examined for those substances which are not glycerides of the fatty acids, or, if it is known that some of the substances above named (1–8) are not present, then such parts of the method as have for their object the removal of these substances, may be omitted. Further, the success of the method does not depend on the order of procedure described above. This may be changed at pleasure.

NOTE.

The Wax of the Bacillariaceae and Its Relation to Petroleum.

In a recent number of the *Berichte* (**32**, 2940) there is an article on this subject by Krämer and Spilker, an abstract of which is herewith given:

"The oil which has long been known to exist in the *Bacillariaceae* (Diatoms) had not been investigated until the authors undertook the task of tracing the probable relationship between it and mineral waxes and oils. These unicellular plants, whose siliceous coverings form immense deposits in some places, are very abundant in peat-bogs. A quantity of the dried material was extracted with benzene, and yielded a brownish-black wax-like mass, which contained a high percentage of sulphur on account of the presence of the so-called 'sulphur bacteria', which set free this element from certain of its compounds. Fortunately, an immense deposit of material nearly free from sulphur was found at Ludwigshof. In the bed of a lake recently drained was a layer of diatom remains of an average thickness of 7 meters and covering an area of 900 hektares (2200 acres). This elastic, slimy mass contained about 10 per cent of dry substance. This yielded 3.6 per cent of wax when extracted, so that the amount obtainable from the entire deposit would be about 250,000 tons.

"The dark-brown wax was scarcely acted on by fuming nitric acid in the cold, but nearly 40 per cent dissolved on warming. The residue, when crystallized from alcohol, yielded a viscous oil, and a white solid in all respects similar to 'lekene', obtained from mineral wax by Beilstein and Wiegand.[1] When distilled the wax gave off methane, the oxides of carbon, sulphuretted hydrogen, and water, besides an oily distillate. Mineral wax (ozocerite) similarly heated gives off only traces of the oxides of carbon and sulphuretted hydrogen, and no water. It is very slightly saponified by alcoholic potash, but about 10 per cent of diatom wax is dissolved. From the alkaline solution ether extracts a brittle gum.

"When distilled under pressure, the two kinds of wax yield very similar products, except that the mineral wax yields no oxides of carbon, no water, and only traces of sulphuretted hydrogen, all of which are given off from diatom wax. In both cases unsaturated gaseous and liquid hydrocarbons are formed. When the liquid products are subjected to fractional distillation, the portions boiling between 130° and 290° are found to be identical.

"For comparison, Carnauba wax and Japan wax were distilled under the same conditions. The gaseous products resembled those from diatom wax, except for the absence of sulphuretted hydrogen, and the liquid distillates were practically identical with those above mentioned. In all four cases the middle fraction (130°–290°) had a molecular weight and composition agreeing fairly well with the formula $C_{11}H_{24}$. This was after the removal of the unsaturated constituents.

"The authors believe that mineral waxes and oils are formed from diatom wax by the combined action of heat, pressure, and ammonium carbonate (formed by the decay of

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[1] Ber. d. chem. Ges., **16**, 1547.

protoplasm). Deposits such as that at Ludwigshof were probably formed in remote ages, and were covered by débris from the surrounding hills, so that great pressure would be exerted on the mass. The heat of the earth's interior would cause a distillation of the wax, and its transformation into the various kinds of petroleum, according to the conditions. The unsaturated hydrocarbons polymerized to form the viscous, heavy oils.

"It is hard to imagine conditions favorable to the accumulation of animal remains in sufficient abundance to form the petroleum deposits, but it is not difficult to believe that, in earlier ages, when the conditions for vegetation were so favorable, there might have been formed layers of diatomaceous material much larger than the one at Ludwigshof. It is not improbable, however, that certain petroleum deposits, *e. g.* in the oil shales, are of animal origin. Unfortunately, no remains of diatoms have been found in the oil sands or in the overlying rocks, but this may be due to the corroding action of ammonium carbonate on the very delicate siliceous coverings. Further, the overlying rock contains a very high percentage of silica, as it should if formed mainly of the remains of diatoms. O. N. Witt,[1] in discussing Engler's petroleum theory, suggested that diatoms ought possibly to be taken into account. Finally, however, he gave up the idea because no remains of diatoms have been found earlier than the tertiary deposits. The authors suggest that such remains would have been so corroded by percolating water in the course of ages that they would be unrecognizable.

"A. F. Stahl, also,[2] states that the theory of the formation of petroleum from animal fat is not supported by his observations in the Kalmuch and Kirgis steppes. He believes the oil was formed from diatoms, but made no experiments along this line.

"There may be points in regard to the above theory which geologists may object to, and it is evident that the correct solution of the problem cannot be attained without the aid of both geologists and chemists."

C. E. W.

OBITUARY.

JOHANN CARL WILHELM FERDINAND TIEMANN.

News has recently reached us of the death of Prof. Tiemann, which occurred November 14. He was born in 1848 and took his Ph.D. degree at Göttingen in 1870. Since 1882 he has

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[1] Prometheus, 1894, 349, 365.

[2] Chem. Ztg., Feb. 22, 1899.

been Professor of Chemistry in the University of Berlin and editor of the "*Berichte der deutschen chemischen Gesellschaft.*" He has always been active in the field of pure chemistry, his work on camphor being perhaps his best known contribution to the science. His energies have been, however, on account of his connection with the firm of Haarman & Reimer, especially directed toward the development of commercial products. He introduced artificial vanillin, prepared at first from coniferin and later from eugenol, and succeeded in perfecting a method for the preparation of ionone, a substance he had discovered and shown to be the essential principle of the odor of the violet. His work on the geraniol alcohols and citral is also a valuable contribution to that branch of the science. He was closely related by marriage to both Hofmann and Kuno Fischer. J. E. G.

REVIEWS.

THEORETISCHE CHEMIE. Vom Standpunkte der Avogadro'schen Regel und der Thermodynamik. Von DR. WALTER NERNST, o. Professor und Direktor des Instituts für physikalische Chemie an der Universität Göttingen. Zweite Auflage, mit 36 in den Text gedruckten Abbildungen. Stuttgart: Verlag von Ferdinand Enke. pp. 703. 1898.

The three great books which mark the progress of physical chemistry towards the close of the nineteenth century are the *Lehrbuch* and *Grundriss* of Ostwald, and the *Theoretische Chemie* of Nernst. The subject-matter is treated quite differently by Ostwald and by Nernst, and each of these works has its peculiar and distinctive advantage. The third edition of the *Grundriss* has just appeared, and the second edition of the *Lehrbuch*, though not completed, seems to be already exhausted. The second edition of the *Theoretische Chemie* has now appeared, just five years after the first. The method of treatment adopted by Nernst in the new edition is essentially the same as in the first. The volume is divided into four books: The General Properties of Substances; The Atom and Molecule; The Transformations of Matter; and The Transformations of Energy. But each book is enlarged, incorporating the work of the last few years. This applies especially to the sections on electrochemistry. This field, in which Nernst has played such a prominent rôle, was discussed very briefly in the first edition, presumably because of its exhaustive development by Ostwald in the Lehrbuch. In the new edition electrochemistry is treated more fully and in a broader way. A section is devoted to the general facts pertaining to electrolytic conduction, electrolysis, etc. This is followed by an application of thermodynamics to the action of the cell, which we owe primarily to Helmholtz and Thomson. In this section paragraphs are devoted to the transformation of chemical energy into electrical, the calculation of electromotive force from thermodynamics, the application of thermodynamics to the lead accumulator. In the final section the application of the laws of osmotic pressure and the theory of electrolytic dissociation, to the problem of the electromotive force of elements, is made at some length. And this is the most interesting and important chapter in electrochemistry, since it has given us, for the first time, a rational theory of the cell. Paragraphs are devoted to the way in which currents are produced in solutions, solution of metals, theory of the origin of the galvanic current, concentration elements, the gas battery, etc.

The only criticism that can fairly be made is that the work is a masterpiece, containing new and original suggestions at every turn. But this is just what we should expect from a leader.

The lack of an adequate appreciation of the great merit of this work, manifested in a recent review in this country, is a source of deep regret to the writer of this notice.

HARRY C. JONES.

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CHEMICAL JOURNAL

Contributions from the Chemical Laboratory of Cornell University.

ANETHOL AND ITS ISOMERS.

[SECOND PAPER.[1]]

By W. R. Orndorff and D. A. Morton.

ANETHOL.

I. Physical Properties.

The anethol used in this work was a product of exceptional purity[2]. It melted at 19°–21°.5 C., and distilled completely between the temperatures 231°.5 and 232°.5 C. (uncorr.). A sample portion distilled completely with steam, leaving no residue. A still purer product was obtained by recrystallization of the commercial anethol from ordinary alcohol (93.7 per cent). After recrystallization the product melted at 22°.5 C., and this melting-point remained unchanged after further recrystallization from this or other solvents. The boiling-point of this purest product was taken, using a standard thermometer, the mercury column of which was entirely surrounded with the vapor of the boiling liquid, and found to be 233°.6 C. at 731 mm. barometric pressure.[3]

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[1] See This Journal, **19**, 845, for the first paper on this subject.

[2] This anethol was purchased from Fritzsche Bros., of N. Y. City, a branch of Schimmel & Co., of Leipsic.

[3] This thermometer registered 0°.1 too high at this temperature according to the Prüfungs-Bescheinigung of the Physikalisch Technische Reichsanstalt, Abtheilung II, Charlottenburg, Germany. The correct boiling-point is therefore 233°.5 C.

The pure product still possessed a slight anise odor, but this was not nearly so pronounced as in the commercial product. It is soluble in all proportions in chloroform, ether, acetic ether, acetone, benzene, absolute alcohol, carbon disulphide, aniline, and petroleum ether. It is less soluble in ordinary alcohol (93.7 per cent), and may be crystallized from this solvent by cooling the solution down to 0° C. In water it is very slightly soluble, but sufficiently to impart its characteristic taste and odor to this liquid. From petroleum ether it may be crystallized by cooling the solution sufficiently.

The freezing-point of the commercial anethol, using the Beckmann freezing-point apparatus, was found to be 20°.55 C. as the mean of three very careful observations. When recrystallized from alcohol twice the purified product solidified at 21°.4 C., and further recrystallization from alcohol or from petroleum ether did not change this freezing-point. Hence the product must be regarded as pure.

The statement is made by Grimaux[1] that when heated to 100° C. for some time, the melting-point of anethol is lowered in consequence of the formation of polymers. In repeating this work it was found that, after heating anethol for nine hours on the water-bath, its melting-point was lowered about 5°. Further heating at its boiling-point (230° C.) for three hours lowered the melting-point about 1° more, and the product now left an appreciable residue when distilled in steam. This residue was a dark-colored, thick, viscous oil, heavier than water, and appeared to be identical with the product called isoanethol, obtained by Kraut and Schlun[2] by heating fluid metanethol in sealed tubes at 330° C. for several hours. In purifying anethol by distillation it is therefore better to distil in steam or under reduced pressure in order to avoid this polymerization as much as possible. The method of purification by crystallization is of course not open to this objection and is to be preferred to all others.

From alcohol anethol crystallizes in extremely thin, rectangular plates, which show parallel extinction and a biaxial optical interference figure in converged polarized light. The

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[1] Bull. Soc. Chim. (Paris), (III), **15**, 778.

[2] Arch. d. Pharm. (2), **116**, 241.

acute bisectrix is apparently at right angles to the flat plates; hence the symmetry is most probably orthorhombic, though possibly monoclinic.

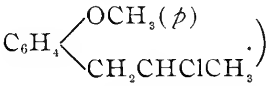
II. Chemical Conduct.

A. The Action of Iodine on Anethol.—A concentrated solution of iodine in acetone or potassium iodide acts at once on anethol, with evolution of heat, converting it into its polymer anisoin. Iodine alone effects this change on standing with anethol for a long time, or immediately, if the two are heated together. On the other hand, a concentrated alcoholic solution of iodine has no polymerizing action on anethol.

B. The Action of Hydrochloric Acid on Anethol. Anethol Hydrochloride.—The method employed in the preparation of this compound was slightly different from the one used by Saussure[1] and Cahours[2] in the respect that, instead of subjecting the solid anethol to the action of the gas, the latter was conducted into the melted substance, care being taken to maintain as low a temperature as possible and still keep the anethol in fluid condition. The anethol was first weighed, then hydrochloric acid gas passed in until the weight no longer increased. The reaction-product was a thick oil and had a reddish or greenish tinge when first prepared.

The amount of hydrochloric acid that anethol can absorb was determined in a few cases, as follows:

10 grams anethol absorbed 3 grams of dry hydrochloric acid gas. (Theory requires 2.5 grams for the compound,



$$C_6H_4\left\langle\begin{matrix}OCH_3(p)\\ CH_2CHClCH_3\end{matrix}\right..)$$

30 grams anethol absorbed 8.5 grams HCl. (Theory 7.5 grams.)

14.26 grams anethol absorbed 3.43 grams HCl. (Theory 3.52 grams.)

In the last determination the weighings were carefully made

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[1] Ann. chim. phys. (1), **13**, 282 (1820).

[2] *Ibid.* (III), **2**, 279 (1841).

and the results are correspondingly accurate. The other determinations were merely approximate.

Grimaux[1] states that the quantity of hydrochloric acid absorbed by anethol does not appear to be definite since he found it to vary by as much as 2 per cent in different experiments. He considers that the action is not an additive but a polymerizing one, the anethol being changed to isoanethol which holds in solution a variable amount of hydrochloric acid. The results of our work, however, do not bear out this supposition. On the contrary, they agree with the results obtained by Saussure and Cahours, both of whom found that anethol absorbed exactly the amount of hydrochloric acid required by theory for the formation of a compound of the formula, $C_{10}H_{12}O.HCl$.

The anethol hydrochloride is very unstable, and gives off hydrochloric acid fumes constantly on standing at ordinary temperatures, the decomposition being apparently the same as that which takes place on distillation; namely, the splitting off of hydrochloric acid and formation of isoanethol. Apparently this decomposition takes place to a slight extent even during the preparation of the anethol hydrochloride. If it is allowed to go too far anomalous analytical results are to be expected.

When anethol hydrochloride is treated with alcoholic caustic potash several products result. Besides isoanethol and solid metanethol a light oil is formed which distils with steam and has a pleasant mint-like odor. This is an alcohol addition-product of anethol and will be described in another part of this paper.

C. The Action of Picric Acid on Anethol.—The picrate of anethol has been described by Ampola[2] as a solid crystallizing from alcohol in carmine-red needles melting at 60° C.

In order to compare closely the conduct of anethol with that of fluid metanethol the action of picric acid on both these compounds was investigated.

The picrate of anethol was easily formed by adding the calculated amount of picric acid to a solution of anethol in alco-

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[1] Bull. Soc. Chim. (Paris), (III), **15**, (1896) 778.

[2] Gazz. chim. ital., **24** (1894), 432.

hol. The picrate could then be precipitated out with water or crystallized out by evaporation of the alcohol. The pure substance melted with decomposition at about 70° C. On standing in the air it gradually breaks down into anethol, which volatilizes, and picric acid. Alcoholic caustic potash decomposes it immediately into anethol and potassium picrate.

D. The Action of Bromine on Anethol. Anethol Dibromide.—This compound was prepared by Ladenburg's method.[1] It decomposes so readily that its crystallographic constants could not be determined. The melting-point of the pure crystals was determined as 63°–64° C. (according to Ladenburg 65° C.), but as the substance decomposes at its melting-point or even at a still lower temperature, an accurate determination could not be made.

Monobromanethol Dibromide.—Following the directions of Hell and Gärttner,[2] this compound was prepared by adding gradually to a cold ethereal solution of anethol slightly more than 2 molecules of bromine. The first half of the bromine should be added gradually, as the reaction is violent, until all the anethol is converted into the dibromide. The remainder of the bromine can then be added all at once, as the substituting action is slow. The ethereal solution, if left to evaporate spontaneously, will then deposit the crystalline monobromanethol dibromide.

Hell and Gärttner purified this product by repeated crystallization from petroleum ether, but this method is slow and unsatisfactory, since, in the first place, the compound does not dissolve easily in petroleum ether, and, in the second place, it requires a number of recrystallizations to remove the impurities. It was found, however, that the compound could be easily and quickly purified by dissolving it in a small amount of chloroform and then adding alcohol to this solution until precipitation began. The monobrom dibromide is then deposited in the form of slender prisms, which melt sharply at 102° C., the melting-point being unchanged by recrystallization from chloroform-alcohol or from ether. When heated

[1] Ann. Chem. (Liebig), Suppl. Bd. 8, 87 (1872).

[2] J. prakt. Chem., **51** (1895) 424 ; see also *Ibid.*, **52**, 193 (1895).

rapidly the melting-point is somewhat higher than the one just given.

The same monobrom dibromide results, either by shaking anethol with bromine water until no more bromine is absorbed and then treating the resulting dibromide in ethereal solution with another molecule of bromine ; or, by adding the calculated amount of bromine directly to anethol.

Monobromanethol dibromide is slowly decomposed if its solution in acetone, ether, chloroform, or chloroform-alcohol is kept warm for any length of time. It was therefore difficult to obtain very good crystals, although it is a substance that would otherwise crystallize unusually well. The best crystals were obtained by allowing the chloroform-alcohol solution to cool somewhat slowly.

The crystals are doubly refracting. They show the biaxial optical interference figure in converged polarized light, but in no case parallel extinction. The optical properties as well as the form of the crystals show them to belong to the triclinic system.

The four angles in one crystal zone were measured in order to compare them with the same angles on the crystals of the corresponding fluid metanethol compound. For the obtuse angles the best measurements were : 97°43′, 97°42′, 97°48′, and 97°44′ ; for the acute angles : 82°22′ and 82°14′. Average 97°44′ and 82°18′.

E. The Action of Nitrogen Trioxide on Anethol.—The nitrosite and its anhydride were prepared by the method of Tönnies[1] for the purpose of comparing their properties with those of the analogous fluid metanethol derivatives. The following method of preparation was finally adopted.

The theoretical amount of sodium nitrite, dissolved in water, was added to a solution of anethol in three times its volume of glacial acetic acid. The mass immediately became viscous and turbid, but it was only after standing several hours that it became nearly solid from the formation of crystalline material. It was then filtered and the contents of the filter recrystallized from ether. Crystals separated from this solvent in the form of long, slender prisms showing very clear

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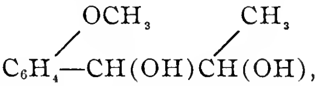
[1] Ber. d. chem. Ges., 11, 1511 (1878).

faces and melting at 98° C. This compound is the anethol nitrosite anhydride or, as Boeris[1] calls it, diisonitrosoanethoil peroxide.

The nitrosite itself was obtained in small quantity by allowing the sodium nitrite and alcohol solution to react together for a much shorter time—about one-half hour—and treating the resulting viscous mass with ether. A portion of the mass dissolves in the ether and another part is deposited in fine needles which melt at about 130° C., and agree in properties with the anethol nitrosite described by Tönnies.

An attempt to prepare the glycol,  $\overset{OCH_3}{C_6H_4}\text{—}CH(OH)\overset{CH_3}{CH}(OH)$, from this compound, following as closely as possible the directions of Tönnies, proved unsuccessful. Attempts to make it by Wagner's[2] method, by the oxidation of anethol with a 1 per cent solution of potassium permanganate, were equally unsuccessful.

The anhydride of the nitrosite crystallized exceedingly well and appeared to be perfectly stable at ordinary temperatures.

A microscopical examination showed the crystals to be doubly refracting and biaxial, and to contain a single plane of symmetry perpendicular to a binary axis of symmetry. They are consequently monoclinic holohedral. A large number of measurements of the six angles in the orthopinacoid zone gave closely agreeing numbers. The average measurements for the angles were: 98°46′, 33°10′.5, and 48°2′, respectively.

F. The Action of Nitrosyl Chloride on Anethol.[3]—The nitrosochloride was prepared in several different ways, all of them based on the use of nascent nitrosyl chloride. The best results were obtained by passing hydrochloric acid gas into an ethereal solution of anethol and amyl nitrite, as follows:

A slow current of dry hydrochloric acid gas was conducted into a mixture of 10 grams anethol and 8 grams amyl nitrite dissolved in 30 grams of ether. Each bubble of hydrochloric acid gas produced a transient brown color. In a few minutes

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[1] Gazz. chim. ital., **21**, 183 (1891).

[2] Ber. d. chem. Ges., **24**, 3488 (1891).

[3] Tönnies: Ber. d. chem. Ges., **12**, 169 (1879); Tilden and Forster: J. Chem. Soc., **65**, 330 (1894).

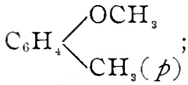
the mixture became nearly solid with the nitrosochloride crystals. These were then filtered off and hydrochloric acid gas again passed into the mother-liquor until it once more became nearly solid with crystals. After this operation had been repeated three or four times the addition of hydrochloric acid gas to the mother-liquor no longer produced a precipitate, but still more of the nitrosochloride separated from the mother-liquor on the addition of alcohol. Finally, the addition of water to the remaining liquid precipitated a small amount of oily matter. The total yield of anethol nitrosochloride obtained by this method was somewhat more than 50 per cent of the theoretical amount. The product was very nearly pure when first prepared, and it is probable that a much larger yield could have been obtained by this method by careful manipulation and the use of pure amyl nitrite instead of the commercial product.

The pure nitrosochloride, when heated slowly, melts with violent decomposition at 123° C. Tilden and Forster give its melting-point as 127° C. It dissolves easily in chloroform, is moderately soluble in toluene, benzene, and acetic ether, slightly soluble in hot absolute alcohol and acetone; and almost insoluble in ordinary alcohol, ether, carbon disulphide, and petroleum ether. It decomposes when heated in solution in chloroform, toluene, acetone, or glacial acetic acid.

The crystals separate from chloroform in the form of tabular plates. An examination of their optical properties showed them to be biaxial, and to give oblique extinction whether examined perpendicularly to their broad surfaces or in cross section. They are therefore triclinic.

FLUID METANETHOL.

The preparation of this compound was carried out in the usual way; namely, by distillation of anisoin and careful separation of the resulting products. For this purpose only pure anisoin, precipitated carefully from acetone solution by alcohol, was used.

The distillation-products of the anisoin were separated by fractional distillation into three distinct compounds. One, of boiling-point 175° C., has been identified as the methyl ether of paracresol,  $C_6H_4\begin{cases}OCH_3\\CH_3(p)\end{cases}$; the second, which boils at 228°–232° C., is fluid metanethol; and the third, whose boiling-point is above 360° C., is the substance known as isoanethol.

The purification of the fluid metanethol was a tedious process. It underwent slight change when distilled under atmospheric pressure so that only an approximate degree of purity could be attained by this means. By distillation under diminished pressure (40 mm.), the purification was carried much farther, although even then slight change appeared to take place, and it was only after seven complete fractionations that a product of sharp boiling-point (142°–143° C. under 40 mm. pressure), and freezing-point (10°.4–10°.7 C.), was isolated.

This compound was finally obtained completely pure by repeated crystallization from alcohol. After one crystallization its melting-point rose to 18°–19° C. Recrystallized once more it became 22°.5 C., and after another recrystallization it still melted at 22°.5 C. This then is the melting-point of pure fluid metanethol, and it is exactly the same as the melting-point of pure anethol. The odor and taste also of this product could not be distinguished from the odor and taste of pure anethol, and its boiling-point was found to be the same as that of pure anethol.

The crystals of the fluid metanethol from alcohol could, in no way, be distinguished from the crystals of anethol from the same solvent. They formed very thin, nearly square, rectangular plates, showing the same biaxial interference figure and probable orthorhombic symmetry as the anethol crystals.

Towards chemical reagents the fluid metanethol was found to behave in every instance in exactly the same way as anethol, as the following experiments show:

A. The action of iodine in concentrated solution in aqueous potassium iodide on fluid metanethol gave a brown, tarry mass, which dissolved easily in acetone and was precipitated from this solvent, by the addition of alcohol, as a white, amorphous powder, having the same appearance and properties as anisoin.

B. A current of dry hydrochloric acid gas passed into fluid metanethol changed it into a heavier oil which could not be distinguished from a specimen of anethol hydrochloride prepared at the same time. Ten grams of the fluid metanethol absorbed 2.5 grams of dry hydrochloric acid gas—2.47 grams being the theoretical amount required for the formation of fluid metanethol hydrochloride, $C_{10}H_{12}O.HCl$. On treating this hydrochloride with alcoholic caustic potash and distilling the resulting product with steam, a light oil passed over. This had a peculiar mint-like odor and yielded anethol on distillation. The oil which resulted by similar treatment of anethol hydrochloride had these same properties and was identified as the alcohol addition-product of anethol,

$$C_{10}H_{12}O.C_2H_5OH.$$

C. The addition of picric acid to an alcoholic solution of fluid metanethol immediately caused the solution to turn red, owing to the formation of the picrate. On evaporation, or by addition of water to the solution, the picrate separates out in the form of bright-red needles, which melt approximately at 70° C. The compound decomposes at its melting-point and is identical in appearance and properties with the corresponding anethol compound.

D. Dibromide of fluid metanethol: This compound was prepared in the same way as the anethol dibromide: that is, by adding bromine, drop by drop, from a burette to a cooled solution of fluid metanethol in ether, until a drop imparted its color to the whole solution. The excess of bromine was removed by shaking the mixture with water saturated with sulphur dioxide. The washed ethereal solution then left behind on evaporation a mass of needle-shaped crystals, which were easily obtained pure by recrystallization from petroleum ether. Their melting-point was determined at 63°.5 C. This compound could, in no way, be distinguished from anethol dibromide.

Monobromine derivative of the dibromide of fluid metanethol: This compound was prepared in exactly the same way as the corresponding anethol compouud. The melting-point of the pure product was determined as 102° C. As to its crystal appearance, solubility, and stability, it is only necessary to repeat what has been said in this connection about the corresponding anethol compound. A microscopical examination showed the crystals to belong to the triclinic system. The same angles were measured as in the case of the monobromanethol dibromide and the following results obtained: Average for the obtuse angles 97° 56′; for the acute angles 82° 6′.

E. The nitrosite and nitrosite anhydride of fluid metanethol, prepared in the same way as the anethol compounds, did not differ from them in any way so far as could be detected. Only a small amount of the nitrosite was obtained, but enough to determine its melting-point, which was found to be 125°–130° C. The anhydride was formed in larger quantity and was more carefully examined. The following characteristics were determined: The compound crystallizes in long, slender, slightly yellow crystals which melt at 98° C. Crystallographically they differ in no respect from the crystals of anethol nitrosite anhydride. The angles in the orthopinacoid zone of a number of crystals were measured, the average angles being found to be 98°46′.5, 33°11′, and 48°2′, respectively.

F. The action of nascent nitrosyl chloride on fluid metanethol produces a compound of the same appearance, melting-point, solubility, and stability as the nitrosochloride of anethol. The symmetry and optical properties of the crystals were determined and the same results obtained as in the case of the anethol compound.

By a comparison of the entire conduct of fluid metanethol with that of anethol it will be seen that it is the same substance. There is therefore no longer any need of the name fluid metanethol to designate the chief product of the distillation of anisoin, as it is, in reality, anethol.

A few other investigations will now be described, first considering the action of alcoholic caustic potash on anethol hydrochloride.

The Alcohol Addition-product of Anethol, $C_{10}H_{12}O.C_2H_6OH$.

The addition of a slight excess of alcoholic caustic potash to anethol hydrochloride at first produced no visible effect, but the mixture soon began to get warm and deposited a copious precipitate of potassium chloride. The mixture was then washed with water, to remove the alcohol and inorganic compounds, and distilled with steam.

Two products were obtained by this treatment in about equal quantities. One, an oil resembling anethol, passed over with the steam. The other remained in the distilling-flask as a semi-solid mass, heavier than water, and was found to consist chiefly of isoanethol and solid metanethol.

The part of the mixture that passed over with the steam was a thin, colorless oil, lighter than water, and had a strong, pleasant, mint-like odor, entirely different from that of anethol. The following experiments showed this substance to be an alcohol addition-product of anethol of the formula

$$C_{10}H_{12}O.C_2H_5OH.$$

(1) The purest product, in ether solution, would take up only one-twelfth the amount of bromine that the same weight of anethol would absorb. It is consequently saturated, there being no doubt that, when entirely free from anethol, it would not absorb bromine at all.

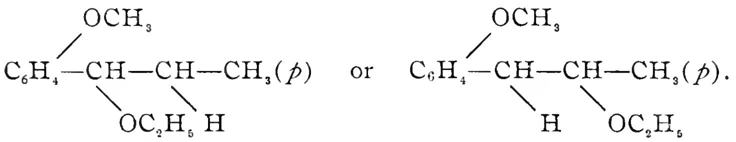
(2) When heated no change is visible until the temperature reaches 200°–210° C. Bubbles then begin to rise from the bottom of the flask and, as the temperature is further increased, the liquid boils vigorously. On distillation, 13 grams of the compound yielded the following products:

(*a*) 2.5 grams of a liquid having the odor and boiling-point of alcohol, and yielding iodoform when treated with potassium hydroxide and iodine. This liquid is evidently alcohol.

(*b*) Approximately 9 grams of a liquid boiling at 225°–230°. This solidified in a freezing-mixture of hydrochloric acid and ice and, by its odor, melting-point, and boiling-point, was identified as anethol.

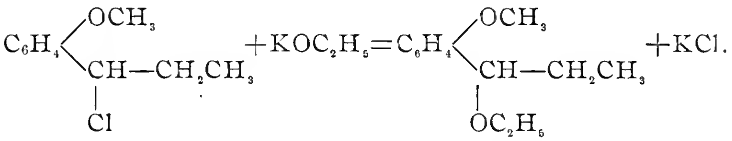
(*c*) There still remained in the distilling-flask about 2 grams of a reddish liquid from which crystals of solid metanethol separated on cooling.

The relative quantities of anethol and alcohol obtained in this experiment indicate that they were present molecule for molecule in the original compound, to which we must accordingly assign the formula $C_{10}H_{12}O.C_2H_5OH$. Structurally it should probably be represented by one of the two following formulas:



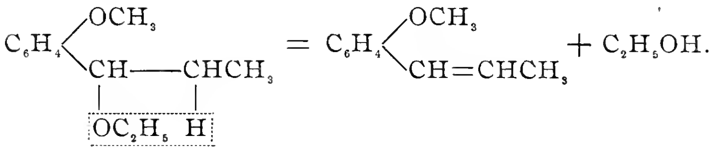
$$\overset{OCH_3}{C_6H_4}-\underset{OC_2H_5}{CH}-\underset{H}{CH}-CH_3(p) \quad \text{or} \quad \overset{OCH_3}{C_6H_4}-\underset{H}{CH}-\underset{OC_2H_5}{CH}-CH_3(p).$$

This alcohol addition-product of anethol probably results from the anethol hydrochloride in accordance with the following equation:



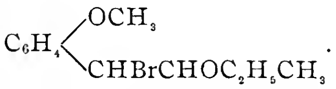
$$C_6H_4\left\langle\begin{array}{l}OCH_3\\ \underset{Cl}{CH}-CH_2CH_3\end{array}\right.+KOC_2H_5=C_6H_4\left\langle\begin{array}{l}OCH_3\\ \underset{OC_2H_5}{CH}-CH_2CH_3\end{array}\right.+KCl.$$

The decomposition of the product on heating would be represented as follows:



$$C_6H_4\left\langle\begin{array}{l}OCH_3\\ \underset{OC_2H_5}{CH}-\underset{H}{CHCH_3}\end{array}\right. = C_6H_4\left\langle\begin{array}{l}OCH_3\\ CH=CHCH_3\end{array}\right. + C_2H_5OH.$$

Perhaps the product obtained by Hell and von Gunthert[1] by the prolonged action of boiling alcohol on anethol dibromide has an analogous constitution. This compound, from the percentage of bromine it contained, was judged to have the formula $C_{10}H_{12}BrO.C_2H_5OH$, and might be regarded as the alcohol addition-product of bromanethol,



$$C_6H_4\left\langle\begin{array}{l}OCH_3\\ CHBrCHOC_2H_5CH_3\end{array}\right..$$

The alcohol addition-product of anethol is but slightly decomposed when distilled with steam. When distilled directly under diminished pressure (40 mm.) the decomposition is greater, but still the larger part remains unaltered.

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[1] J. prakt. Chem., **52**, 199 (1895).

Anethol Hydrobromide.

The hydrobromide of anethol is not mentioned in the literature. It is formed by the action of dry hydrobromic acid gas on anethol in the same way that anethol hydrochloride is formed by the action of dry hydrochloric acid.

A current of dry hydrobromic acid gas was passed into 20 grams of liquid anethol until further addition no longer increased the weight. It was found that 12.5 grams of hydrobromic acid had then been absorbed. In order to remove any excess of hydrobromic acid air was then passed through the liquid until the fumes of the acid, which were copiously evolved at first, ceased to be given off, and even its odor could not be detected. By this treatment with air the product lost 1.5 grams in weight, hence there remained 11 grams of hydrobromic acid in combination with the anethol. The calculated amount with which 20 grams of anethol should unite to form the hydrobromide, $C_{10}H_{12}O.HBr$, is 10.95 grams; and, as succeeding experiments confirmed these results, there can be but little doubt that this formula correctly represents the compound formed in this reaction.

The freshly prepared, crude hydrobromide was tinged slightly green, but became colorless when washed with water. It had previously been noticed that anethol hydrochloride sometimes had this same color when first prepared.

Anethol hydrobromide is a heavy oil of the same consistency and general appearance as the hydrochloride. It does not decolorize a trace of bromine and is consequently saturated. When it is decomposed with alcoholic caustic potash and the resulting oil is distilled, the products are the same as result from the distillation of anethol hydrochloride—anethol and isoanethol.

The hydrobromide reacts readily with aniline, pyridine, piperidine, or zinc dust, yielding resinous products that were not fully identified, but which consisted in part of isoanethol and solid metanethol.

The Action of Sulphuric Acid on Anethol.

Anethol itself apparently does not dissolve in sulphuric acid. Dilute sulphuric acid has no appreciable effect upon it unless the two are left in contact for a considerable time. The concentrated acid polymerizes it at once into anisoin, and the latter dissolves slowly, yielding a red solution. Hot concentrated, or fuming, sulphuric acid acts violently on anethol, causing a rapid evolution of sulphur dioxide and completely charring the mass which is left.

It is stated by Cahours[1] that the red solution, formed by the action of sulphuric acid on anisoin, contains an acid substance which unites with baryta and lime with the formation of resinous products. These he did not further examine.

In order to determine the nature of this acid we have prepared and examined it as follows: 5 grams of anethol were treated, drop by drop, with concentrated sulphuric acid until about 20 grams of the latter had been introduced. The anisoin, which was first formed, dissolved very slowly, but at the end of two days had wholly disappeared. After standing still another day the addition of a liter of water to the red solution did not produce the least turbidity. This diluted solution was nearly neutralized with precipitated chalk, filtered, and the filtrate, after the addition of a little lime-water, evaporated to small bulk on the water-bath. The residue was a resinous mass which dried to a powder on still longer standing, the latter being extremely soluble in water, although very insoluble in alcohol, acetone, or ether. Attempts were made to crystallize it from water or a mixture of water with methyl or ethyl alcohols, but the same gummy product always separated out. It was not sufficiently soluble to crystallize from solvents containing no water, and, when any water was present, enough would be taken up by the substance to form a resinous mass.

The substance was finally dissolved in alcohol (50 per cent) and reprecipitated by the addition of alcohol (90 per cent). The white powder thus obtained was subjected to the same treatment again and then dried at 120° C. until its weight was constant. An analysis of this dried product for calcium gave the following results:[2]

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[1] Ann. chim. phys. (III), 2, 274 (1841).

[2] In the calculation of all the analyses in this work the atomic weights used were: C = 12, O = 16, H = 1, S = 32, Ca = 40.

I. 0.2550 gram substance gave 0.0723 gram $CaSO_4$.
II. 0.2454 gram substance gave 0.0679 gram $CaSO_4$.

	Calculated for $(C_{10}H_{13}OSO_4)_2Ca$.	Calculated for $(C_{10}H_{11}OSO_3)_2Ca$.	Found. I.	Found. II.
Ca	7.54	8.1	8.34	8.13

Although from the method of preparation and properties of the salt it was expected that it would agree in composition with the first formula, the analyses indicate that the second formula is correct. Gerhardt[1] made an acid by the action of concentrated sulphuric acid on the so-called fluid metanethol, to which he gave the name sulphanethinic acid. From this acid he prepared the barium salt, which resembled the above calcium salt closely and on analysis gave results in accord with the formula $(C_{10}H_{11}OSO_3)_2Ba + 2H_2O$.

Anethol Dihydride (Parapropyl Anisol).[2]

The reduction of anethol was accomplished by adding to its solution in absolute alcohol three times the theoretical amount of sodium necessary for the formation of the dihydro addition-product. The sodium was introduced in bits the size of a pea, the whole operation taking perhaps two hours. The yield of the reduction-product was found to be much larger when the reaction took place at as low a temperature as possible than when it took place at the boiling temperature of the alcohol. Under the former conditions a 50 per cent yield was obtained.

The addition of water to the reaction-products precipitated an oil which, after being washed, dried, and fractionally distilled, was found to contain, besides anethol, a liquid which boiled at 210°–214° C. This would unite directly with only about 0.1 the amount of bromine that would be absorbed by the same weight of anethol. It was evident from this conduct that the reduction-product was a saturated compound but still containing as an impurity a small quantity of anethol. This remaining trace was completely removed by dissolving the mixture in a concentrated solution of iodine in acetone and heating to boiling for a few minutes. Alcohol was then

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[1] J. prakt. Chem., **36**, 275 (1845).

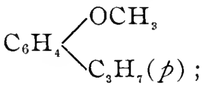
[2] See also Ladenburg: Ann. Chem. (Liebig), Supl. Bd. **8**, 89 (1872); Landolph: Ber. d. chem. Ges., **13**, 144 (1880); and Klages: *Ibid.*, **32**, 1436 (1899).

added to precipitate the anisoin, the mixture boiled with zinc dust to remove the iodine, and filtered. Water added to the filtrate precipitated an oil which was then further purified by being washed with water, dried, and redistilled. The distillate would not unite with bromine and was consequently free from anethol. Its boiling-point was determined as 212°.5–213°.5 C. (corr.) at 728 mm. barometric pressure. A combustion gave the following results :[1]

0.1771 gram substance gave 0.5178 gram CO_2, and 0.1538 gram H_2O.

	Calculated for $C_{10}H_{14}O$.	Found.
C	80.00	79.73
H	9.33	9.65

From its boiling-point and percentage composition we must conclude that this substance is parapropylanisol,



$$C_6H_4\begin{cases}OCH_3\\C_3H_7(p)\end{cases};$$

and, as it is formed by the reduction of anethol, it is probably the normal propyl compound. It was identical with one of the compounds formed by heating anethol under pressure.[1]

ANISOIN.

Of the methods described for the preparation of anisoin the two which have been especially recommended are : (1) The polymerization of anethol by means of concentrated sulphuric acid ; and (2) The polymerization by means of a concentrated solution of iodine in aqueous potassium iodide. There are disadvantages to both of these methods. Unless the substances are left in contact for a long time, the anisoin formed will retain included some unchanged anethol, as well as a certain quantity of the reagent, and will consequently be difficult to purify.

A method which on repeated trial in this work has been found to give much better results is the one described below. To a moderately concentrated solution of anethol in acetone,

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[1] This analysis was made by Mr. J. E. Teeple, to whom we wish here to express our thanks.

[2] This JOURNAL, **19**, 863.

iodine is added until no more will dissolve. The mixture is heated to boiling for a few minutes, after which the iodine is removed by adding zinc dust, little by little, to the warm solution until it becomes nearly colorless. This solution, which must not be too concentrated, is then filtered slowly into several times its volume of alcohol. The anisoin is thus thrown down as a white powder, nearly pure.

No anisoin is formed by adding anethol to a concentrated solution of iodine in alcohol even though the mixture be heated to boiling.

Methyl Ether of Paracresol.

When anisoin is distilled there is one product formed in so small quantity that it has not hitherto been isolated. By distilling a large amount of anisoin (500 grams) and carefully fractionating the resulting products, we obtained, together with approximately 250 grams of anethol and 80 grams of isoanethol, about 20 grams of a liquid which distilled at 173°–175° C.

This liquid doubtless still contained a slight trace of anethol, but so little that it could scarcely be detected by testing an ethereal solution with bromine. One-fiftieth part of a gram of bromine imparted its color to an ethereal solution of 1 gram of the substance. Hence it follows that the substance not only does not contain anethol, but is itself a saturated compound. Combustion analyses gave the following results :[1]

I. 0.2465 gram substance gave 0.1727 gram H_2O, and 0.8084 gram CO_2.

II. 0.1986 gram substance gave 0.1475 gram H_2O, and 0.5719 gram CO_2.

	Calculated for $C_8H_{10}O$.	Found. I.	II.
C	78.68	78.38	78.54
H	8.19	7.79	8.25
O	13.13	13.83	13.21

The analyses show that the compound is correctly represented by the formula $C_8H_{10}O$.

This same compound was obtained in our previous investi-

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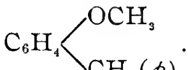
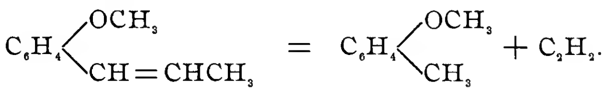
[1] These analyses were made by Mr. J. E. Teeple, to whom we wish here to express our thanks.

gation by heating anethol under pressure, and analyses of this product and molecular weight determinations showed it to have the composition $C_8H_{10}O$.

The percentage composition of the compound, its boiling-point and its other properties, show it to be identical with the methyl ether of paracresol described in the literature. It consequently has the structural formula,  $C_6H_4\Big\langle\begin{matrix}OCH_3\\CH_3(p)\end{matrix}$. It is probably formed by the action of heat on the anethol (or fluid metanethol), resulting from the decomposition of anisoin according to the following equation:

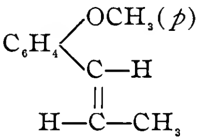


$$C_6H_4\Big\langle\begin{matrix}OCH_3\\CH{=}CHCH_3\end{matrix} \quad = \quad C_6H_4\Big\langle\begin{matrix}OCH_3\\CH_3\end{matrix} + C_2H_2.$$

SUMMARY OF RESULTS.

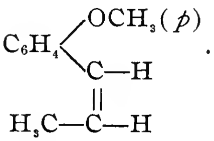
Anethol and Fluid Metanethol.

The properties and reactions of anethol and fluid metanethol have been given especial prominence in this work because, from the results of our earlier investigations, it seemed probable that they were stereoisomers of the maleic-fumaric acid type and would be represented by the two formulas:

I. 

$$C_6H_4\Big\langle\begin{matrix}OCH_3(p)\\ \begin{matrix}C{-}H\\ \| \\ H{-}C{-}CH_3\end{matrix}\end{matrix}$$

and

II. 

$$C_6H_4\Big\langle\begin{matrix}OCH_3(p)\\ \begin{matrix}C{-}H\\ \| \\ H_3C{-}C{-}H\end{matrix}\end{matrix}.$$

It was to be expected that two stereoisomers of this type would resemble each other very closely; and that, with many reagents, they would yield exactly the same products. Consequently it was only after the two substances were very carefully examined and found to exhibit no differences whatever, either in their own conduct or in the conduct of their derivatives, that their complete identity was finally established. The facts upon which this conclusion is based may be briefly summarized as follows:

1. The physical properties of the two are identical. In

odor, taste, boiling-point, melting-point, specific gravity, and crystal form, the pure products exhibit no differences.

2. Both substances show exactly the same chemical conduct.

They yield the same dibromide and monobrom dibromide, which conduct is a strong proof of their identity since stereoisomers of the formulas given above should not yield identical derivatives of this character.

They yield the same hydrochloride, nitrosite, nitrosite anhydride, nitroso chloride, and picrate. This conduct might not preclude the possibility of their being stereoisomers, but it at least shows conclusively that they are structurally identical.

The identity in conduct of these compounds toward polymerizing and oxidizing agents might also be cited, but the evidence seems already conclusive that anethol and fluid metanethol are one and the same compound.

That the true character of fluid metanethol was not earlier discovered is doubtless due to the difficulty of separating it from the methyl ether of paracresol which is formed simultaneously with it. The presence of this impurity, even in small quantity, lowers the melting-point of anethol many degrees and completely masks its odor.

Anethol Hydrochloride.

The conclusion of Saussure and Cahours that the product formed by the action of hydrochloric acid on anethol is a chemical compound of the formula $C_{10}H_{12}O.HCl$, has been confirmed by the results obtained in this investigation. One molecule of anethol has been found to absorb exactly 1 molecule of hydrochloric acid. The resulting product will not take up bromine in the cold and hence contains no free anethol. Moreover, by the action of alcoholic caustic potash, it yields an alcohol addition-product of anethol,

$$C_{10}H_{12}O.C_2H_5OH,$$

the formation of which it is difficult to explain without assuming that the hydrochloride is first formed. Also, the fact that anethol absorbs exactly 1 molecule of hydrobromic acid, with the formation of a saturated chemical compound, would lead us to infer by analogy that its union with hydrochloric acid is of the same character.

The Alcohol Addition-product of Anethol.

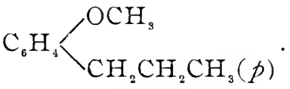
A compound of the formula $C_{10}H_{12}O.C_2H_5OH$ is formed by the action of alcoholic caustic potash on anethol hydrochloride. This compound has a pleasant mint-like odor. It is a thin liquid, lighter than water, and is but slightly decomposed when distilled with steam. When distilled alone it breaks down completely, yielding alcohol, anethol, and higher-boiling products. It is not attacked by bromine in the cold.

Anethol Hydrobromide.

Anethol rapidly absorbs hydrobromic acid gas until it has taken up the amount required for the formation of a compound of the formula $C_{10}H_{12}O.HBr$. The hydrobromide is a heavy oil closely resembling anethol hydrochloride in appearance and conduct. When decomposed by alcoholic caustic potash and distilled, it yields as the chief products anethol and isoanethol.

Parapropylanisol.

This compound results from the action of sodium on an alcoholic solution of anethol, and is also formed as one of the products when anethol is heated at a high temperature under pressure. Analyses and molecular weight determinations show its formula to be $C_{10}H_{14}O$; and, since it is formed by the addition of two hydrogen atoms to the anethol molecule, its structure is most probably represented by the formula,



$$C_6H_4\left\langle\begin{array}{l}OCH_3\\CH_2CH_2CH_3(p)\end{array}\right..$$

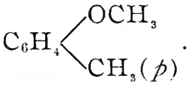
Anisoin.

It has been found most practicable to prepare anisoin by adding anethol to a saturated solution of iodine in acetone and heating the resulting mixture to boiling for a few minutes. By this means the anethol appears to be rapidly and completely converted into anisoin.

When distilled, anisoin is completely decomposed, yielding the compounds anethol, isoanethol, and the methyl ether of paracresol.

Methyl Ether of Paracresol.

One of the products formed by the breaking down of anisoin on distillation is a light, colorless oil, of pungent odor, which boils at a temperature of 175° C. This same compound has been previously obtained by the action of heat and pressure on anethol. Perhaps, in its formation from anisoin, the latter is first converted into anethol, and this is then partially decomposed into the lower-boiling product. The physical properties of this compound, as well as its percentage composition and molecular weight, identify it as the methyl ether of paracresol,



$$C_6H_4\begin{cases}OCH_3\\CH_3\,(p)\end{cases}.$$

Cornell University, Ithaca, N. Y.,
December, 1899.

THE SUPPOSED ISOMERIC POTASSIUM SODIUM SULPHITES.[1]

By Geo. S. Fraps.

INTRODUCTION.

The prevailing view in regard to the structure of sulphurous acid is that it is asymmetrical and has the formula $\mathrm{H{-}SO_2{-}OH}$. From this formula it is theoretically possible to derive two isomeric sodium potassium sulphites; namely, $\mathrm{K{-}SO_2{-}ONa}$ and $\mathrm{Na{-}SO_2{-}OK}$. Descriptions of these salts are on record. By neutralizing a concentrated aqueous solution of acid potassium sulphite with sodium carbonate, and precipitating with alcohol, A. Röhrig[2] obtained fine lustrous crystals of the composition $KNaSO_3 + 2H_2O$, which he believed to be isomeric with crystals of the same composition made in a similar manner from acid sodium sulphite and potassium carbonate. The statement was probably based on the assumed reactions:

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[1] This work was suggested by Prof. Ira Remsen, and conducted under his direction in the laboratory of the Johns Hopkins University.

[2] J. prakt. Chem. [2], **37**, 250.

$$2H—SO_2—OK + Na_2CO_3 = 2Na—SO_2—OK + CO_2 + H_2O;$$
$$2H—SO_2—ONa + K_2CO_3 = 2K—SO_2—ONa + CO_2 + H_2O.$$

H. Schwicker[1] prepared the salts in a similar manner, but, instead of precipitating with alcohol, he evaporated the solutions in a desiccator over sulphuric acid. The crystals contained different amounts of water of crystallization. The one from acid potassium sulphite and sodium carbonate separated in crystals having the composition $NaKSO_3 + 2H_2O$; the crystals of the other, from acid sodium sulphite and potassium carbonate, had the formula $NaKSO_3 + H_2O$.

By the aid of the reaction between ethyl iodide and a sulphite, in which the metal united to the sulphur is replaced by ethyl, thus:

$$C_2H_5I + Na—SO_2—ONa = C_2H_5—SO_2—ONa + NaI,$$

we might be able to determine if the salts described above are isomeric or identical, since, if different, the one should yield a sodium ethylsulphonate, the other a potassium ethylsulphonate:

$$C_2H_5I + K—SO_2—ONa = C_2H_5—SO_2—ONa + KI;$$
$$C_2H_5I + Na—SO_2—OK = C_2H_5—SO_2—OK + NaI;$$

or more correctly, the double salt $4C_2H_5SO_3Na + KI$ could be extracted from the reaction-product of the first, and the salt $4C_2H_5SO_3K + NaI$ from that of the other.

According to Schwicker, when the sodium potassium sulphite made from acid sodium sulphite and potassium carbonate is heated in aqueous solution in a sealed tube with ethyl iodide and the product recrystallized from alcohol, it contains sodium and potassium in the ratio Na : K : : 4 : 1, corresponding to the double salt $4C_2H_5SO_3Na + KI$. The salt from acid potassium sulphite and sodium carbonate under the same conditions yielded a product containing Na : K : : 1 : 4, corresponding to the double salt $4C_2H_5SO_3K + NaI$. This indicates that isomeric salts have been prepared, having the formulas $K—SO_2—ONa$ and $Na—SO_2—OK$. Schwicker states further that, by boiling the isomeric sulphites with ammonium

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[1] Ber. d. chem. Ges., **22**, 1728.

polysulphide, they are converted into isomeric thiosulphates, which, when heated with ethyl bromide (Bunte's reaction), yield, the one the sodium salt, $C_2H_5S_2O_3Na + H_2O$, the other the potassium salt, $C_2H_5S_2O_3K$.

More recently this work has been repeated by K. Barth[1] in the course of an investigation on the complex salts of sulphurous acid. The acid sulphite was formed by passing sulphur dioxide into a strong solution of sodium (or potassium) hydroxide, and neutralized by the requisite quantity of a solution of potassium (or sodium) hydroxide. Alcohol precipitated both salts as water-free crystals, not the crystals

$$NaKSO_3 + 2H_2O,$$

of Röhrig. Under ordinary conditions, the crystals formed by evaporation over sulphuric acid in a desiccator were water-free, but, when cooled, crystals separated which had the composition of those obtained by Schwicker.

Barth heated the equally concentrated solutions of the water-free salts—the concentration is not given—with ethyl iodide in a sealed tube at 130° for three hours, evaporated to dryness, extracted the residue with 97 per cent alcohol, and recrystallized from 99 per cent alcohol. The product was analyzed by igniting with sulphuric acid, and determining the sulphuric acid in the residue, from which the ratio Na : K was calculated. The potassium sodium sulphite from acid sodium sulphite and caustic potash yielded a product containing Na : K : : 1 : 1.3 (mean of two preparations); theory requires for the salt $4C_2H_5SO_3Na + KI$, Na : K : : 4 : 1. The salt from acid potassium sulphite and sodium hydroxide yielded a product containing Na : K : : 1 : 2.9 (mean of two) instead of Na : K : : 1 : 4 as required by the theory. The two sodium potassium sulphites yielded different products, and must therefore be different.

Barth explained the deviation of the results from the theoretical in terms of the theory of electrolytic dissociation. He showed that the salts dissociate into three ions. When the ions K, Na, SO_3, from the salt KSO_2ONa, for example, are caused to reunite, as by evaporation of the solution, or precipitation

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[1] Ztschr. phys. Chem., 9, 77.

with alcohol, there is no reason to suppose the salt KSO_2ONa to be formed again, but rather a mixture of the salts $NaSO_2OK$, KSO_2ONa, Na_2SO_3, and K_2SO_3, and the pure salt KSO_2ONa could not be obtained. Again, when the reaction betweed the ethyl iodide and the salt has taken place, the potassium iodide and the sodium ethylsulphonate must be dissociated to some extent, and potassium ethylsulphonate and sodium iodide must be formed when the solution is evaporated to dryness. The alcohol from which the salt is recrystallized must exert some influence on its composition also. Hence one could not expect the ratio of sodium to potassium to agree with that required by theory. Barth states that "an infallible conclusion as to the different constitution of the sulphites cannot be drawn from the results obtained, but only that in one solution more molecules of KSO_2ONa were present, in the other more molecules of $NaSO_2OK$, and hence the probability of the isomerism of the solid bodies."

The conclusion does not appear to be accepted. Hantzsch[1] asserts that structural isomerism is unknown among inorganic compounds. A Sabanejeff[2] observes that the isomerism of the potassium sodium sulphites can by no means be regarded as proved.

The stability of the salts appears incompatible with the theory of electrolytic dissociation, since they dissociate into three ions. If dissociation is conceived as a dynamic condition, in which the molecules are in a constant vibration of decomposition and recombination, it is difficult to see how the salts $K—SO_2—ONa$ and $Na—SO_2—OK$, supposing them to exist as solids, could long retain their individuality even in concentrated solutions. In a certain time the undissociated portion of the salts must assume a condition of equilibrium of the salts K_2SO_3, Na_2SO_3, $KNaSO_3$, which would be the same whether sodium potassium sulphite or potassium sodium sulphite were the starting-point. That is to say, isomeric salts of such a nature could not remain different in aqueous solution, even if they exist in the solid state.

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[1] Ann. Chem. (Liebig), **292**, 342; **296**, 100, 111.

[2] Ztschr. anorg. Chem., **17**, 481.

The same objection applies to the reaction used to prove that the two salts are different, or Guldberg and Waage's law of mass action may be applied. Supposing the following reactions to take place:

$$C_2H_5I + KSO_2ONa = C_2H_5SO_2ONa + KI;$$
$$C_2H_5I + NaSO_2OK = C_2H_5SO_2OK + NaI.$$

The reaction

$$C_2H_5SO_2ONa + KI \rightleftarrows C_2H_5SO_2OK + NaI$$

must surely be a reversible one, and the condition of equilibrium would be the same from either starting-point; at 130° the adjustment would not take long.

These considerations throw doubt upon the work before cited, and it was repeated. Before going into details, a brief summary of the experiments will be given. Four sets of the double salts were prepared, under conditions judged most favorable to the appearance of isomerism, one member of the set from acid sodium sulphite and potassium carbonate or hydroxide, the other from acid potassium sulphite and sodium carbonate or hydroxide. The salts in each set were made under exactly similar conditions and at the same time, with the exception of set I, as hereafter noted. In set I the salts were not analyzed; in set II they were slightly different in composition; and in sets III and IV they had practically the same composition.

The two salts, which it was thought might be isomeric, were heated with ethyl iodide, the products extracted with alcohol and analyzed, the supposed isomers being subjected to conditions as nearly identical as possible. Seven experiments were thus made, in which the strength of alcohol, time of heating, etc., were varied slightly. If the salts were isomers, analysis should show a difference in the ratio of sodium to potassium; in none of the experiments was there any decided variation. It is believed that the conditions were as favorable for the isomerism to reveal itself as it was possible to make them. The writer therefore feels justified in making the statement that we have no evidence that isomeric potassium sodium sulphites exist.

The table shows the ratio of sodium to potassium as found by analysis of the double sulphonate prepared from the two salts.

	$NaSO_2OK$.	KSO_2ONa.
Na : K required by theory....	1 : 4	4 : 1
" found by Barth	1 : 2.9	1 : 1.3
" Experiment I	1 : 1.57	1 : 1.40
" " II	1 : 1.43	1 : 1.37
" " III	1 : 1.89	1 : 2.17
" " IV	1 : 1.59	1 : 1.57
" " V	1 : 2.09	1 : 2.10
" " VI	1 : 2.06	1 : 2.01
" " VII	1 : 1.82	1 : 1.73

The variation in the ratio Na : K in the different experiments is ascribed to the difference in the conditions. The stronger the alcohol used, the wider the ratio. Recrystallization from alcohol increased the ratio also, as may be seen by comparing Experiments I, II, and IV, in which the sulphonate was not recrystallized, with Experiments III, V, VI and VII, in which it was recrystallized from alcohol. The slight variation between the two members of a set was to be expected and is probably due to the alcohol.

EXPERIMENTAL.

Experiment I.—Sulphur dioxide was passed into a cooled solution of 11.5 grams of potassium carbonate in 75 cc. water until the weight gained was that required for the formation of acid potassium sulphite. Nine grams of sodium carbonate were added, air drawn through to remove carbon dioxide, and the salt precipitated with alcohol. It was not analyzed.

Ten grams of the above salt, 11 grams ethyl iodide, and 15 cc. water were heated two and a half hours in a sealed tube to 130°–140°, and the tube allowed to cool over night. The solution was evaporated to dryness, and the product extracted with laboratory alcohol. It was not recrystallized.

Analysis showed the ratio of sodium to potassium to be Na : K : : 1 : 1.57. Theory for $4C_2H_5SO_3K + NaI$, 1 : 4.

(1) 0.3381 gram substance, ignited with sulphuric acid, gave 0.1922 gram sulphates, yielding 0.2771 gram barium sulphate.

Per cent SO_3 in sulphates = 49.52. Na : K : : 1 : 1.54.

(2) 0.2848 gram substance gave 0.1612 gram sulphates, yielding 0.2320 gram barium sulphate.

Per cent SO_3 in sulphates = 49.43. Na : K : : 1 : 1.59.

Proceeding exactly as above, and performing the operations at the same time and under the same conditions, but using a solution of 9 grams sodium carbonate in 32 cc. of water, and adding 11.5 grams of potassium carbonate, the supposed isomeric salt was prepared. It was treated with ethyl iodide under the same conditions, at the same time as the above, the product extracted with the same alcohol, and analyzed. The ratio of sodium to potassium was 1 : 1.40; a slight difference, but no evidence of isomerism.

(1) 0.3892 gram substance gave 0.2117 gram sulphates, yielding 0.3067 gram barium sulphate.

Per cent SO_3 in sulphate = 49.77 Na : K : : 1 : 1.38.

(2) 0.2858 gram substance gave 0.1545 gram sulphates, yielding 0.2235 gram barium sulphate.

Per cent SO_3 in sulphates = 49.69. Na : K : : 1 : 1.41.

In the experiment above described, the two salts were prepared in solution of different concentrations, for the reason that it seemed to be desirable to use as concentrated solutions as possible, and acid potassium sulphite is less soluble than acid sodium sulphite. In succeeding experiments the salts are prepared in solutions of equivalent concentration.

Experiment II.—The salts were prepared as in Experiment I, with the exception that the solutions were of different concentration, *i. e.*, 23 grams of potassium carbonate in 120 cc. water, and 18 grams of sodium carbonate in the same quantity.

Analysis of the salts:

(*a*) Salt from acid potassium sulphite and sodium carbonate:

(1) 0.3344 gram substance, with sulphuric acid, gave 0.3657 gram mixed sulphates, which yielded 0.5403 gram barium sulphate. Na : K : : 1 : 0.94.

(2) 0.2899 gram substance gave 0.3180 gram sulphates, yielding 0.5403 gram barium sulphate. Na : K : : 1 : 0.99.

(*b*) Salt from acid sodium sulphite and potassium carbonate:

(1) 0.4505 gram substance gave 0.4756 gram sulphates, yielding 0.7119 gram barium sulphate. Na : K : : 1 : 0.72.

(2) 0.5432 gram substance gave 0.5762 gram sulphates, yielding 0.8614 gram barium sulphate. Na : K : : 1 : 0.74.

The ratio of sodium to potassium in the two salts is different. The analyses show the crystals to be water-free.

Ten grams of the salt (*a*), from acid potassium sulphite and sodium carbonate, 11 grams ethyl iodide, and 21 cc. water, were heated three hours in a sealed tube to 130°–140°. The solution was evaporated to dryness, the product extracted with laboratory alcohol, and analyzed. The ratio Na : K was found to be 1 : 1.43.

(1) 0.1881 gram substance, ignited with sulphuric acid, gave 0.1004 gram sulphates, which yielded 0.1452 gram barium sulphate.

Per cent SO_3 in sulphates = 49.67. Na : K : : 1 : 1.44.

(2) 0.2580 gram substance gave 0.1389 gram sulphates, yielding 0.2010 gram barium sulphate.

Per cent SO_3 in sulphates = 49.70. Na : K : : 1 : 1.41.

Ten grams of salt (*b*) was treated as above and at the same time. The ratio of Na : K in the product was 1 : 1.37. Salt (*a*) was not different from salt (*b*).

(1) 0.1500 gram substance gave 0.0798 gram sulphates, yielding 0.1162 gram barium sulphate.

Per cent SO_3 in sulphates = 50.01 Na : K : : 1 : 1.23.

(2) 0.2179 gram substance gave 0.1164 gram sulphates, yielding 0.1679 gram barium sulphate.

Per cent SO_3 in sulphates = 49.54. Na : K : : 1 : 1.51.

The composition of the two products was practically the same.

It will be noted that laboratory alcohol of unknown strength was used in the foregoing experiments. The strength of the alcohol must have some effect on the composition of the product, since that double salt would crystallize out that was most insoluble under the conditions of the experiment. For this reason it was determined to repeat the work, using alcohol of different strength.

The double sulphites used in the experiments about to be described were prepared as follows: A solution of caustic potash was prepared, containing 172.2 grams of caustic potash in a liter, the strength being determined by titration with standard acid, and also a solution of caustic soda containing 124.2 grams per liter. 100 cc. of the solution were cooled with ice-water, and sufficient dry sulphur dioxide (from sodium sulphite and sulphuric acid) passed in to form the acid salt, controlling the amount of sulphur dioxide by weighing. In case an excess of sulphur dioxide was absorbed, the volume of the solution containing the required amount of the proper alkali was added, keeping the liquid cool. The acid sulphite so formed was neutralized with the requisite volume of the other alkali and the double salt precipitated immediately with 500 cc. of alcohol, washed with alcohol, and dried on drying-paper. It is believed that these conditions are most favorable to the production and retention of the isomerism, if it exists.

Experiments III and IV.—Salts were prepared as just described, and analyzed.

(*a*) From acid potassium sulphite and caustic soda:

(1) 0.5150 gram substance gave 0.5705 gram sulphates, and yielded 5 × 0.1637 gram K_2PtCl_6.

K_2O = 30.69 per cent. Na : K : : 1 : 0.86.

(2) 0.5200 gram substance gave 0.5759 gram sulphates, and 5 × 0.1664 gram K_2PtCl_6.

K_2O = 30.85. Na : K : : 1 : 0.87.

(*b*) Salt from acid sodium sulphite and caustic potash.

(1) 0.5409 gram substance gave 0.5956 gram sulphates, and yielded 5 × 0.1703 gram K_2PtCl_6.

K_2O = 30.40. Na : K : : 1 : 0.85.

(2) 0.5080 gram substance gave 0.5585 gram sulphates, and yielded 5 × 0.1583 gram K_2PtCl_6.

K_2O = 30.08. Na : K : : 1 : 0.84.

The salts had practically the same composition and were anhydrous.

Experiment III.—Ten grams of each of the above salts, 21 grams water, and 11 grams ethyl iodide, were heated in sealed tubes for three hours at 130°–140°. The tubes cooled over night. Their contents were then evaporated to dryness, extracted with 500 cc. of alcohol, sp. gr. 0.839, and recrystallized from 250 cc. of alcohol of sp. gr. 0.7975.

Analysis of the products .

(*a*) From salt (*a*).

(1) 0.2421 gram substance gave 0.1325 gram sulphates, and yielded 0.2546 gram K_2PtCl_6.

$$K_2O = 20.3. \quad Na : K :: 1 : 1.79.$$

(2) 0.7376 gram substance gave 0.4050 gram sulphates, and yielded 5/2 × 0.3206 gram K_2PtCl_6.

$$K_2O = 20.98. \quad Na : K :: 1 : 1.99.$$

(*b*) From salt (*b*).

(1) 0.2753 gram substance gave 0.1526 gram sulphates, and yielded 0.3092 gram K_2PtCl_6.

$$K_2O = 21.68. \quad Na : K :: 1 : 2.14.$$

(2) 0.5876 gram substance gave 0.3256 gram sulphates, and yielded 5/2 × 0.2675 gram K_2PtCl_6.

$$K_2O = 21.97. \quad Na : K :: 1 : 2.21.$$

This experiment was supposed to be as nearly as possible a repetition of Barth's, but it did not confirm his results.

Experiment IV.—Six grams of the above salts, 7 grams ethyl iodide, and 12 grams water were heated to 130°–136° for three hours. The contents of the tube were evaporated to dryness the same day, and extracted with alcohol of sp. gr. 0.804. The product was not recrystallized.

Analysis of the products :

(*a*) From salt (*a*).

1.0211 gram substance gave 0.5557 gram sulphates, which gave 5 × 0.2057 and 5 × 0.2049 gram K_2PtCl_6.

$$K_2O \begin{cases} 19.45. \\ 19.40 \end{cases} \quad Na : K \begin{cases} 1 : 1.60. \\ 1 : 1.59 \end{cases}$$

(*b*) From salt (*b*).

1.1822 gram substance gave 0.6421 gram sulphates, which gave 5 × 0.2370 and 5 × 0.2363 gram K_2PtCl_6.

$$K_2O \left\{ \begin{array}{l} 19.36. \\ 19.30 \end{array} \right. \qquad Na : K \left\{ \begin{array}{l} 1 : 1.58. \\ 1 : 1.57 \end{array} \right.$$

The ratio of sodium to potassium is the same in the products from both salts. It will be noted that the ratio is different from that in Experiment III, which is 1 : 1.89 and 1 : 2.21. Recrystallization from stronger alcohol increases the ratio.

Experiments V, VI, and VII.—The supposed isomeric potassium sodium sulphites were prepared exactly as for Experiments III and IV.

Analysis of the salts:

(*a*) Salt from acid potassium sulphite and caustic soda.

(1) 0.5527 gram substance gave 0.6090 gram sulphates, yielding 5 × 0.1709 gram K_2PtCl_6.

$K_2O = 29.85$. Na : K : : 1 : 0.82.

(2) 0.5051 gram substance gave 0.5588 gram sulphates, yielding 5 × 0.1578 gram K_2PtCl_6.

$K_2O = 30.08$. Na : K : : 1 : 0.83.

(*b*) From acid sodium sulphite and caustic potash.

(1) 0.5035 gram substance gave 0.5565 gram sulphates, yielding 5 × 0.1574 gram K_2PtCl_6.

$K_2O = 30.18$. Na : K : : 1 : 0.84.

(2) 0.5167 gram substance gave 0.5727 gram sulphates, 5 × 0.1607 gram K_2PtCl_6.

$K_2O = 30.02$. Na : K : : 1 : 0.82.

The salts were anhydrous and had practically the same composition.

Experiment V.—The operation was carried on the same as Experiment III, and under the conditions there described.

Analysis of the products:

(*a*) From salt (*a*).

0.3275 gram substance gave 0.1802 gram sulphates, yielding 0.3626 gram K_2PtCl_6.

$K_2O = 21.37$. Na : K : : 1 : 2.09.

(*b*) From salt (*b*).

0.2115 gram substance gave 0.1076 gram sulphates, yielding 0.2169 gram K_2PtCl_6.

$K_2O = 19.80$. Na : K : : 1 : 2.10.

There is no evidence of isomerism ; the ratio of sodium to potassium is nearly as in Experiment III.

Experiment VI.—Ten grams of the double sulphites described above, 11 grams ethyl iodide, and 20 grams water, were heated as in the preceding experiment. The contents of the tube were evaporated to dryness the same day, the residue extracted with 500 cc. alcohol (sp. gr. 0.803) and recrystallized from 250 cc. alcohol of 0.795 sp. gr.

Analysis of the products :

(*a*) From salt (*a*).

0.8606 gram substance gave 0.4710 gram sulphates, and yielded 5 × 0.1887 gram K_2PtCl_6.

$K_2O = 21.16$. Na : K : : 1 : 2.06.

(*b*) From salt (*b*).

0.2361 gram substance gave 0.1297 gram sulphates, and yielded 0.2602 gram K_2PtCl_6.

$K_2O = 21.28$. Na : K : : 1 : 2.01.

Experiment VII.—Ten grams of the double sulphites described above, 11 grams ethyl iodide, and 20 grams water, were heated in sealed tubes at the same time as Experiment III. The contents of the tubes were evaporated to dryness the same day. The product was extracted with alcohol of 0.808 sp. gr. and recrystallized from alcohol of 0.803 sp. gr.

Analysis of the products :

(*a*) From salt (*a*).

(1) 0.9116 gram substance gave 0.4978 gram sulphates, yielding 5 × 0.1910 gram K_2PtCl_6.

$K_2O = 20.23$. Na : K : : 1 : 1.78.

(2) 1.0257 grams substance gave 0.5602 gram sulphates, yielding 5 × 0.2180 gram K_2PtCl_6.

$K_2O = 20.25$. Na : K : : 1 : 1.86.

(*b*) From the salt (*b*).

(1) 0.9551 gram substance gave 0.5123 gram sulphates, of which 0.4632 gram gave 5 × 0.1768 gram K_2PtCl_6.

$K_2O = 19.77$. Na : K : : 1 : 1.75.

(2) 1.2675 gram substance gave 0.6916 gram sulphates, yielding 5 × 0.2617 gram K_2PtCl_6.

$K_2O = 19.93$. Na : K : : 1 : 1.70.

No evidence of isomerism.

Conclusion and Summary.

It has been stated that two isomeric potassium sodium sulphites exist, which can be distinguished from each other by their action upon ethyl iodide, the one yielding a salt approaching the composition $4C_2H_5SO_2ONa + KI$, the other approaching $4C_2H_5SO_2OK + NaI$.

Under the most favorable conditions that could be devised, and working on salts supposed to be isomers, in these experiments practically no difference could be observed in the composition of the products obtained by the action of ethyl iodide on the salts. In seven experiments only slight variations could be observed, and this could be explained by changes in the strength of the alcohol.

There appears, therefore, to be no evidence that isomeric potassium sodium sulphites exist.

CHEMICAL LABORATORY,
JOHNS HOPKINS UNIVERSITY,
December, 1898.

CONDENSATION COMPOUNDS OF AMINES AND CAMPHOROXALIC ACID.

FIFTH COMMUNICATION ON THE INTERACTION OF ETHYLIC OXALATE AND CAMPHOR.[1]

BY J. BISHOP TINGLE AND ALFRED TINGLE.

THEORETICAL.

In the preceding paper on this subject (*loc. cit.*) we described three compounds obtained from aniline and camphoroxalic acid, to which we assigned the formulæ

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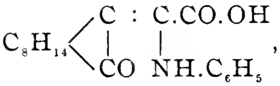
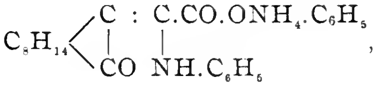
[1] This JOURNAL, **21**, 238 (1899); *Ibid.*, **20**, 318 (1898); *Ibid.*, **19**, 393 (1897); J. Chem. Soc. (London), **57**, 652 (1890).

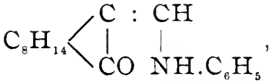


$$C_8H_{14}\left\langle\begin{matrix}C & : & C.CO.OH\\ | & & |\\ CO & & NH.C_6H_5\end{matrix}\right.,$$



$$C_8H_{14}\left\langle\begin{matrix}C & : & C.CO.ONH_4.C_6H_5\\ | & & |\\ CO & & NH.C_6H_5\end{matrix}\right.,$$

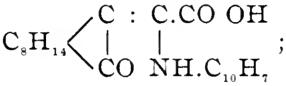
and



$$C_8H_{14}\left\langle\begin{matrix}C & : & CH\\ | & & |\\ CO & & NH.C_6H_5\end{matrix}\right.,$$

and designated them phenylcamphoformeneaminecarboxylic acid, anilinephenylcamphoformeneaminecarboxylate, and phenylcamphoformeneamine, respectively. We have now obtained a number of other condensation compounds of camphoroxalic acid and its ethylic salt with various aliphatic and aromatic amines, and have gathered further evidence in favor of the above formulæ. The majority of the compounds from aliphatic amines will be described in a subsequent communication and will only be referred to here in so far as is necessary to elucidate theoretical points.

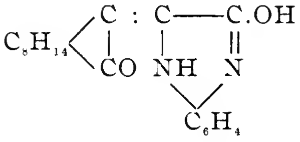
By the action of α-naphthylamine on camphoroxalic acid (as sodium salt), in alcoholic solution, at 100°, under pressure, a compound is obtained crystallizing from benzene in well-developed, transparent, amber-colored crystals; at 100°–105° these gradually become opaque and finally change to a light-brown powder, which, like the crystals, melts and decomposes at 170°. The compound has well-marked acidic properties and readily dissolves in a solution of sodium carbonate; it gives no coloration with ferric chloride and alcohol. This substance is strictly analogous with the first of the aniline compounds mentioned above, and is therefore termed α-naphthylcamphoformeneaminecarboxylic acid,

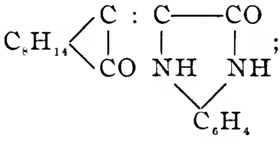


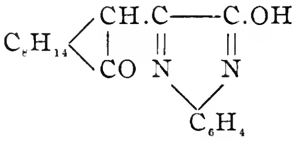
$$C_8H_{14}\left\langle\begin{matrix}C & : & C.CO\ OH\\ | & & |\\ CO & & NH.C_{10}H_7\end{matrix}\right.;$$

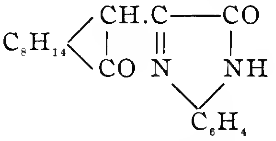
the crystals contain 0.5 molecule benzene of crystallization. The corresponding derivative of β-naphthylamine is formed in an analogous manner; it quickly dissolves in toluene, but in benzene, although its solubility is ultimately considerable, it dissolves very slowly; the supersaturated solution formed on cooling is relatively stable, as crystals are deposited only gradually. The compound is obtained from either solvent in bright-yellow needles melting and decomposing at 173°. In its acidity and other properties it closely resembles the α-naphthyl derivative.

Orthophenylenediamine readily condenses with sodium or potassium camphoroxalate, in equimolecular proportion, when heated at 100°, in alcoholic solution, under pressure. The yield is extremely good. The compound has the formula $C_{18}H_{20}N_2O_2$. It is readily soluble in benzene, and is deposited in bright-yellow needles melting at 246°. It dissolves to some extent in hot water, in boiling hydrochloric acid, and sodium hydrate solution, all of which are practically without action on it. With concentrated sulphuric acid, at the ordinary temperature, a red solution is obtained resembling that produced by a crystal of potassium bichromate. After remaining during eight days without heating the compound is recovered unchanged on dilution, except for the formation of a little resinous matter. The same substance is also formed from orthophenylenediamine and ethylic camphoroxalate under similar conditions. The properties of the compound characterize it as a quinoxaline derivative with one of the following formulæ:

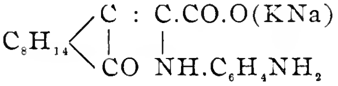
(1)  ;

(2)  ;

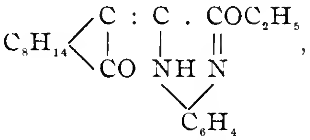
(3)  ;

(4)  ;

The relationship between 1 and 3, and 2 and 4, respectively, is similar to that between the enolic and ketolic forms of camphoroxalic acid, and may, for present purposes, be ignored, the choice thus falling between 1 and 2. From analogy with the preceding compounds we should expect to obtain from the alkali camphoroxalate as primary, intermediate product a compound of the formula

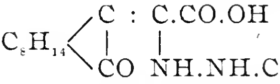
 ;

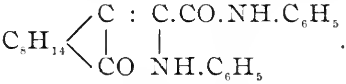
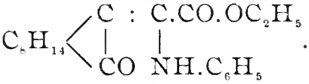
then, by the further elimination of water this should give rise to the substance  $C_8H_{14}\left\langle\begin{array}{lll} C & : C & \text{———}C.O(KNa) \\ | & \;\, | & \qquad\quad \| \\ CO & NH.C_6H_4 & N \end{array}\right.$, which on acidification would produce the compound 1. Ethylic camphoroxalate should, in an analogous manner, eliminate water and alcohol successively, and yield the compound 2. We must therefore conclude either that one of these is unstable and immediately changes into the other, or that the excess of diphenylamine employed in the preparation of the ester condensation-product has hydrolyzed the intermediate product,

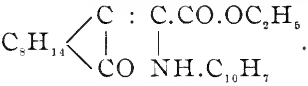


$$C_8H_{14}\left\langle\begin{array}{lll} C & : C & . COC_2H_5 \\ | & \;\, | & \;\;\| \\ CO & NH & N \end{array}\right. ,\quad NH, N \searrow\swarrow C_6H_4$$

to the compound 1. We regard the former view as the more probable, since otherwise it is difficult to understand why the ethylic camphoroxalate itself should not have been hydrolyzed. But this would have led to the formation of a phenylenediamine salt which, as no acid was used in the purification, should have been isolated. A second argument, tending in the same direction, is based on the fact that meta- and paraphenylenediamine, under similar conditions, did not hydrolyze the ester at all, although, from their total failure to react in any way, they were present in larger excess than was the ortho-compound. Finally, the yield from the ortho-amine is relatively large, and is scarcely affected by reducing the quantity of amine to somewhat below 1 molecular proportion.

Two substances are formed by the interaction of semicarbazide and potassium camphoroxalate in presence of alcohol, under pressure, at 100°. For the present we will term them simply the α- and β-semicarbazides of camphoroxalic acid. They are separated by means of their different solubility in ether; the α-compound, which readily dissolves, is deposited from acetone in small white needles, melting and decomposing at 218°. It is soluble in a warm solution of sodium carbonate, is reprecipitated in a gelatinous condition on acidification, and gives no coloration with ferric chloride and alcohol. The β-derivative is formed in smaller quantity than its companion; it is not soluble in the ordinary neutral organic media, but slowly dissolves in boiling glacial acetic acid, and is gradually deposited from the solution, on the addition of alcohol, in colorless, microscopic needles aggregated into characteristic cubical forms; it melts and decomposes at 209°–210°. The substance resembles the α-derivative in its behavior towards ferric chloride and sodium carbonate, but from solution in the latter, acids precipitate the α-compound. Both bodies agree closely in their content of carbon and hydrogen, which is that required for semicarbazylcamphoformenecarboxylic acid,  $C_8H_{14}\left\langle\begin{array}{ll} C & : C.CO.OH \\ | & \quad | \\ CO & NH.NH.CO.NH_2 \end{array}\right.$; pending further experimental evidence we shall abstain from discussing their relationship and constitution.

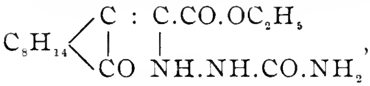
We have previously shown (*loc. cit.*) that at 130° ethylic camphoroxalate combines with two molecular proportions of aniline forming phenylcamphoformeneaminecarboxylic anilide,  $C_8H_{14}\left\langle\begin{array}{ll} C & : C.CO.NH.C_6H_5 \\ | & \quad | \\ CO & NH.C_6H_5 \end{array}\right.$. At 100°, under pressure, in alcoholic solution, ethylic camphoroxalate and aniline, or preferably aniline hydrochloride and potassium hydroxide, in the above proportions, yield ethylic phenylcamphoformeneaminecarboxylate,  $C_8H_{14}\left\langle\begin{array}{ll} C & : C.CO.OC_2H_5 \\ | & \quad | \\ CO & NH.C_6H_5 \end{array}\right.$. It readily crystallizes from benzene in white, microscopic needles melting and decomposing at 158°–160°. By the action of alkalies the corresponding acid (m. p. 174°) is obtained. It has been previously prepared by us from aniline and camphoroxalic acid or sodium camphoroxalate.

β-Naphthylamine resembles aniline in its behavior towards ethylic camphoroxalate and yields ethylic β-naphthylcamphoformeneaminecarboxylate,  $C_8H_{14}\left\langle\begin{array}{ll} C & : C.CO.OC_2H_5 \\ | & \quad | \\ CO & NH.C_{10}H_7 \end{array}\right.$. This is somewhat sparingly soluble in boiling benzene, and is deposited in colorless microscopic needles which soften at about

160°, and melt and decompose at 174° when rapidly heated, otherwise at a lower temperature. The compound is insoluble in hot water, and, except for a slight superficial yellow color, unchanged by boiling with a solution of sodium carbonate.

Semicarbazide hydrochloride and ethylic camphoroxalate react in dilute alcoholic solution, at the ordinary temperature, in the presence of potassium acetate. The same product is formed at 100° if potassium hydroxide, in quantity slightly less than is sufficient to liberate the base, is substituted for the acetate.

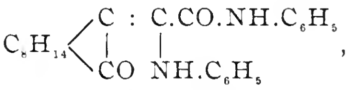
Ethylic semicarbazylcamphoformenecarboxylate,



$$C_8H_{14}\left\langle \begin{array}{ll} C & : C.CO.OC_2H_5 \\ | & \quad | \\ CO & NH.NH.CO.NH_2 \end{array} \right.$$

, readily dissolves in ethylic acetate, chloroform, and ether; moderately in benzene and acetone, and is practically insoluble in ligroin. It crystallizes from ethylic acetate in colorless needles melting at 202°. When prepared at 100° with potassium hydroxide in the manner referred to above, a second compound is formed in small quantity. This is very sparingly soluble in boiling ether, and in water at the ordinary temperature. It crystallizes in colorless needles and melts at 255°.

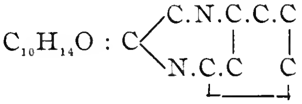
Ethylic camphoroxalate also condenses with ammonia, methylamine, and ethylamine. The compounds formed differ in type from those described above, but resemble the phenylcamphoformeneaminecarboxylic anilide,



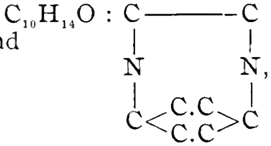
$$C_8H_{14}\left\langle \begin{array}{ll} C & : C.CO.NH.C_6H_5 \\ | & \quad | \\ CO & NH.C_6H_5 \end{array} \right. ,$$

prepared by heating ethylic camphoroxalate and aniline at 130°, and described by us in the previous paper (*loc. cit.*). The conditions under which they are obtained are similar to those employed for the production of the above ethylic β-naphthylcamphoformeneaminecarboxylate, and, together with the compounds themselves, will be fully detailed in a subsequent communication. At present we merely desire to draw attention to the striking distinction in behavior between the two classes of amines. That this difference is not due simply to the "aromatic" or "aliphatic" nature of the bases is shown by the behavior of semicarbazide. We regard the difference as being dependent primarily on the basicity of the amine, the strongly basic ones being capable of attacking the carbethoxyl group ($CO.OC_2H_5$) at 100°, aniline only at 130°, whilst the naphthylamines, which are still more feebly basic, are either incapable of reacting with it at all under the conditions we have tried, or at any rate cannot do so at temperatures below that at which ethylic camphoroxalate itself suffers decomposition.

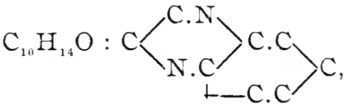
We have hitherto failed to obtain condensation compounds with ethylic camphoroxalate or potassium camphoroxalate, and ethylaniline, dimethylaniline, meta- and paraphenylenediamine, and urea, whilst ethylic camphoroxalate did not react with α-naphthylamine and dimethylamine. We have no explanation to offer for the failure with α-naphthylamine. Perhaps in the case of urea the cause is to be sought in its comparatively feeble basic properties. The inhibition of the reaction in the case of the two phenylenediamines is doubtless due to the relative difficulty experienced in producing rings of seven and eight members,



and



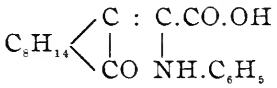
as compared with the six-membered ring,



which is actually formed in the case of orthophenylenediamine.

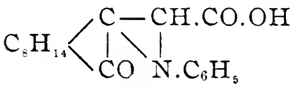
The failure with dimethylaniline is only what would be expected from the nature of the reaction, since, being a tertiary base, there is no hydrogen to form water with the hydroxyl of the ethylic camphoroxalate. The case is otherwise, however, with ethylaniline and dimethylamine. We shall reserve the discussion of the latter for a subsequent communication and at present confine ourselves to the former.

In our previous paper on this subject (*loc. cit.*) we suggested two formulæ for phenylcamphoformeneaminecarboxylic acid (m. p. 174°); *viz.*,



$$C_8H_{14}\begin{cases}C : C.CO.OH \\ \;| \qquad | \\ CO \;\; NH.C_6H_5\end{cases}$$

and



$$C_8H_{14}\begin{cases}C - CH.CO.OH \\ \;| \;\diagdown\; | \\ CO \;\; N.C_6H_5\end{cases},$$

expressing our preference for the former. We have obtained crystalline compounds from the corresponding amine (m. p. 166°) with benzoyl chloride, phenylsulphonic chloride, and acetic anhydride. Should further investigation prove these to be simple acyl derivatives the first formula would be established, but in this case there is no very obvious reason why a secondary amine should not react like aniline. The second of the above formulæ, whilst furnishing a satisfactory explanation of the failure of the group R_2NH to react, does not lead us to expect the production of a benzoyl, phenylsulphonyl, or acetyl derivative. Pending further experimental evidence we prefer not to commit ourselves to a decided opinion. It is possible that the chlorides cause cission of the ring, or that, somewhat on the lines of Bischoff's "dynamical theory," stereo-conditions of the two radicals linked to nitrogen prevent the reaction. We hope later to be able to throw light on this point. The compound from benzoyl chloride and phenylcamphoformeneamine mentioned above crystallizes from benzene in prisms resembling those of potassium nitrate, and forming characteristic cruciform aggregates. It melts at 160°–161°. With phenylsulphonic chloride the amine yields a colorless, crystalline compound, which melts at 133° and is insoluble in a solution of sodium hydroxide, indicating the secondary nature of the original amine.

Phenylcamphoformeneamine and acetic anhydride also yield a crystalline product which, after being well drained on tile, melted at 134°. It was, however, contaminated with resinous matter, and repeated recrystallization from alcohol, or preferably ethylic acetate and ligroin, failed to produce a separation, as each crystallization caused some decomposition.

EXPERIMENTAL.

Camphoroxalic Acid and α-Naphthylamine.

Camphoroxalic acid (4.4 gram = 1 mol.), α-naphthylamine (1.4 grams = 0.5 mol.), sodium hydrate (0.8 gram = 1 mol.), and 95 per cent alcohol (about 50 cc.) were heated in a pressure bottle at 100°, during four hours. The alcohol was then evaporated on the water-bath, and the residue treated with water, acidified with dilute sulphuric acid, and extracted with ether. The ethereal solution, after drying with calcium chloride, was distilled, and the residue crystallized twice from benzene. The yield of α-naphthylcamphoformeneaminecarboxylic acid is very good, but is not materially affected by doubling the quantity of amine, as, when this is done, a precipitate of α-naphthylamine sulphate forms on acidifying and hinders the satisfactory extraction of the acid. The crystals deposited from benzene contain 0.5 mol. C_6H_6, and consist of well-developed amber prisms. At 100°–105° they become opaque, and finally change to a yellow powder, which, like the crystals themselves, melt and decompose at 170°.

Analysis:

I. 0.6574 gram substance gave 1.8634 grams CO_2, and 0.3942 gram H_2O.

II. 0.3796 gram substance lost 0.0393 gram at 105°.

	Calculated for $C_8H_{14}\left\langle\begin{array}{l} C : C.COOH.\frac{1}{2}C_6H_6 \\ \mid \quad\;\; \mid \\ CO \;\; NH.C_{10}H_7 \end{array}\right.$	Found.	
		I.	II.
C	77.32	77.30	....
H	6.70	6.66	....
C_6H_6	10.05	....	10.35

The acid readily dissolves in a solution of sodium carbonate.

Camphoroxalic Acid and β-Naphthylamine.

The experiments in this case were carried out exactly as with the α-amine, and with similar results. In all preparations made with equimolecular proportions of acid and amine a portion of the latter was precipitated as sulphate. Potassium hydrate was found to give better results than sodium hydrate on account of its greater solubility in alcohol. It was observed that sometimes pieces of sodium hydrate did not dissolve, and produced a series of small cracks on the inner surface of the glass at the point of their contact with it. This was apparently not the case with potassium hydrate. The crude β-naphthylcamphoformeneaminecarboxylic acid, obtained after the removal of the ether, is purified by quickly extracting it once or twice with hot benzene. It is then recrystallized from toluene and is deposited in bright-yellow needles, melting and decomposing at 173°. The readiness with which it forms supersaturated solutions with benzene has been mentioned above. The yield is excellent.

Analysis:

0.2236 gram substance gave 0.6246 gram CO_2, and 0.1410 gram H_2O.

	Calculated for $C_{22}H_{23}NO_3$.	Found.
C	75.64	76.18
H	6.59	7.00

The slight error in the carbon is doubtless due to the crystals containing a trace of toluene which contains 91.30 per cent of carbon.

Camphoroxalic Acid and Orthophenylenediamine.

The experiments with these compounds were carried out in the same manner as those with the naphthylamines. We found it most convenient not to prepare the free diamine, but to use the hydrochloride together with three molecular proportions of potassium hydrate. The condensation-product does not require to be extracted with ether. It is sufficient to dissolve the alcoholic residue in water, acidify, filter, wash with a little water, and dry the precipitate on a porous plate in the air. After two crystallizations from benzene the compound is deposited in bright-yellow needles melting at 246°. It is slightly soluble in hot water, is practically unchanged by boiling with hydrochloric acid, and is only slightly acted upon by prolonged heating with a solution of sodium hydrate. It dissolves quickly in concentrated sulphuric acid at the ordinary temperature, giving a red coloration, the change being similar in appearance to that produced by potassium chromate under analogous conditions. After remaining during eight days at the ordinary temperature a white precipitate is obtained on dilution. This rapidly turns yellow and then consists of unchanged crystals. The addition of a crystal of potassium bichromate to the sulphuric acid solution does not produce any characteristic color. If the acid solution is heated alone decomposition gradually takes place. It readily dyes unmordanted cotton bright-yellow. The yield is practically quantitative. The constitution of the compound is discussed in the first part of this paper.

Analyses :

I. 0.2550 gram substance gave 0.6785 gram CO_2, and 0.1590 gram H_2O.

II. 0.1216 gram substance gave 10.8 cc. N at 28°.5 and 741 mm.

	Calculated for $C_{18}H_{20}N_2O_2$.	Found. I.	Found. II.
C	72.97	72.56	....
H	6.76	6.92	....
N	9.46	....	9.64

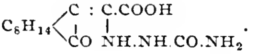
Semicarbazide and Camphoroxalic Acid.

Semicarbazide hydrochloride (4.4 grams = 2 mols.) was mixed with the acid (4.4 grams = 1 mol.), potassium hydrate (3.4 grams = 3 mols.) and alcohol (95 per cent, 50 cc.) were then added, and the solution heated at 100°, under pressure, during four hours. After removal of the alcohol the residue was acidified with dilute sulphuric or hydrochloric acid and extracted with ether. The acid produced a precipitate which did not dissolve in the ether. It was removed by filtration, dried, and frequently extracted with hot ether. The residue constituted the "β-compound," which is insoluble in all ordinary, neutral, organic media. It was purified by solution in boiling glacial acetic acid. On the addition of alcohol minute microscopic needles are deposited, aggregating into characteristic cubical forms. After repeating this treatment several times the product melts and decomposes at 209°–210°. It readily dissolves in a solution of sodium carbonate, is reprecipitated in a gelatinous condition as the α-derivative on the addition of acid, and gives no coloration with ferric chloride.

The "α-compound" constitutes the residue obtained after the distillation of the combined ethereal solutions mentioned above. It crystallizes from acetone in small, colorless needles, which melt and decompose at 218°. The substance does not evolve ammonia when boiled with a solution of sodium hydrate. Towards sodium carbonate and ferric chloride its behavior is identical with that of the β-compound.

Analysis:

0.3053 gram substance gave 0.6129 gram CO_2, and 0.1860 gram H_2O.

	Calculated for  $C_8H_{14}\left\langle\begin{array}{l} C : C.COOH \\ \mid \quad\ \mid \\ CO\ \ NH.NH.CO.NH_2 \end{array}\right.$.	Found.
C	55.51	54.75
H	6.76	6.76

The carbon and hydrogen content of the β-compound is practically identical with that of the α-derivative.

Aniline and Camphoroxalic Acid.

Camphoroxalic acid (1.1 grams = 1 mol.), aniline hydrochloride (1.2 grams = 2 mols.), sodium hydrate (0.84 gram = 3 mols.), and alcohol (95 per cent, 50 cc.), when heated under pressure at 100°, during four hours, yield the phenylcamphoformeneaminecarboxylic acid (m. p. 174°) which we have described in our previous paper. We failed to esterify it by E. Fischer's method, our object being to show that it is really the acid of the ethylic phenylcamphoformeneaminecarboxylate, prepared from ethylic camphoroxalate and aniline, and described below. The proof desired was, however, ultimately obtained in the reverse manner, by hydrolyzing the ester and isolating and identifying the acid.

We desire briefly to describe some unsuccessful attempts to condense camphoroxalic acid:

Meta- and paraphenylenediamine hydrochlorides completely failed to react when treated with camphoroxalic acid, sodium hydrate, and alcohol, under pressure, at 100°, in the proportions and conditions employed in the case of α-naphthylamine. The probable reasons for this we have already mentioned.

Ethylaniline hydrochloride, under the same circumstances, gave a similar result, as also did the free base and acid when mixed and heated at 170° during two hours. No better success was attained by mixing the base and acid with benzene and heating on the water-bath ; some solid separated from the solution, but in quantity too small for further investigation.

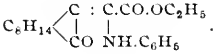
Dimethylaniline also gave a negative result when heated with the acid alone at 180°, or with the acid and benzene on the water-bath.

Ethylic Camphoroxalate and Aniline.

Ethylic camphoroxalate (2.5 grams = 1 mol.), aniline hydrochloride (2.6 grams = 2 mols.), potassium hydroxide (1 gram = less than 2 mols.), and alcohol (95 per cent, 50 cc.) were heated together under pressure at 100° during four hours. After removal of the alcohol the residue was treated with water, extracted with ether, and the ethereal solution dried and distilled. The residue, after recrystallizing from benzene, is deposited in almost white, microscopic needles, which melt and decompose at 158°–160°. The yield is excellent.

Analysis :

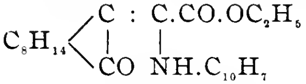
0.2682 gram substance gave 0.7172 gram CO_2, and 0.1810 gram H_2O.

	Calculated for  $C_8H_{14}\left\langle\begin{array}{l}C : C.CO.OC_2H_5 \\ \vert \quad\;\; \vert \\ CO\;\; NH.C_6H_5\end{array}\right.$.	Found.
C	73.39	72.93
H	7.64	7.49

The compound is therefore ethylic phenylcamphoformeneaminecarboxylate, analogous to the phenylhydrazide previously described by us, and its relationship to the corresponding compound from aniline and camphoroxalic acid is proved by its hydrolysis. When heated for about five minutes with warm 10 per cent aqueous-alcoholic sodium hydroxide in excess, it yields the corresponding acid (m. p. 174°). (Cf. p. 218.) Free aniline may be used for the preparation of the compound instead of the hydrochloride and alkali, but a large excess of the base should be avoided as it hinders crystallization. We have found the above method of working with the amine hydrochlorides and alkalies in slight deficiency very convenient, especially when the free base is unstable or readily volatile ; in the latter case the alkali is conveniently enclosed in a sealed tube of thin glass, which is broken after the stopper of the pressure bottle has been securely fastened down. We have not observed any perceptible hydrolysis of the ester by the alkali.

Ethylic Camphoroxalate and β-Naphthylamine.

Ethylic β-Naphthylcamphoformeneaminecarboxylate,



, was prepared in a similar manner to the phenyl derivative, from β-naphthylamine, and ethylic camphoroxalate in alcoholic solution. Any unchanged amine is removed by means of benzene, and the residue then recrystallized from the same solvent. It is deposited in colorless, microscopic needles, which soften at about 160°, and melt and decompose at 174°, but the melting-point varies according to the rapidity with which the bath is heated. The compound is not affected by boiling water nor by boiling aqueous sodium carbonate except for the production of a superficial yellow color.

Analysis:

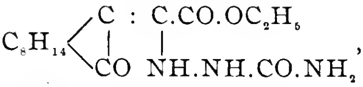
0.3392 gram substance gave 0.9446 gram CO_2, and 0.2242 gram H_2O.

	Calculated for $C_{24}H_{27}NO_3$.	Found.
C	76.39	75.94
H	7.16	7.34

No definite compound could be isolated except apparently unchanged naphthylamine, by heating ethylic camphoroxalate with β-naphthylamine at 140°–145° during three hours.

Ethylic Camphoroxalate and Semicarbazide.

Ethylic Semicarbazylcamphoformenecarboxylate,



, is prepared by heating the ester with semicarbazide hydrochloride (3 mols.), potassium acetate (3.5 mols.), and alcohol (95 per cent), at 100°, under pressure, during four hours, or by allowing the substances to remain at the ordinary temperature in dilute alcoholic solution during seven days. In the former case the compound was extracted by means of ether; in the latter it separated on dilution with water. It is readily soluble in ethylic acetate, chloroform, and ether, moderately so in benzene and acetone, and sparingly in ligroin. It is deposited from ethylic acetate in colorless needles, melting at 202°. The yield is good whichever method of preparation is employed. In one experiment, carried out at 100°, a compound was obtained in small quantity, which did not dissolve in either the ethereal or aqueous layers of liquid, nor in any organic solvent we could employ. It crystallized in needles, melted at 255°, and may be semicarbazide sulphate, as the aqueous solution had been acidified with dilute sulphuric acid. Neither J. Thiele and O. Strange,[1] who first prepared this salt, nor F. Tiemann and P. Krüger,[2] who subsequently employed it, give the melting-points of their preparations.

Analyses:

I. 0.4832 gram substance gave 1.0056 grams CO_2, and 0.3360 gram H_2O.

II. 0.4532 gram substance gave 0.9438 gram CO_2, and 0.3234 gram H_2O.

III. 0.1540 gram substance gave 19.4 cc. N_2 at 27° and 746.6 mm.

	Calculated for $C_{15}H_{23}N_3O_4$. (Mol. wt. = 309.)	Found. I.	II.	III.
C	58.25	56.75	56.79	....
H	7.44	7.72	7.92	....
N	13.59	....	....	13.64

Molecular weight determinations:

Solvent, phenol.

Weight of solvent. Grams.	Weight of substance. Gram.	Δ.	m.
19.6330	0.1145	0.19°	227
19.6330	0.2220	0.36°	232.5

Ethylic Camphoroxalate and Orthophenylenediamine.

The ester reacts with the orthodiamine hydrochloride and

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[1] Ber. d. chem. Ges., **27**, 34.

[2] *Ibid.*, **28**, 1754.

sodium hydrate, in presence of alcohol, at 100°, under pressure. The product was isolated by evaporating off the alcohol and washing with water. Its appearance and melting-point proved it to be identical with the corresponding compound from sodium camphoroxalate. In the first experiments two molecular proportions of amine hydrochloride, together with the equivalent amount of sodium hydrate, were employed; subsequently, in order to avoid any chance of hydrolysis, exactly equimolecular proportions of the ester and amine were taken, with a small deficiency of sodium hydrate, but without appreciably affecting the result. The yield is large.

Unsuccessful Experiments with Ethylic Camphoroxalate.

Meta- and paraphenylenediamine yielded only tarry matter when treated with ethylic camphoroxalate under the same conditions as the ortho-compound. A similar result was obtained in the case of α-naphthylamine, both at 100° under pressure, and at 140°–145°. In both experiments the only products which could be isolated were the original materials. Ethylaniline, both as free base and as hydrochloride, together with sodium hydrate, and dimethylaniline in the free state, at 100°, under pressure, in alcoholic solution, also failed to give any condensation-products.

Experiments with Phenylcamphoformeneamine.

Benzoyl chloride reacts with phenylcamphoformeneamine, in presence of a little sodium hydrate, either when gently warmed or at the ordinary temperature if allowed to remain during thirty-six hours. The latter appears to be the preferable method. The product was well washed with a solution of sodium carbonate, extracted with ether, the ether dried and removed, and the residue recrystallized from benzene. The compound is deposited in cruciform aggregates of prisms resembling potassium nitrate in appearance, and melting at 160°–161°. It has not yet been further investigated. An attempt to prepare it by the ordinary Schotten-Baumann method, in aqueous solution, was not successful, as benzoic acid was the only product that could be isolated in quantity.

Phenylsulphonic chloride does react with the amine by the

Schotten-Baumann method, but when the two are simply heated together they only yield an oil. The product has as yet only been obtained in small amount. It is readily deposited from benzene in colorless needles, melts at 133°, and does not dissolve in a solution of sodium hydrate.

The amine, when boiled with 10 molecular proportions of acetic anhydride during fifteen minutes, yields a brown liquid, which deposits a gummy substance after treatment with a solution of sodium carbonate. Recrystallization from a mixture of ethylic acetate and ligroin yields colorless crystals, which, after draining on a porous plate, melted at 134°. The crystals were always accompanied by resinous matter, and, as repeated recrystallizations failed to effect any separation of the two, further attempts to purify the compound were abandoned. We propose to continue this work in various directions.

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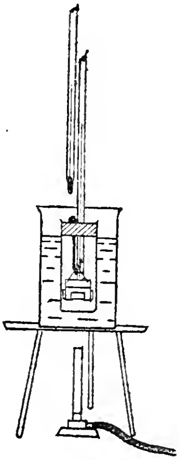
A METHOD FOR THE DETERMINATION OF THE MELTING-POINT.

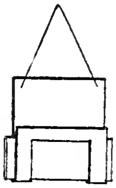
BY M. KUHARA AND M. CHIKASHIGÉ.

Several different methods have hitherto been suggested for determining the melting-point of substances. One of these, that now in common use, consists in heating the substance to be experimented upon in a capillary tube, fastened to a thermometer, and immersed in a bath. It is usual, in this case, to take the temperature at which the substance begins to melt away from the walls of the capillary tube as its melting-point. This method, however, is very liable to give too high results, as it is difficult to observe the exact point of fusion of that portion of the substance which is in contact with the walls of the tube, before the inner portion thereof reaches its melting-point; this is apparently higher than the real melting-point, owing to the bad conductivity of the air contained in the interstices of the substance, and the consequent overheating. We also find another disadvantage in this method; namely, that substances which cannot be pulverized, such as waxes, fats, etc., are, with difficulty, introduced into the capillary tube.

We have recently devised a method which, we think, will eliminate all the disadvantages of the tube method, and which, moreover, can easily be carried out in chemical laboratories.

In this new method, instead of a capillary tube, we make use of a pair of cover-glasses for microscopical purposes, cut in halves, between which the substance to be tested is introduced, either in powder, in crystals, or in thin slices. If the substance is in the state of powder, we can make the layer as thin as possible by pressing and sliding the two pieces with the fingers, so that the heat of the bath may at once be conducted throughout the whole mass. The surface exposed is very large compared with the quantity of the substance taken, and, consequently, its behavior towards heat can be distinctly observed. Before the substance is melted the glass appears opaque, while it becomes transparent when fusion occurs. The thinner the layer the more distinct is the difference ; but with volatile substances, a quantity somewhat in excess of what is apparently essential should be taken, in order to make allowance for loss by volatilization.





The pair of glass-pieces is then fastened to a holder made of platinum foil and tied, if necessary, with a piece of fine wire of the same material. The holder, which can easily be made by folding the foil and cutting it with scissors, as shown in the annexed figure, is suspended in a wide test-tube, into which is inserted a thermometer close to the holder. The test-tube, serving as an air-bath, is immersed in the sulphuric-acid bath almost to its mouth. The further steps of the process require no modification of the old methods.

The glass pieces can be used any number of times, unless they are broken; this is considered another advantage over the tube method.

The result of experiments with our method is given in the following table. The substances taken were purified by repeated crystallization, and the temperatures given are the corrected ones:

Substance.	Exp. I.	Exp. II.	Exp. III.	Mean.	M. P. already known.	Observer.
Chloral hydrate	57°.3	57°.3	57°.0	57°.2	57°	Meyer and Dulk
Urea	132°.1	132°.1	132°.3	132°.2	132°	Lubavin
Phthalic acid	203°.2	202°.7	203°.0	203°.0	203°	Ador
Phthalimide	233°.6	233°.7	233°.6	233°.6	233°.5	Graebe

The melting-point of phthalic acid has been a subject of discussion, the figures given by different observers differing considerably. Lossen[1] gives it as low as 184°, but Ador[2] states that crystallized phthalic acid melts at 213° and the powdered substance at 203°. Remsen[3] ascribes the variation to the fact that phthalic anhydride, formed partly from the acid, lowers the melting-point of the mixture. In order to test his view, small quantities of the acid, introduced into a U-tube, were heated over a paraffin-bath at the temperatures of 140° and 170°, and the melting-point was found to be considerably lower in both cases. This experiment was conducted by one of us a number of years ago, when working in his laboratory. We have found, however, with the new method, that both the crystallized and the powdered substances melt at the same constant temperature of 203°, whether the air-tube is grad-

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[1] Ann. Chem. (Liebig), **144**, 76.

[2] *Ibid.*, **163**, 230.

[3] This JOURNAL, **8**, 30.

ually heated or plunged at once into the bath at a temperature above 205°. This is probably due to the fact that the anhydride formed is freely volatilized in our apparatus through the interstices of the two glass-pieces, and the remaining acid, kept pure, melts at its proper temperature. With our method we have never observed a temperature so high as 213°, nor so low as 184°, while with the capillary-tube method we often noted a melting-point as low as 185°.

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THE SYMMETRICAL CHLORIDE OF PARANITROORTHOSULPHOBENZOIC ACID.[1]

BY F. S. HOLLIS.

Introduction.

The present investigation may be divided into two parts. The first consists of further work on the method of preparation and separation of the chlorides of paranitroorthosulphobenzoic acid. This work was confined largely to the unsymmetrical or low-melting chloride, as this is the one used mainly in the second part of the investigation. The preparation of the unsymmetrical dichloride, first obtained by Remsen and Gray,[2] was found to be a matter of considerable difficulty and uncertainty, unless the crystallization could be conducted out of doors at a very low temperature.

As the result of a series of experiments, undertaken to determine the best conditions for the preparation of the unsymmetrical chloride, a method has been devised by which the unsymmetrical chloride can be prepared in any desired quantity in the laboratory.

The second part of the investigation consists of a study of the action of benzene and aluminium chloride on the chlorides under varying conditions, and the preparation of a series of derivatives of the product formed.

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[1] From the author's dissertation submitted to the Board of University Studies of the Johns Hopkins University, June, 1896, for the degree of Doctor of Philosophy. The investigation was undertaken at the suggestion of Professor Remsen and was carried on under his guidance.

[2] This JOURNAL, **19**, 496.

Remsen and Saunders[1] and Remsen and McKee,[2] working with the chlorides of orthosulphobenzoic acid, found that the action of benzene and aluminium chloride gives the same products with both chlorides.

It was thought that, on account of the greater stability of the paranitroorthosulphobenzoic acid, the action of benzene and aluminium chloride might lead to the formation of two series of derivatives, one derived from the symmetrical chloride and the other from the unsymmetrical chloride, in which the resulting compound would retain the unsymmetrical structure of the chloride. This proved not to be the case, as the product of the action of benzene and aluminium chloride on both of the chlorides was found to be paranitroorthobenzoylbenzenesulphone chloride.

It was found that paranitroorthosulphobenzoic acid does not yield a sulphone corresponding to the one obtained from orthosulphobenzoic acid by Remsen and Saunders,[3] although the reaction was conducted under the conditions used by them, as well as under a variety of different conditions.

Preparation of Material.

The acid potassium salt of paranitroorthosulphobenzoic acid was prepared from paranitrotoluene according to the method described by Kastle,[4] and used later by Remsen and Gray.[5]

One thousand grams of paranitrotoluene gave 1439 grams of the neutral potassium salt of paranitrotolueneorthosulphonic acid. One thousand grams of the potassium salt of paranitrotolueneorthosulphonic acid gave 800 grams of the acid potassium salt of paranitroorthosulphobenzoic acid.

The Action of Phosphorus Pentachloride on the Acid Potassium Salt of Paranitroorthosulphobenzoic Acid.

The action of phosphorus pentachloride on the anhydrous acid potassium salt of paranitroorthosulphobenzoic acid gives rise to the formation of an unsymmetrical and a symmetrical dichloride, as determined by Remsen and Gray,[6] according to the following equations :

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[1] This JOURNAL, **17**, 355.

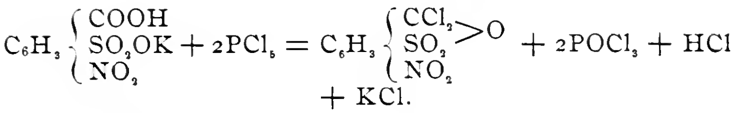
[2] *Ibid.*, **18**, 794.

[3] *Loc. cit.*

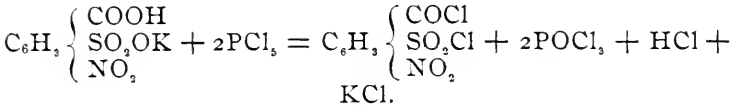
[4] This JOURNAL, **11**, 177.

[5] *Loc. cit.*

[6] *Loc. cit.*



$$C_6H_3\left\{\begin{array}{l}COOH\\ SO_2OK\\ NO_2\end{array}\right. + 2PCl_5 = C_6H_3\left\{\begin{array}{l}CCl_2\\ SO_2\end{array}\!\!>O\right.\!\!\begin{array}{l}\\ \\ NO_2\end{array} + 2POCl_3 + HCl + KCl.$$



$$C_6H_3\left\{\begin{array}{l}COOH\\ SO_2OK\\ NO_2\end{array}\right. + 2PCl_5 = C_6H_3\left\{\begin{array}{l}COCl\\ SO_2Cl\\ NO_2\end{array}\right. + 2POCl_3 + HCl + KCl.$$

Remsen and Gray[1] found that the relative amount of each chloride depends on the temperature and length of time which the phosphorus pentachloride is allowed to act on the acid potassium salt. The largest amount of the unsymmetrical chloride, amounting to 80 or 90 per cent of the total, was formed by heating a mixture of 2 molecules of phosphorus pentachloride and 1 molecule of the anhydrous acid potassium salt to 150° C. for four or five hours in a distilling-bulb, immersed in a sulphuric-acid bath.

Under these conditions, the amount of symmetrical chloride formed amounted to 10 or 20 per cent of the total, but this is increased to 30 per cent by heating in an open dish on a water-bath. The symmetrical chloride was separated by using chloroform as a solvent.

As considerable difficulty was experienced, mainly in the preparation of the unsymmetrical chloride, according to the directions given by Remsen and Gray, a series of experiments was made under different conditions with amounts of the acid potassium salt varying from 20 to 60 grams in order to determine the conditions most favorable for the formation of the unsymmetrical chloride. The results of these experiments are embodied in the following method.

a. The Preparation of the Unsymmetrical Chloride.—A mixture of 1 molecule of the acid potassium salt, previously heated to 150° C. for four hours, and 2.5 molecules of phosphorus pentachloride is carefully ground together in a mortar and introduced into a distilling-bulb having a capacity of about six times that of the volume of the mixture. The outlet tube of the bulb is closed, and a cork, through which runs a glass tube about 3 feet long, the lower end reaching nearly to the surface of the mixture, inserted in the neck.

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[1] *Loc. cit.*

The distilling-bulb, thus closed, is immersed in a sulphuric-acid bath, previously heated to 150° C., and this temperature maintained for five hours.

No reaction takes place on mixing the acid potassium salt and the phosphorus pentachloride, but upon immersing the bulb containing the mixture in the heated bath, vigorous action begins immediately, and the resulting phosphorus oxychloride is conducted back upon the product by means of the condensing-tube. The temperature of 150° C. cannot safely be exceeded, as decomposition of the chloride begins at 160° C.

At the end of five hours the tube is removed from the neck of the flask, the perforated stopper replaced by a solid one, the outlet tube opened, and the phosphorus oxychloride distilled off.

The resulting chloride, which is in the form of a thick, yellow, oily liquid, is poured into a large bottle, nearly filled with cold water, and shaken vigorously so as to break it into small globules. This washing is continued until the chloride hardens to a solid cake, which commonly takes place after washing with five or six successive portions of cold water. The solidified chloride is broken up and dried by pressing between filter-paper, and in this form it may be exposed to the air without undergoing much, if any, decomposition.

By using 2.5 molecules of phosphorus pentachloride, all of the acid potassium salt is converted into the form of the chloride, while, if but 2 molecules are used, varying amounts of the acid potassium salt, in some cases as much as 25 per cent, are unacted upon and may be recovered from the wash-water.

The product obtained by this method consists, with the exception of slight impurities, of only the unsymmetrical chloride, thus making the crystallization from chloroform unnecessary. One hundred grams of anhydrous acid potassium salt gave, on an average, 99 grams of the crude unsymmetrical chloride.

Previous work showed that the crystallization of the unsymmetrical chloride from ligroin (50°–80°) was a difficult matter, unless it could be done out of doors during very cold weather. The same was found to be the case with the unsymmetrical chloride of orthosulphobenzoic acid by Remsen and Saunders.[1]

A solution of the crude chloride in purified ligroin (50°–80°), on standing out of doors at a temperature of 6° F., crystallized in clusters of crystals, some of which measured 3 centimeters in length. An attempt was made to obtain the chloride in the form of crystals by cooling the ligroin solution to 0° C. in a refrigerating box, such as was used by Remsen and McKee.[2] The chloride invariably separated as an oil, and no advantage was derived by drawing a current of cold, dry air through the flask containing the ligroin solution. Some of the oily chloride which separated from the ligroin solution, and from which the ligroin had been decanted, formed an opaque semisolid mass on placing it in a freezing-mixture, but no crystals were deposited.

The first indication of crystallization in the laboratory was obtained on placing some of the oil, which had been dissolved several times in fresh portions of hot ligroin (50°–80°) and allowed to separate out on cooling, in a freezing-mixture, and stirring with a rod. This suggested the possibility that some material, which by its presence retards crystallization, had been dissolved out of the mass by the several portions of ligroin in which it had been dissolved. This was shown to be the case by several tests, and gave rise to the following method of purification and crystallization, in which the further change is made of using ligroin of boiling-point 90°–125° as the solvent. This ligroin is to be preferred to that having a lower boiling-point, as the chloride is apparently much more soluble in it, and crystallizes from the solution at the temperature of the laboratory. The ligroin is purified by shaking in a separating-funnel with concentrated sulphuric acid until it imparts no color to a fresh portion of acid, after which it is treated with a solution of caustic soda to neutralize the acid, and washed free from alkali by water.

The crude chloride, which is always somewhat dark colored and gummy, is placed in an Erlenmeyer flask with purified ligroin (50°–80°) and washed by stirring it with a rod until it yields a granular powder having but little color.

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[1] *Loc. cit.*

[2] *Loc. cit.*

On boiling the chloride thus purified with ligroin (90°-125°), it dissolves, with the exception of slight remaining impurities, and on cooling the solution becomes cloudy, and the excess of chloride separates out as a light-colored oil. It is best to decant the solution from the separated oil after separation has mainly ceased at the temperature at which crystallization is to proceed, but before the solution has become clear. The chloride is obtained from this solution at the temperature of the laboratory in clusters of needles having the form of long monoclinic prisms as observed by Remsen and Gray.[1] The rate of crystallization is increased by keeping the solution at a lower temperature, but no especial advantage is derived unless the temperature is very low, when larger crystals are obtained. The crystals of the chloride thus obtained have a constant melting-point of 57° C. (uncorr.).

The purified chloride which separates from the ligroin as an oil generally crystallizes on standing, but it is better to redissolve it in a fresh portion of ligroin, by which it is further purified, and proceed according to the directions given above.

The principal impurity which causes difficulty in the crystallization of the unsymmetrical chloride seems to be that which is removed by the preliminary treatment with ligroin (50°-80°).

On evaporating the ligroin used in washing the chloride, this impurity remains as a dark-colored, slightly viscous liquid having a strong acid reaction. It showed no tendency to crystallize after standing in the laboratory for five months. A small amount of another impurity was obtained as a flocculent material on dissolving the crude chloride in chloroform. It melts after purification at 100°-105° C., and is probably the anhydride.

b. The Preparation of the Symmetrical Chloride.—One portion of the symmetrical chloride was made in order to test the action of benzene and aluminium chloride, but no comparative tests were made, as in the case of the unsymmetrical chloride. The method used for its preparation differed somewhat from that of Remsen and Gray.

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[1] *Loc. cit.*

The conditions chosen for its preparation were, as far as possible, the opposite of those found to be most favorable for the formation of the unsymmetrical chloride.

The anhydrous acid potassium salt and phosphorus pentachloride, in the proportion of 1 molecule of the former to 2 molecules of the latter, are mixed by grinding them together, and the action commenced by placing the vessel containing the mixture in a sulphuric-acid bath previously heated to 150° C.

The vessel is removed from the bath as soon as the action commences, and allowed to stand until the action is complete, which requires about ten minutes.

The mass is washed, as in the case of the unsymmetrical chloride, by shaking in a bottle with five or six portions of cold water.

The chloride thus washed exists in the form of a light-colored, thick gum. It is dissolved in anhydrous chloroform, the solution dried by means of calcium chloride, and allowed to stand at the temperature of the laboratory. Crystals of the symmetrical chloride are formed only after the chloroform has nearly all evaporated, and crystallization proceeds very slowly.

The chloride was obtained in the form of small monoclinic crystals, having a constant melting-point of 94° C. (uncorr.).

The yield indicated that, under the conditions used, the action of the phosphorus pentachloride is complete, but between 35 and 40 per cent of the product obtained consists of the symmetrical chloride.

The Action of Benzene and Aluminium Chloride on the Chlorides of Paranitroorthosulphobenzoic Acid.

a. The Action on the Unsymmetrical Chloride.—When aluminium chloride is added to a solution of the unsymmetrical chloride in benzene, slight action begins immediately, as is shown by the darkening of the color of the solution and a slight evolution of hydrochloric acid gas.

In the case of small quantities of the chloride, heated with an excess of aluminium chloride, the reaction is complete in from fifteen to twenty minutes. A series of experiments was made in order to determine the best conditions for conducting the reaction and for separating and purifying the product.

Under some conditions the product contains a considerable amount of a dark-purple material which separates as an impurity on crystallization. As a result of these experiments, the following method was adopted :

Twenty grams of the unsymmetrical chloride is dissolved in 100 cc. of benzene in a flask provided with a return-condenser, and about 10 grams of aluminium chloride in small pieces added. This is heated with a small flame for from one to two minutes, at the end of which time vigorous action commences and continues without further heating for ten minutes.

After the action is over the flask is heated repeatedly so as to maintain an even evolution of hydrochloric acid gas for about eight minutes, at the end of which the reaction is complete. The resulting product is poured into 750 cc. of water in a liter separating-funnel, 75 cc. of hydrochloric acid (sp. gr. 1.12) added and the mixture well shaken.

After the benzene layer has risen the water is drawn off and the small amount of the product suspended in it separated by filtration. The greater part of the product is in the form of a pinkish-white powder, which remains in suspension in the benzene, from which it is separated by filtration, dried, and purified with the portion obtained from the water. The product is purified by dissolving in benzene and adding rather more than an equal volume of anhydrous ether, which causes a more rapid crystallization. By this method it is obtained in clusters of small, apparently monoclinic crystals, having a rhombohedral habit, or as a granular powder if crystallization takes place rapidly.

Some of the larger crystals measured 4 or 5 mm. on an edge. The larger crystals have a purple or green color, and the granular form is generally slightly green. Both forms yield a white powder. The pure crystalline product has a constant melting-point of 177° C. (uncorr.).

The portion of the product which remains in solution in the benzene is mixed with a small amount of the purple impurity before described, but it is obtained in a crystalline form of fair purity by drying the benzene solution, evaporating it to about one-third of its volume, and adding rather more than an equal volume of absolute ether. The dark impurity may be largely removed by washing with absolute alcohol, in which it dissolves readily.

An attempt was made to prevent the darkening of the benzene solution during evaporation by conducting the evaporation in a current of sulphur dioxide, as it was believed that the darkening was due, in part at least, to the action of the air.

The product was not materially improved, and a certain amount of free acid was always found to be present after such treatment. The rapid evaporation of the dried benzene solution and the addition of an equal volume of absolute ether to insure rapid crystallization is greatly to be preferred.

Twenty grams of the unsymmetrical chloride gave 16 grams of the product as first obtained. This was slightly decreased by recrystallization.

The product has a characteristic disagreeable odor.

b. The Action on the Symmetrical Chloride.—The reaction was conducted exactly as in the case of the unsymmetrical chloride, the same relative quantities and method of treatment being used. The method of separation was also the same.

The product gave, on purification, crystals of the same form, size and color as those obtained from the unsymmetrical chloride.

The melting-point of the purest crystals is also the same, 177° C. (uncorr.).

Two grams of the symmetrical chloride gave 1.5 grams of the product.

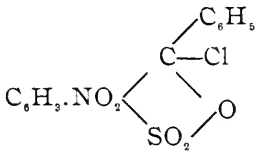
Analyses of the product of the action of benzene and aluminium chloride on the unsymmetrical chloride :

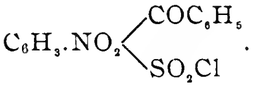
0.2051	gram	gave	0.3632	gram	CO_2
0.2992	“	“	0.5249	“	“
0.1994	“	“	0.0535	“	H_2O
0.2992	“	“	0.0819	“	“
0.2508	“	“	9.03	cc.	N
0.3496	“	“	12.88	“	“
0.2601	“	“	0.1957	gram	$BaSO_4$
0.2058	“	“	0.1584	“	“
0.2602	“	“	0.1888	“	“

0.2492 gram gave 0.1878 gram $BaSO_4$
0.2424 " " 0.1811 " "
0.2434 " " 0.1072 " AgCl
0.2058 " " 0.0925 " "
0.2602 " " 0.1161 " "

	Calculated for $C_{13}H_8O_5NSCl$.	Found. I.	II.	III.	IV.	V.
C	47.92	48.29	47.84	....	....	....
H	2.45	2.97	3.04	....	....	....
N	4.30	4.32	4.42	....	....	....
S	9.83	10.33	10.56	9.96	10.34	10.26
Cl	10.90	10.90	11.11	11.03	....	....

The two following structural formulæ are possible for a substance derived from the unsymmetrical chloride, and having the composition indicated by the analyses.





$C_6H_3.NO_2<\begin{matrix}COC_6H_5\\SO_2Cl\end{matrix}$.

The fact that the product is apparently not acted upon by alcoholic potash, together with its high melting-point and its properties generally favor the belief that it has the structure represented by the first.

The formation of the same product by the action of benzene and aluminium chloride on the symmetrical chloride seems to indicate that the product derived from each chloride is paranitroorthobenzoylbenzenesulphone chloride. This view agrees with the results obtained by the action of benzene and aluminium chloride on orthosulphobenzoic acid by Remsen and Saunders[1] and Remsen and McKee.[2]

It is clear from the analysis that but one of the chlorine atoms of the chloride is replaced by this reaction. All attempts to prepare the diphenyl derivative or paranitroorthobenzoylbenzenesulphone were unsuccessful, although the conditions were varied widely, both as to temperature and the length of time which the heating was continued.

The conditions already described give the best yield and also the purest product.

[1] *Loc. cit.*

[2] *Loc. cit.*

By allowing the mixture to stand for a day with occasional heating nearly to the boiling-point of the benzene, similar good results are obtained.

By heating to the boiling-point of benzene, for three hours, using a return-condenser, the yield is decreased, and a large amount of a black, tarry matter obtained, which is almost insoluble in benzene. This dissolves readily in absolute alcohol, from which solution it is precipitated as a dark red-colored powder on adding water, and after being thrown out of solution in this way, it becomes less soluble in absolute alcohol.

It swells up on heating and gives an odor like that obtained on burning sulphonic acids. On burning off the organic portion a considerable amount of alumina remains. Hydrochloric acid dissolves the alumina, leaving the organic portion in the form of a black, tarry mass.

The Action of Hydrochloric Acid on Paranitroorthobenzoylbenzenesulphone Chloride.

a. The Action of Dilute Hydrochloric Acid (sp. gr. 1.12).—The action of dilute hydrochloric acid was determined by boiling the sulphone chloride in a flask, provided with a return-condenser, with an excess of the acid until it was all dissolved, which usually requires about six hours. The solution is then filtered and evaporated on a water-bath, and the heating continued until no odor of hydrochloric acid remains. The resulting acid is obtained in the form of a dark, solid substance, which dissolves readily in water and takes up water on standing in the air.

Barium Salt.—The barium salt was prepared by adding barium carbonate to a solution of the acid in water, filtering off the excess of barium carbonate, and evaporating the solution under a bell-jar by means of a current of dry air. The solution cannot be concentrated safely by boiling, as it causes a decomposition of the salt.

The salt was obtained in the form of small, light-colored crystals, arranged in tufts.

In the following analyses of salts, the base, as well as the sulphur, is calculated on the basis of the anhydrous salt.

I. 0.2039 gram substance lost 0.0119 gram at 180° C., and gave 0.0586 gram $BaSO_4$.

II. 0.2892 gram substance lost 0.0179 gram at 180° C., and gave 0.0810 gram $BaSO_4$.

	Calculated for $(C_{13}H_8O_6NS)_2Ba + 3H_2O$.	Found. I.	II.
H_2O	6.72	5.84	6.18
Ba	18.29	18.12	17.65

The barium salt of another portion of acid, prepared in the same way, was obtained in the form of short, thick, monoclinic prisms, which seemed to be made up of a series of plates.

I. 0.2010 gram substance lost 0.0260 gram at 210° C., and gave 0.0557 gram $BaSO_4$.

II. 0.2021 gram substance lost 0.0250 gram at 210° C., and gave 0.0562 gram $BaSO_4$.

III. 0.2263 gram substance gave 0.1262 gram $BaSO_4$.

IV. 0.2109 gram substance gave 0.1201 gram $BaSO_4$.

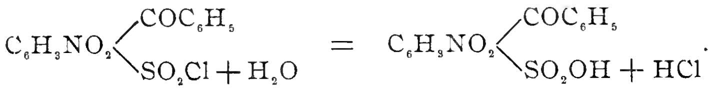
	Calculated for $(C_{13}H_8O_6NS)_2Ba + 6H_2O$.	Found. I.	II.
H_2O	12.60	12.93	12.66
Ba	18.29	18.64	18.70
S	8.54	8.76	8.93

This salt became opaque on standing in a specimen tube for one month, due to the loss of water of crystallization.

0.2133 gram of the opaque salt lost 0.0139 gram at 210° C.

	Calculated for $(C_{13}H_8O_6NS)_2Ba + 3H_2O$.	Found.
H_2O	6.72	6.56

The results of the analysis indicate that paranitroorthobenzoylbenzenesulphone chloride is converted into paranitroorthobenzoylbenzenesulphonic acid by boiling with dilute hydrochloric acid, according to the following equation:



$$C_6H_3NO_2\begin{cases}COC_6H_5\\SO_2Cl\end{cases} + H_2O = C_6H_3NO_2\begin{cases}COC_6H_5\\SO_2OH\end{cases} + HCl.$$

b. The Action of Concentrated Hydrochloric Acid (sp. gr. 1.17).—The action of concentrated hydrochloric acid was determined by heating the sulphone chloride with a large excess of acid in a sealed tube.

The tube was first heated for six hours in a water-bath, but, as no action seemed to take place, it was transferred to a Carius furnace and heated for six hours at a temperature of 175° C. The substance dissolved, with the exception of a few dark flakes, and the acid was colored brown. The flakes were removed by filtration, the acid solution evaporated to dryness on a water-bath, and the heating continued until the resulting acid had no odor of hydrochloric acid. The barium salt was prepared as in the case of the acid derived from the sulphone chloride by the action of dilute hydrochloric acid. It crystallized in the form of light-colored, fine needles, which were arranged in loose tufts or clusters. A few darker crystals in the form of larger monoclinic crystals with rhombohedral habit were obtained from the mother-liquor.

I. 0.2103 gram of the needles lost 0.0164 gram at 210° C., and gave 0.0609 gram $BaSO_4$.

II. 0.2083 gram of the needles lost 0.0158 gram at 210° C., and gave 0.0595 gram $BaSO_4$.

	Calculated for $(C_{13}H_8O_6NS)_2Ba + 3\frac{1}{2}H_2O$.	Found. I.	II.
H_2O	7.75	7.69	7.59
Ba	18.29	18.21	18.20

0.1053 gram of the larger, dark crystals lost 0.0152 gram at 210° C., and gave 0.0279 gram $BaSO_4$.

	Calculated for $(C_{13}H_8O_6NS)_2Ba + 7H_2O$.	Found.
H_2O	14.40	14.43
Ba	18.29	18.20

The Action of Dilute Sulphuric Acid on Paranitroorthobenzoylbenzenesulphone Chloride.

The action of sulphuric acid on the sulphone chloride was determined by heating in a flask with a return-condenser until it dissolved. The resulting product was an acid, which was converted into the barium salt by adding an excess of barium carbonate, as in the previous experiments.

The barium salt was obtained in the form of short needles arranged in clusters.

0.1943 gram substance lost 0.0119 gram at 180° C., and gave 0.0570 gram $BaSO_4$.

	Calculated for $(C_{13}H_8O_6NS)_2Ba + 3H_2O$.	Found.
H_2O	6.72	6.12
Ba	18.29	18.48

The Action of Water on Paranitroorthobenzoylbenzenesulphone Chloride.

The action was determined by boiling the sulphone chloride in a flask with a return-condenser until it dissolved. It was necessary to boil somewhat longer to dissolve the substance than in the experiments in which acids were used.

The resulting product was an acid which, by treating in the usual way with barium carbonate, gave a barium salt which crystallized in well-formed monoclinic crystals.

0.1610 gram substance lost 0.0207 gram at 210° C., and gave 0.0443 gram $BaSO_4$.

	Calculated for $(C_{13}H_8O_6NS)_2Ba + 6H_2O$.	Found.
H_2O	12.60	12.85
Ba	18.29	18.56

The Action of Absolute Alcohol on Paranitroorthobenzoylbenzenesulphone Chloride.

The action of absolute alcohol on the sulphone chloride was determined by boiling in a flask with a return-condenser until it dissolved. It dissolved rather more rapidly than in the experiments in which acid was used, and the boiling was continued for a short time after all the material was dissolved. After a part of the alcohol was evaporated, a few drops of the solution showed indications of crystallization on evaporating rapidly on a watch-glass, but, on further evaporation, the solution darkened and the resulting product was an acid as in the previous experiments.

The barium salt was prepared as in the previous experiments. The crystals first obtained were in the form of small, light-colored needles arranged in clusters, but later well-formed monoclinic crystals were obtained from the same solution.

0.1957 gram of the needle-shaped crystals lost 0.0153 gram at 210° C., and gave 0.0559 gram $BaSO_4$.

	Calculated for $(C_{13}H_8O_6NS)_2Ba + 3\frac{1}{2}H_2O$.	Found.
H_2O	7.75	7.81
Ba	18.29	18.21

0.2007 gram of the larger crystals lost 0.0285 gram at 210° C., and gave 0.0535 gram $BaSO_4$.

	Calculated for $(C_{13}H_8O_6NS)_2Ba + 7H_2O$.	Found.
H_2O	14.40	14.26
Ba	18.29	18.27

The above analyses indicate that the action of dilute or concentrated hydrochloric acid, sulphuric acid, water and alcohol on paranitroorthobenzoylbenzenesulphone chloride converts it into paranitroorthobenzoylbenzenesulphonic acid.

Comparison of the Barium Salts.

The analyses of the barium salt of the acids, derived from the action of the various substances on the sulphone chloride, show that the acid is in every case the same and that the salts contain the same amount of barium when calculated upon the basis of the anhydrous salt. The amount of water of crystallization varies widely in the different salts, depending on the conditions under which crystallization takes place.

The needles are obtained from the more concentrated solutions, and crystals of this form are first obtained from a solution which has been evaporated by heating before placing it under a bell-jar. All crystals having this form contain 3 or 3.5 molecules of water of crystallization.

The larger monoclinic crystals which form in the same solution after the formation of needles ceases, or when a cold solution is evaporated to the point of crystallization under a bell-jar, contain 6 molecules of water of crystallization. On exposure to the air or even in a stoppered tube these lose water of crystallization and become opaque.

The only analysis made of a crystal that had changed in this way shows that it contains 3 molecules, while it crystallized with 6.

Those crystals which contain 7 molecules of water of crystallization are obtained on slow crystallization, on standing in the air, from a dilute solution or from a mother-liquor from which crystals containing a less amount of water of crystallization have been deposited.

Although all the barium salts containing different amounts of water of crystallization appear to crystallize in the monoclinic system, they show clearly a variation in form.

Owing to lack of time, no comparative study could be made of the relation existing between the amount of water of crystallization and the crystallographic constants.

The barium salt of paranitroorthobenzoylbenzenesulphonic acid is characterized by an intense bitter taste.

Preparation of Other Salts from the Barium Salt of Paranitroorthobenzoylbenzenesulphonic Acid.

These were prepared from an aqueous solution of the barium salt by precipitating the barium exactly by means of sulphuric acid and neutralizing the free acid exactly with the carbonate of the base.

The solutions were evaporated to crystallization under a bell-jar by means of a current of dry air.

In the analyses the amount of the base is calculated on the basis of the anhydrous salt.

a. The Sodium Salt.—The sodium salt was obtained in the form of fine white crystals composed apparently of monoclinic prisms.

They appear to undergo no change on exposure to the air.

I. 0.1898 gram substance lost 0.0105 gram at 210° C., and gave 0.0384 gram Na_2SO_4.

II. 0.2022 gram substance lost 0.0111 gram at 210° C., and gave 0.0402 gram Na_2SO_4.

	Calculated for $(C_{13}H_8O_6NS)Na + H_2O$.	Found.	
		I.	II.
H_2O	5.19	5.53	5.49
Na	6.99	6.93	6.82

b. The Potassium Salt.—The potassium salt was obtained in the form of fine white needles which were too small to indicate the form of crystallization. They became opaque on exposure to the air.

I. 0.2118 gram substance lost 0.0014 gram at 210° C., and gave 0.0546 gram K_2SO_4.

II. 0.2041 gram substance lost 0.0013 gram at 210° C., and gave 0.0518 gram K_2SO_4.

	Calculated for $(C_{13}H_8O_6NS)K$.	Found.	
		I.	II.
K	11.33	11.63	11.46

c. The Magnesium Salt.—The magnesium salt was obtained in the form of tabular monoclinic crystals having a marked pearly luster. Some of the crystals measured nearly a centimeter in length. They appear to undergo no change on exposure to the air.

I. 0.1940 gram substance lost 0.0408 gram at 210° C., and gave 0.0294 gram $MgSO_4$.

II. 0.1997 gram substance lost 0.0425 gram at 210° C., and gave 0.0303 gram $MgSO_4$.

	Calculated for $(C_{13}H_8O_6NS)_2Mg + 9\frac{1}{2}H_2O$.	Found.	
		I.	II.
H_2O	21.17	21.03	21.28
Mg	3.83	3.88	3.90

d. The Calcium Salt.—The calcium salt was obtained in the form of thin, pearly plates having no regular bounding planes. They become opaque on exposure to the air and crumble to a white powder.

I. 0.1373 gram substance lost 0.0096 gram at 210° C., and gave 0.0280 gram $CaSO_4$.

II. 0.1199 gram substance lost 0.0082 gram at 210° C., and gave 0.0242 gram $CaSO_4$.

	Calculated for $(C_{13}H_8O_6NS)_2Ca + 3H_2O$.	Found.	
		I.	II.
H_2O	7.65	6.99	6.88
Ca	6.13	6.44	6.39

e. The Lead Salt.—The lead salt was obtained in clusters of small, tabular, monoclinic crystals, which became opaque very slowly on exposure to the air.

I. 0.2121 gram substance lost 0.0219 gram at 210° C., and gave 0.0711 gram $PbSO_4$.

II. 0.2039 gram substance lost 0.0213 gram at 210° C., and gave 0.0699 gram $PbSO_4$.

III. 0.1543 gram substance lost 0.0166 gram at 210° C., and gave 0.0509 gram $PbSO_4$.

	Calculated for $(C_{13}H_8O_6NS)_2Pb + 5\frac{1}{2}H_2O$.	Found. I.	II.	III.
H_2O	10.78	10.32	10.44	10.75
Pb	25.25	25.43	25.95	25.23

The copper salt underwent decomposition on evaporation.

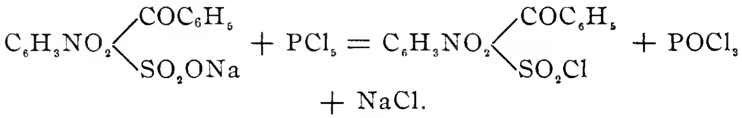
The Action of Phosphorus Pentachloride on the Sodium Salt of Paranitroorthobenzoylbenzenesulphonic Acid.

The sodium salt and phosphorus pentachloride in the proportion of 1 molecule to 1.5 were mixed by grinding together in an evaporating dish. There was no evidence of action, even upon adding a considerable quantity of phosphorus oxychloride, but on heating there was slight action.

The heating was continued for about ten minutes, and the pasty mass was then treated with a considerable volume of cold water. Most of the material dissolved, but a part hardened to a solid mass. After carefully washing with water this material was washed with absolute alcohol, dissolved in benzene, and crystallized out by adding an equal volume of anhydrous ether. The product separated out as clusters of small, light-colored crystals, which melted at 174°–176° C. (uncorr.) and as a scale, around the sides of the beaker, which melted at 160°–170° C. (uncorr.). It was entirely free from the dark-purple material obtained as an impurity in the preparation of paranitroorthobenzoylbenzenesulphone chloride by the action of benzene and aluminium chloride.

A considerable portion of the material was insoluble in benzene and melted at 240°–245° C. (uncorr.).

The method of formation of this material, together with its melting-point, its solubility in benzene, from which it crystallizes readily upon the addition of absolute ether, indicate that it is paranitroorthobenzoylbenzenesulphone chloride. The method of formation from the sodium salt is indicated by the following equation :



$$C_6H_3NO_2\left\langle\begin{matrix}COC_6H_5\\SO_2ONa\end{matrix}\right. + PCl_5 = C_6H_3NO_2\left\langle\begin{matrix}COC_6H_5\\SO_2Cl\end{matrix}\right. + POCl_3 + NaCl.$$

The material melting at 174°–176° C. was boiled in a flask with a return-condenser, with an excess of dilute hydrochloric acid until it was completely dissolved. This required seven hours. The solution was filtered and evaporated to dryness on a water-bath, and the heating continued until all hydrochloric acid was driven off. The product was a dark solid, similar to that obtained by the action of acid on paranitroorthobenzoylbenzenesulphone chloride. An excess of barium carbonate was added to an aqueous solution of the product, the excess of carbonate filtered off, and the solution, which had the characteristic bitter taste of the barium salt of paranitroorthobenzoylbenzenesulphonic acid, evaporated under a bell-jar. On evaporation the solution yielded a small amount of a crystalline barium salt.

The formation of paranitroorthobenzoylbenzenesulphonic acid by the action of hydrochloric acid on the product of the action of phosphorus pentachloride on the sodium salt of paranitroorthobenzoylbenzenesulphonic acid, and its conversion into the barium salt confirms the view already expressed that the action of phosphorus pentachloride on the sodium salt gives the sulphone chloride.

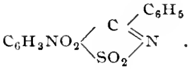
The Action of Concentrated Ammonia on Paranitroorthobenzoylbenzenesulphone Chloride.

As the result of several experiments it was found that, by heating the chloride in a sealed tube for two or two and a half hours in a water-bath, it is mainly converted into a clear, granular product, which melts at 234° C. (uncorr.).

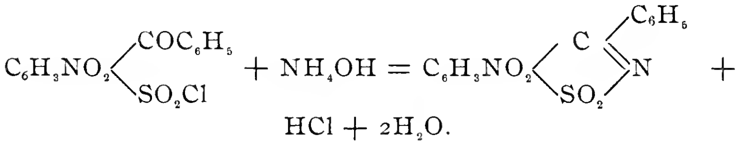
A small amount of a dark, high-melting product is also formed as a thin coating, and can easily be removed mechanically or dissolved in alcohol, which dissolves it readily without dissolving the main product.

The material thus prepared is obtained in the form of a light-green, granular powder, having a constant melting-point of 234° C. (uncorr.). The substance contains no chlorine.

I. 0.2014 gram substance gave 15.81 cc. N.
II. 0.1970 gram substance gave 15.67 cc. N.
III. 0.2075 gram substance gave 0.1756 gram $BaSO_4$.
IV. 0.2011 gram substance gave 0.1692 gram $BaSO_4$.

	Calculated for  $C_6H_3NO_2{<}\begin{matrix}C{<}^{C_6H_5}_{\gg N}\\ SO_2\end{matrix}$.	Found. I.	II.
N	9.72	9.86	9.99
S	11.11	11.60	11.55

The results of analysis, together with those described in the following section, indicate that the main product of the action of concentrated ammonia on the chloride is the lactim of paranitroorthobenzoylbenzenesulphonic acid. The reaction by which it is formed is represented as follows:



$$C_6H_3NO_2{<}\begin{matrix}COC_6H_5\\ SO_2Cl\end{matrix} + NH_4OH = C_6H_3NO_2{<}\begin{matrix}C{<}^{C_6H_5}_{\gg N}\\ SO_2\end{matrix} + HCl + 2H_2O.$$

The lactim is insoluble in water, only slightly soluble in alcohol and readily soluble in benzene.

The formation of the lactim of the sulphonic acid by the action of concentrated ammonia agrees with the formation of the lactim of orthobenzoylbenzenesulphonic acid by the action of dry ammonia gas on the sulphone chloride as observed by Remsen and Saunders.[1]

The Action of Concentrated Ammonia on the Lactim of Paranitroorthobenzoylbenzenesulphonic Acid.

The presence of a red-colored, amorphous product, melting above 275° C. (uncorr.), with the lactim formed by the action of ammonia on the chloride, together with the fact that the amount of this product was increased as the length of time of heating was increased, indicated that another product was formed by the continued action of ammonia. A considerable quantity of this material was prepared by heating some of the paranitroorthobenzoylbenzenesulphone chloride in a sealed tube until the only product consisted of the red-colored substance desired. It was found necessary to heat it to the temperature of the water-bath for twenty-four hours in order to effect this transformation, while two and a half hours were sufficient to transform the sulphone chloride into the lactim.

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[1] *Loc. cit.*

The product is insoluble in water, but dissolves readily in absolute alcohol, giving a red solution with a marked green fluorescence. It is thrown out of solution by adding a considerable volume of water.

On evaporating the alcoholic solution it is deposited as a red-colored crust which seems to possess no crystalline structure.

0.2150 gram gave 19.24 cc. N = 11.24 per cent N.

0.1615 gram gave 0.1200 gram $BaSO_4$ = 10.20 per cent S.

The results of the analysis show that while the percentage of sulphur remains about the same as in the lactim, the percentage of nitrogen is increased, but not to an amount corresponding to the composition of any substance likely to be derived from the lactim by the further action of ammonia.

These results, together with the impossibility of obtaining the product in crystalline condition and its properties generally indicate that it is probably not a definite chemical compound, and that the lactim probably undergoes decomposition by the further action of ammonia.

The Action of Dilute Hydrochloric Acid on the Lactim of Paranitroorthobenzoylbenzenesulphonic Acid.

The action of hydrochloric acid on the lactim was first tried by boiling in a flask, provided with a return-condenser, with an excess of acid. The lactim showed but little change after boiling with the acid for thirty hours. The acid was colored yellow, but this was found to be due to solution of the lactim. By evaporating off the acid, the lactim is recovered with its melting-point unchanged.

By heating the lactim with a large excess of hydrochloric acid in a closed tube to 150°–175° C. in a furnace for five hours, about half of the lactim is dissolved and is not deposited on cooling. On heating to 200° C. for seven hours longer, all of the lactim goes into solution, and is not deposited on cooling, and the acid has a dark-yellow color. On evaporating the filtered acid solution, a yellow, crystalline product is obtained, which has not a constant melting-point. The melting-point, immediately after pressing out between filter-paper, is 100°–160° C. (uncorr.), and it is charred by heating to 210°

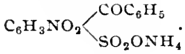
C. (uncorr.) in an air-bath. If, however, it is first carefully dried, it appears to melt at a much higher temperature.

This indicates that the product is a salt which melts in its water of crystallization.

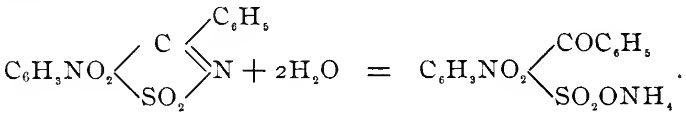
Analysis of a sample carefully dried:

0.2009 gram gave 14.33 cc. N.

0.1692 gram gave 0.1264 gram $BaSO_4$.

	Calculated for  $C_6H_3NO_2\begin{cases}COC_6H_5\\SO_2ONH_4\end{cases}$.	Found.
N	8.64	8.95
S	9.88	10.24

The results of analysis indicate that the product is the ammonium salt of paranitroorthobenzoylbenzenesulphonic acid. The transformation takes place according to the following equation:



The ammonium salt thus obtained has generally the form of a yellow crystalline powder, but under the conditions existing in one of the experiments, a few thick, needle-shaped crystals about a centimeter long were obtained. It dissolves readily in water.

Summary.

The principal results obtained in the foregoing investigation may be briefly stated as follows:

By using phosphorus pentachloride in the proportion of 2.5 molecules to 1 of the anhydrous acid potassium salt and heating for five hours under the conditions indicated, the unsymmetrical chloride is the only product.

This may be crystallized readily at the temperature of the laboratory by using ligroin (90°–125°) as the solvent, provided the impurities are first removed by washing with ligroin (50°–80°).

The action of benzene and aluminium chloride on the symmetrical and on the unsymmetrical chloride gives, in both cases, paranitroorthobenzoylbenzenesulphone chloride.

The action of hydrochloric acid, concentrated or dilute, dilute sulphuric acid, water, and alcohol on paranitroorthobenzoylbenzenesulphone chloride is the same. The product formed is, in each case, paranitroorthobenzoylbenzenesulphonic acid.

The action of phosphorus pentachloride on the sodium salt of paranitroorthobenzoylbenzenesulphonic acid gives rise to the formation of paranitroorthobenzoylbenzenesulphone chloride identical with that from which the acid was derived by the action of acids or water.

The action of concentrated ammonia on paranitroorthobenzoylbenzenesulphone chloride for a limited length of time gives the lactim of paranitroorthobenzoylbenzenesulphonic acid.

The further action of concentrated ammonia gives a substance of indefinite composition, which probably indicates a decomposition of the lactim first formed.

The continued action of concentrated hydrochloric acid at a high temperature in a sealed tube converts the lactim into the ammonium salt of paranitroorthobenzoylbenzenesulphonic acid.

Contribution from the Kent Chemical Laboratory of the University of Chicago.

STEREOISOMERS AND RACEMIC COMPOUNDS.

By Herman C. Cooper.

I. Solubility of Stereoisomers in an Indifferent Active Solvent.

The possibility of a difference in solubility of two optical isomers in an active solvent has been recognized ever since the researches of Pasteur.[1] In a recent paper[2] the writer, together with Heinrich Goldschmidt, who first directed his attention to the matter, presented experimental evidence indicating that the two optically active carvoximes have the same solubility in *d*-limonene. Tolloczko[3] had by a different method previously come to similar conclusions in the cases of the tartaric acids in amyl alcohol and the mandelic acids in

[1] Ann. chim. phys. [3], **38**, 437; Cf. also Van 't Hoff-Eiloart, Atoms in Space, 1898, p. 45.

[2] Ztschr. phys. Chem., **26**, 711.

[3] *Ibid.*, **20**, 412.

levulose solution. Kipping and Pope,[1] however, announce that, on allowing a racemic mixture to crystallize from an optically active solution, the first fractions show a preponderance of crystals of one of the isomers. Thus, the first crystallization of sodium ammonium racemate from aqueous dextrose solution at a temperature below the transition-point was found to consist chiefly of dextrotartrate. As this seems to suggest a difference of solubility of the two active tartrates in dextrose solution, it appeared desirable to use the same simple method employed in the carvoxime-limonene test[2] to obtain more light on this matter.

On account of the rather large solubility of the sodium ammonium tartrates in water and their tendency to weather, the stable sodium hydrotartrates were first examined. In the light of the present structural theory of optical isomers it is very unlikely that the addition of an NH_3 group each to both isomers would alter their relative behavior towards an active solvent. The probability of electrolytic dissociation of tartrates in such a solution renders this all the less likely.

Sodium Hydrotartrates in Aqueous Dextrose Solution.—The dextrotartrate was prepared by mixing the theoretical amounts of sodium carbonate and ordinary c. p. tartaric acid in water; the laevo salt in a similar manner from *l*-tartaric acid obtained by the Pasteur-Anschütz crystallization method.[3] After recrystallization the salts were tested as to rotatory

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[1] Proc. Chem. Soc., 1898, 113.

[2] Goldschmidt and Cooper: *Loc. cit.*

[3] A careful comparison of the three well-known Pasteur methods has shown the crystallization process to be the most reliable in securing a satisfactory yield about whose rotatory power no anxiety need be felt. By the improved cinchonine method (Ber. d. chem. Ges., **29**, 42) much time is consumed in the recovery and purification of the racemic acid and cinchonine unless one is working on a large scale, while with a little care a concentrated solution of Scacchi salt can after a short period in a cold room be made to yield homogeneous crystals of 1–5 grams each. The first one that can be crystallographically identified as laevo should be used to prepare a calcium-tartrate solution, and the neat Anschütz test (Ann. Chem. (Liebig), **226**, 193) at once applied to all the other crystals. If the sample is taken from different parts of the crystals, the ones so recognized as laevo will be found, after recrystallization from 60 per cent alcohol, to furnish a tartrate of unquestioned purity, from which the laevo acid is easily obtained by treatment with lead acetate and hydrogen sulphide.

Sowing the original solution with laevo crystals is of advantage for the first one or two crops but supersaturation with reference to the dextrotartrate soon becomes so great that laevo crystals are dissolved while dextro crystals are formed. For this reason it is better to sow dextro and laevo crystals simultaneously at different places in the solution.

power with a thoroughly reliable Laurent half-shadow polarimeter.

1. d-$NaC_4H_5O_6 + H_2O$. 1.5350 grams dissolved in water to 25 cc.; $c = 6.1400$; $t = 21^\circ$; $l = 2\text{dm}$; $\alpha = +2^\circ 42'.3$; $[\alpha]_D^{21} = +22^\circ.03$.

2. l-$NaC_4H_5O_6 + H_2O$. 1.5350 grams dissolved in water to 25 cc.; $c = 6.1400$; $t = 19^\circ.5$; $l = 2\text{dm}$; $\alpha = -2^\circ 42'$; $[\alpha]_D^{19.5} = -21^\circ.98$.

A comparison of these figures with the table of Thomsen[1] shows that the substances may be considered perfectly pure. The dextrose solution used possessed a density of 1.14, a strength of 32.5 per cent, and a rotatory power of $[\alpha]_D^{20} = 53^\circ.8$.

Weighed quantities of tartrate and dextrose solution were sealed up in small glass tubes and the temperature determined at which complete solution took place.[2] By working with a No. 20 beaker-glass and carefully avoiding disturbing air currents the temperature could easily be held constant to 0°.1 below 50°, and to at least 0°.2 between 50° and 70°. The tubes were allowed to rotate about 60–70 times a minute. In cases where the concentration, and consequently the solution-temperature, was high the question as to just when complete solution took place was decided by removing the tube and allowing it to remain several hours at room temperature. If all solid particles had disappeared, supersaturation resulted and no separation of solid matter followed; otherwise the tube was replaced and the test continued. A table of results follows:

d-Tartrate in Dextrose Solution.

Gram tartrate.	Grams dextrose solution.	Grams tartrate to 100 grams dextrose solution.	Solution temperature.
0.1782	2.3202	7.68	32°.9
0.1984	1.8949	10.47	43°.6+
0.1946	1.1200	17.38	61°.6

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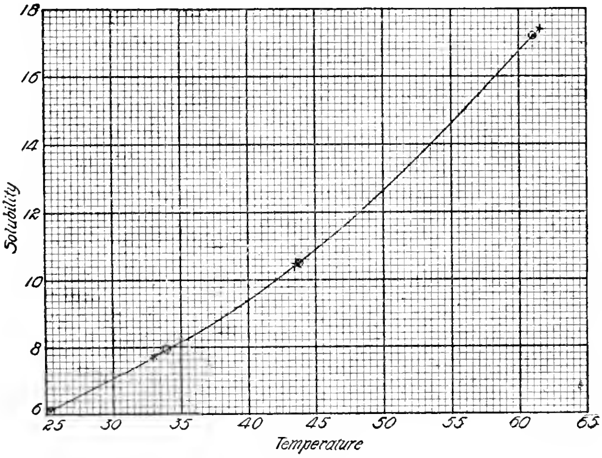
[1] J. prakt. Chem. [2], **31**, 85.

[2] For description of apparatus see Ztschr phys. Chem., **26**, 713; and also Fig. 125, Ostwald-Walker's Physico-chem. Measurements (1894).

l-Tartrate in Dextrose Solution.

0.1756	2.8700	6.12	25°.2
0.2006	2.5330	7.92	34°.0
0.1998	1.9066	10.48	43°.7
0.1943	1.1301	17.19	61°.1

The parallelism of the results in the two cases is better shown by plotting them as curves. Let the figures in the third column, representing solubility, be the ordinates and those in the fourth column, representing the corresponding temperatures, be the abscissae. The crosses indicate *d*-tartrate, the circles *l*-tartrate.



As a further check on the results we may apply the solubility formula, $S = a + bt + ct^2$, which, using the values at 25°.2, 34°.0, and 43°.7, becomes $S = 3.72 + 0.01443t + 0.003211t^2$ for dextrotartrate. Interpolating for 32°.9 we have $S = 7.67$. 7.68 was found experimentally for *l*-tartrate. It is plain that there is no justification for the assumption of two separate curves and we must conclude that there is no difference in solubility.

Sodium Ammonium Tartrates in Aqueous Dextrose Solution.—A few experiments were then similarly made with the sodium ammonium tartrates. Each of these salts was recrystallized from 60 per cent alcohol, the solution being agitated to produce small crystals, and the resulting crystals were washed with alcohol and dried first on filter-paper and then a few minutes in a vacuum desiccator. In each experiment nearly equal proportions of dextro and laevo salt were used and the two tests carried out simultaneously (temp. as under I). After subsequent cooling each experiment was repeated (II).

Exp. I.—Material obtained from Neutralizing the Previously Prepared Hydrotartrates with Ammonia.

	Gram $NaNH_4C_4H_4O_6 + 4H_2O$.	Grams dextrose sol.	Grams tartrate to 100 grams dextrose sol.	Solution temperature.	
				I.	II.
Dextro	0.6668	1.0846	6.15	27°.3	27°.4
Laevo	0.6682	1.0870	6.14	27°.6	27°.6+

Exp. II.—Material from Freshly Separated Tartrates.

Dextro	0.5222	1.0652	4.90	22°.1	21°.9
Laevo	0.5300	1.0733	4.94	21°.8	21°.9

Exp. III.—Material as in Exp. II.

Dextro	0.4918	0.9886	4.97	22°.2	22°.2
Laevo	0.4920	0.9891	4.97	22°.15	22°.2

The slight variation in the results seems to be due to the rather large experimental error, anticipated above, and we are hardly justified in assuming any considerable difference in solubility. It is therefore very probable that a solution of an externally compensated mixture of the sodium ammonium tartrates, in a concentration strong enough to cause crystallization, will in time yield practically equal quantities of the two modifications. Nevertheless, if the dextrose molecules exert even the slightest influence, so that the first crystal molecule formed is dextro, that individual will have the same effect on the crystallization as the introduction of a dextro crystal. No intrusion on the field of Messrs. Kipping and Pope is planned, but it is to be hoped that they will ascertain whether a laevo-rotatory solvent has the opposite effect from that of dextrose solution.

II. *Properties of Inactive Mixtures.*

Melting-point.—The following data supplement the interesting work of Centnerszwer.[1] Sodium hydrotartrate decomposes at 234°, a point sharply indicated by a sudden rise of substance in the m. p. tube. The racemate decomposes at 219°, and a mixture of approximately equal parts of the optical isomers at 222°.

A mixture of approximately equal parts of the active carvoximes was found to melt at the same temperature as inactive carvoxime; *viz.*, 93°. A slight shrinking was to be observed at 72°, the melting-point of the active body.

Solubility.—On mixing equal amounts of the active sodium hydrotartrates in water, a cloudy precipitate of racemate appears and does not disappear till the temperature of the solution of the racemate is reached. A similar mixture of the active carvoximes in aqueous alcohol gives no precipitate of racemic compound, but, nevertheless, has the same solubility as an amount of racemic carvoxime equal to the weight of the mixture.

III. Partial Racemism.

The credit of having established the existence of partial racemic compounds must be ascribed to Ladenburg, who identified racemic quinine pyrotartrate[2] as the first example. Other examples have been subsequently announced by Ladenburg and Doctor,[3] and by Pope and Peachey.[4] It will be noticed that there is no essential difference between them, each being made up of two components which possess the same chemical composition, differing only as $+A+B$ and $+A-B$ or $+A+B$ and $-A+B$, in which A represents an acid, B a basic radical. Is it not possible, however, for a racemic compound to exist whose active components are not chemically equivalent? When one considers the facility with which some optical isomers unite to form racemic compounds of distinctly different physical properties, the question easily arises whether a slight modification of one isomer, such as substitution in a position remote from the asymmetric carbon atom, necessarily renders racemic association impossible.

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[1] Ztschr. phys. Chem., **29**, 715.

[2] Ber. d. chem. Ges., **31**, 524, 937.

[3] *Ibid.*, **31**, 1969.

[4] Ztschr. Kryst. u. Min., **31**, 11.

Such a case, if discovered, would certainly broaden our ideas of racemic bodies. Reasoning somewhat in this way, Küster[1] has suggested the possibility of chlorbenzoyl-*d*-tartrate and brombenzoyl-*l*-tartrate uniting to form a partial racemate.

In Pasteur's notable monograph[2] entitled "Nouvelles Recherches," ammonium bimalate is said to form a definite compound with dextroammonium bitartrate, not, however, with laevoammonium bitartrate. This discovery of a half century ago has apparently been frequently overlooked, no mention of it being found in Bischoff-Walden's "Stereochemie" or Van 't Hoff-Eiloart's "Arrangement." The compound was found to consist of 1 molecule of *d*-ammonium bitartrate and 1 molecule of *l*-ammonium bimalate. Inasmuch as the atomic difference between the two molecules is very slight, it seems quite likely that we have here to deal with a case of partial racemism as above suggested. A repetition and extension of Pasteur's experiments is planned, covering all the tartro-malic compounds, and the much discussed "criteria" of racemic compounds will be carefully applied. Some preliminary experiments with sodium bitartrate and sodium bimalate have disclosed interesting relations.

OBITUARY.

CARL FRIEDRICH RAMMELSBERG.

The long and useful life of Carl Friedrich Rammelsberg ended on December 28th of the past year. He was born in Berlin, April 1st, 1813, and after a thorough school training spent five years as an apothecary. He then matriculated at the university and devoted himself to physics, chemistry, mineralogy, and botany under the most distinguished teachers of that day, working in the laboratory of Mitscherlich. Later he established the first laboratory specially devoted to the instruction of students in inorganic analysis. He became in succession privatdocent, extraordinary, and ordinary professor in the University. Meantime his marvelous industry showed itself in the publication of numerous papers on mineral chemistry, the number of these alone amounting to more than 150. He made also valuable investigations in many branches

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[1] Ber. d. chem. Ges., **31**, 1853.

[2] Ann. chim. phys. [3], **38**, 460.

of pure inorganic chemistry, and as an excellent crystallographer did much to further the study of crystalline form as an essential part of descriptive chemistry. The list of his special treatises, handbooks, and introductions is a long one and many of them even now have a real value as works of reference and well illustrate the broad view which he took of his own favorite branches of science. He was able to pursue his laboratory work long after the age when most chemists are obliged to content themselves with only looking on at the progress of their science. Personally he was much beloved by his pupils and was conscientious as a teacher as well as an investigator. The writer of this brief notice, as one of Rammelsberg's pupils, offers these words of appreciation of the man and of his work. W. G.

NOTES.

Polonium and Radium.

Some years ago Becquerel, while working with uranium and some of its salts, found that certain of the salts, although they are not fluorescent, nevertheless have the power of emitting rays which are different from the Roentgen rays. These new rays have the power of rendering gases through which they pass conductors of electricity and of producing impressions on photographic plates. They are also capable of being transmitted through opaque bodies, but suffer greater absorption than the Roentgen rays.

Shortly after Becquerel's work, Schmidt found that thorium and its salts emit the same kind of rays as uranium and its salts, but that the former are less intense than the latter.

While investigating pitchblende and other minerals closely allied to it, which contain uranium and thorium, M. and Mme Curie[1] discovered the new substance which they called polonium, after the native country of Mme. Curie. They called the property of emitting Becquerel rays "radioactivity", and found that the sample of pitchblende with which they were working was two or three times as radioactive as uranium. Since the salts of uranium are less active than metallic uranium, they concluded that the great radioactivity of pitchblende is due to the presence of a small amount of some strongly radioactive substance. They passed hydrogen sulphide into an acid solution of the pitchblende. The uranium and thorium remained in solution, and besides lead, bismuth, copper, arsenic, and antimony, a very active substance was pre-

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[1] Compt. rend., **127**, 175 (1898); Chem. News, **78**, 40 (1898).

cipitated. The active sulphide is insoluble in ammonium sulphide, which separated it from arsenic and antimony. The sulphides insoluble in ammonium sulphide were dissolved in nitric acid, and the lead precipitated with sulphuric acid. Some of the active substance is carried down with the lead, and can be covered by treating the lead sulphate with dilute sulphuric acid, which dissolves the active substance. There were then in solution the active substance, bismuth and copper. Ammonia precipitated the first two completely, thus separating them from the copper. It was impossible to separate the active substance from bismuth in the wet way. On dissolving them both in nitric acid and adding water, it was found that the portions first precipitated are by far the most active. Further, when the mixed sulphides from pitchblende are heated in a vacuum in a glass tube to about 700°, the active substance sublimes in the portion of the tube heated to 250°–300°, while the bismuth remains in the warmer part of the tube. By these methods the investigators obtained a substance which was 400 times as active as uranium. Specimens of it were sent to Demarçay to be examined spectroscopically, but his results were unsatisfactory.

While working on polonium M. and Mme. Curie[1] discovered a second new radioactive substance, closely allied to barium and different from polonium, which they called radium. This new radioactive substance is obtained from pitchblende together with barium, and it has not been possible to separate it from barium. It is not precipitated by hydrogen sulphide, ammonium sulphide, nor ammonia ; its sulphate is insoluble in water and acids ; its carbonate is insoluble in water ; the chloride is very soluble in water, but insoluble in concentrated hydrochloric acid and in alcohol. The substance, as first obtained by its discoverers, was in the form of the chloride and then had a radioactivity 60 times as great as that of uranium. On dissolving the chloride in water and precipitating with alcohol, the portions first precipitated are the most active. In this way a substance was finally obtained which was 17000 times as radioactive as uranium. Demarçay[2] examined the spectrum of this substance and found in it the barium lines, the platinum lines due to the electrodes, the calcium and lead lines, which were very weak, probably due to impurities, and a series of new lines which were fully as intense as the barium lines, and which could not possibly belong to any of the known elements. The new lines in the spectrum were comprised between $\lambda = 4826.3$

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[1] Compt. rend., **127**, 1215 (1898) ; Chem. News, **79**, 1 (1899).

[2] Compt. rend., **127**, 1218 (1898) ; *Ibid.*, **129**, 716 (1899) ; Chem. News, **29**, 13 (1899) ; *Ibid.*, **80**, 269 (1899).

and λ = 3649.6. The strongest new line, which was as strong as the strongest barium line, had λ = 3814.7. The results of the spectroscopic examination, together with the fact that barium and its compounds are not in the least radioactive, led M. and Mme. Curie to the conclusion that they had a new substance to deal with.

The atomic weight[1] of the metal contained in some of the most active specimens of radiferous barium chloride was determined with the following results:

a.	*M.*	*Ba.*
3000	140.0	138.1
4700	140.9	137.6
7500	145.8	137.8

a represents the activity of the chloride, the activity of uranium being taken as 1, *M* represents the atomic weight of the metal in the radiferous chloride, and *Ba* represents the atomic weight of barium from pure, inactive barium chloride, whose atomic weight was determined each time that the metal in the radiferous chloride was determined. The atomic weights were determined by estimating the amount of chlorine in the anhydrous chlorides with silver nitrate.

Becquerel rays and the rays from polonium and radium seem to be essentially the same in character, but they differ in intensity. The rays from radium are the strongest, those from thorium the weakest. The radium rays will produce an impression on a photographic plate in half a minute, while under the same conditions the uranium rays require an hour to produce the same impression. Rays from polonium and radium excite fluorescence in barium platinocyanide, weaker to be sure than that caused by Roentgen rays, but uranium and thorium rays excite no fluorescence at all on account of their weaker radioactivity. Radioactive substances also have the power of inducing radioactivity in inactive substances, and this induced radioactivity continues for several days after the originally radioactive substance has been removed. In this respect Becquerel rays differ markedly from Roentgen rays which produce a secondary effect in bodies only as long as the rays strike such bodies.

Becquerel rays seem to have the power of inducing chemical action.[2] It was observed that when bottles containing radiferous barium chloride were opened, the odor of ozone was very perceptible. This odor was dissipated after the bottle had stood open for some minutes, but was noticeable again when the bottle was opened after having been closed for

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[1] Compt. rend., **129**, 760 (1899); Chem. News, **80**, 281 (1899).

[2] Compt. rend., **129**, 1823 (1899).

some time. Also, the glass of bottles in which the chloride is kept assumes a violet color where it comes in contact with the salt. Villard[1] noticed a similar effect when glass is subjected to the action of Roentgen rays, while at the same time it is protected from the cathode rays. It is concluded that this coloration of the glass is due to the oxidation of manganese which is contained in it. Further, the action of Becquerel rays on barium platinocyanide seems to be of a chemical nature. The salt under the effect of these rays becomes fluorescent and turns yellow. It then loses its fluorescence and becomes dark-brown. If now it is exposed to the sunlight, it again acquires the property of becoming fluorescent when struck by Becquerel rays.

To account for the continuous disengagement of energy from radiferous bodies, several views have been advanced. It might be due to a phosphorescence of very long duration, caused by the action of light, or it might be due to an emission of matter accompanied by a loss of weight of the radiferous bodies. Again, it might be a secondary emission provoked by rays which are constantly in existence in space and which are absorbed only by certain elements.

Quite recently, M. Debierne[2] has obtained another radioactive substance from pitchblende, which is closely allied to titanium in its chemical properties. It differs from radium in that it is not luminous in the dark, while radium is luminous.

C. E. C.

Asymmetric Optically Active Nitrogen Compounds.

Messrs. Pope and Peachey[3] have recently published an interesting article on the above subject. From this the following extracts are taken:

"The only direct evidence pointing to the existence of asymmetrically optically active nitrogen compounds is Le Bel's observation[4] that on cultivating *Penicillium glaucum* in solutions of isobutylpropylethylmethylammonium chloride the liquid acquires a rotatory power of —0°25′ or —0°30′ under favorable conditions. The value of this important observation is, however, considerably lessened by the fugitive nature of the optical activity and by the failure of Marckwald and von Droste-Huelshoff[5] to confirm Le Bel's results. (Le Bel has recently replied to Marckwald and von Droste-Huelshoff's criticism,[6] and has confirmed his previous results.)

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[1] Compt. rend., **129**, 882 (1899).

[2] *Ibid.*, **129**, 593 (1899).

[3] J. Chem. Soc., December, 1899.

[4] Compt. rend., 1891, **112**, 724.

[5] Ber. d. chem. Ges., **32**, 560.

[6] Compt. rend., **129**, 548.

"Many futile attempts have been made to directly resolve quaternary bases of the type $N(OH)X_1X_2X_3X_4$ into optically active antipodes by means of optically active acids. Thus Marckwald and von Droste-Huelshoff[1] attempted to resolve Le Bel's base by the aid of tartaric, camphoric, and mandelic acids, whilst Wedekind[2] endeavored to resolve α-benzoylphenylallylmethylammonium hydroxide by means of tartaric and camphoric acids; in no case, however, was an optically active base obtained.

"A consideration of the facts led to the opinion that the failure of these and other attempts had its origin in the facility with which tetralkylammonium salts are decomposed by water and converted into tertiary base and alcohol; we, therefore, prepared α-benzylphenylallylmethylammonium iodide by Wedekind's[3] method and were successful in resolving it into isomeric optically active bases by using hydroxyl-free solvents containing only small quantities of water. A number of methods, differing in detail, were applied, but we ultimately adopted the following process as affording the best results:

"Carefully purified α-benzylphenylallylmethylammonium iodide was mixed with a molecular proportion of the anhydrous silver salt of Reychler's dextrocamphorsulphonic acid and boiled for an hour or so on the water-bath with a mixture of about equal parts of acetone and, ethylic acetate, a few drops of water being added when necessary. After separating silver iodide from the gummy solution by filtration the solvent was distilled off, and, on cooling, the residue solidified to a crystalline mass consisting of a mixture of dextro- and laevobenzylphenylallylmethylammonium dextrocamphorsulphonate.

"By fractionally crystallizing the mixture of dextrosulphonates from boiling acetone the less soluble constituent, dextro-α-benzylphenylallylmethylammonium dextrocamphorsulphonate, was readily obtained in colorless, diamond-shaped plates melting at 169°–170°."

The authors show that the molecular rotatory power of the basic radical of this salt is $+150°$.

The corresponding laevo salt was obtained from the acetone mother-liquors, and this was found to have a marked laevo rotatory power.

From the two dextrosulphonates the corresponding iodides and bromides were obtained.

In concluding their article the authors say:

"In the present paper it is proved that quaternary ammo-

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[1] *Loc. cit.*

[2] Ber. d. chem. Ges., **32**, 517.

[3] *Loc. cit.*

nium derivatives in which the five substituting groups are different, contain an asymmetric nitrogen atom which gives rise to antipodal relationships of the same kind as those correlated with an asymmetric carbon atom. The method which has enabled us to deal with quaternary bases is now being applied to various other types of substituted ammonium derivatives in order to ascertain the stereochemical nature of pentad nitrogen. We hope shortly to be in a position to publish results obtained with sulphonium derivatives of the type $SX_1X_2X_3I$." I. R.

REVIEWS.

LES SUCRES ET LEURS PRINCIPAUX DÉRIVÉS. Par L. MAQUENNE, Professeur au Muséum d' Histoire Naturelle. Paris : Georges Carré et C. Naud, éditeurs. 1900. 1032 pp.

The author of this handbook has done chemists a service by compiling from the great mass of papers appearing within the last few years on the sugars and closely allied substances—largely due to the labors of E. Fischer and his pupils and co-workers—a general *résumé* of our present knowledge in the field in question. Not only are the general principles of stereoisomeric chemistry applied systematically to the classification and nomenclature of the sugars, but the preparation and properties of the now numerous substances of this class are described with a very fair degree of detail, considering the moderate size of the book, and its value is greatly enhanced for the practical worker by copious references to the original papers which have been collated, French, Russian, and other sources being drawn upon as well as German. The transformations by hydrolysis, fermentation, etc., are gone into in brief but intelligible fashion, connecting the sugars with each other and with their chief derivatives of other classes, and methods of determination for the principal sugars are discussed in their practical bearings. The notice taken of some allied substances, such as starch and cellulose, seems to be hardly in proportion to the work upon them which has been done in recent years, though there are references to the more important memoirs. In agreeable contrast with the usage of most French writers, the author has appended a convenient index, as well as the usual table of contents. J. W. M.

MODES OPÉRATOIRES DES ESSAIS DU COMMERCE ET DE L'INDUSTRIE. Par L. CUNIASSE et R. ZWILLING, Chimistes-Experts de la Ville de Paris. Paris : Georges Carré et C. Naud, éditeurs. 1900. 302 pp.

In the preface to this little book, by M. Ch. Girard, it is suggested that it is intended for the use of young men who expect to enter industrial laboratories, and is to occupy an intermediate place between the large treatises for professional men and the small text-books for beginners. There is included much good matter, in general clearly presented and in highly condensed form, but condensation has been carried so far that, for many of the topics treated of, the work can hardly be considered as more than an index, and must prove of small value in the absence of larger handbooks. Thus, the whole subject of iron is disposed of in about three and a half small pages (no notice is taken of steel), glass in a page and a quarter, fuel in less than three pages, soap in a little more than three pages, and butter in about a page. Some other subjects have more space devoted to them, as, for example, there are ten and a half pages on milk, fifteen pages on sugar, and nearly twenty pages on wine. A few materials are included which are not commonly found in the smaller manuals of this kind, such as wood- and coal-tar creosote, vulcanized india-rubber, and gutta percha. J. W. M.

WATER AND WATER SUPPLIES. By JOHN C. THRESH, D.Sc. (London). Philadelphia : P. Blakiston's Son & Co. (printed in England). 1900. 431 pp.

A generally well-compiled and well-balanced summary of the most important facts—geological, chemical, bacteriological, and engineering—bearing upon natural water as obtainable for human use. In regard to most of the questions which have given rise to difference of opinion the author seems to fairly, and without partisanship, sum up the present state of our knowledge, as, for instance, in the chapters on the interpretation of water analyses and the so-called self-purification of rivers. The book is written essentially from an English point of view, and would be increased in value if more extended notice were taken of the investigations made and results obtained in other countries. The three subjects which receive distinctly inadequate notice are: the effects of various kinds of natural waters upon metallic pipes and iron or steel boilers; the relations of natural waters to special manufacturing uses, such as brewing, dyeing, and paper-making, and the effects on streams of special manufacturing refuse; and the rapid mechanical filtration of water on the great scale, aided by coagulants, as now largely practiced in the United States. J. W. M.

OUTLINES OF INDUSTRIAL CHEMISTRY. By FRANK HALL THORP, PH.D., Instructor in Industrial Chemistry in the Massachusetts Institute of Technology. New York : The Macmillan Company. New edition, revised. 1899. 541 pp.

The appearance of a second edition of this work a year after its first publication is a favorable indication of its having proved acceptable. As the author says in his new preface that he has limited himself to the correction of errors which have been noticed, and has made no material change in the text, there seems to be occasion for little more than a repetition of the remarks made in a former notice in this JOURNAL (Vol. **21**, p. 181). It is to be hoped that the press of other work referred to as the reason for not extending or recasting any parts of the book may not long prevent the bringing out an edition with such changes and improvements, particularly in regard to the illustrations, as might easily develop the work into a very useful manual for students. J. W. M.

INTRODUCTION TO PHYSICAL CHEMISTRY. By JAMES WALKER., D.SC., PH.D., Professor of Chemistry in University College, Dundee. New York and London: Macmillan & Co. 1899. 335 pp.

This work does not aim to be a systematic text-book covering the whole field of physical chemistry, but treats certain chapters at considerable length. Dr. Walker states the purpose which he had in mind in writing this book, as follows: "I have found in the course of ten years' experience in teaching the subject, that the average student derives little real benefit from reading the larger works which have hitherto been at his disposal, owing chiefly to his inability to effect a connection between the ordinary chemical knowledge he possesses and the new material placed before him. He keeps his every-day chemistry and his physical chemistry strictly apart, with the result that instead of obtaining any help from the new discipline in the comprehension of his systematic or practical work, he merely finds himself cumbered with an additional burden on the memory, which is to all intents and purposes utterly useless. This state of affairs I have endeavored to remedy in the present volume."

Some of the subjects treated are: The Atomic Theory and Atomic Weights; The Simple Gas Laws; The Periodic Law; Solubility; Fusion and Solidification; Vaporization and Condensation; The Kinetic Theory and van der Waals' Equation; The Phase Rule; Relation of Physical Properties to Composition and Constitution; The Properties of Dissolved Substances; Osmotic Pressure and the Gas Laws for Dilute Solutions; Methods of Molecular Weight Determination; Electrolysis and Electrolytes; Electrolytic Dissociation; Balanced Actions; Rate of Chemical Transformation; Relative Strengths of Acids and Bases; Applications of the Dissociation Theory; Thermodynamical Proofs.

The chapter on the Phase Rule is by far the clearest and most concise treatment of this subject which has thus far appeared.

Under methods for determining molecular weights, in addition to those ordinarily employed for vapors and solutions, we find a brief account of the beautiful method of Ramsay and Shields, by which the molecular weight of pure liquids can be determined by measuring their surface-tension. It is unfortunate that this method is too delicate for general laboratory use, since much of importance would undoubtedly be brought to light by its further application.

It seems a little out of keeping with the remainder of the work, that the very defective method of Nernst and Loeb should be recommended for determining the relative velocities of ions, now that we have methods which are so much more refined.

The work, as a whole, is admirably written in a clear and attractive style and can be heartily recommended to any one who is beginning the study of physical chemistry.

H. C. J.

A TEXT-BOOK OF PHYSICAL CHEMISTRY. By DR. R. A. LEHFELDT, Professor of Physics at the East London Technical College. London: Edward Arnold. 1899 308 pp.

The author points out what is generally recognized, that the new physical chemistry has not been accorded the hearty welcome in England which it deserves. "It is time, too, to appeal for wider recognition in England, where, as yet, not a single professorship exists to mark the appearance of a new science that on the continent has long been regarded as wide enough to require a man's whole energy." A brief quotation from the preface will show what is the aim of this little book: "The present book is intended to contain what a student—with limited time and many subjects to learn—may usefully read. * * The author hopes that the style adopted will put the reader, as far as possible, in touch with the constant stream of experimental and theoretical research that makes physical chemistry at present such a fascinating subject to follow."

The subject is dealt with in seven chapters: Determination of Molecular Weight; Physical Constants in Relation to Chemical Constitution; The Principles of Thermodynamics; Chemical Dynamics of Homogeneous Systems; Chemical Dynamics of Heterogeneous Systems; Application of Thermodynamics to Chemical Equilibrium; Electrochemistry.

The work is clearly written and is quite up to date. The abbreviation *Ostw.* for Zeitschrift für physikalische Chemie, is not customary, and is a little perplexing until one consults the list of abbreviations, since we should naturally think that this referred to Ostwald's Lehrbuch. But this is of little consequence. The book will doubtless contribute much to the advancement of physical chemistry wherever it is used.

H. C. J.

OPTICAL ACTIVITY AND CHEMICAL COMPOSITION. By DR. H. LANDOLT, Professor of Chemistry in the University of Berlin. Translated with the author's permission by JOHN MCCRAE, PH.D. London and New York: Whittaker & Co. 1899. 158 pp. Price, $1.00.

This is a translation of the eighth chapter of the first volume of Graham-Otto's "Lehrbuch der Chemie." Professor Landolt is the highest authority on the subject of optical activity and chemical composition, and his writings are always clear and accurate. In the original the chapter here translated is well known to chemists. Its appearance in English and in separate form will no doubt give it a wider circulation than it could secure as a part of an unwieldy and expensive book. The translation reads smoothly—something quite unusual in translations of chemical books from German into English. The translator has made certain notes and additions for the purpose of bringing the matter up to date.

I. R.

A SHORT HISTORY OF THE PROGRESS OF SCIENTIFIC CHEMISTRY IN OUR OWN TIMES. By WILLIAM A. TILDEN, D.Sc., Lond., D.Sc. Dub., F.R.S., Fellow of the University of London, Professor of Chemistry in the Royal College of Science. London: Longmans, Green & Co. 276 pp.

This is a well-written and interesting book, and one that will be helpful to students. It is, as the title indicates, a *short* history of the progress of chemistry. It consists of ten chapters, each of which deals with some important facts of the subject, and students of chemistry, even those who have a good knowledge of the history of their science, will find these chapters profitable reading. The titles are: I. Matter and Energy; II. The Chemical Elements: Their Distribution in Nature, and Recognition by the Chemist; III. Rectification and Standardization of Atomic Weights; IV. Numerical Relations among the Atomic Weights: Classification of the Elements; V. Origin and Development of the Ideas of Valency and the Linking of Atoms; VI. The Development of Synthetical Chemistry; VII. The Origin of Stereo-Chemistry—Constitutional Formulæ in Space; VIII. Electricity and Chemical Affinity; IX. Discoveries Relating to the Liquefaction of Gases; X. Summary and Conclusion.

In his preface the author says: "In the following pages I have endeavored to provide for the student such information as will enable him to understand clearly how the system of chemistry, as it now is, arose out of the previous order of things; and for the general reader, who is not a systematic student, but who possesses a slight acquaintance with the elementary facts of the subject, a survey of the progress of chemistry as a branch of science during the period covered by the lives of those chemists, a few of whom only remain among us, who were young when Queen Victoria came to the throne."

And again he says: "Finally, I desire to point out that this does not profess to be a text-book giving a complete picture of the state of knowledge and of theory at the moment. Its object, as already stated, is to show by what principal roads we have arrived at the present position, in regard to questions of general and fundamental importance."

The book is cordially recommended to chemists, old and young. I. R.

THE KINETIC THEORY OF GASES. By O. E. MEYER. Translated from the second revised edition by ROBERT E. BAYNES. London and New York: Longmans, Green & Co. 1899. 472 pp.

The first edition of this book appeared in 1877 and was soon exhausted. The preparation of a revised edition was, however, postponed from time to time; and it was not published until a year ago. English readers are to be congratulated on the fact that the publishers secured the services as translator of Mr. Baynes, of Christ Church, Oxford. The translation is in every case accurate, fluent, and lucid, and the added notes are always valuable. The publishers have given us a book of convenient size and with excellent paper and type, so that it is a pleasure to read it.

The author divides his subject into two sections, relegating the more mathematical portions—the complicated formulæ and the manifold discussions—to "Mathematical Appendices" at the end of the book. These occupy over 100 pages of rather fine type and give, on the whole, a fair and ample discussion of the intricate questions which have excited so much interest among mathematicians and physicists. It is true that one does not feel, while reading these sections, the presence and strength of an original mind grappling with the difficulties, as one does in the two recent text-books on the kinetic theory of gases by Watson and by Burbury; but, in spite of this, the reader is given sufficient information to make all the later critical papers by Rayleigh, Boltzmann, and Planck interesting and intelligible.

The portion of the present book, however, which is the most valuable and which will be more widely read is included in the first 350 pages. This is divided into three parts: Molecular Motion and Its Energy; The Molecular Free Paths and the Phenomena Conditioned by Them; On the Direct Properties of Molecules. There are ten chapters: Foundations of the Hypothesis; Pressure of Gases; Maxwell's Law; Ideal and Actual Gases; Molecular and Atomic Energy; Molecular Free Paths; Viscosity of Gases; Diffusion of Gases; Conduction of Heat; On the Direct Properties of Molecules. Each of these subjects is treated largely from an historical standpoint and in such a direct non-mathematical manner that it is delightful reading. The presentation of the various questions is of such a nature as to make them easily understood by all, even by those who may have had no previous knowledge of the subject. The mathematical formulae on the kinetic theory are deduced; the experimental determinations are described, full references being given; and discrepancies between theory and observation are critically discussed. One cannot speak too highly of this portion of the book. At times, naturally, exception may be taken to the use or definition of a word, or to the importance given certain hypotheses, but such criticisms do not deserve recording. The book is such a storehouse of observations, theoretical discussions, and experimental formulae, that it is invaluable for reference. The arrangement of the subject-matter is clear and logical, and the index—which we owe to Mr. Baynes—is full and accurate.

J. S. AMES.

THE COMPENDIOUS MANUAL OF QUALITATIVE CHEMICAL ANALYSIS OF C. W. ELIOT AND F. H. STORER, as revised by W. R. NICHOLS. Nineteenth edition. Newly revised by W. B. LINDSAY, Professor of General and Analytical Chemistry in Dickinson College, and F. H. STORER, Professor of Agricultural Chemistry in Harvard University. New York: D. Van Nostrand Co. 1899. 202 pp.

Among the multitude of works upon qualitative chemical analysis it is rare indeed to find a manual which has reached its nineteenth edition, and this fact alone would seem to render comment upon the merits of this work almost superfluous. It has proved itself to be, in many hands, a reliable guide alike for the general student, to whom it presents an excellent example of scientific methods of study, and for the professional student, who, within its scope, derives from it an excellent training in the manipulation, reasoning, and capacity for observation, which are essential for the successful analyst. The passage from this manual to those of wider scope is easy and natural for the student who has conscientiously followed its teachings.

The present edition has been rewritten and revised, although the changes are those of details, and do not alter the general character of the work. A notable change is that in the scheme for the separation of the members of the arsenic group, the fusion of the mixed sulphides with sodium carbonate and nitrate having been replaced by the separation by means of hydrochloric acid and the use of the generator. Some of the material has been rearranged, many subheadings have been introduced, and a great many additional and helpful comments and suggestions have been scattered through the text. Since much of the material of this character, new and old, has been printed in type smaller than that of the main body of the text, the size of the volume is not increased.

It is difficult to understand why, in the revision of this manual, the teaspoon has been retained as the standard of measure throughout the work. The graduated cylinder is as common a laboratory utensil as the beaker or test-tube, and the expenditure of time or thought in acquiring a concrete notion of the volume of 5 cc., which is stated in a foot-note to be the equivalent of the teaspoonful, is surely not serious. To find the use of a "teaspoonful of strong nitric acid" prescribed on one of its pages is disturbing in a work which has been prepared with such an evident and careful purpose to present the subject from a scientific standpoint.

H. P. TALBOT.

DESCRIPTIVE GENERAL CHEMISTRY. A TEXT-BOOK FOR SHORT COURSE. By S. E. TILLMAN, Professor of Chemistry, Mineralogy, and Geology, United States Military Academy. Second edition. New York: John Wiley & Sons. 8vo. 429 pp. $3.00, net.

In the preface to this new edition of the text-book in use at West Point, the author says that the time which can be allotted to the study of chemistry at that institution is very short, and the belief of the instructors has been "that the laboratory method alone, or mainly, in so short a course, could not be made of as much value to the pupils as the method making the acquisition of knowledge the essential feature; and that the best results could be reached through careful study of the proper text, well-conducted recitations accompanied by experimental and explanatory lectures. While accepting the general correctness of this conclusion, the author would add a small amount of well-selected laboratory practice."

Of course, if the time allotted to the study of chemistry is insufficient, the instructor must modify his instruction to fit the circumstances, but Professor Tillman, after speaking of the care given to the selection of the information in the book, continues: "The chemical knowledge most requisite to the average professional soldier differs but little from that essential to other educated men."

At first sight one might infer that in the author's opinion a similar system of instruction would be in place in colleges, instead of the prevailing laboratory system. Few teachers would accept such a conclusion, nor indeed is it probable that the author means more than to suggest that the text-book found best for West Point would be equally valuable in colleges. This may be doubted. With time and facilities for laboratory work, text-books which constantly direct the attention of the student to experimental verification of the statements given will be preferred by most teachers.

For the students, for whose use it is primarily intended, the book is good. A more careful revision of the text of the new edition in the light of modern chemical knowledge would have been an improvement. For example, the statements that " ammonia is primarily organic in its origin," that " all hydrocarbons are primarily derived from the organic kingdom" cannot stand without ample qualification in view of what we know of the formation of nitrides and carbides at high temperatures, and of the action of water on these substances.

E. R.

THE ARITHMETIC OF CHEMISTRY. Being a simple treatment of the subject of chemical calculations. By JOHN WADDELL, PH.D. New York: Macmillan Co. 136 pp. 90 cents.

This little book will be helpful to those college students who find difficulty in making chemical calculations, and will also be of service to teachers, showing them how to explain a subject, like the measurement of gases, in a clear way. Several useful tables and a number of problems taken from English and American university examination papers add to the value of the book.

E. R.

EXPERIMENTELLE EINFÜHRUNG IN DIE UNORGANISCHE CHEMIE. Von HEINRICH BILTZ. Leipzig: Veit & Co. 1900.

In this little laboratory manual Professor Biltz has added to the usual simple reactions of inorganic compounds a number which are based on the current theory of aqueous solutions. The book is clear and modern.

E. R.

QUALITATIVE ANALYSE UNORGANISCHER SUBSTANZEN. Von HEINRICH BILTZ. Leipzig: Veit & Co. 1900.

This, too, is a small laboratory manual. The analytical methods recommended are the best and newest.

E. R.

LES PARFUMS ARTIFICIELS. Par EUGÈNE CHARABOT, Chimiste Industriel, Professeur d'Analyse chimique a l'Institut Commercial de Paris. Paris: J. B. Baillièr et Fils. 1900. 296 pp.

There have been rapid advances in the field of the chemistry of perfumes during the past few years, and it will therefore be of interest to chemists to read this book, which gives a brief and clear account of the principal discoveries of importance in the field. The titles of the chapters are: I. Nitro

Compounds; II. Alcohols and Ethers; III. Phenols and Ethers of Phenols; IV. Aldehydes; V. Ketones; VI. Olides. The many varieties of artificial musk are treated of in Chapter I. There appears to be a great demand for this perfume, though why, it would be hard to say. There are to be sure some odors to which it is to be preferred, but not many.

The author says: "The synthetical perfumes which, from the point of view of their applications, are most interesting are *terpineol*, *vanilline*, *piperonal* or *heliotropine*, *ionone* or *artificial violet*, and *artificial musk*." Terpineol is made by the dehydration of terpenes. It was put upon the market in 1889 and is now very extensively used for perfuming soaps. It also enters into the composition of a large number of bouquets, especially syringa and lilac. The story of ionone or artificial violet is the most interesting in the book, from the scientific as well as from the commercial point of view. According to the author: "The discovery of ionone, which is now extensively employed, has not worked any injury to the cultivation of the violet in the department of the Maritime Alps. In fact, this cultivation has extended since 1893 without leading to a lowering of the price of the flower."

It is interesting to note that piperonal or heliotropine, which in 1879 cost 3790 francs a kilogram, cost only 37.5 francs a kilogram in 1899. I. R.

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THE ELECTRICAL CONDUCTIVITY OF LIQUID AMMONIA SOLUTIONS.

BY EDWARD C. FRANKLIN AND CHARLES A. KRAUS.

In a recent paper[1] the authors pointed out some analogies between the properties of liquid ammonia and those of water, showing, among other things, that of all known electrolytic solvents ammonia most closely approaches water in its power of forming solutions which conduct the electric current. The interest which attaches to the study of liquids with such high conducting power has led the authors to undertake more careful measurements of the conductivity of ammonia solutions than have yet been attempted.

None of the measurements hitherto made on ammonia solutions[2] can be used for more than a qualitative comparison with aqueous and other solutions; and from somewhat extended experiments on the part of the authors it became evident that reliable quantitative results were not to be obtained with any of the simple forms of apparatus used in previous investigations. It was therefore found necessary to devise a form of apparatus by means of which the solvent could be purified and isolated for a considerable length of time. It was also essential to arrange the apparatus so that both solvent and solute could be added safely and conveniently. At the

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[1] This JOURNAL, **21**, 8 (1899).

[2] Cady: J. phys. Chem., **1**, 707 (1897); and Goodwin and Thompson: Phys. Rev., 8, 38 (1899).

same time it was necessary to be able to remove known portions of the solution from the resistance vessel, and to supply the place of the removed solution by fresh solvent. Finally the escape of large quantities of gaseous ammonia into the air of the laboratory had to be avoided.

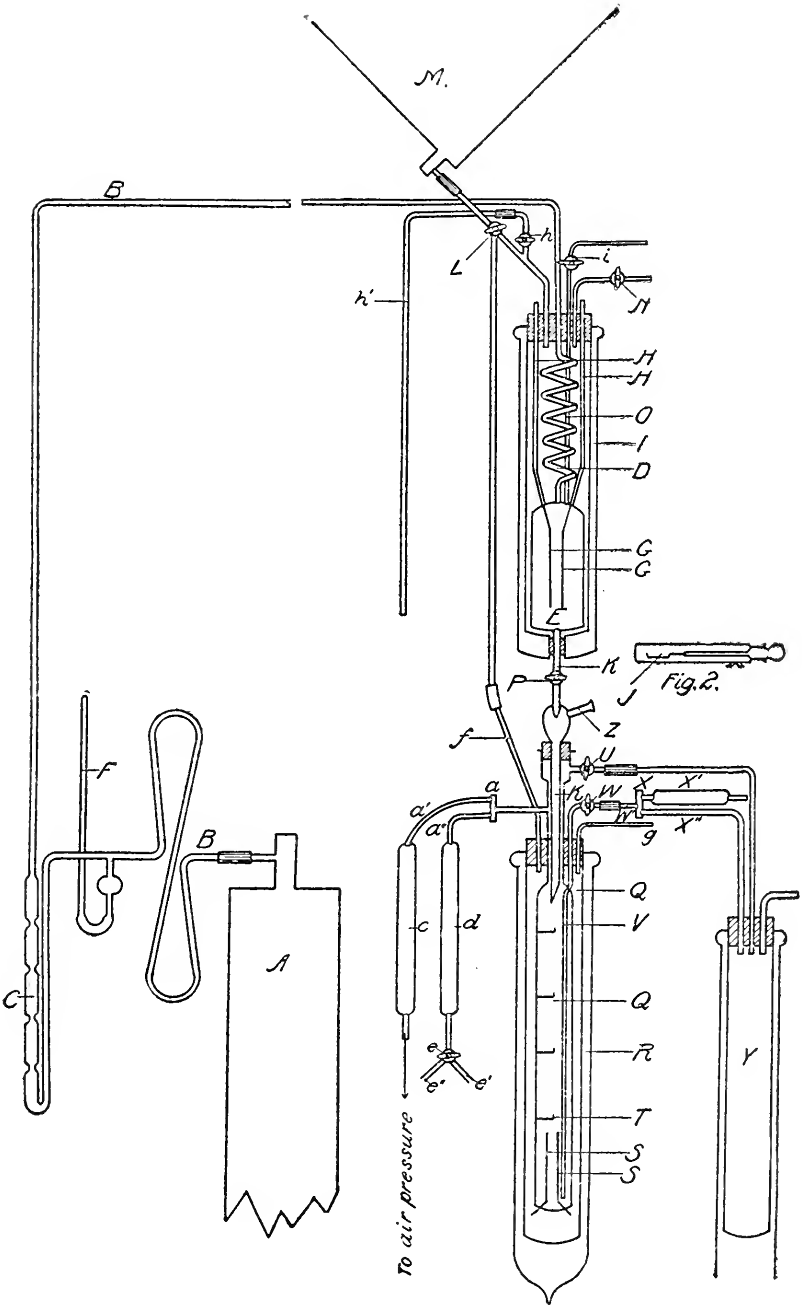
The following is a description of the form of apparatus which the authors found to be well adapted to meet the above enumerated requirements.

Description of the Apparatus.

The steel cylinder *A*, containing the liquid ammonia which is to be purified, is provided with a valve of a pattern which permits the easy regulation of the flow of gas. The metal delivery tube of the valve was connected with the glass tube *B* by means of a piece of rubber tubing, which, to withstand the pressure, was first tightly tied and then wrapped with tape.

On opening the valve the gas passes from the cylinder *A* through the glass tube *B*, which carries an asbestos filter, *C*, into the condensing spiral *D*, whence it runs as a liquid into the receptacle *E*. To the tube *B* is attached a pressure gauge *F*, for the purpose of assisting the manipulator to regulate more easily the flow of gas. The asbestos filter is a glass tube filled with carefully dried asbestos. The constrictions are for the purpose of preventing the packing of the asbestos into one end of the tube when the pressure from *A* is turned on. The asbestos used was the serpentine variety which, unless freed of its water of crystallization by long heating over the blast-lamp, continued indefinitely to give up sufficient moisture to the ammonia to affect materially its conductivity.

The filter is an important part of the purifying apparatus, its object being to retain minute particles of solid material which may be carried over by the stream of gas. That foreign matter was carried over from the stock cylinder is proved by the following observations: Other conditions being the same it was not possible without the filter to obtain a distillate with anything like the high resistance of the pure solvent. With fresh sodium in the cylinder *A*, a sufficient quantity of the metal was carried over to give the ammonia in the receptacle *E*, a decided blue color, and to reduce the resistance in


M.
B
h
L
i
h'
N
H
H
O
I
D
G
G
E
K
J
Fig. 2.
P
Z
f
F
U
a
X
X'
k
W
a'
a"
W'
g
X"
B
Q
V
c
d
A
Q
C
R
Y
e
e"
e'
T
S
S
To air pressure

this cell to less than a hundredth of its value under other conditions.

The purity of the solvent was determined by making measurements of its conductivity, for which purpose a pair of electrodes, *GG*, was sealed into the receiver *E*. The electrodes are in metallic connection with the exterior and the measuring apparatus through the glass tubes *HH*, sealed around the connecting wires and filled with mercury. The receptacle and spiral were kept cold by surrounding them with a bath of liquid ammonia contained in the vacuum-jacketed vessel *I*. During the investigations this vessel developed a crack, and, the necessary tubing not being at hand to replace it, an air jacket was substituted in its stead with satisfactory results. A little alcohol between the walls of the air jacket served to absorb the moisture which otherwise would have frozen on the walls and obscured the view of the receptacle and its contents. The opening in the lower end of the vessel *I* is closed by a rubber stopper through which passes the delivery tube *K* from the receiver *E*. Care had to be taken to have this stopper fit well, as otherwise a little pressure is liable to force out liquid ammonia, which almost inevitably breaks the jacket. The upper end of the vessel, *I*, is likewise closed with a rubber stopper, which is fitted with holes, first, for the tube *L* through which ammonia is drawn from the stock cylinder *M* into the bath *I*; second, for the escape tube *N*, for carrying off the gas; and third, for the tube *O*, through which the bath may be emptied of its contents by simply closing the stop-cock *N*. Besides these, the tubes *HH*, making connection with the electrodes, also pass through this stopper. The tubes *B*, *L*, *N*, and *O* are fitted gas-tight into the stopper, while for the tubes *HH* large holes were made so that the stopper might be forced tightly into place without danger of breaking these tubes loose from their connections with the receiver *E*. When all the tubes were in place, the stopper was tied firmly to the vessel *I*, and the space around the tubes *HH* was filled up with laboratory wax.

The condensation of the gas in the spiral *D* and the receiver *E* is produced at the expense of an equivalent quantity of liquid ammonia which evaporates from the bath *I*. The gas escapes through the tube *N* and is thence conducted into a carboy containing water where it is recovered as aqua ammonia.

When a sufficient quantity of liquid has been collected in the receiver *E*, the stop-cock *P* is opened and the ammonia runs into the conductivity vessel *Q*. This vessel is provided with a pair of electrodes, *SS*, which is connected with the exterior and the measuring apparatus by means of glass tubes filled with mercury in the same manner as are the electrodes *GG* in the upper receptacle. Connections for the electrodes *SS* are not shown in the figure. Five fine glass pointers, *T*, were sealed into the resistance cell *Q*, point upwards. The volume of the cell up to these different points was determined by filling with water at 25° until the respective points were just breaking the surface, and caculating the observed volumes to the volume at the boiling-point of ammonia. Sealed into the cell *Q* at *Q′* and reaching to the bottom, is a glass tube, *V*, which has capillary dimensions from the point at which it enters the resistance vessel to its lower end. This tube is provided with a stop-cock, *W*, just beyond which connection is made with the tube *W′*. *W′* carries a two-way stop-cock *X*. One way leads to the open air through the soda-lime drying tube *X′*, while the other, *X″*, leads to the vacuum-jacketed tube *Y*. The purpose of this vessel *Y* will appear below.

The tube *KK′* leading from the receiver *E* to the vessel *Q* reaches well through the neck of the latter into which it is fitted by means of a rubber stopper. A short distance above this stopper the tube *K* is enlarged and the tube from above is sealed in so that it projects about 1 centimeter within the enlargement, as shown in the figure. In the side of the enlargement, and with an upward slant, is sealed a tube, *Z*, through which the solute is introduced into the conductivity cell.

The solute is weighed out in a small platinum spoon, *J*, enclosed in a weighing tube as shown in Figure 2. In order to introduce the solute, the spoon is removed from the weighing tube and placed in position in the tube *Z*. A half turn on the axis of the spoon holder empties the contents into the cell *Q*. Any portions of the solute which may remain clinging to the spoon or to the side of the tube are washed down by the ammonia drawn from the receiver *E*.

Just below the stopper, through which *K′* enters the neck of the resistance receptacle, is sealed a tube provided with a stop-cock, *U*, and leading to the vessel *Y*. This attachment enables the operator to wash out the neck of the vessel *Q* as described below.

To the neck of the vessel *Q* is sealed a second tube carrying a two-way stop-cock, *a*, one branch of which, *a′*, leads through the phosphorus pentoxide drying tube *c* to the pressure reservoir containing dry air free from carbon dioxide. The other branch, *a″*, leads through a soda-lime drying-tube, *d*, to a two-way stop-cock, *e*, one branch, *e′*, of which opens to the air, while the other, *e″*, leads to a collecting bottle containing water.

Preparatory to making a series of measurements, the resisance vessel *Q* must be well washed out and supplied with pure solvent from the receptacle *E*. To accomplish this, ammonia is drawn down by opening the stop-cock *P* until the electrodes *SS* are well covered, the stop-cocks *a* and *e* having previously been set to open the way through *a″* and *e″*, and the stop-cocks *W* and *U* having been closed. By this arrangement of the stop-cocks the ammonia vapor escapes through *e″* into the absorption bottle. The stop-cocks *W* and *X*, through *X″*, are then opened, and *a* is set to close *a″* and open *a′*. The pressure from the air reservoir on the surface of the liquid forces this latter out through the tube *V* into the vessel *Y*, thus emptying *Q*. After emptying the resistance cell the stop-cocks are turned back to their original positions and a fresh quantity of ammonia is drawn down into the cell. This operation is repeated until tests of the resistance in the cell *Q* show that all soluble material has been removed. *U* is then opened, and with *W* and *a* closed, the liquid is run down into the lower vessel until it fills the cell completely and runs over into *Y* through *U*. The stopper is then removed from *Z* and a quantity of ammonia is allowed to blow out through this portion of the apparatus. The ammonia is then run out through *V* in the manner described above. In this way the resistance cell is thoroughly washed. The next lot of ammonia run down is tested, and in case its resistance indicates sufficient washing of the cell *Q* the operator proceeds to the addition of the solute.

The previously weighed solute is introduced in the manner described above, and, with the stop-cocks properly set, ammonia is let down into the resistance cell until the first pointer is slightly more than covered. The stop-cock *e* is then set to open the way through *e'* to the outside air; *W* is opened, and *X* is set to open the way through *X''*. With this arrangement of the stop-cocks, the back pressure from the vessel *Y* forces ammonia vapor through the liquid in the resistance cell. This current of ammonia gas, warmed by its passage through *X''*, *W*, and *V*, evaporates ammonia from the resistance cell and at the same time thoroughly mixes the solution. After passing the vapor for a few moments, *X''* is closed and *X'* is opened. Both the tubes *V* and *e'* being, with this arrangement of the stop-cocks, open to the air, the liquid in *Q* and *V* comes into pressure equilibrium. If, after this operation, the tip of the glass pointer is not visible just breaking through the surface of the solution, the above-described operation is repeated until the point just touches the surface. The resistance is then measured. The solution is then diluted, stirred, adjusted to the next pointer, and the resistance again read. This operation is repeated until the last point is reached, after which the solution is forced out through the tube *V* in the manner described above, until the lowest point is reached, when the stop-cock *W* is closed. This leaves a known quantity of solute in the resistance cell. More solvent is then added, the volume adjusted to the second pointer, and the resistance again measured. In this manner measurements may be made on solutions carried to any desired degree of dilution.

The Constant Temperature Bath.—In order to maintain the resistance vessel *Q* at a constant temperature it is immersed in a bath of liquid ammonia contained in the Dewar tube *R*. To overcome the considerable superheating which ammonia exhibits in glass vessels, it was at first attempted to boil the liquid in the bath by means of a spiral of platinum wire heated by a current of electricity. This plan was soon abandoned, however, for the much simpler and quite as efficient method of placing blackened platinum tetrahedra in the bottom of the bath and warming them by the radiations from an ordinary incandescent lamp. No errors from changes in the temperature of the bath could be observed.

The mouth of the vessel *R* is fitted with a rubber stopper which supports the resistance cell *Q*, and in which provision is made for the mercury connecting tubes, and for the tubes *f* and *g* for introducing the liquid and carrying off the gas, respectively. The mercury connecting tubes are not shown in the figure. Liquid ammonia is introduced into the bath *R* by opening the stop-cock *L* through *f* and then opening the valve on the steel cylinder *M*.

Recovery of Liquid Ammonia from Receptacle Y.—A glass tube carrying a stop-cock, *h*, is sealed to the tube *L*, through which ammonia is drawn from the stock cylinder to the baths *I* and *R*. If this stop-cock is opened and an aspirator attached to the exit tube *N*, then liquid from without may be drawn into the bath *I* by connecting a tube *h'* to *h*, and immersing the end of the former in the liquid. Thus, ammonia which has been used in the resistance cell can be drawn from the vessel *Y* into the bath *I* and utilized for cooling the receiver.

To Empty the Condensing Bath, I.—After considerable liquid has been evaporated from the bath *I*, the residue becomes so impure that the frothing of the liquid in boiling interferes with the distillation. By opening the stop-cock *i* on the tube *O*, and closing the stop-cock on the exit tube *N*, the pressure of the boiling ammonia forces out the liquid through *O*, thus emptying the bath of its contents. This was always necessary at the end of a series of experiments.

The apparatus is somewhat complicated, but after a little practice on the part of the operators, measurements can be carried out easily and with a fair degree of accuracy. With everything in order, from two to three series of measurements can be made in half a day.

The Solvent.—The ammonia used in these experiments was the "Liquid Anhydrous Ammonia" of commerce, such as is used for refrigerating purposes. An earlier plan, of distilling the ammonia once or twice before its final distillation from the cylinder *A* of the purifying apparatus, was later abandoned for the simpler and entirely satisfactory plan of drawing the liquid from the stock cylinder directly into the smaller cylinder, into which latter a quantity of metallic sodium had previously been introduced. The sodium dissolves in the ammonia, and any water present in solution is at once acted upon by the metal with the formation of insoluble sodium hydroxide. The sodium not used up by the water present reacts slowly with the ammonia to form sodamide and hydrogen. The sodamide is somewhat soluble and is an efficient drying agent. The ammonia distilled from sodamide into the receptacle *E* was very pure, as was shown by tests of its resistance, which, after the introduction of a good asbestos filter in the train, was found to be uniformly very high. In fact, the resistance was so great that it was not possible to measure it, even approximately, with the measuring apparatus in its present form, and, moreover, the high resistance did not diminish when the liquid remained in the cell for some hours, proving that, contrary to the behavior of water, liquid ammonia is without appreciable action on glass. Attempts to obtain the purest possible ammonia in the receiver *E* were not made, partly for the reason that the means were not at hand for measuring very high resistances, but principally for the reason that other sources of impurity were present which could not be overcome in the present experiments.

While ammonia of a specific conductivity below 0.01×10^{-6} was easily obtained in the receiver, it was not possible to produce a liquid which, after being run into the resistance cell *Q*, showed a specific conductivity lower than about 0.10×10^{-6}.[1]

Certainly one of the sources of impurity, to which reference has just been made, is moisture which enters the stop-cock *P*. Water lowers the resistance of liquid ammonia. As a result of the contact of cold ammonia with the stop-cock, moisture condenses on the latter, and small, but sufficient, quantities work in around it to reduce the resistance of the solvent very

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[1] Goodwin and Thompson [Phys. Rev., 8, 47 (1899)] give 1.6×10^{-4} as the mean specific conductivity of liquid ammonia at temperatures between $-30°$ and $-12°$, a value very much greater than the minimum obtained in these experiments.

materially. Nor is this defect easily remedied. An ordinary glass stop-cock cannot be ground to be absolutely tight without the use of lubricant, which must, of course, be omitted from a cock used for the present purpose. After experimenting with a number of different styles of stop-cocks, a mercury-seal cock was finally used for the measurements recorded in this paper. The mercury, however, was left out and the empty spaces on either end of the key opened into the air through pieces of small rubber tubing of considerable length. The ammonia which leaked through the stop-cock was thus allowed to escape, while the deposition of moisture was confined to the exterior of the stop-cock. Even with this stop-cock, which gave much better results than any other form used, the specific conductivity of the solvent in the resistance cell Q could not be reduced much below 0.10×10^{-6}. The specific conductivity varied between 0.10×10^{-6} and 0.15×10^{-6}, or even more, and could not be accurately controlled.

Solutes.—With the exception of sodamide, all the salts and other substances used in these experiments were carefully purified and thoroughly dried before being used. The concentration of the sodamide solutions for which measurements are given were arrived at by calculation from a weighed quantity of sodium added to the solvent.

Measuring Apparatus, Constants, and Units.—The bridge and telephone method of Kohlrausch was used in making the measurements of conductivity recorded in this paper. With the highest dilutions the resistance reached 20,000 ohms. At this resistance the telephone minimum became so poor that it was not practicable with the present form of the apparatus to carry the dilutions higher. Besides the errors introduced by the variable conductivity of the solvent, some of the inaccuracies in the measurements at high dilutions are to be attributed to the difficulty of accurately setting the bridge at such high resistances. Another source of error which is easily introduced is insufficient stirring. The solutions were usually stirred until no further change could be detected in the conductivity, but doubtless some errors are due to this cause.

The units recently introduced by Kohlrausch[1] were used in calculating the values given below.

The resistance capacity of the cell, determined by means of a fiftieth-normal solution of potassium chloride of specific conductivity 0.002397[2] at 18°, was 0.07344.

The volumes of the conductivity cell at the boiling-point of ammonia for the five points was 45.70 cc., 67.67 cc., 94.75 cc., 117.09 cc., and 141.16 cc., respectively. The volume to the first point plus the volume of the stirring tube V was 46.62 cc.

The atomic weights recently recommended by the committee of the German Chemical Society, which are calculated on the basis of oxygen = 16, were used.

The correction made for the conductivity of the solvent was 0.13×10^{-6}, which was approximately the mean conductivity of the solvent as measured in the resistance cell Q, after thoroughly washing out the latter. The correction for the highest dilutions amounts to about 4 per cent.

Numerical Results.—In the following tables are given the results of measurements on twenty-five different substances. Besides these substances measurements were also made on potassium iodide, sodium nitrate, ammonium bromide, and silver nitrate, but because of the uncertain value of the resistance capacity of the cell at the time of making these measurements, they are not included in the tables below.

The dilutions, expressed in liters per gram molecule, are denoted by v, the molecular conductivities by μ_v, which correspond respectively to $\varphi 10^{-3}$ and $\varDelta$ in Kohlrausch's[3] notation.

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[1] Kohlrausch und Holborn : Das Leitvermögen der Electrolyte, p. 1 (1899); Kohlrausch, Holborn, und Diesselhorst : Wied. Ann., **64**, 417 (1898).

[2] Kohlrausch : *Loc. cit.*

[3] *Ibid.*

Table I—Potassium Bromide.

v.	μ_v.	v.	μ_v.
301.9	210.6	7093.0	324.6
447.0	228.3	8553.0	323.9
625.9	242.3	12410.0	329.7
773.4	251.7	17380.0	333.5
932.6	259.5	21480.0	336.1
1354.0	272.9	25900.0	337.0
1895.0	286.8	37590.0	338.7
2343.0	293.7	52640.0	339.6
2824.0	299.8	65040.0	340.2
4099.0	308.5	78430.0	340.4
5740.0	317.6		

Table II—Potassium Nitrate.

v.	μ_v.	v.	μ_v.
324.0	192.7	7614.0	314.9
479.9	210.1	9181.0	318.8
671.9	226.0	13330.0	322.1
830.2	236.7	18660.0	327.9
1001.0	245.0	23060.0	330.1
1453.0	261.7	27800.0	331.4
2082.0	274.9	40360.0	333.7
2514.0	282.9	56510.0	337.4
3032.0	289.3	69820.0	338.6
4401.0	301.4	84200.0	337.6
6162.0	309.9		

Table III—Potassium Metanitrobenzenesulphonate.

v.	μ_v.	v.	μ_v.
144.8	135.5	4522.0	242.8
214.5	147.2	6332.0	250.9
371.1	166.8	9190.0	257.3
538.7	179.8	12870.0	263.0
754.3	192.5	18680.0	268.6
1095.0	204.1	26150.0	271.0
1533.0	215.5	37960.0	276.1
2225.0	225.8	53160.0	281.2
3116.0	234.5		

Table IV—Sodium Bromide.

v.	μ_v.	v.	μ_v.
287.0	200.0	6744.0	287.7
425.0	214.5	8132.0	289.9
595.1	227.4	11810.0	292.0
735.4	234.7	16530.0	296.0
886.8	240.2	20420.0	297.9
1287.0	251.7	24630.0	298.2
1802.0	262.5	35750.0	298.1
2227.0	266.8	50050.0	299.8
2686.0	271.1	61840.0	303.0
3898.0	277.6	74580.0	302.1
5458.0	283.8		

Table V—Sodium Bromate.

v.	μ_v.	v.	μ_v.
342.3	179.4	1535.0	229.5
506.9	193.4	2150.0	238.6
709.8	205.1	2656.0	244.0
877.0	212.5	3203.0	247.8
1058.0	218.7	4648.0	255.2

Table VI—Sodium Bromate.

v.	μ_v.	v.	μ_v.
323.4	177.6	7600.0	263.7
479.0	191.5	9164.0	265.9
670.7	210.8	13300.0	269.1
828.7	211.0	18620.0	271.1
999.3	217.1	23020.0	273.4
1451.0	227.9	27760.0	273.9
2031.0	238.0	40280.0	275.1
2509.0	243.1	56400.0	275.8
3026.0	247.5	69690.0	276.7
4392.0	253.9	84040.0	275.7
6150.0	260.9		

Table VII—Ammonium Chloride.

v.	μ_v.	v.	μ_v.
298.9	159.0	7023.0	280.5
442.6	176.3	8468.0	285.6
619.8	191.2	12290.0	292.0
765.8	200.3	17210.0	296.2
923.4	208.7	21270.0	298.8
1340.0	224.4	25650.0	301.1
1877.0	238.9	37220.0	303.7
2319.0	246.5	52120.0	303.9
2796.0	253.1	64400.0	301.4
4059.0	264.7	77660.0	304.4
5684.0	274.2		

Table VIII—Ammonium Nitrate.

v.	μ_v.	v.	μ_v.
105.1	169.7	6057.0	286.6
155.8	183.8	7385.0	288.9
218.1	195.3	9024.0	291.4
269.5	203.1	13100.0	294.2
324.9	210.4	18340.0	296.3
471.6	222.4	22660.0	296.6
660.4	233.7	27330.0	297.0
816.0	240.5	39670.0	297.1
984.0	245.6	55540.0	295.5
1428.0	256.9	68640.0	298.5
2000.0	266.8	82760.0	298.7
2471.0	271.1	120100.0	294.3
2980.0	276.1	168200.0	299.4
4325.0	281.4		

Table IX—Silver Iodide.

v.	μ_v.	v.	μ_v.
212.1	71.06	4984.0	198.1
314.1	83.50	6011.0	205.9
439.8	96.29	8724.0	221.1
543.5	100.9	12210.0	233.9
655.4	107.9	15100.0	242.1
951.3	122.7	18200.0	247.5
1332.0	137.1	26420.0	256.3
1646.0	146.5	36990.0	265.2
1985.0	155.5	45710.0	270.6
2881.0	175.2	55120.0	274.0
4034.0	188.2	80000.0	276.0

Table X—Silver Cyanide.

v.	μ_v.	v.	μ_v.
44.77	20.21	556.6	21.52
66.30	20.53	779.4	21.65
92.84	20.78	1131.0	21.54
134.84	20.88	1584.0	21.65
188.7	21.17	2299.0	21.45
273.8	21.31	3219.0	21.50
383.4	20.64		

Table XI—Mercuric Cyanide.

v.	μ_v.	v.	μ_v.
24.17	1.20	6.92	1.44
35.79	1.18	10.25	1.35
50.12	1.17	14.35	1.30
72.75	1.16	20.83	1.25
101.9	1.16	29.17	1.23
147.9	1.16	42.34	1.23
207.1	1.17	59.28	1.22
		86.04	1.20
		120.5	1.20
		174.9	1.19
		244.9	1.19

Table XII—Metadinitrobenzene.

v.	μ_v.	v.	μ_v.
354.5	131.6	5590.0	217.0
525.0	144.1	8114.0	221.3
735.0	155.7	11360.0	(225.8)
1067.0	168.6	14040.0	232.5
1494.0	178.7	20380.0	234.3
2226.0	190.4	29570.0	236.0
3231.0	203.7		

Table XIII—Strontium Nitrate.

v.	μ_v.	*v.*	μ_v.
286.2	145.0	8108.0	299.0
423.9	160.2	11770.0	321.5
593.3	173.7	16480.0	344.4
733.2	182.6	20360.0	359.3
884.1	190.6	24550.0	371.1
1283.0	207.0	35640.0	403.4
1797.0	221.9	49900.0	431.4
2220.0	232.1	61660.0	449.0
2677.0	240.8	74350.0	466.2
3886.0	258.1	107900.0	491.9
5441.0	275.8	151100.0	514.2
6724.0	288.4		

Table XIV—Sodamide.

v.	μ_v.	*v.*	μ_v.
27.49	4.923	169.2	15.69
38.49	6.013	236.9	19.53
47.56	6.896	343.8	23.84
57.35	7.739	481.4	28.17
83.23	9.698	698.7	32.35
116.5	12.09	978.6	35.52

Table XV—Acetamide.

v.	μ_v.	*v.*	μ_v.
5.020	0.2841	30.71	0.4507
9.434	0.3134	43.00	0.4850
10.41	0.3413	62.41	0.5266
15.11	0.3768	87.39	0.5670
21.15	0.4130		

Table XVI—Benzenesulphonamide.

v.	μ_v.	*v.*	μ_v.
42.00	18.03	731.0	58.43
62.19	21.70	1061.0	67.25
87.08	24.41	1485.0	76.72
126.4	28.45	2156.0	87.86
177.0	32.65	3019.0	106.9
256.9	38.01	4382.0	122.4
359.7	43.62	6136.0	137.2
522.0	51.05	8916.0	151.9

Table XVII—Orthomethoxybenzenesulphonamide.

v.	μ_v.	v.	μ_v.
101.2	14.13	2811.0	59.09
141.8	16.34	3937.0	67.67
175.2	17.92	4864.0	73.16
211.2	19.44	5866.0	79.36
306.6	22.88	8514.0	90.24
429.3	26.53	11920.0	101.1
530.4	29.10	14730.0	108.3
639.6	31.61	17760.0	115.7
928.3	37.33	25780.0	127.6
1300.0	42.88	36100.0	139.7
1606.0	46.79	44610.0	147.7
1937.0	51.05		

Table XVIII—Metamethoxybenzenesulphonamide.

v.	μ_v.	v.	μ_v.
57.96	23.92	1809.0	91.03
85.82	27.85	2533.0	102.2
148.5	34.71	3677.0	114.9
215.5	40.81	5149.0	124.5
301.7	45.93	7473.0	140.9
438.0	53.57	10460.0	153.5
613.3	60.91	15190.0	165.9
890.2	70.20	26280.0	183.2
1247.0	79.60		

Table XIX—Paramethoxybenzenesulphonamide.

v.	μ_v.	v.	μ_v.
55.50	11.27	1326.0	47.16
77.70	13.23	1924.0	54.93
122.8	15.51	2694.0	63.20
157.9	17.96	3910.0	73.55
229.2	21.05	5475.0	83.71
320.9	25.13	7947.0	96.01
465.8	30.01	11130.0	109.4
652.2	34.74	16150.0	126.1
946.7	40.92	22620.0	140.2

Table XX—Metanitrobenzenesulphonamide.

v.	μ_v.	v.	μ_v.
85.68	89.54	2164.0	184.6
126.9	99.70	3031.0	193.3
177.6	109.1	4399.0	200.9
257.9	119.7	6159.0	207.3
361.0	130.4	8940.0	213.9
524.0	142.0	12520.0	219.6
733.8	153.3	18170.0	222.7
1065.0	164.3	25440.0	224.1
1491.0	174.8	36930.0	227.1

Table XXI—Benzoic Sulphinide.

v.	μ_v.	v.	μ_v.
118.1	85.98	2983.0	167.5
174.8	94.45	4177.0	176.3
244.8	101.7	6062.0	184.0
355.3	110.5	8488.0	191.8
497.6	119.0	12320.0	196.6
722.1	129.3	17250.0	203.8
1011.0	139.5	25040.0	207.3
1468.0	149.6	35060.0	211.4
2055.0	159.2		

Table XXII—Trinitrotoluene.

v.	μ_v.	v.	μ_v.
158.0	164.4	2427.0	203.1
233.9	170.4	3398.0	208.0
404.8	178.0	4932.0	212.8
587.5	180.4?	10030.0	223.9
822.7	187.5	14040.0	228.1
1194.0	193.2	20380.0	233.8
1672.0	198.6		

Table XXIII—Nitromethane.

v.	μ_v.	v.	μ_v.
8.99	9.01	646.4	47.95
13.31	10.02	938.2	56.12
18.64	11.15	1306.0	64.66
27.06	12.76	1907.0	75.24
37.89	14.52	2670.0	85.92
55.00	16.89	3876.0	99.68
77.00	19.38	5426.0	114.5
111.8	22.55	7876.0	131.5
156.5	26.15	11030.0	147.3
227.1	30.55	16010.0	162.5
318.1	35.37	22410.0	181.3
461.6	41.45		

Table XXIV—Orthonitrophenol.

v.	μ_v.	v.	μ_v.
366.2	82.76	6963.0	190.6
542.3	95.11	8604.0	192.8
759.3	106.6	10380.0	203.9
938.2	114.0	15060.0	213.3
1131.0	120.7	21090.0	222.5
1642.0	135.3	26060.0	226.2
2299.0	148.3	31420.0	230.3
2841.0	157.1	45610.0	234.9
3426.0	164.5	63860.0	240.1
4973.0	178.7		

Table XXV—Benzaldehyde.

v.	μ_v.	v.	μ_v.
15.53	1.695	133.0	3.385
23.00	1.950	193.1	3.736
32.20	2.198	270.3	4.058
46.74	2.493	392.4	4.328
65.45	2.770	549.4	4.561
95.00	3.078		

Discussion of Results.

Besides the measurements above given, quantitative determinations of the molecular conductivity of potassium iodide, sodium iodide, ammonium iodide, cuprous iodide, silver bromide, silver nitrate, lead iodide, mercuric iodide, mercuric chloride, zinc iodide, cupric nitrate, iodine, sulphur, paranitrophenol, dinitrophenol, trinitrophenol, vanilline, ethyl formate, ethyl acetate, metallic potassium, and metallic lithium have also been made, but the results are not given here for the reason that the measurements were made in an earlier form of apparatus which did not permit of sufficient accuracy of measurement. Qualitative tests have been made on several hundred substances, which show that all soluble salts and a great variety of organic compounds form conducting solutions.

Binary Salts.—The limit of molecular conductivity of binary salts in solution in ammonia at —38° lies between 270 and 340 Kohlrausch units. This is more than twice the maximum conductivity of the same salts in water solutions at the ordinary temperature, and is far above the conductivity of electrolytes in any other known solvent. At 100°, however, the limit of molecular conductivity in aqueous solution is somewhat greater[1] than the maximum conductivity of the same salts in solution in ammonia at its boiling-point.

The values for the maximum molecular conductivities of a number of salts in five of the best electrolytic solvents are given in the following table, which is made up from data taken from Dutoit and Friderich,[2] and from Carrara,[3] together with values obtained for ammonia solutions by the authors.

see errata p. 532

	Acetone.	Aceto- nitrile.	Methyl alcohol.	Water.	Ammonia. -38°
NaI	140	160	90	121	...
NaBr	...	...	88	122	302
KI	154	...	98	143	340?
KBr	...	...	97	144	340
NH_4I	153	...	105	143	...
NH_4Cl	...	...	100	144	304
KNO_3	...	...	...	133	338
NH_4NO_3	...	...	...	114	297
$AgNO_3$	...	160	...	121	280?
HCl	2.21	...	133	360	...

Notwithstanding the fact that for the most part ammonia solutions conduct electricity with greater facility than do

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[1] Krannhals: Ztschr. phys. Chem., **5**, 250 (1890); and Schaller: *Ibid.*, **25**, 497 (1898).

[2] Bull. Soc. Chim. (3), **19**, 336 (1898).

[3] J. Chem. Soc. Abstracts, **72**, II, 471 (1897).

water solutions of the same concentration, the solute in ammonia is dissociated to a much less extent than it is in water. The accompanying table shows, for nine salts dissolved in these two solvents, the dilution at which the dissociation reaches respectively 50, 75, and 90 per cent.

Solute	Degree of dissociation.	Water. at 18°	Ammonia. at −38°
KI	0.50	....	80
	0.75	0.4	400
	0.90	20.0	2000
KBr	0.50	....	100
	0.75	....	800
	0.90	20.0	4000
KNO_3	0.50	0.5	200
	0.75	5.0	1200
	0.90	25.0	5000
NaBr	0.50	....	125
	0.75	....	500
	0.90	32.0	2500
$NaNO_3$	0.50	0.5	....
	0.75	5.0	800
	0.90	33.0	4000
NH_4Cl	0.50	....	250
	0.75	1.0	1500
	0.90	25.0	5000
NH_4Br	0.50	....	75
	0.75	....	700
	0.90	....	3500
NH_4NO_3	0.50	....	100
	0.75	....	500
	0.90	....	4000
$AgNO_3$	0.50	0.6	125
	0.75	5.0	350
	0.90	40.0	1500

Aqueous solutions of binary salts practically reach their limit of molecular conductivity at a dilution of 1,000 to 5,000 liters, while ammonia solutions must be carried to a dilution of 25,000 to 50,000 to come as near the limit. In accordance with the Thomson-Nernst hypothesis, this behavior of ammonia solutions was to be expected from the low dielectric constant as found by Goodwin and Thompson[1], and later by Cool-

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[1] Phys. Rev., 8, 38 (1899).

idge.[1] The low degree of dissociation is also in accordance with measurements of the boiling-point elevations of ammonia solutions of salts.[2] At the concentrations at which these measurements were made the dissociation is so low that it would be difficult to detect the effect of dissociation on the rise of the boiling-point of a solvent with such a low constant of molecular elevation as that of ammonia.

The very high conductivity of ammonia solutions seems hence to be due to the high velocity of migration of the ions as a result of the low viscosity of the solvent.

Ostwald's law of dilution holds approximately for ammonia solutions of a number of binary salts, the only solutes which have so far been tested. The constant diminishes in value with the dilution but the change is of a very different order from that which is found in the case of water solutions of the same salts. The values for the constants for three salts, calculated from the formula

$$K = \frac{\alpha^2}{(1-\alpha)v},$$

in which the symbols have their usual significance, are given below for both ammonia and water. The values for the water solutions are calculated from Kohlrausch's data.[3]

Ammonium Chloride.

α.	NH_3.	H_2O.
52.30	0.1919	....
58.00	0.1809	....
62.89	0.1760	49.68
65.89	0.1662	45.47
68.64	0.1628	38.54
73.81	0.1553	22.86
78.58	0.1536	11.53
81.09	0.1533	5.981
83.25	0.1481	5.527
87.08	0.1445	3.777
90.20	0.1460	2.506
92.26	0.1568	1.749
93.91	0.1932	1.264
96.05	0.1897	0.8435

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[1] Wied. Ann., **69**, 130 (1899).

[2] The Authors: This JOURNAL, **20**, 852 (1898).

[3] Leitfähigkeit der Electrolyte, p. 159.

Potassium Nitrate.

a.	NH_3.	H_2O.
57.00	0.2277	12.79
62.12	0.2074	11.55
66.85	0.2006	10.20
70.02	0.1970	9.528
72.48	0.1906	8.754
77.41	0.1826	6.269
81.32	0.1740	4.509
83.66	0.1706	4.006
85.59	0.1677	3.389
89.15	0.1623	2.893
91.66	0.1635	2.332
93.15	0.1664	1.885
94.30	0.1699	1.710
95.28	0.1444	1.443

Potassium Bromide.

a.	NH_3.	a.	NH_3.
61.76	0.330	90.47	0.210
66.94	0.303	93.12	0.220
71.06	0.279	94.97	0.210
73.81	0.269	96.67	0.222
76.09	0.260	97.79	0.250
80.02	0.237	98.56	0.315
84.10	0.235	98.81	0.321
86.12	0.228		

Silver Halides.—Measurements of the conductivity of the halides of silver is a matter of interest in view of the fact that, because of their resistance to the action of most ordinary solvents,[1] their conductivities have not been measured.

Silver iodide in solution in ammonia is a good conductor, but it is not as strongly dissociated as is the nitrate of silver, a fact which is not unexpected when the behavior of mercuric chloride and the halides of some other heavy metals in resisting the dissociating action of water is recalled.

Mercuric Chloride.—This salt reacts with liquid ammonia to form mercuriammonium chloride, but since at the same time a small quantity of an insoluble compound was formed, quantitative measurements of the conductivity of mercuriammonium solutions have not yet been made.

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[1] According to St. v. Lasczynski and St. v. Gorski [Ztschr. Electrochem., 4, 290 (1897)], a pyridine solution of silver iodide is a non-conductor of electricity.

The results of a brief investigation of the action of liquid ammonia on mercuric chloride may be given here. When mercuric chloride is sealed up in a tube with liquid ammonia, a heavy liquid of the composition represented by the formula

$$HgCl_2.2NH_3.10NH_3$$

is formed, as is shown by the following analytical data :

I. 2.0000 grams mercuric chloride united with 1.4033 grams ammonia. The compound thus formed lost 1.1679 grams ammonia at 20°.

II. 3.0000 grams mercuric chloride united with 2.0638 grams ammonia. The compound thus formed lost 1.6882 grams ammonia at 20°.

	Calculated for $HgCl_2.2NH_3.10NH_3$.	Found. I.	II.
NH_3 lost at 20°	35.79	34.32	33.56
" retained at 20°	7.15	6.92	7.41

The liquid, which is slightly soluble in ammonia, has a specific gravity of 1.56, and is stable only under pressure. At low temperatures it solidifies, and the solid formed melts at —9°. If the pressure is removed from this solid, 10 molecules of ammonia are dissociated off, and there remains behind a compound of the formula $HgCl_2.2NH_3$, which seems to be identical with mercuri-diammonium chloride. The compound melts with some decomposition, as does the fusible white precipitate. Mercuri-diammonium chloride, prepared by precipitation from a solution of mercuric chloride in a concentrated solution of ammonium chloride, when sealed in a tube with liquid ammonia, takes up 10 molecules of ammonia to form the heavy liquid described above.

Mercuric Cyanide.—This salt is very easily soluble in ammonia, even deliquescing in the vapor from the cold liquid. In water, mercuric cyanide is not at all dissociated,[1] while in ammonia it forms a solution possessed of a distinct conductivity. The molecular conductivity, however, instead of increasing, decreases with the dilution. The decrease is small, and the rate diminishes as the dilution becomes greater. Three independent measurements on different specimens of the salt gave similar results in this respect.

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[1] Ostwald : Wissenschaft Grundlag. d. analyt. Chem., p. 147 (1894).

No instance in which the molecular conductivity decreases with dilution is known in aqueous solution, but such behavior has been observed in the case of certain ether and amyl alcohol solutions[1] and in the case of solutions in benzonitrile.[2]

Silver Cyanide.—Silver cyanide is readily soluble in ammonia, forming a solution which is a fair conductor. As is true of mercury cyanide, the molecular conductivity of the salt is low and varies but slightly[3] with changes in the concentration. Contrary to the behavior of mercury cyanide, however, the molecular conductivity of silver cyanide increases somewhat with the dilution.

Ternary Salts.—But one ternary salt, strontium nitrate, has been measured. It has a much higher molecular conductivity than the binary salts, and although the dilution was carried beyond $v = 100,000$, the limit was not reached, the ammonia solution behaving in this respect like aqueous solutions of the ternary salts.

Phenols.—Phenol, the cresols, the dihydroxybenzenes, pyrogallol, and guaiacol form solutions which show a distinct conductivity, while solutions of ortho- and paranitrophenol, dinitrophenol, and picric acid approach salt solutions in their power to conduct the current. Accurate quantitative measurements have been made on orthonitrophenol only, which, as the data given in the tables show, is a very much better conductor in ammonia than in water.[4]

Nitrohydrocarbons.—The aromatic nitrohydrocarbons are, so far as they have been tested,[5] more or less soluble in ammonia, forming solutions which in some cases are brilliantly colored. Solutions of nitrobenzene and of the nitrotoluenes are but slightly colored and conduct the current but little, if at all, while dinitrobenzene and trinitrotoluene approach the salts in their conducting power.

Dinitrobenzene.—The interesting observation was made upon this substance that the conductivity of its solution upon dilu-

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[1] Kablukoff: Ztschr. phys. Chem., **4**, 429 (1889).

[2] Euler: *Ibid.*, **28**, 623 (1899).

[3] Euler (*loc. cit.*) has observed that the molecular conductivity in nitrobenzene solutions increases but slightly, if at all, with increasing dilution.

[4] Bader: Ztschr. phys. Chem., **6**, 296 (1890).

[5] This JOURNAL, **20**, 832 (1898).

tion did not at once come to its full value, but that the resistance dropped continuously for about half an hour, the total fall amounting to about 2 or 3 per cent. After reaching its full value the resistance remained constant. In one experiment the resistance, after becoming constant, did not change perceptibly after the lapse of fourteen hours. The only analogous case recorded is an observation by Euler,[1] who noticed that when solutions in nitrobenzene were diluted the conductivity did not become constant until after some time, the total increase in this case amounting to about 10 per cent. It was also observed that the blue color of the freshly prepared ammonia solution gradually changes to a fine red.

It is worth while to note that contrary to the behavior of dinitrobenzene, no appreciable time was necessary for the solution of trinitrotoluene to take on its final conductivity value upon dilution.

Nitromethane.—Nitromethane, which is miscible with ammonia, is not dissociated to as great an extent as are the aromatic nitro compounds, but it nevertheless forms a good conducting solution. While nitromethane itself is but very slightly soluble in water, it very readily dissolves in a solution of an alkaline hydroxide, forming a compound in which the metal takes the place of hydrogen in the nitromethane.[2] No record of measurements of the conductivity of the salts of nitromethane or of nitromethane itself in aqueous solution could be found.

Basic and Acid Amides.—The amides of potassium, sodium, and lithium are fair conductors of electricity in ammonia solution as are also a considerable number of acid amides.

Of the class of basic amides, measurements of the molecular conductivity have been made only in the case of sodamide. In preparing the solution of sodamide a weighed quantity of metallic sodium was introduced into the resistance cell, when by the action of the ammonia, the metal was soon changed into sodamide. The end of the reaction was recognized by the complete disappearance of the blue color of the sodammonium, and by the final constant value of the resistance of the

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[1] Ztschr. phys. Chem., **28**, 619 (1899).

[2] Meyer und Jacobson: Lehrb. d. organ. Chem., **1**, 254 (1893).

solution. The difficulty of weighing metallic sodium accurately makes a confirmation of the values given in the table above desirable, a matter which will have the attention of one of us in the near future. Quantitative measurements of the conductivity of potassamide and lithamide solutions have also been made. Sodamide is slightly soluble in ammonia ; potassamide is very soluble.

The acid amides generally dissolve readily in ammonia, most of them forming solutions which are conductors. They vary a great deal, however, in the extent of dissociation which they undergo ; benzamide and paracettoluide, for example, do not conduct the current perceptibly, acetamide and urea conduct very poorly, while succinimide conducts well, and metanitrobenzenesulphonamide approaches the salts in the facility with which its solution conducts the current.

The only measurements so far recorded of the conductivity of acid amides in aqueous solution are those of Bader[1] on a number of substituted cyanamides, of Walden[2] on succinimide, and of Trübsbach[3] on a few ureides. The substituted cyanamides and some of the substituted ureides form solutions which are fairly good conductors, while the solutions of succinimide, urea, and some simple ureides are very poor conductors. Qualitative measurements by the authors on a number of acid amides, including acetamide and benzenesulphonamide, justifies the conclusion that in general this class of bodies is but slightly dissociated in aqueous solution. On the other hand, ammonia has the power of dissociating many of them to a very considerable extent, as the measurements given above show. An interesting question in connection with these solutions is whether the positive ion is hydrogen or ammonium. From the action of ammonia on hydrogen ions in aqueous solution it is to be presumed that the positive ion is ammonium, but if this is the case it would seem that the dissociation curves of these substances might be expected to follow more closely the curves for salts, instead of resembling, as they do, those of weak acids in aqueous solution. If ammonium salts are formed in solution they are so unstable that,

[1] Ztschr. phys. Chem., **6**, 304 (1890).

[2] *Ibid.*, **8**, 484 (1891).

[3] *Ibid.*, **16**, 708 (1895).

on evaporating away the solvent and warming up to the laboratory temperature, they decompose, leaving behind the free acid amides.[1] On the other hand, if the positive ion is hydrogen, then the migration of the positive ion is strikingly low.[2]

Reactions of the Amides in Liquid Ammonia.—If acid and basic amides bear to ammonia a relation analogous to that borne to water by the ordinary oxygen acids, then, since the former are dissociated in liquid ammonia, they should react in ammonia something after the manner of acids and bases in water.

Numerous reactions suggest themselves, a few of which take place in aqueous solution while others have been carried out in benzene and other non-electrolytic solvents.[3] Titherly especially, in his investigations on the action of sodamide on a variety of substances, has prepared a number of salts of acid amides. By continued heating of benzene solutions of formamide, acetamide, propionamide, and benzamide, respectively, with sodamide, Titherly obtained sodium formamide, $HCONHNa$, sodium acetamide, $CH_3CONHNa$, sodium propionamide, $C_2H_5CONHNa$, and sodium benzamide, $C_6H_5CONHNa$.

Only a few such reactions have yet been studied in ammonia solution, and these only qualitatively.

If an ammonia solution of benzenesulphonamide is allowed to act on sodamide, after a time a well-crystallized substance separates from the solution which is presumably benzenesulphonamide in which sodium is substituted for amide hydrogen.

Solutions of benzenesulphonamide, succinimide, benzoic sulphinide, acetamide, and urea dissolve metallic sodium, metallic magnesium, and, to some extent, metallic zinc, with the evolution of hydrogen, and well-crystallized products separate from the solutions. The amount of hydrogen given off

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[1] This statement was proved by experiment to be true in the cases of benzoic sulphinide, acetamide, and benzenesulphonamide. Orthonitrophenol retains 1 molecule of ammonia. Trinitrotoluene retains 3 molecules of ammonia.

[2] Hydrochloric acid in acetone shows an abnormally low conductivity. Carrara: Ztschr. phys. Chem., **27**, 184 (1898).

[3] Dessaignes: Ann. Chem. (Liebig), **82**, 231 (1852); Strecker: *Ibid.*, **103**, 324 (1857); Gal: Bull. Soc. Chim., **39**, 647 (1883); Curtius: Ber. d. chem. Ges., **23**, 3037 (1891); Blacher: *Ibid.*, **28**, 432 and 2352 (1895); Titherly: Jour. Chem. Soc. (London), **71**, 461 (1897).

when magnesium was dissolved in a solution of acetamide, was measured and found to be equivalent to the amount of magnesium dissolved. In the case of the action of magnesium on benzenesulphonamide the volume of hydrogen obtained was much less than the calculated amount, a fact which may have its explanation in the reducing action of the nascent hydrogen on the acid amide.

Silver oxide dissolved sparingly in a solution of acetamide, and copper oxide dissolved in a solution of benzoic sulphinide; after a time well-crystallized substances separated from the solutions, and these were presumably silver and copper salts of acetamide and benzoic sulphinide, respectively.

In this connection the fact may also be mentioned that, in general, the salts of ammonium, which bear to ammonia a relation in some respects analogous to the relation which the oxygen acids bear to water, dissolve the alkali metals and magnesium, and in some cases other metals, with the evolution of hydrogen. Ammonium nitrate, for example, dissolves magnesium very energetically and after a time a well-crystallized product separates from the solution.

Further, on the basis of the relations which the ammonium salts and the acid amides on the one hand, and the metallic amides on the other, bear to ammonia as an electrolytic solvent, it ought to be possible to find indicators which give color reactions in ammonia after the manner of indicators in aqueous solutions. Such indicators in fact exist.

Phenolphthalein dissolves in ammonia forming a pale-red solution. Addition of sodamide greatly intensifies the color of the solution, while in turn the color is completely discharged by addition of benzoic sulphinide or ammonium bromide.

Carmine dissolves sparingly, forming a dirty red solution which sodamide changes to a fine blue. The blue color is changed to a fine red by the addition of ammonium bromide.

Saffranine dissolves abundantly, forming a beautiful crimson solution. Sodamide or potassamide changes this color to blue, and acid amides or ammonium salts restore the crimson color.

The strong colors of a considerable number of other substances in solution in ammonia, among which may be mentioned metadinitrobenzene, trinitrotoluene, and orthonitrophenol are but slightly affected by either the addition of basic or acid amides. A large excess of an ammonium salt of an acid amide changes the blue solution of alizarin to a mixed color.

See errata p. 532.

The Alkali Metals.—The most remarkable observations made in connection with the work on liquid ammonia is the fact that solutions of the alkali metals conduct electricity with great facility, without any separation of products at the electrodes and without the least sign of polarization. The authors have confirmed the statements of Cady[1] to this effect. The greatest difficulty in the way of measuring the conductivity of these solutions lies in the fact that the metals react with the solvent rapidly enough to introduce a large and uncontrollable error. For example 56 mg. of sodium in 45 cc. of ammonia at its boiling-point, were completely changed into sodamide in the course of fifteen minutes. An approximate value of the molecular conductivity of a sodium solution was obtained by introducing a known weight of sodium into the resistance cell of the conductivity apparatus, and as soon thereafter as possible, taking a reading of the resistance. This gave for $v = 18.56$, a molecular conductivity of 392.6, or if the molecule be assumed to contain 2 atoms of sodium, as some previous investigators[2] on these solutions indicate, then the molecular conductivity becomes 785.2.

See errata p. 532.

An attempt was made to determine what change, if any, takes place in the molecular conductivity on diluting the solution. To this end the above solution was again measured and, as rapidly as possible, ammonia was added from the receiver until the second point in the conductivity cell was covered. The solution was then stirred and the resistance read. The molecular conductivity calculated from these two measurements was for $v = 1856$, $\mu_v = 332.6$; and for $v = 27.49$, $\mu^v = 335.4$. Approximate measurements made by Cady[3] gave for $v = 4.28$, 3.97, and 3.8, $\mu_v = 420$, 441, and 479,

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[1] J. phys. Chem., **1**, 707 (1897).

[2] Joannis : Compt. rend., **115**, 820 (1898).

[3] *Loc. cit.*

respectively. Certainly the molecular conductivity does not change much with the dilution. Because of a mishap to the apparatus, further measurements on these solutions have not yet been made.

See Errata p. 532

An attempt was also made to measure the temperature coefficient of the alkali metal solutions, but here too the action between the metal and the solvent[1] interposed a serious difficulty which was only partially overcome by making the measurements at temperatures much below the boiling-point of ammonia at atmospheric pressure. Under these conditions the temperature coefficient which could not be at all accurately determined was found to be between 0.5 and 1.5 per cent per degree, and to be of positive sign.

As stated above, Joannis has shown that in these metallic solutions 2 atoms of the metal are united with 2 molecules of ammonia to form, for example in the case of sodium, a compound having the formula $Na_2N_2H_6$, to which he has given the name sodammonium. It has not been shown, however, that the ammonia combined with the metal in this compound plays the same part as does ammonia in the ammonium compounds. The solution behaves in many respects as a simple solution of the metal in ammonia in which the former is combined with the ammonia rather after the manner of substances with water of crystallization than as a constituent of a stable compound of the ordinary kind. Or the ammonia is coordinated with the metal in the sense in which Werner uses this expression. Water of crystallization in combination with compounds has no effect on the conductivity of their aqueous solutions, nor does it take part in the reactions of the compounds as ordinarily considered. The same is in all probability true of salts with ammonia of crystallization in ammonia solutions. It may be doubted therefore whether the compound sodammonium has any further analogy with the hypothetical compound ammonium than the fact that it may be brought under the same formula.

The following facts seem to indicate that sodium solutions

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[1] By comparing the rate of reaction between sodium and ammonia on the one hand, and sodium and water on the other, some idea of the relative number of hydrogen ions present in liquid ammonia is obtained. The number must be very much less in ammonia, which is in agreement with the high resistance found for the pure liquid.

occupy a very interesting position between ordinary electrolytic conductors and some vapors.

J. J. Thomson[1] has shown that sodium vapor is blue, that it conducts electricity remarkably well, and without polarization at the electrodes, properties which an ammonia solution of sodium likewise exhibits. While, however, in the form of vapor the molecule and atom of the alkali metals are identical,[2] in solution in ammonia the molecule contains 2 atoms.[3]

Whatever may be the nature of the substance in solution, it conducts the current with remarkable facility. It would seem that the process of conduction must consist in the wandering of charged bodies through the solution, and the fact that the temperature coefficient is of positive sign and of considerable magnitude lends probability to this view.

As there are molecules of but one kind in solution it is impossible to assume that 1 molecule should be able to take on only a positive charge and another only a negative charge. Consequently it would seem that one and the same particle must be able to take on a charge of either positive or negative electricity with which it wanders to the oppositely charged electrode, there to loose its charge and to take on one of opposite sign, or meeting an oppositely charged particle to thus lose its charge.[4] At any rate enormous quantities of electricity may pass through such solutions without producing any visible effects other than a deepening of the blue color in the vicinity of the electrodes in dilute solutions.

Investigations on these metal solutions will be continued during the present year by one of us (Kraus) in the laboratories at Johns Hopkins University.

In the appended plates, in which the ordinates represent molecular conductivities and the abcissae the cube roots of the dilution, the dependence of the molecular conductivity upon the dilution of the solutions is shown graphically.

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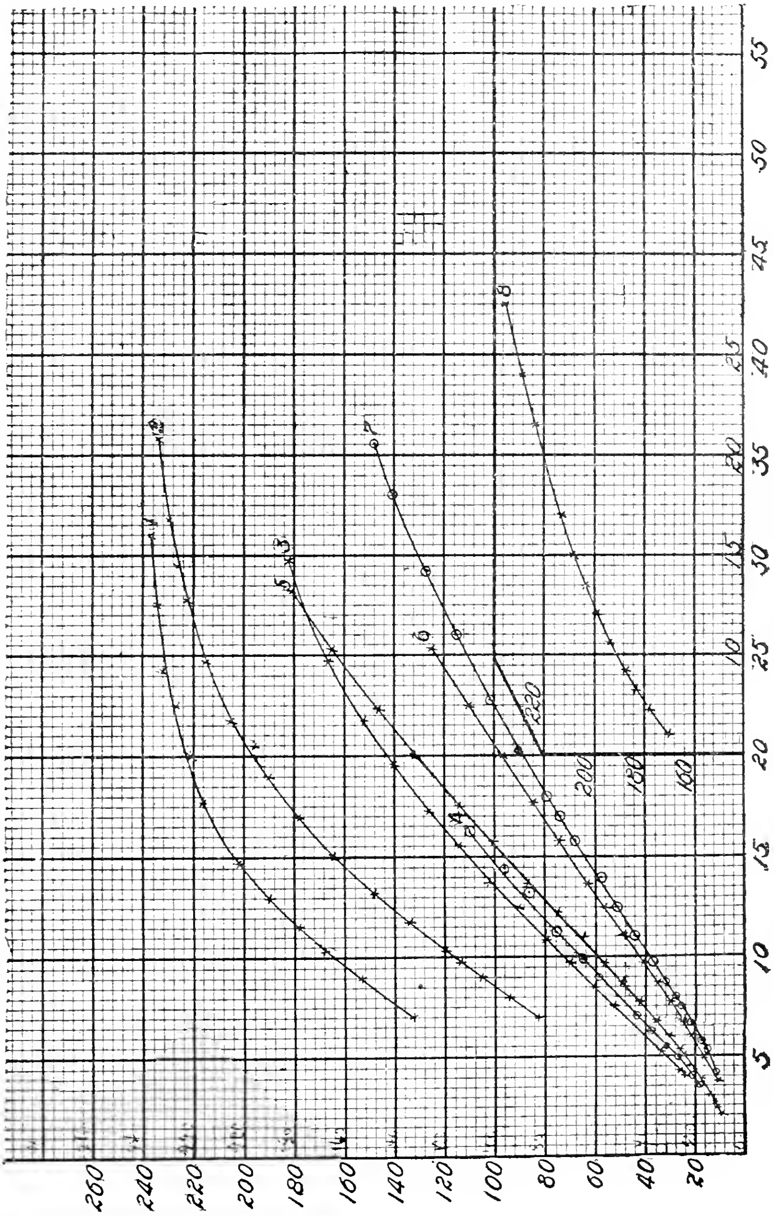
[1] Phil. Mag. (5), **29**, 441 (1890). It is interesting to note in this connection that sodium chloride which has been heated in the vapor of sodium takes on a permanent blue color. (Geisel: Ber. d. chem. Ges., **30**, 158 (1897).)

[2] Scott: Trans. Roy. Soc., Edinburgh, **14**, 410 (1887).

[3] Joannis: *Loc. cit.*

[4] This is approximately the hypothesis upon which J. J. Thomson explains the conductivity of the vapor of sodium and some other substances. (*Loc. cit.*)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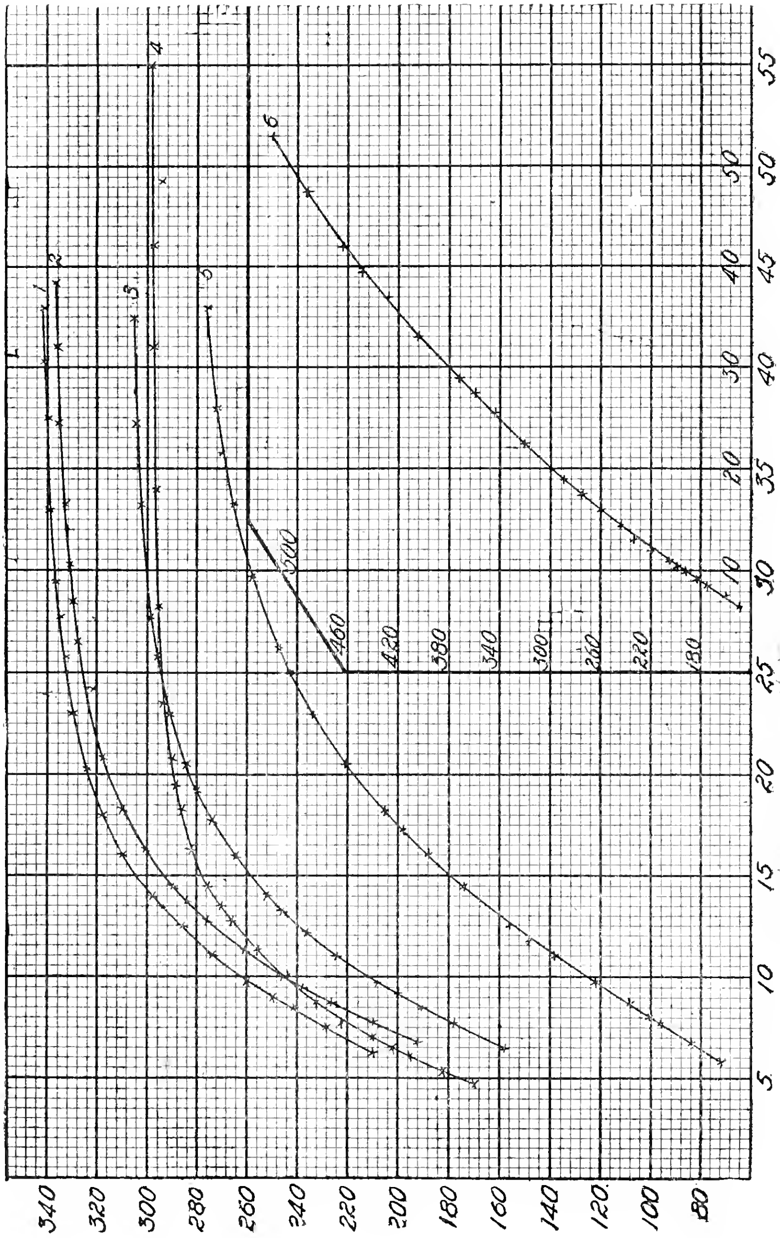
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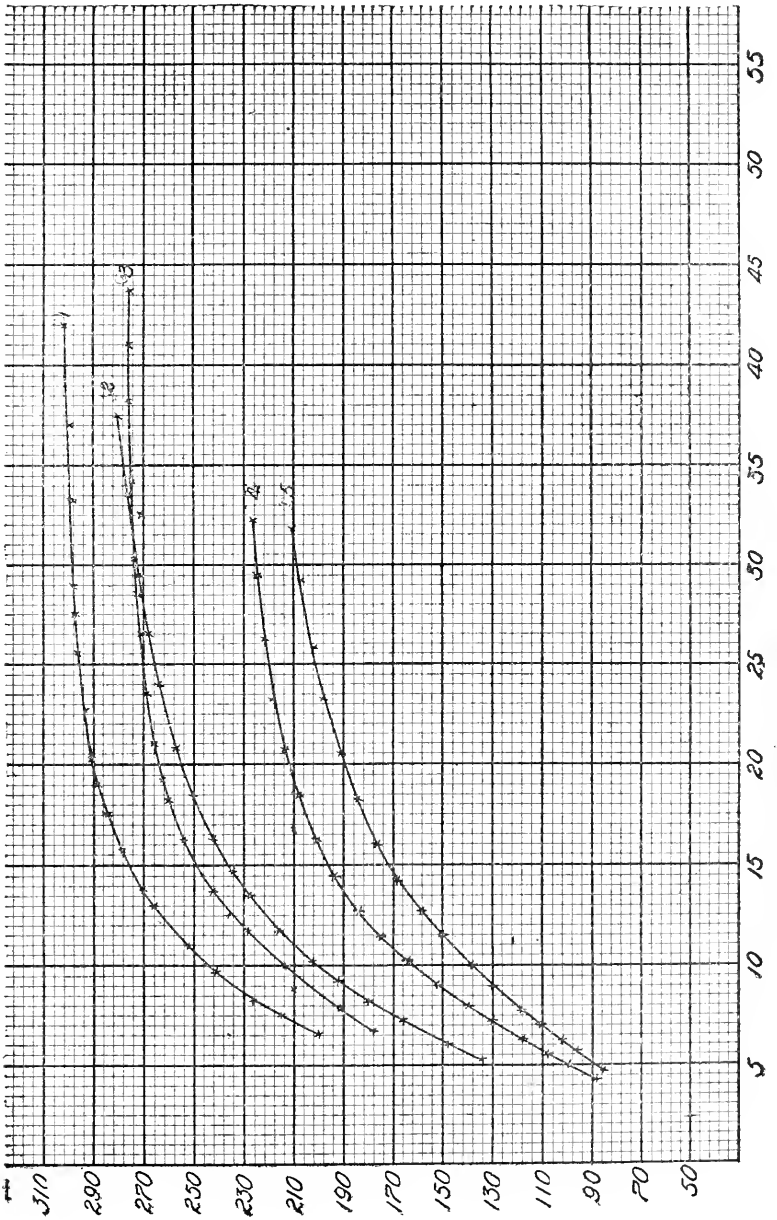
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Summary of Results.

The results of the work described in this paper may be briefly summed up as follows:

1. The problem of obtaining pure liquid ammonia has been successfully solved and a form of apparatus has been constructed which is well adapted to the study of the conductivity of liquids of low boiling-points.

2. With a few exceptions salts are dissociated to a less degree in ammonia than in water.

3. The limit of molecular conductivity of binary salts in ammonia at —38° ranges from about 290 to 340 Kohlrausch units, which is much above the conductivity of the same salts in solution in water at 18°.

4. Ostwald's law of dilution holds approximately for binary salts. Other solutes have not been tested.

5. Silver iodide is dissociated in ammonia solution, although not to so great an extent as other binary salts.

6. Mercuric chloride reacts with ammonia to form the compound $HgCl_2.12NH_3$, which loses 10 molecules of ammonia on being warmed up at atmospheric pressure. The compound $HgCl_2.2NH_3$ is identical with mercuri-diammonium chloride.

7. Mercuric cyanide and silver cyanide conduct in ammonia, but the conductivity in neither case changes much with the dilution. The molecular conductivity of the former falls slightly, the latter rises somewhat.

8. The one ternary salt measured has a high molecular conductivity, and, as in water solution, it approaches its maximum more slowly than do the binary salts.

9. Many of the nitro compounds are good conductors in ammonia solution. Some of them approach the binary salts in their power to carry the current.

10. The acid and basic amides generally dissolve in ammonia to form good conducting solutions. The conducting power of the acid amides ranges from the fraction of a unit to that of the binary salts.

11. The acid and basic amides may be considered as acid and bases derived from ammonia in the same manner as the

oxygen acids and bases are derived from water. This relation is borne out by the chemical behavior of the amides in solution in ammonia and by their action on color indicators.

12. As found by Cady ammonia solutions of the alkali metals conduct electricity without polarization at the electrodes. The conductivity changes but slightly, if at all, with the concentration.

These solutions exhibit positive temperature coefficients.

In conclusion, the authors wish to express their appreciation of the kindness of Professor Lucien I. Blake in placing at their disposal the facilities of the Department of Physics and Electrical Engineering.

THE UNIVERSITY OF KANSAS,
LAWRENCE, September, 1899.

ON THE CAUSE OF THE EVOLUTION OF OXYGEN WHEN OXIDIZABLE GASES ARE ABSORBED BY PERMANGANIC ACID.

BY H. N. MORSE AND H. G. BYERS.

It was suggested in a former communication[1] that the evolution of oxygen which occurs when hydrogen or carbon monoxide is absorbed by acidified solutions of potassium permanganate is due to the action of the peroxide which is formed upon the excess of the permanganic acid; and, further, that the cause of this action of the oxide upon the acid may be a tendency on the part of the simpler peroxide molecules to polymerize to more complex ones at the expense of the acid.

It was affirmed by V. Meyer and M. von Recklinghausen[2] that when hydrogen and carbon monoxide are absorbed by a neutral solution of potassium permanganate, there is no liberation of oxygen. Previous to this, however, it had been stated by one of us[3] that "the reduction of potassium permanganate by the superoxide in a neutral solution is too slow for convenient observation." If, now, the evolution of oxygen which occurs when gases are absorbed by acidified solu-

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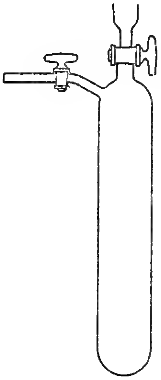
[1] Morse and Reese: This JOURNAL, **20**, 721.

[2] Ber. d. chem. Ges., **29**, 2551.

[3] This JOURNAL, **18**, 413.

tions of permanganate is due to the action of the oxide on the permanganic acid, as maintained by us[1] in opposition to V. Meyer and H. Hirtz,[2] then the oxide which is formed in neutral solutions and is *inactive* should become *active* whenever—after the disappearance of the gas—the solution containing the oxide in suspension is acidified. Our experiments show, as regards carbon monoxide, that when this gas is absorbed by neutral solutions of permanganate, there is no evolution of oxygen; but when an acid is afterwards added, there is an evolution of oxygen similar in all respects to that which is observed when an equal volume of the gas is absorbed by an acidified solution of permanganate of the same concentration.

Again, if the cause of the reduction of the acid is, as suggested, the tendency on the part of the peroxide to become more complex at the expense of the acid, then the evolution of oxygen should gradually diminish in rapidity as the polymerization progresses. Our experiments prove that as a matter of fact the rate of evolution does constantly decrease whether the gas is absorbed in an acid solution or in a neutral one which is afterwards acidified. It is shown, moreover, that when the gas is absorbed in an acid solution the period of rapid evolution does not terminate with the disappearance of the gas as it should if the gas is the direct cause of the liberation of oxygen.



Finally, if polymerization of the oxide is the cause of the decomposition of the acid, the quantity of the gas absorbed remaining fixed, the volume of oxygen liberated within a given time should increase with increasing concentration of the permanganic acid. Our experiments show that it does so increase.

The apparatus which was employed by us is shown in the accompanying figure. It consisted of a glass tube having a capacity of 100 cc. The liquid reagents were introduced through the larger horizontal stop-cock at the top, and the gas through the stop-cock in the nearly capillary side-tube.

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[1] This JOURNAL, **20**, 521.

[2] Ber. d. chem. Ges., **29**, 2828.

To make room for the gas within, a volume of air equal to, or somewhat greater than, that of the gas to be introduced was first withdrawn from the tube. To secure proper mixing of the contents and a uniform condition of temperature, the tubes were attached transversely to a shaft which passed through a thermostat and was revolved at the rate which appeared to secure the greatest agitation of the contents of the tube. A nearly constant temperature of 35° was maintained in the bath. The gas experimented with was carbon monoxide, of which 12 cc.—or the volume which would reduce to that under standard conditions of temperature and pressure—were employed in every case. With this fixed volume of carbon monoxide, various quantities of potassium permanganate were agitated both in neutral and in acidified solutions. The volume of the acidified solutions, however, was always raised to 50 cc. by the addition of water. 12 cc. of carbon monoxide reduce 56.44 mgms. of potassium permanganate to the peroxide condition, and the weights of the salt introduced into the tubes were always some multiple of this quantity. Hence the oxide resulting from the absorption of the gas and the excess of permanganic acid bore to each other in every case definite, known, molecular ratios. For example, when 169.32 ($= 56.44 \times 3$) mgms. of the salt were agitated with 12 cc. of the gas, the ratio of $HMnO_4$ to MnO_2 was 2 to 1; and when 1549.64 ($= 56.44 \times 31$) mgms. of the salt were used, the ratio was 30 to 1. The ratios actually employed were 2 : 1, 5 : 1, 10 : 1, 15 : 1, 20 : 1, 25 : 1, 30 : 1, and in one case 7.5 : 1. In working with acidified solutions, the same degree of acidity was always produced, the quantity of sulphuric acid which was added being in every instance equivalent to the potassium in the permanganate reduced by the gas plus three times the potassium in the excess of the salt. The amount of the reduction was measured by titrating the contents of the tubes, after agitation, against standard solutions of oxalic acid or of potassium tetroxalate.

Our first step was to determine the length of time required to absorb the gas by neutral solutions of various concentrations. The results are given in Table I.

Table I.

Ratio of $HMnO_4$ to MnO_2.	Time of agitation. Hours.	CO unabsorbed. cc.	Apparent reduction. cc. of O_2.
2 : 1	5	1.0	—0.08
	5	0.85	—0.10
	9	0.2	0.01
	9	0.4	—0.01
	10	0.0	—0.02
	10	0.0	—0.01
5 : 1	3	0.6	—0.14
	3	0.2	—0.00
	4	0.2	—0.02
	4	0.4	0.03
	5	0.0	0.03
	5	0.0	0.03
10 : 1	1½	1.3	—0.13
	1½	1.5	—0.13
	2	0.0	—0.13
	2	0.0	—0.26
20 : 1	1	0.4	—0.26
	1	0.9	—0.87
	1½	0.4	—0.07
	1½	0.0	0.00
	2	0.0	0.00
	2	0.0	—0.53
30 : 1	1	0.3	—0.09
	1	0.2	0.26
	1¼	0.0	0.17

Having found the time which neutral solutions of various concentrations required for the complete absorption of the gas, we proceeded to ascertain what would happen if, after the absorption, the solutions were acidified. In Table II, which gives the conditions and results of our experiments in this direction, the duplicates are bracketed together, and letters are employed to indicate what tubes were in the bath at the same time.

Table II.

Ratio of $HMnO_4$ to MnO_2.		Hours of agitation.		Oxygen liberated.	Percentage reduction.
		Neutral.	Acid.	cc.	
2 : 1		11	24	0.89	7.34
		11	24	0.98	8.37
		22	24	1.16	9.76
		22	24	0.98	8.37
		26	24	1.06	8.92
		26	24	1.14	9.65
		13½	150	5.67	47.51
		13½	150	5.66	47.39
5 : 1	a	4	24	1.88	6.29
		4	24	1.45	4.87
	a	24	00	0.06	....
		24	00	0.11	....
	b	24	24	1.68	5.67
		24	24	1.74	5.84
	b	48	00	0.06	....
		48	00	0.06	....
		4	150	7.44	24.85
		4	150	7.44	24.85
10 : 1	c	2	24	2.09	3.51
		2	24	2.15	3.57
	c	24	00	—0.13	....
		24	00	—0.06	....
	d	24	24	2.29	3.82
		24	24	2.35	3.89
	d	48	00	0.00	....
		48	00	0.06	....
		3	150	11.46	18.33
		3	150	11.17	18.04
20 : 1	e	1½	24	3.40	2.84
		1½	24	3.54	2.94
	e	25½	00	0.13	....
		25½	00	0.07	....
	f	24	00	0.00	....
		24	00	—0.33	....
	f	2	24	3.00	2.50
		2	24	3.00	2.50
		24	24	3.24	2.61
		24	24	3.75	3.01
	g	48	00	—0.06	....
		48	00	0.06	....
		2	24	3.34	2.77
		2	24	4.00	3.33
		2	150	11.62	9.69
		2	150	12.95	10.78

30 : 1	h	1¼	24	4.56	2.54
		1¼	24	5.10	2.86
	h	24	00	—0.09	....
		24	00	—0.17	....
	i	24	24	4.74	2.62
		24	24	5.42	3.01
	i	48	00	0.35	....
		48	00	0.52	....
		2	150	18.40	10.10
		2	150	19.27	10.84

We next proceeded to determine how long a time acidified solutions of permanganate of different concentrations require for the absorption of the gas, and what volumes of oxygen are liberated previous to the disappearance of the last traces of the gas. Table III gives the results :

Table III.

Ratio of $HMnO_4$ to MnO_2.	Time of agitation. Hours.	CO unabsorbed. cc.	O_2 liberated. cc.	Percentage reduction.
2 : 1	5	0.85	0.22	1.76
	6	0.60	0.28	2.25
	7	0.35	0.29	2.51
	8	0.0	0.34	2.85
	8	0.0	0.34	2.85
5 : 1	2	1.65	0.73	2.39
	2	0.95	0.53	1.41
	3	0.0	0.88	2.92
	3	0.0	0.88	2.92
10 : 1	1½	0.55	1.65	2.71
	1½	0.20	1.40	2.27
	2	0.0	1.84	3.04
	2	0.0	1.65	2.73
20 : 1	1	2.6	2.80	2.31
	1	0.9	2.80	2.33
	1½	0.0	3.33	2.77
	1½	0.0	3.74	3.11
30 : 1	1	0.30	5.27	2.92
	1¼	0.0	5.36	2.98
	1¼	0.0	5.63	3.00

Finally, we absorbed the gas in acid solutions of various concentrations, agitated for periods of 6, 24, and 150 hours, and determined the amount of oxygen which had been liberated. The results are contained in Table IV.

Table IV.

Ratio of $HMnO_4$ to MnO_2.	Time of agitation.								
		6 hours.			24 hours.			150 hours.	
		O_2 liberated. cc.	Per cent reduction.		O_2 liberated. cc.	Per cent reduction.		O_2 liberated. cc.	Per cent reduction.
2 : 1		CO not all absorbed			0.80	6.85		1.91	16.02
					0.73	6.10		2.49	20.81
					0.72	6.07			
					0.71	5.95			
5 : 1	a	1.49	4.96	b	2.46	8.21	c	3.88	12.99
		1.35	4.46		2.30	7.64		3.88	12.99
7½ : 1	c	1.90	4.25	e	2.77	6.16	c	5.80	12.91
		1.90	4.25		2.77	6.16		5.96	13.25
	a	2.06	4.37	d	2.77	6.16			
		...	...		2.94	6.49			
10 : 1	d	2.93	4.90	e	3.57	5.95	c	7.80	13.05
		2.63	4.90		3.57	5.95		...	....
	f	3.20	5.34	g	3.84	6.43	h	7.80	13.05
		2.89	4.84		3.84	6.43		7.64	12.79
		3.20	5.34		3.87	6.49			
		3.13	5.21		4.14	6.87			
15 : 1	f	3.84	4.21		5.26	5.78	h	9.54	10.47
		3.87	4.24		5.26	5.78		9.70	10.84
20 : 1	f	4.79	3.99		5.89	4.89	l	10.75	8.86
		5.13	4.29		5.75	4.75		11.44	9.51
	i	5.10	4.24	k	5.30	4.38	h	10.81	8.99
		4.62	3.68		...	...		....	...
		4.95	4.14	k	5.74	4.72		10.81	8.99
		5.30	4.38		5.89	4.90		11.03	9.16
25 : 1	i	5.90	3.92	k	6.06	4.02	l	13.66	9.09
		5.90	3.92		6.37	4.24		14.30	9.39
30 : 1	i	6.38	3.53	k	7.48	4.15	l	15.25	8.46
		6.53	3.56		7.48	4.15		16.83	9.36
					7.32	4.06			

It appears from Table I that when carbon monoxide is absorbed by a neutral solution of potassium permanganate there is no liberation of oxygen during the absorption; and from certain experiments included in Table II, where no acid was added, it appears that the neutral permanganate may be agitated for many hours with the peroxide which is produced in it by the absorption of the gas without suffering any sensible reduction. The inactive state of the oxide under these conditions may be due to the fact that the salt is more stable than the acid, or to the fact that the peroxide precipitated in a neutral solution contains large quantities of potassium and is therefore already saturated ; or, what is more likely, the failure to liberate oxygen may be due to both of these causes. As regards the quantity of alkali which such an oxide may contain, it has been shown[1] that when a neutral solution of the permanganate undergoes complete, so-called spontaneous reduction to the peroxide, the precipitate contains the whole of the potassium.

Table II shows that when carbon monoxide has been absorbed by an excess of neutral permanganate, giving an inactive oxide, and the liquid is afterwards acidified, there is a liberation of oxygen just as when the gas is absorbed by an acid solution. Moreover, the general characteristics of the reaction are the same in both cases, pointing to a common cause. The amount of oxygen liberated within a given time increases with the concentration of the acid, and the rate of evolution in any given case decreases with time, the decrease being most marked in the more concentrated solutions. These phenomena are most easily explained by supposing the peroxide molecule in its simpler state to be unsaturated in the sense that it is capable of uniting with other molecules of its own kind and that its power to do this enables it to break up adjacent molecules of permanganic acid. Its failure to liberate oxygen when formed in neutral solutions would be explained, as previously stated, by the fact that when it is so formed it is in combination with potassium.

Table III shows that when a fixed quantity of carbon monoxide is absorbed by acid solutions of permanganate, the quantity of oxygen which is liberated during the absorption increases with the concentration of the solution. This result was anticipated and the experiments were made with a view to testing the hypothesis as to the cause of the liberation of oxygen. It was reasoned that if the reduction of the acid is

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[1] This Journal, 18, 411.

due to the inclination of the peroxide molecules to abstract still other molecules of the oxide from the acid in order to unite with them, then the rate of the reduction, and consequently of the liberation of oxygen, should increase with the concentration of the permanganic acid.

From Table IV it appears that the quantity of oxygen which is liberated in a given period *after* the gas has disappeared increases with the concentration just as it does during the absorption, and as it does also when the gas is first absorbed in a neutral solution to which acid is afterwards added. Moreover, the rate of evolution diminishes with time in the former as it does in the latter case. Nevertheless, the evolution is still relatively rapid for a time—especially in the more dilute solutions—after the disappearance of the gas, as if the causes of the evolution during the absorption and afterwards were identical. These relations will be rendered clearer by an inspection of Table V, in which the averages of the results contained in Tables III and IV are given :

Table V.

				Agitation. 6 hours.		Agitation 24 hours.		Agitation. 150 hours.	
Ratio of $HMnO_4$ to MnO_2.	Time required for the absorption of the CO. Hours.	O_2 evolved during the absorption of the gas. cc.	Percentage reduction during the absorption of the gas.	O_2 evolved. cc.	Percentage reduction.	O_2 evolved. cc.	Percentage reduction.	O_2 evolved. cc.	Percentage reduction.
2 : 1	8	0.34	2.85	...	...	0.74	6.24	2.20	18.42
5 : 1	3	0.88	2.92	1.42	4.71	2.38	7.93	3.88	12.99
7½ : 1	..	...	...	1.95	4.29	2.81	6.24	5.88	13.08
10 : 1	2	1.75	2.89	3.05	5.09	3.81	6.35	7.75	12.99
15 : 1	..	...	...	3.86	4.23	5.26	5.78	9.62	10.66
20 : 1	1⅓	3.54	2.94	4.82	4.12	5.71	4.73	10.97	9.11
25 : 1	..	...	...	5.90	3.92	6.22	4.13	13.98	9.24
30 : 1	1¼	5.50	2.99	6.45	3.55	7.43	4.12	16.04	8.91

A comparison of Tables II and IV will show that the oxide formed in acidified solutions is, in general,—especially in the more concentrated ones—more active during the first twenty-four hours than that formed in neutral solutions; while if the agitation is continued for one hundred and fifty hours, the latter oxide exhibits, in all cases, the greater activity. Table VI, in which averages are given, will show this more clearly.

Table VI.

Ratio of	24-hour period.		150-hour period.	
	Acid.	Neutral.	Acid.	Neutral.
$HMnO_4$ to MnO_2.	O_2 cc.	O_2 cc.	O_2 cc.	O_2 cc.
2 : 1	0.74	1.03	2.20	5.67
5 : 1	2.38	1.69	3.88	7.44
10 : 1	3.81	2.22	7.55	11.29
20 : 1	5.71	3.38	10.97	12.28
30 : 1	7.43	4.95	16.04	18.84

If we grant that the evolution of oxygen, when the peroxide is agitated with an acidified solution of permanganate, is due to the abstraction of more peroxide from the acid with subsequent polymerization, and that the decline in the activity of the oxide is a consequence of such polymerization, the question naturally arises whether polymerization may not also take place between those molecules which are formed in consequence of the oxidation of the gas, as well as between these and others which must be derived from neighboring molecules of the acid. The experience of V. Meyer and M. von Recklinghausen[1] seems to indicate that such a polymerization may occur. It was found by them that when hydrogen or carbon monoxide is allowed to stand quietly over an acidified solution of permanganate, there is little liberation of oxygen ; in other words, the agitation of the gas with the solution is essential to any considerable evolution of oxygen. The explanation which we would suggest for this phenomenon is that the absorption and oxidation of the gas taking place only at the surface of the liquid, the solution becomes dilute at that point, and the molecules of peroxide therefore unite with each other to a great extent instead of with molecules of oxide derived from the acid. It may be due in part to the same cause that the evolution of oxygen during the absorption of the gas is so much more rapid in concentrated than in dilute solutions.

CHEMICAL LABORATORY,
JOHNS HOPKINS UNIVERSITY,
February, 1900.

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[1] *Loc. cit.*

Contribution from the Chemical Laboratory of Wesleyan University.

ABSORPTION APPARATUS FOR ELEMENTARY ORGANIC ANALYSIS.

BY FRANCIS GANO BENEDICT.

Since the time of Liebig, granulated calcium chloride and potassium hydroxide solution have been almost universally used for the absorption of water and carbon dioxide, respectively, in elementary organic analysis. Numerous forms of apparatus for holding these reagents have been devised but no satisfactory substitute for either absorbent has been generally accepted. In a former article[1] a special form of soda-lime that had given satisfactory results in the absorption of carbon dioxide was described, and it was mentioned that sulphuric acid was used to absorb the water formed in the process of the combustion. In the system here described sulphuric acid is used as the absorbent of water and soda-lime as the absorbent of carbon dioxide.

A fundamental error of most absorbing systems, including the one described in the article referred to, is the unequal drying which the gases receive on entering and leaving the carbon dioxide absorber. All dehydrating agents have not the same absorptive power, and hence a gas dried by one reagent will differ considerably in absolute moisture content from that dried by another. It is essential in determining the correct weight of carbon dioxide that no moisture be added to or removed from the absorbing system. In the earlier forms no provision was made to collect the moisture carried away by the gas which passes through a potash bulb, as it was considered that the moisture and carbon dioxide of the air used in the final aspiration, counterbalanced any error arising from evaporization of moisture.[2] As generally conducted at present the gas dried by fused calcium chloride enters the potash bulb and escapes through a small extension tube containing fragments of solid potassium hydroxide, and, while it is true that the issuing gas is thereby dried, it is by no means true

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[1] J. Am. Chem. Soc., **21**, 389.

[2] Die Entwicklung der organischen Elementaranalyse, W. Dennstedt, p. 21.

that it is dried to the same degree as it was before entering the carbon dioxide absorbing system. Where the greatest refinement of method is not required this unequal drying may be considered negligible. In the method of combustion in oxygen gas, already referred to,[1] but a small quantity of gas (700 to 1000 cc.) issues from the carbon dioxide absorbers, and consequently the error is not great. Where, however, a current of air instead of oxygen is used in the combustion, sufficient gas may pass through the system to exert a material influence on the result if the gas is unequally dried.

While doubtless different drying agents produce the greatest differences in the absolute amount of moisture remaining in a gas, the same drying agent will not always produce the same result, and as Dudley and Pease[2] have said, the mechanical condition as well as the freshness of calcium chloride may be a serious source of error when two different forms of this reagent are used for drying the gas before and after leaving the absorber.

Calcium chloride, being a solid, has many advantages over sulphuric acid, a liquid, for the absorption of water vapor. It is, however, not without its disadvantages. Probably the greatest difficulty in its use is the fact that it often contains basic chlorides, which absorb carbon dioxide as well as water. This impurity is so constantly present that it becomes necessary to pass dry carbon dioxide through a freshly filled calcium chloride tube for several hours before the basicity is destroyed. It is then necessary to remove the carbon dioxide by passing a current of dry air through the tube for some time. But as Winkler[3] has shown, this operation of saturating the calcium chloride is not thoroughly remedial since it is only the surface of the lumps of calcium chloride that is thus saturated, and later, as the solid absorbs water and deliquesces, fresh surfaces of basic chlorides are exposed and consequently carbon dioxide retained.

Moreover, calcium chloride deliquesces when used for some time, and the semiliquid portions are liable to clog the tube

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[1] J. Am. Chem. Soc., **21**, 389.

[2] *Ibid.*, **15**, 540.

[3] Ztschr. anal. Chem., **21**, 545.

and prevent the passage of the gas. A number of years ago Löwe[1] suggested a simple remedy for this, however, which consists in greasing the inside of the U-tube with clean tallow, and thus preventing the liquid from adhering to the walls.

Concentrated sulphuric acid, though a liquid reagent, has advantages that would seem to outweigh those of calcium chloride for use as an absorbent. It is a much better dehydrating agent than calcium chloride, does not retain carbon dioxide, and, in addition, serves to indicate the rate of passage of the gas. In an actual experiment to show the great avidity of this reagent for water, 64 grams of ordinary commercial concentrated sulphuric acid contained in a Drechsel gas washing bottle removed nearly 11 grams of water from an air current passing at the rate of 1 liter per minute. Less than 0.1 gram remained unabsorbed in the air leaving the absorbing bottle.

A property of sulphuric acid which is often of value in making combustions, is the fact that if unburned carbonaceous volatile products escape from the combustion tube they are mainly retained by the sulphuric acid, which soon becomes blackened. This indication often saves much time in forestalling unnecessary weighing and calculating.

In combustions of most organic substances more water is generally formed than is sufficient to saturate the gas leaving the combustion tube; hence, a varying amount of water condenses about the stopper in the exit end of the tube. The water formed in the process of a combustion is generally collected in a U-tube having a bulb on the arm nearest the combustion tube, which serves to collect the condensed water and thus to prevent unnecessary exhaustion of the absorbing agent. As this bulb fills it may be emptied, and consequently a number of combustions may be made with the same absorbing tube. The Volhard and the Marchand form of U-tube are most commonly used.

In the absorber indicated in the figure a small glass vial placed in one limb of a plain 5-inch U-tube $\frac{5}{8}$ of an inch in diameter serves the purpose of the bulb in the earlier forms. This vial, which should be 3 or 4 mm. less in diameter than the

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[1] Ztschr. anal. Chem., **11**, 403.

U-tube, is so supported on a bit of glass rod flattened at one end that the glass tube conducts the products of combustion into the neck of the vial. Water condensing in the tube falls in drops to the bottom of the vial and the gas saturated with aqueous vapor at the temperature of the apparatus passes through the U-tube into the carbon dioxide absorbers.

A plug of coarse glass-wool is inserted in the other arm and extends from the cork to the point where the bend begins. Enough commercial concentrated sulphuric acid is slowly poured through the glass-wool to saturate it thoroughly and just seal the bend at the bottom of the U in such a way that the gas will have to bubble through it. The lower end of the glass-wool will then be about 1 centimeter above the surface of the liquid, the air space preventing too much acid from being carried up mechanically into the glass-wool. When this happens it is not unusual for the acid to be carried over into the carbon dioxide absorbers. The air space is otherwise valuable as it permits isolation of each bubble and consequently better regulation of the rate of the combustion. If the bend is just sealed, the minimum pressure only is necessary to force the gas through the tube. The greater part of the water vapor is retained by the acid in the bend of the tube as the gas bubbles through, while the last traces are removed by the acid adhering to the glass-wool. Thus in one plain U-tube are incorporated three distinct drying operations;

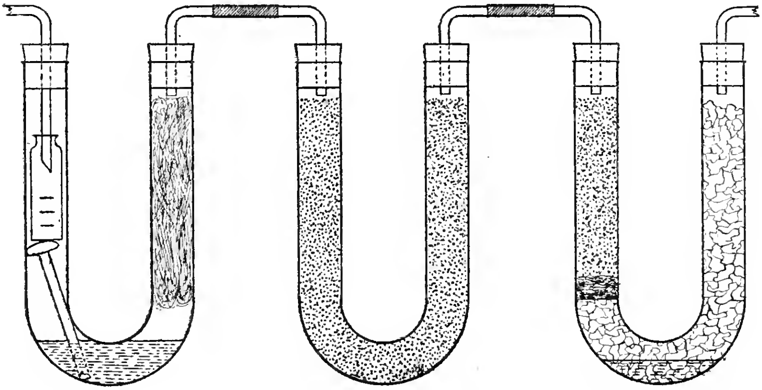

Fig. 1.

condensation of excessive moisture, removal of the major part of the water vapor, and final absorption of remaining traces of moisture. The tubes are closed with well-fitting, one-holed rubber stoppers furnished with glass elbows. One elbow extends far enough below the stopper to be thrust into the neck of the vial. The tubes are finally closed with short bits of red rubber tubing fitted with short glass plugs. Inasmuch as all the tubes in the absorbing train can be used for a number of combustions before refilling, the rubber stoppers can be replaced by corks which are crowded down and cut off flush with the ends of the U-tube. The corks may then be coated with sealing-wax. This precaution was not taken in the determinations reported in the following article. Rubber stoppers gave entire satisfaction. A tube prepared in this manner may safely be relied on to absorb about 1 gram of water vapor exclusive of the water condensed in the vial. In a series of experiments on the combustion of sugar where approximately 0.12 gram of water was weighed each time, it was found that about three-fourths of the water condensed in the vial. No direct estimate can be made, however, on the length of time such a tube will last, though if the vial is marked with a file scratch at the points indicating cubic centimeters and the amount of condensed water deducted from the increase in weight of the tube, a ready check on the amount of water vapor actually absorbed is at hand.

This form of absorber is characterized by great efficiency. As sulphuric acid is a much stronger dehydrating agent than calcium chloride, less moisture remains in the air current. Repeated tests have shown that all the moisture that can be retained by sulphuric acid will be absorbed in such a tube when the air current is much faster than would ever be permissible in the process of a combustion (150 cc. per minute), a rapidity of desiccation unattainable with calcium chloride. The use of a liquid absorbent renders the attachment of a special apparatus to indicate the rate of flow unnecessary. Where potassium hydroxide solution is used to absorb the carbon dioxide no indicator is needed, but in systems using solid absorbents for both water and carbon dioxide it has been customary to insert between the combustion tube and the water-absorbing tube a small U-tube containing either mercury, water, or sulphuric acid[1] to note the rate of flow.

This form of U-tube is very easy to wipe dry with a cloth while other forms, including as they do bulbs and enlargements, are not so readily cleaned.

The friability of many other forms of drying apparatus is not shared by this form. Plain glass U-tubes are not, of course, indestructible, but when properly handled the risk of breakage is very small, while if broken they can be replaced at one-half the cost of any other form.

The carbon dioxide absorbing system is a slightly modified form of that described in the article previously referred to,[2] and consists of a U-tube containing specially prepared soda-lime followed by a U-tube one-third filled with soda-lime and two-thirds filled with pumice stone saturated with concentrated sulphuric acid. This differs from the earlier form in the substitution of the pumice stone and sulphuric acid for calcium chloride as a final dryer in the train. The actual amount of moisture leaving a soda-lime tube is small, not more than 3 to 5 mgms. per liter of gas escaping from the absorbers, and of this quantity the greater portion would be retained by calcium chloride, as was found by repeated tests, but of necessity there would still be a loss of moisture amounting to from 0.5 to 1 mgm., that in accurate work should not be neglected. Sulphuric acid, on the other hand, retains all of the moisture, *i. e.* the issuing gas is dried to the same extent as that which enters.

The soda-lime is practically a mixture of equal weights of sodium hydroxide and calcium oxide to which sufficient water has been added to slake the lime and dampen the whole mixture. The preparation of this form of soda-lime is very simple. One kilogram of commercial caustic soda "Greenbank Lye" is dissolved in 750 cc. of water in an iron kettle and 1 kilogram of finely-pulverized quicklime is added to the solution with constant stirring until the lime is slaked and the water is all absorbed. The product is then broken into lumps

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[1] Monatshefte (1889), 398; Ann. Chem. (Liebig), **285**, 385; Ztschr. anal. Chem., **11**, 403.

[2] J. Am. Chem. Soc., **21**, 389.

and, after cooling, placed in securely sealed bottles. For use it should be damp but not so moist that the particles glisten in strong light. If too dry it is easily moistened by adding a few drops of water and rubbing up in a mortar. If too much water is accidentally added the mixture may be brought to the proper consistency by the addition of dry soda-lime. The finished product should be pulverized as finely as is consistent with the passage of the gas. For use in the carbon dioxide absorbers the pieces should not be larger than 2 mm. in diameter. As the soda-lime is damp there is no danger that particles will be carried along mechanically with the gas.

The second tube of the carbon dioxide absorbing system serves the dual purpose of retaining any moisture lost from the first soda-lime tube and any traces of carbon dioxide that might escape absorption in the first tube in case it became exhausted. With soda-lime the change in color is a very accurate indication of the absorption of carbon dioxide, and hence it is only necessary to replace the tube with a fresh one before it has been completely whitened.[1] The increase in weight of the second tube is ordinarily not more than 7 mgms. for each combustion, and, consequently, when the increase is greater it is an additional sign that the first tube is nearly exhausted.[2] It has been the custom in this laboratory to use the first tube until the increase in weight of the second tube is more than 10 mgms. One arm and the bend of the second tube of the carbon dioxide absorber is filled with dry lump pumice stone. Concentrated sulphuric acid is then allowed to trickle slowly down over the pumice until it becomes thoroughly saturated, but there must not be acid enough left in the bottom of the U-tube to seal the bend. A 10 mm. layer of glass-wool is then laid over the pumice-stone in the partially filled arm and the remaining space filled with soda-lime. The glass-wool must not come in contact with acid at any point.

In case sufficient carbon dioxide to exhaust the soda-lime does not enter the tube, it should last for 25 or more combustions, since the sulphuric acid would completely absorb at

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[1] J. Am. Chem. Soc., **21**, 394.

[2] A tube freshly filled with soda-lime will last for from 6 to 14 combustions, the number depending on the size of the lumps of soda-lime, the quantity in the tube, and the weight of carbon dioxide absorbed in each combustion.

least 0.5 gram of water; and if 10 mgms. were retained from each combustion the possible efficiency would be 50 combustions. The ease with which the last tube is prepared, however, renders it more satisfactory to change it after 25 or 30 combustions.

An absorbing system consisting of three separate pieces necessitates, it is true, an additional weighing with its delays and possible error. While the introduction of error in weighing the third tube cannot be avoided, this form of water absorber does away with the necessity of shaking the water out of the bulb after each weighing, and consequently a weighing with its possible source of error is avoided. The number of weighings required is the same in each case. Furthermore, in many forms the carbon dioxide absorber is in two pieces, and, in such cases, the advantage in accuracy and weighing lies with the system under consideration.

Aside from the great efficiency of the absorbing agents which have been discussed elsewhere[1] the greatest advantage to be derived from this form of absorber is the ability to make accurate analyses independent of the weather. The condensation of moisture, not to speak of gases on the surface of potash bulbs and other similar forms of absorbers, is a fluctuating factor dependent on atmospheric conditions, and it has been considered impossible by some[2] to make accurate determinations of carbon and hydrogen in damp or stormy weather. That the condensation of moisture on the surface of the absorbing system is not a negligible factor is seen from the precautions ordinarily given to wipe the absorber and allow it to stand in the balance room for at least half an hour. While doubtless this procedure gives a close approximation to correct results, the differences in the amount of condensation, on days in which the atmospheric conditions are not the same, are very considerable. When the conditions to which the glass is exposed in the course of a combustion are considered, *i. e.*, the wiping, the handling with moist fingers, the sojourn of at least an hour in close proximity to a combustion furnace, together with the considerable internal heat from the absorp-

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[1] *Loc. cit.*, p. 393.

[2] J. Am. Chem. Soc., **15**, 451; and **20**, 528.

tion of the carbon dioxide by the reagent, the assumption that the surface condition remains the same after as before, even with all precautions, is rather broad.

It is possible, however, to have constant surface conditions before and after analysis. By carefully wiping the absorber with clean, dry cheese-cloth it is possible to clean the apparatus till there is no longer any loss in weight. This point is taken as the standard condition, and the tubes are so wiped before and after each combustion. In an operation of this kind, the simpler the form of the absorber and the smaller the surface, the more readily can the apparatus be brought into condition for weighing. Such a method would be impossible when applied to a Liebig or Geissler potash bulb.

The operation as practiced in this laboratory with many hundred combustions, including those reported in the accompanying paper, is as follows: A piece of stout copper wire is so bent as to hang on the arm of the balance and act as a hook on which a U-tube can be readily supported. The rubber plugs are removed from the first U-tube, which is then wiped thoroughly with a piece of clean, dry cheese-cloth in each hand in such a way that the glass does not come in contact with the fingers. It should receive a very hard, thorough rubbing. The tube is then placed on the balance and brought to equilibrium and then removed, thoroughly wiped again, and weighed. It will probably lose somewhat in weight. The operation is continued until the weight remains constant. After a little experience it is seldom necessary to wipe the tube more than three times. No difficulty was experienced with the electric charges noted by Miller.[1] The tube is then plugged and the weight recorded. At the end of the combustion the operation is repeated and the condensation on the surface of the glass thereby eliminated. The importance of using clean, dry cheese-cloth cannot be too much emphasized. A tube so cleaned rapidly increases in weight owing to the condensation on its surface, but the increase is not too rapid to prevent making an accurate record of the weight.

To make an especially efficient purifier for the air or oxygen used in the combustion, the reagents may conveniently

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[1] J. Am. Chem. Soc., **20**, 428.

be placed in a calcium chloride jar. The gas is conducted through sulphuric acid placed in the lower compartment of the jar, through soda-lime filled in around a large glass tube thrust through the constriction, and after descending to the bottom of the jar, issues over a long column of pumice-stone drenched with concentrated sulphuric acid. The details of construction are shown in Fig. 2.

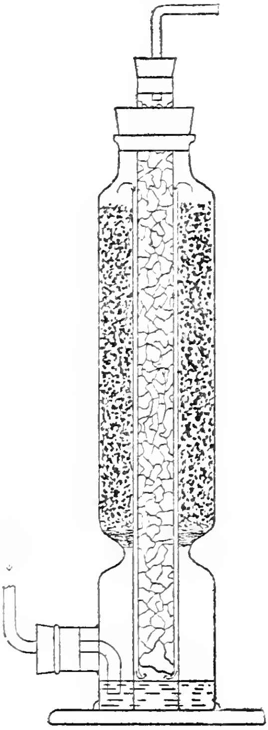
Fig. 2.

A "12-inch" calcium chloride jar, preferably with the tubulature as near the top of the lower compartment as possible, is selected, and a piece of glass tubing, of an external diameter a little less than the internal diameter of the constriction in the jar, is cut off long enough to rest on the bottom, and to reach to within 30 mm. of the top of the jar. A cork on the end of a glass rod is loosely inserted in the upper end of the tube and a layer of glass-wool or long-fiber asbestos is packed around the tube to a depth of 3 or 4 mm. Soda-lime prepared as described above and pulverized into pieces approximately 2 mm. in diameter is then introduced, and the jar filled to within 1 centimeter of the top of the inner tube. A "12-inch" jar will require about 175 grams of soda-lime. A long glass tube, approximately 10 mm. external diameter, is thrust through the one-holed rubber stopper inserted in the mouth of the jar. This tube is slightly tapered at the lower end and is filled with pumice-stone, which is subsequently drenched with concentrated sulphuric acid. The glass tube extends from about 10 mm. above the stopper to within 20 mm. of the bottom, and should be of a diameter small enough to slide easily through the upright tube passing through the constriction in the jar. The upper end of the tube is closed with a one-holed red rubber stopper carrying a glass elbow and a piece of rubber tubing with a screw pinch-cock. This stopper may be sealed with paraffin or wax if desired.

Concentrated sulphuric acid is poured down the central tube, thoroughly drenching the pumice-stone and collecting in the base. The first lot of acid should be poured out of the tubulature and finally sufficient acid poured through the tube to fill the lower compartment to within 5 mm. of the one-holed rubber stopper which has been inserted in the tubulature. The cork is then replaced in the upright tube and the screw pinch-cock closed. A glass tube bent downward is thrust through the hole in the rubber stopper in the tubulature in such a manner that a current of gas passing through it bubbles through the acid in the base of the jar. The gas then rises, passing through a long column of soda-lime at a very slow rate, turns and passes down through the annular space between the two glass tubes, and finally, entering the base of the tube filled with pumice-stone, issues at the top. The greater portion of the water is removed as the gas bubbles through the acid; the carbon dioxide is completely removed by the soda-lime and the unabsorbed moisture, including that lost from the slightly moist soda-lime, is removed as the gas passes over the pumice-stone and sulphuric acid. The gas issuing at the top is free from carbon dioxide and as free from moisture as is possible with sulphuric acid.

The ordinary form of "12-inch" calcium chloride jar has the tubulature in such a position that about 20 cc. of acid can be introduced without flowing out of the orifice or coming in contact with a rubber stopper inserted in the tubulature. A jar having the tubulature nearer the top is preferable and may be obtained at a slight increase in cost.[1] The chief advantage of the form of jar having the tubulature near the top of the base is that there is less liability of getting concentrated acid on the rubber stopper in the tubulature. The extra amount of acid that can be placed in the lower compartment increases the length of service of the purifier, but 20 cc. of acid will, it is calculated, remove 6 grams of water vapor from the air. If

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[1] Whitall, Tatum & Co., of Philadelphia, have furnished the writer with several 12-inch jars with the tubulature inserted at various specified points, with but slight addition to the price of stock jars.

the temperature of the gasometer is taken as 28° C., the gas leaving it would contain 27 mgms. of water vapor per liter. An average of 1.5 liters of oxygen are used for each combustion in the method as here conducted, hence the amount of acid conveniently placed in the base of a regular "12-inch" jar would suffice for 200 combustions.

In case the sulphuric acid should become exhausted, it is only necessary to drain the acid out of the lower compartment through the tubulature and pour fresh acid through the tube containing pumice-stone to regenerate the purifier. This is done in this laboratory after every 50 combustions. The soda-lime need not be renewed until it becomes three-fourths white.

MIDDLETOWN, CONN.

Contribution from the Chemical Laboratory of Wesleyan University.

THE ELEMENTARY ANALYSIS OF ORGANIC SUBSTANCES CONTAINING NITROGEN.

BY FRANCIS GANO BENEDICT.

The chemical processes involved in organic elementary analysis where the combustion of a substance is made with cupric oxide are, as a rule, extremely simple. When carbon and hydrogen, with or without oxygen, are the only elements in the substance, the carbon is burned to carbon dioxide and the hydrogen to water. When, however, the molecule contains nitrogen the reaction is not so regular, for while in many cases all of the nitrogen is liberated uncombined, in certain classes of compounds a portion, at times a no inconsiderable portion, is combined with the oxygen of the molecule, of the gaseous medium, or of the cupric oxide, in the form of nitric oxide, which in the presence of free oxygen forms nitrogen peroxide. This latter compound, whose presence is shown by the appearance of red fumes in the exit end of the combustion tube and by the acidity of the water condensed in the small bulb of the water-absorbing tube, introduces a serious error in the determination of carbon and hydrogen, owing to its solubility in most of the reagents ordinarily used for the absorption of water and carbon dioxide. While in many instances the influence of this abnormality is so slight as to be unimportant, its possibilities are great enough to necessitate special modifications of the methods of combustion to eliminate the errors caused by the formation and the subsequent absorption of the oxides of nitrogen. Especially is this true in determining the composition and the nature of organic substances of fundamental importance, compounds which serve as the basis of new theories in organic chemistry. It is in such instances that the vital importance of the greatest degree of accuracy in organic analytical operations is apparent.

Owing, perhaps, to its technical importance, the determination of carbon has been brought to a state of perfection rarely attained by the methods of analytical chemistry. The technical methods for the determination of carbon are, however, not readily applicable in the analysis of organic compounds and, furthermore, in most technical methods of analysis no provision is made for the determination of hydrogen ; but the determination of hydrogen is of almost as great, if not of equal, importance and the method most commonly used in the laboratory for the determination of carbon, *i. e.*, combustion with cupric oxide in a current of air or oxygen, permits of the determination of hydrogen.

The formation of oxides of nitrogen in the combustion of organic substances containing nitrogen by the cupric oxide method was first noted by Gay-Lussac.[1] Nitrogen, while ordinarily a most inert substance, unites at high temperatures with the oxygen of the air to form nitric oxide. This phenomenon is readily observed in all cases of combustion in air where a high temperature is attained.

In the method of combustion adopted in the work here reported the substance is first charred in the closed tube, *i. e.*, with no current of air or oxygen, and, after complete charring, oxygen is admitted to oxidize the non-volatile residue, and the copper that has been reduced by the volatile products of the dry distillation. As the oxygen is admitted the carbon ignites and glows, and here it is true there may be a temperature sufficiently high to cause a union of the nitrogen in the tube with the oxygen. That no appreciable quantities of

[1] Ann. Chim., **95**, 184 ; **96**, 53.

oxides of nitrogen[1] are formed in this way, is seen by the fact that they cannot be detected when non-nitrogenous organic substances yielding carbonaceous residues are burned in a current of air or oxygen.

In considering the formation of the oxides of nitrogen in the combustion tube it is necessary to subdivide all organic nitrogenous substances into two classes: one in which the nitrogen is attached to an oxygen atom, and the other in which no oxygen is connected with the nitrogen. To the first class belong nitro, nitroso, isonitroso, and azoxy bodies, oximes, etc., while the second class includes practically all other nitrogenous organic compounds: amines, amides, nitriles, etc.

The bodies belonging to the first class would be expected to yield oxides of nitrogen all the more readily as the nitrogen is to a certain extent partially oxidized, and nitro compounds, according to this assumption, owing to the high state of oxidation of the nitrogen atom, would serve as types of the substances which would most readily liberate their nitrogen in the oxidized form.

In the amido and other unoxidized nitrogen compounds on the other hand, it would be necessary to have an actual oxidation of the nitrogen atom to obtain oxides of nitrogen. In an examination of the influence of the method of combustion on the formation of the oxides of nitrogen it was found that in burning urea, for example, in a current of oxygen, *i. e.*, without previous charring in the closed tube, the oxides of nitrogen were formed to such an extent as to cause the presence of red fumes in the absorbing system. Obviously in this case there was a direct oxidation of the nitrogen and at a comparatively low temperature. Other amidic compounds gave similar results.

In the absolute determination of nitrogen by mixing the substance with finely pulverized cupric oxide and burning in a vacuum, Klingemann[2] found in the case of certain oxygen-free azines and glyoxalines that very considerable quantities of the oxides of nitrogen were formed. In this case the

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[1] The general term 'oxides of nitrogen' is applied to all products formed by the reaction between nitric oxide, oxygen, and water.

[2] Ber. d. chem. Ges., **22**, 3066.

nitrogen must have come from the compound and the oxygen from the copper. Klingemann explains the formation of the oxides of nitrogen as the action of the nascent nitrogen on the copper oxide. It is interesting to note the evidence presented by Klingemann to support the theory that the use of a copper spiral in the regular carbon and hydrogen determination of substances containing nitrogen is unnecessary.

O. F. Tower[1] has shown in an admirable treatment of the subject that amidic nitrogen bodies, of which urea, hippuric acid, and *p*-toluidine are taken as types, when burned in the manner described on p. 335, yield no appreciable quantities of oxides of nitrogen. Nitro bodies, such as dinitrobenzene and nitraniline, also yield, according to his results, no oxides of nitrogen. Trinitrophenol, on the other hand, liberates sufficient quantities to affect materially the percentage of both carbon and hydrogen.

In burning the amidic and "unoxidized nitrogen" compounds in a closed tube, the combustion apparently proceeds as follows: The substance, if not volatilized unchanged, undergoes dry distillation, and the gases given off reduce the first portions of the cupric oxide in the combustion tube. If any oxides of nitrogen are formed, they are decomposed in the presence of the reducing gases, the carbonaceous residue, and the reduced copper. After dry distillation is complete, the greater portion of the nitrogen is probably in the gaseous form, though the charred residue may, according to some writers, contain considerable quantities of nitrogen.

In volatile substances the combustion is practically all accomplished by the oxygen of the cupric oxide, though it is possible that portions of the volatilized material, when passing through the hot reduced copper, may be decomposed by the heat with a deposition of carbon.

Nitro and allied bodies, on the other hand, yield, when burned as above, nitric oxide in appreciable quantities. According to the investigations of Liebig,[2] Klingemann,[3] and Tower,[4] nitric oxide is probably the only oxide of nitrogen

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[1] J. Am. Chem. Soc., **21**, 596.

[2] Pogg. Ann., **18**, 357.

[3] Ber. d. chem. Ges., **22**, 3066.

[4] J. Am. Chem. Soc., **21**, 596.

formed directly in the combustion of nitrogenous substances. By means of secondary reactions with oxygen and water, there may be formed almost any or all of the oxides of nitrogen, the chief of which is, however, nitrogen peroxide.

Nitric oxide itself would have no material influence on the operation, for it is not absorbed by any of the reagents commonly used in this analytical process; *i. e.*, concentrated sulphuric acid or fused calcium chloride for the absorption of water vapor, or concentrated potassium hydroxide solution or soda-lime for the absorption of carbon dioxide.

Nitrogen peroxide, however, is always formed by the union of nitric oxide with the oxygen in the tube or in the absorbing system, and is absorbed by all the above reagents except calcium chloride, thereby introducing the error.

In many cases the amount of oxides of nitrogen is not large, and consequently is all retained by the sulphuric acid when this reagent is used to absorb water, though in highly nitrated bodies, especially those burning with explosive violence, the percentage of carbon is often increased by the absorption of the oxides of nitrogen in the carbon dioxide absorber.

A large number of combustions of oxidized and unoxidized nitrogenous bodies were made to determine, if possible, the cause of the variations in the amounts of the oxides of nitrogen. The analyses were made by first charring the material in the closed tube; *i. e.*, without the current of oxygen which was finally admitted at the end of the combustion, each combustion requiring about one hour for completion. The modified form of purifying apparatus and absorbing system described in the preceding paper were used in all analyses.

Jena glass combustion tubes have given excellent satisfaction, four tubes having withstood the heating in 97, 99, 104, and 116 combustions, respectively.

Table I gives a series of analyses of a number of pure substances burned with this method without the use of the copper spiral, those of non-nitrogenous substances being added for a dual purpose; *i. e.*, first to show the accuracy of the method of analysis and second to show the purity of the products used in some subsequent operations.

Table I.

Substance.	Weight taken.	Weight water found.	Weight carbon dioxide found.	Hydrogen.		Carbon.	
	Gram.	Gram.	Gram.	Found. Per cent.	Theory. Per cent.	Found. Per cent.	Theory. Per cent.
Sucrose	0.2028	0.1175	0.3129	6.48	6.48	42.08	42.08
$C_{12}H_{22}O_{11}$.	0.2011	0.1161	0.3103	6.46	....	42.08	....
	0.2262	0.1317	0.3488	6.51	....	42.06	....
Benzoic acid,	0.1414	0.0629	0.3566	4.98	4.95	68.78	68.88
C_6H_5COOH.	0.1419	0.0638	0.3581	5.03	....	68.83	....
	0.1443	0.0646	0.3639	5.01	....	68.78	....
Naphthalene,	0.1049	0.0612	0.3598	6.53	6.30	93.54	93.70
$C_{10}H_8$.	0.1031	0.0601	0.3542	6.52	....	93.70	....
	0.1024	0.0592	0.3511	6.47	....	93.51	....
Urea,	0.4022	0.2399	0.2960	6.67	6.70	20.07	19.96
$CO(NH_2)_2$.	0.4014	0.2454	0.2941	6.84	....	19.98	....
Glycocoll,	0.2528	0.1555	0.2972	6.88	6.71	32.06	31.96
$CH_2.NH_2.COOH$.	0.2053	0.1242	0.2412	6.77	....	32.04	....
Hippuric acid,	0.1733	0.0773	0.3829	4.99	5.06	60.26	60.30
$C_9H_9NO_3$.	0.1714	0.0767	0.3791	5.01	....	60.32	....
	0.1716	0.0782	0.3790	5.09	....	60.24	....
	0.1722	0.0794	0.3806	5.15	....	60.28	....
	0.1544	0.0691	0.3412	5.01	....	60.27	....
Uric acid,	0.2214	0.0485	0.2887	2.45	2.40	35.56	35.67
$C_5H_4N_4O_3$.	0.2506	0.0560	0.3266	2.50	....	35.54	....
Caffein, $C_8H_{10}N_4O_2$.	0.2026	0.0937	0.3668	5.18	5.19	49.38	49.42
Azobenzene,	0.1207	0.0609	0.3506	5.65	5.53	79.22	79.05
$(C_6H_5N)_2$.	0.1259	0.0622	0.3646	5.53	....	78.98	....

Table I (Continued).

Substance.	Weight taken.	Weight water found.	Weight carbon dioxide found.	Hydrogen		Carbon.	
				Found.	Theory.	Found.	Theory.
	Gram.	Gram.	Gram.	Per cent.	Per cent.	Per cent.	Per cent.
Nitroguanidine,							
$NH_2.C : NH.NH.NO_2$.	0.2545	0.0898	0.1075	3.95	3.87	11.52	11.52
Dinitrobenzene,	0.1555	0.0367	0.2445	2.64	2.40	42.88	42.83
$C_6H_4(NO_2)_2$.	0.1563	0.0352	0.2456	2.52	....	42.86	....
	0.1564	0.0349	0.2457	2.50	....	42.85	....
	0.1521	0.0366	0.2390	2.68	....	42.85	....
Nitraniline,	0.2055	0.0823	0.3935	4.48	4.38	52.22	52.13
$C_6H_4.NO_2.NH_2$.	0.2023	0.0809	0.3876	4.47	....	52.25	....
Dinitraniline,	0.2277	0.0595	0.3295	2.92	2.75	39.46	39.32
$C_6H_3(NO_2)_2.NH_2$.	0.2046	0.0551	0.2936	3.01	....	39.14	....
Trinitrobenzene,	0.2005	0.0361	0.2528	2.02	1.38	34.39	33.78
$C_6H_3(NO_2)_3$.	0.2012	0.0318	0.2539	1.77	....	34.41	....
	0.2008	0.0315	0.2501	1.76	....	33.97	....
Trinitrophenol,							
$C_6H_2(NO_2)_3.OH$.	0.2903	0.0454	0.3346	1.75	1.32	31.44	31.42
Dinitronaphthol,	0.1957	0.0611	0.3708	3.49	2.58	51.67	51.25
$C_{10}H_5(NO_2)_2.OH$.	0.1500	0.0464	0.2827	3.46	....	51.40	....
Guanidine nitrate,							
$NH_2C:NH.NH_2,HNO_3$.	0.2150	0.1001	0.0845	5.21	4.95	10.72	9.82
Urea nitrate,							
$CO(NH_2)_2,HNO_3$.	0.2537	0.0985	0.0943	4.34	4.09	10.14	9.74

Atomic weights used: C = 12.001; H = 1.0075; N = 14.045; O = 16.00.

An examination of the results of the table shows that with the exception of the nitro bodies the percentages of hydrogen and carbon, as a rule, are near the theory. The inability to get perfectly pure oximes, azines, and glyoxyalines precluded experimenting with those compounds. The specimen of uric acid was found to contain 0.2 per cent of moisture and, if allowance be made for this, the percentages of hydrogen and carbon still more closely approach the theoretical.

In the case of dinitrobenzene the first discrepancy of any magnitude is observed. Here the percentage of hydrogen is invariably somewhat high, though the substance was found to be perfectly anhydrous.

Great difficulty was experienced in burning many of these compounds, as on heating they decomposed readily, and at times with explosive violence. It was found nearly impossible to obtain a regular combustion of picramide, picric acid, or dinitronaphthol. This latter compound, while relatively much less nitrated than either of the other two, gave off dense red fumes, completely filling the combustion tube. Guanidine and urea nitrates, though yielding large quantities of oxides of nitrogen, burned with great regularity.

While the oxides of nitrogen were, as a rule, wholly retained by the sulphuric acid in the water-absorbing tube a portion escaped into the carbon dioxide absorbers when trinitrobenzene, dinitronaphthol, guanidine nitrate, and urea nitrate were burned.

It thus appears that when burned as above described, compounds containing "unoxidized nitrogen" yield no oxides of nitrogen, at least none that is absorbed by sulphuric acid or soda-lime. Compounds containing the nitro group, on the other hand, do yield appreciable quantities of the oxides of nitrogen, which are absorbed in sulphuric acid and soda-lime. Nitraniline, though containing the nitro group, gave results differing but little from theory, and it is this fact that led to the method here described. Dinitrobenzene, when burned, yielded nitric oxide, while when one nitro group is reduced the resulting product, nitraniline, gave none. It appears, therefore, that when there is sufficient reducing material, such as carbon and hydrogen, in the molecule, and not too great a proportion of nitro groups, the reducing material effects a reduction of the nitro group, and the nitrogen is then not reoxidized under the conditions of the combustion. Were a large number of combustions of nitrated bodies made, it would doubtless not be difficult to establish a relative proportion between the number of nitro groups and the carbon and hydrogen in the molecule necessary to effect the reduction of the oxides of nitrogen.

It is evident, however, that the nitric acid molecule existing in the two nitrates burned is not as readily reduced, for, while nitroguanidine gave theoretical results, the nitrate containing one more molecule of water yields large quantities of the oxides of nitrogen. Nitroguanidine therefore contains enough reducing material in its molecule to reduce completely the nitro group. The nitric acid molecule of the two nitrates is probably much more loosely combined and hence escapes reduction.

In the ordinary methods of combustion, it is customary to take some special precaution to eliminate any possible effect of the oxides of nitrogen on the final results. These precautions consist of one of two essentially different operations. In one case the oxides formed are absorbed by lead peroxide, manganese dioxide, potassium chromate, etc., or, more commonly, they are reduced by metallic copper and, in certain special methods, by metallic silver.

The absorption of the oxides is almost always adapted to special methods and is open to grave objections.

Gay-Lussac,[1] in 1815, used hot metallic copper turnings to reduce the oxides of nitrogen formed in the combustion of organic substances with cupric oxide, and this method is to-day almost universally used. As ordinarily described, a 10 centimeter length of cupric oxide is removed from the combustion tube and a reduced spiral of copper wire or a roll of copper gauze of the same length is inserted in the end of the combustion tube to which the absorbing train is connected. This operation is of itself time-consuming, but can be avoided if two combustion tubes are held prepared, one with the copper spiral and the other without it. Considerable difficulty

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[1] Ann. d. chim., **95**, 184; **96**, 53.

has been experienced in satisfactorily reducing the copper spiral. If hydrogen is used, the gas must be specially purified and, as Neumann[1] has shown, copper obstinately retains material quantities of hydrogen which are later oxidized and weighed as water. Reduction by means of methyl or ethyl alcohol or formic acid has the advantage of being much quicker and less laborious than that in which hydrogen is used, but the copper retains the vapors of these bodies which are later oxidized, and materially increase the percentage of both hydrogen and carbon. It is often recommended to dry out the spiral in a current of hydrogen at a sufficiently high temperature to drive off the alcohol vapors, but in this operation considerable hydrogen is occluded. In drying out the spiral reduced by alcohol in a current of carbon dioxide, it has been found that enough carbon dioxide may be retained to vitiate the results. The reduced spirals are often dried in air though they are then rapidly coated with a superficial layer of copper oxide, and their efficiency thereby much impaired. The most satisfactory way is to allow the reduced spirals to remain a number of hours in a vacuum desiccator though, as is readily seen, this takes time, and a good vacuum desiccator is not always at hand.

A further objection to the use of copper spirals is the fact that, unless the air or oxygen is swept out of the combustion tube, the spiral becomes somewhat oxidized on heating. It is essential to replace the oxygen in the combustion tube with air, an operation requiring a gasometer or other supply of air.

The method here reported is the outcome of an attempt to secure a reduction of the copper with no danger of adding unknown amounts of carbon dioxide and water to the materials to be weighed. Those nitro compounds in whose molecule there is a deficiency of carbon and hydrogen are burned with an admixture of a known amount of a carbonaceous material of known composition. In this way the carbonaceous material including volatile gaseous products, and reduced copper, are all in the position to react with any oxides of nitrogen formed and effect their reduction.

The importance of pure materials cannot be overstated and

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[1] Monatshefte, **13**, 40.

for the purposes of this research, sucrose in the form of well-powdered rock-candy and Kahlbaum's pure benzoic acid, were found to be very satisfactory.

In many of the analyses sucrose was used, though the reducing material, the carbon (the hydrogen being theoretically at least all oxidized) is but 42 per cent of the weight of the substance. Benzoic acid and naphthalene are, weight for weight, much more active as reducing agents than sucrose. Nevertheless, in a large number of cases, the latter was used with excellent results.

Sucrose of a remarkable degree of purity and dryness may be obtained by pulverizing good crystals of rock candy after carefully removing the strings. This material is not very hygroscopic, and, unless the air is very moist, requires no further precaution for its preservation than to be placed in a well-stoppered bottle. In very damp weather, however, two hours' drying, after pulverization, in the water- or air-bath at not over 95°, will insure thorough dryness. All of the material used in connection with the analyses here given was not previously dried. As it was used in the analyses of sucrose given in Table I, it is seen to be chemically pure. The sucrose, owing to its purity, is always useful for check combustions to test the accuracy of the method of combustion.

In general, it has been found desirable to place the substance in the boat in such a manner as to leave a free space about a centimeter in length in the forward end. The greater portion of the sucrose, benzoic acid, or naphthalene is placed in this space and the remainder sprinkled over the top of the layer of substance. The end of the boat containing the sucrose is first inserted in the combustion tube, and the boat pushed in till it nearly touches the asbestos plug holding the layer of cupric oxide. The boat should not directly touch the cupric oxide but be separated by a centimeter layer of air. After heating the spiral in the anterior end of the tube, the heat is brought toward the boat from the middle of the combustion furnace; hence the cupric oxide becomes thoroughly heated before the end of the boat containing the reducing material is heated. The sucrose melts at 143° and distils towards 200°, giving off empyreumatic vapors which reduce a portion of the contiguous cupric oxide, which becomes still more heated as the flames are turned on. The melted sucrose often mixes with or possibly partially dissolves the substance to be burned, and when the sucrose finally chars there is a large excess of carbon to aid in reducing the nitro group. Furthermore, the hot reduced copper may produce a decomposition of the gases with a deposition of finely divided carbon.

When benzoic acid is used, the greater portion of the acid is vaporized at a moderately low temperature, and no appreciable quantity of carbonaceous residue is left. In this case, therefore, the cupric oxide is reduced for a distance of several centimeters, but no carbon is left to aid in reducing oxides of nitrogen, save what may be formed on the hot reduced copper by the decomposition of the benzoic acid vapor, which passes over it. Hence it would appear that a carbonaceous residue in the boat is not essential to the reduction of the oxides of nitrogen.

When a new combustion tube is used, the presence of reduced copper is readily seen as a layer some 2 or 3 centimeters long in front of the boat, while the end of the rear cupric oxide spiral inserted after the boat is always seen to be partially reduced. Consequently there is a sufficient quantity of metallic copper to reduce thoroughly the maximum amount of oxides of nitrogen that can be formed.

Few nitro bodies are decomposed with an evolution of oxides of nitrogen below the temperatures necessary to secure the vaporization of benzoic acid or naphthalene or the dry distillation of sucrose. It may be necessary, however, in some cases to place the reducing material in a small copper boat a little ahead of the porcelain boat containing the material to be analyzed. In this case the copper could be reduced before the material was heated.

One gram of pure sucrose, when completely oxidized, yields 1.5430 grams of carbon dioxide and 0.5791 gram of water.

One gram of pure benzoic acid, when completely oxidized, yields 2.5235 grams of carbon dioxide and 0.4428 gram of water.

One gram of pure naphthalene, when completely oxidized, yields 3.4357 grams of carbon dioxide and 0.5627 gram of water.

To determine the amount of carbon dioxide and water added by reason of the combustion of the sugar or benzoic acid or naphthalene, it is only necessary to multiply the weight of the material used in grams by the factors for carbon dioxide and water. The quantities of water and carbon dioxide calculated as being derived from the sucrose or benzoic acid used are then subtracted from the actual weights found and the resulting weights used as in the regular method of calculation.

Table II shows the results of analyses of various nitro bodies, using sucrose or benzoic acid to reduce the oxides of nitrogen formed :

The results given therein indicate what may be expected of the method, and it will be noticed that in all cases where discrepancies appear the quantity of water actually weighed is very small, and hence the error of weighing might, in many cases, cause a discrepancy no smaller than those obtained. The evidence, however, seems to indicate that no material, absorbed by the sulphuric acid or soda-lime, other than water and carbon dioxide, leaves the combustion tube.

Furthermore, as it is unnecessary to replace the oxygen left in the tube by air, the necessity of a second gasometer is obviated. Indeed, by this method one can make combustions of nitrogenous or non-nitrogenous bodies with no change in the manipulation other than the addition to the boat of a known weight of pure sucrose or benzoic acid.

While sucrose and benzoic acid are here recommended as reducing agents, many others may, of course, be used. Naphthalene suggests itself as the ideal substance, but it has been a matter of considerable difficulty to obtain perfectly pure naphthalene.

The explosive character of several of these compounds rendered combustion very difficult. It was found, however, that by mixing the finely powdered material with three or four volumes of pure, ground quartz the combustions proceeded with much greater regularity. Accordingly, many of the combustions above tabulated were made with an admixture of finely powdered silica. The silica contained no moisture and

Table II.

Material.	Weight taken. Gram.	Weight water found. Gram.	Weight carbon dioxide found. Gram.	Hydrogen.		Carbon.	
				Found. Per cent.	Theory. Per cent.	Found. Per cent.	Theory. Per cent.
Dinitrobenzene.							
Substance + sucrose	0.1959	0.0882	0.3049	....	....	....	....
Sucrose	0.1149	0.0665	0.1774	....	....	....	....
Substance	0.0810	0.0217	0.1275	2.38	2.40	42.93	42.83
Substance + sucrose	0.2057	0.0849	0.3200	....	....	....	....
Sucrose	0.1110	0.0643	0.1713	....	....	....	....
Substance	0.0947	0.0206	0.1487	2.43	2.40	42.82	42.83
Dinitrophenol.							
Substance + benzoic acid	0.2139	0.0566	0.3707	....	....	....	....
Benzoic acid	0.0595	0.0263	0.1502	....	....	....	....
Substance	0.1544	0.0303	0.2205	2.20	2.19	38.95	39.11
Substance + sucrose	0.2613	0.0963	0.3863	....	....	....	....
Sucrose	0.1137	0.0658	0.1754	....	....	....	....
Substance	0.1476	0.0305	0.2109	2.31	2.19	38.97	39.11
Trinitrobenzene.							
Substance + sucrose	0.2574	0.0813	0.3515	....	....	....	....
Sucrose	0.1069	0.0618	0.1650	....	....	....	....
Substance	0.1505	0.0195	0.1865	1.45	1.38	33.80	33.78

Table II (Continued).

Material.	Weight taken. Gram.	Weight water found. Gram.	Weight carbon dioxide found. Gram.	Hydrogen. Found. Per cent.	Hydrogen. Theory. Per cent.	Carbon. Found. Per cent.	Carbon. Theory. Per cent.
Substance + sucrose	0.2583	0.0809	0.3543	....	....	....	....
Sucrose	0.1053	0.0610	0.1625	....	....	....	....
Substance	0.1530	0.0199	0.1918	1.45	1.38	34.09	33.78
Substance + sucrose	0.2605	0.0832	0.3559	....	....	....	....
Sucrose	0.1084	0.0628	0.1673	....	....	....	....
Substance	0.1521	0.0204	0.1886	1.50	1.38	33.80	33.78
Substance + sucrose	0.2862	0.0931	0.3935	....	....	....	....
Sucrose	0.1295	0.0750	0.1998	....	....	....	....
Substance	0.1567	0.0181	0.1937	1.29	1.38	33.71	33.78
Substance + sucrose	0.2523	0.0789	0.3432	....	....	....	....
Sucrose	0.1017	0.0589	0.1570	....	....	....	....
Substance	0.1506	0.0200	0.1862	1.49	1.38	33.72	33.78
Trinitrophenol.							
Substance + benzoic acid	0.2130	0.0473	0.3306	....	....	....	....
Benzoic acid	0.0629	0.0279	0.1587	....	....	....	....
Substance	0.1501	0.0194	0.1719	1.45	1.32	31.24	31.42

Table II (Continued).

Material.	Weight taken. Gram.	Weight water found. Gram.	Weight carbon dioxide found. Gram.	Hydrogen. Found. Per cent.	Hydrogen. Theory. Per cent.	Carbon. Found. Per cent.	Carbon. Theory. Per cent.
Substance + benzoic acid	0.2297	0.0562	0.3833	....	....	....	....
Benzoic acid	0.0870	0.0385	0.2195	....	....	....	....
Substance	0.1427	0.0177	0.1638	1.39	1.32	31.31	31.42
Substance + benzoic acid	0.2207	0.0466	0.3373	....	....	....	....
Benzoic acid	0.0610	0.0270	0.1539	....	....	....	....
Substance	0.1597	0.0196	0.1834	1.37	1.32	31.32	31.42
Substance + benzoic acid	0.2151	0.0493	0.3454	....	....	....	....
Benzoic acid	0.0717	0.0317	0.1809	....	....	....	....
Substance	0.1434	0.0176	0.1645	1.38	1.32	31.29	31.42
Trinitraniline.							
Substance + benzoic acid	0.2498	0.0832	0.3269	....	....	....	....
Benzoic acid	0.0992	0.0574	0.1531	....	....	....	....
Substance	0.1506	0.0258	0.1738	1.92	1.77	31.48	31.55
Substance + benzoic acid	0.2256	0.0581	0.3652	....	....	....	....
Benzoic acid	0.0758	0.0336	0.1913	....	....	....	....
Substance	0.1498	0.0245	0.1739	1.79	1.77	31.66	31.55

Table II (Continued).

Material.	Weight taken. Gram.	Weight water found. Gram.	Weight carbon dioxide found. Gram.	Hydrogen. Found. Per cent.	Hydrogen. Theory. Per cent.	Carbon. Found. Per cent.	Carbon. Theory. Per cent.
Substance + benzoic acid	0.2125	0.0525	0.3314	....	....	....	....
Benzoic acid	0.0625	0.0277	0.1577	....	....	....	....
Substance	0.1500	0.0248	0.1737	1.85	1.77	31.58	31.55
Substance + benzoic acid	0.2042	0.0479	0.3125	....	....	....	....
Benzoic acid	0.0556	0.0246	0.1403	....	....	....	....
Substance	0.1486	0.0233	0.1722	1.75	1.77	31.60	31.55
Dinitronaphthol.							
Substance + benzoic acid	0.2109	0.0609	0.4321	....	....	....	....
Benzoic acid	0.0577	0.0255	0.1456	....	....	....	....
Substance	0.1532	0.0354	0.2865	2.55	2.58	51.00	51.25
Substance + benzoic acid	0.1750	0.0527	0.3611	....	....	....	....
Benzoic acid	0.0514	0.0228	0.1297	....	....	....	....
Substance	0.1236	0.0299	0.2314	2.71	2.58	51.06	51.25
Dinitraniline.							
Substance + benzoic acid	0.2094	0.0636	0.3659	....	....	....	....
Benzoic acid	0.0587	0.0260	0.1481	....	....	....	....
Substance	0.1507	0.0376	0.2178	2.79	2.75	39.41	39.32
Trinitrotoluol.							
Substance + benzoic acid	0.2197	0.0603	0.3733	....	....	....	....
Benzoic acid	0.0651	0.0288	0.1640	....	....	....	....
Substance	0.1546	0.0315	0.2093	2.28	2.22	36.92	36.98

Table II (Continued).

Material.	Weight taken. Gram.	Weight water found. Gram.	Weight carbon dioxide found. Gram.	Hydrogen. Found. Per cent.	Hydrogen. Theory. Per cent.	Carbon. Found. Per cent.	Carbon. Theory. Per cent.
Trinitroxylol.							
Substance + benzoic acid	0.1789	0.0572	0.3169	....	....	....	....
Benzoic acid	0.0530	0.0235	0.1337	....	....	....	....
Substance	0.1259	0.0337	0.1832	2.99	2.92	39.69	39.81
Substance + benzoic acid	0.1733	0.0544	0.3084	....	....	....	....
Benzoic acid	0.0528	0.0234	0.1332	....	....	....	....
Substance	0.1205	0.0310	0.1752	2.88	2.92	39.65	39.81
Urea nitrate.							
Substance + benzoic acid	0.3235	0.1236	0.2531	....	....	....	....
Benzoic acid	0.0640	0.0283	0.1615	....	....	....	....
Substance	0.2595	0.0953	0.0916	4.11	4.09	9.63	9.74
Substance + benzoic acid	0.3359	0.1290	0.2754	....	....	....	....
Benzoic acid	0.0720	0.0319	0.1817	....	....	....	....
Substance	0.2639	0.0971	0.0937	4.12	4.09	9.68	9.74
Guanidine nitrate.							
Substance + benzoic acid	0.3165	0.1408	0.2512	....	....	....	....
Benzoic acid	0.0627	0.0278	0.1582	....	....	....	....
Substance	0.2538	0.1130	0.0930	4.98	4.95	9.99	9.82
Substance + benzoic acid	0.3309	0.1455	0.2792	....	....	....	....
Benzoic acid	0.0741	0.0328	0.1870	....	....	....	....
Substance	0.2568	0.1127	0.0922	4.91	4.95	9.79	9.82

apparently exercised no injurious effect on the combustion of the material, for the percentages of carbon and hydrogen are in almost every case well within the limits of error when the quantity of material taken as well as its purity are considered. Furthermore, numerous combustions of sucrose and benzoic acid were made with a similar admixture of silica. In no case was any discrepancy in the analyses obtained. The residue remaining in the boat after the combustions was always perfectly white, indicating the absence of unoxidized material.

Singularly enough the admixture with silica has a direct influence on the reduction of the oxides of nitrogen and, though they are by no means completely reduced, they are present in the products of combustion in much smaller quantities.

Table III.

Substance.	Weight taken.	Weight water found.	Weight carbon dioxide found.	Hydrogen.		Carbon.	
				Found.	Theory.	Found.	Theory.
	Gram.	Gram.	Gram.	Per ct.	Per ct.	Per ct.	Per ct.
Trinitrobenzene	0.2069	0.0293	0.2580	1.58	1.38	34.01	33.78
Trinitrophenol	0.2893	0.0409	0.3340	1.58	1.32	31.49	31.42
	0.2791	0.0389	0.3228	1.56	...	31.54	....
	0.2838	0.0373	0.3277	1.47	...	31.49	....
Trinitraniline	0.2877	0.0469	0.3316	1.87	1.77	31.46	31.55
	0.2996	0.0502	0.3468	1.87	...	31.57	....

In Table III several combustions of highly nitrated bodies mixed with silica are given. It is seen that, while the percentages of hydrogen are still somewhat too high, the discrepancies are not as great as when the combustion is made of the material by itself, while the percentages of carbon are sufficiently accurate for most purposes.

The materials used in this investigation were for the most part of Kahlbaum's make, only those specimens showing widest variation from the theoretical being obtained elsewhere.

My thanks are due to Mr. Emil Osterberg, assistant in this laboratory, whose experimental skill has made the prosecution of this research possible.

The application of this method of reducing the oxides of nitrogen to the absolute determination of nitrogen, by the Dumas method, is to be investigated at an early date.

MIDDLETOWN, CONN.

Contribution from the Chemical Laboratory of the University of Utah.

AN APPARATUS FOR DETERMINING MOLECULAR WEIGHTS BY THE BOILING-POINT METHOD.

BY HERBERT N. MCCOY.

The boiling-point method possesses two obvious natural advantages over the freezing-point method. In the former any solvent may be used, while the latter is restricted to a comparatively small number of solvents. At the boiling-point substances are, as a rule, much more soluble than at the freezing-point. Nevertheless, as a means of determining molecular weights, the freezing-point method has been very largely used in preference to the boiling-point method. This has been chiefly due to certain disadvantages attending the use of most forms of apparatus designed for boiling-point determinations.

The rather long time required to attain a constant boiling-point may lead to appreciable errors on account of intervening barometric changes. Further, the weight of the solvent placed in the boiling vessel does not represent the true weight that is effective in forming the solution, as a fraction, indefinite in amount, always exists in the state of vapor. In most forms of apparatus the cold liquid, formed by the condensation of this vapor, constantly drops back into the boiling liquid, hindering greatly the establishment of equilibrium. However, this latter disturbing influence is largely eliminated in the forms of apparatus devised by Hite[1] and Jones.[2]

The main difficulty has lain in obtaining regular boiling without superheating. Numerous devices, such as glass beads, garnets, balls of platinum gauze, and a platinum wire, sealed into the glass, have been used, as is well known, to avoid this difficulty. While it is true that these have been more or less successful in accomplishing the desired end, at the same time they have complicated the apparatus and made the working of the methods more troublesome.

A distinct innovation was introduced by Sakurai,[3] who

[1] This JOURNAL, **17**, 514.

[2] *Ibid.*, **19**, 58.

[3] J. Chem. Soc., **61**, 993.

prevented superheating and produced regular boiling by passing the vapor of the pure solvent into the liquid whose boiling-point was to be measured, external heat being also applied.

Following up this advance, Landsberger has described a method[1] by which many of the difficulties of the older boiling-point methods have been overcome. The apparatus is simple. The process is very rapid, and the results are fully as good as those obtained by means of the elaborate apparatus of Beckmann.[2]

According to Landsberger's method a state of equilibrium between the liquid and vapor phases is quickly attained by substituting for the direct source of heat usually employed to raise the liquid to its boiling-point, the latent heat of the vapor of the pure solvent. The liquid whose boiling-point is to be determined according to Landsberger's method is contained in a large test-tube, holding also the thermometer, and surrounded also by a larger tube which serves as a jacket. The vapor is generated in a flask by direct heat and is conducted into the liquid in the inner tube, rapidly bringing it to its boiling-point. A hole in the side of the inner test-tube near the cork allows the excess of vapor to pass into the jacket and a side neck of the latter leads the uncondensed portion of the vapor from the jacket to an ordinary condenser.

That a solution, even a saturated one, may be heated to its boiling-point by the vapor of the pure solvent, has long been known. It is obvious, however, that no superheating can occur as the liquid and vapor can exist in contact at but one definite temperature. No beads or garnets, etc., are required. Thorough mixing of the liquid and vapor is insured. No cold liquid runs back into the boiling vessel and radiation is largely prevented by the jacket which is filled with hot vapor. Since a determination can be made in half an hour, barometric changes have little effect on the results.

Walker and Lumsden[3] have improved Landsberger's apparatus by using a graduated inner tube and measuring the volume of the solution instead of weighing it; a procedure

[1] Ber. d. chem. Ges., **31**, 458.

[2] Ztschr. phys. Chem., **8**, 226.

[3] J. Chem. Soc., **73**, 502.

which Beckmann[1] has shown to be equally applicable. The graduated tube allows a determination of the real volume of the solution. This is preferable to a knowledge of the whole amount of solvent present, part of which necessarily exists as vapor at the time the boiling-point is measured, thus rendering the solution more concentrated than the amount of solvent weighed out would indicate. Of greater importance is the fact that several determinations of the molecular weight may be made with the same quantity of substance, by observing the boiling-point at different dilutions, the corresponding volumes being read off on the graduated tube.

In the method just described the jacket must be kept filled with vapor at the temperature of the boiling-point of the solvent. To do this requires a more rapid current of vapor passing through the solution than would otherwise be necessary to establish equilibrium between vapor and the solution. Now, as the solution is heated solely by the latent heat of this vapor, there is with some solvents, notably benzene, a rapid condensation of the vapor in the inner tube. The condensation is greater the smaller the ratio of the latent heat to the specific heat of the solvent employed. The dilution thus caused soon increases the volume of the solution beyond the capacity of the apparatus and so limits the number of duplicate determinations to one or two.

In applying Walker and Lumsden's modification of Landsberger's method, it occurred to me that the difficulty just mentioned would be remedied and other advantages would be gained by combining the functions of the boiling-flask and the jacket. As a result the apparatus shown in the figure has been devised.[2]

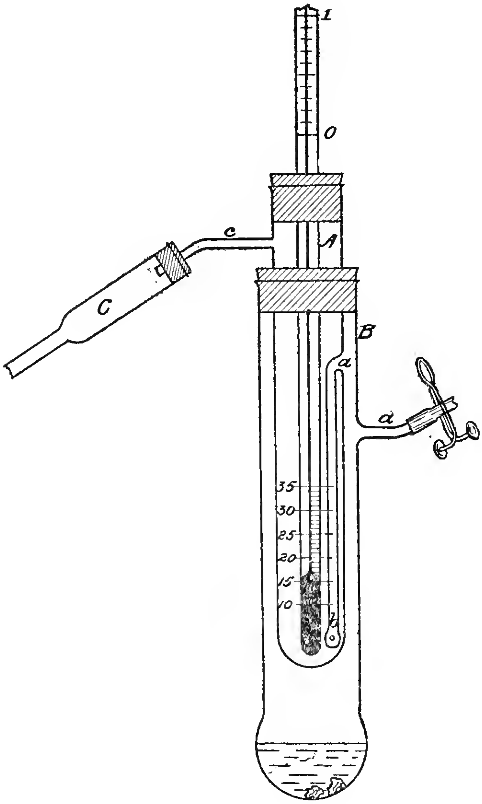
The vessels *A* and *B* are of glass. The smaller one, *A*, in which the thermometer is placed, is 20 cm. long and 2.7 cm. wide. Its lower portion is graduated between the points marking 10 cc. and 35 cc. It has a narrow tube *ab*, opening to the exterior at *a*, 7.5 cm. from the open end. The tube *ab* is closed at the lower end *b* and perforated with five small holes. Another tube, *c*, 2.5 cm. from the mouth of *A*, leads to a Liebig's condenser *C*. The jacket *B* is 22 cm. long and

[1] Ztschr. phys. Chem., 6, 472.

[2] This apparatus may be obtained from Eimer & Amend, New York.

4 cm. wide, excepting near the bottom where it is somewhat enlarged. A short tube *d*, bent upward slightly, is attached to the jacket about 7 cm. from the mouth. The tube *d* is closed by a rubber tube and Mohr's pinch-clamp. A is held in position by a cork fitting tightly into the jacket.

When a determination is to be made the apparatus is supported by a universal clamp and the tube *c* is connected with a Liebig's condenser. About 50 cc. of the pure solvent and a small piece of clay tile are placed in the jacket and 12–16 cc. of the solvent in the inner tube. The liquid in the jacket is heated to boiling by a small flame, best protected from air currents by a small iron chimney, such as is used in analytical work. The bit of tile promotes regular boiling and the vapor



heats the liquid in the graduated tube nearly to its boiling-point by contact with the outside of the inner tube. But as soon as the liquid in the graduated tube has become hot, the vapor rises in the jacket and forces its way through the tube *ab* into the liquid in the graduated tube and brings it to its boiling-point. Before this point is reached the liquid in the jacket may be allowed to boil briskly, but now the heat is to be adjusted so that the liquid in the inner tube boils slowly but regularly, and a very slow distillation into the condenser takes place.

When the thermometer is constant, or does not change more than 0.001 of 1° in thirty seconds, the reading is taken as the boiling-point of the pure solvent. This point is reached, as a rule, in from five to ten minutes after the heating is commenced. The pinch-clamp closing the tube *d* is now removed and then the flame is withdrawn. If the flame be withdrawn before admitting air through *d* the liquid in the inner tube runs over into the jacket through the tube *ab*.

The weighed substance, whose molecular weight is to be determined, is now introduced by raising the stopper carrying the thermometer, *d* is closed, and the solvent in the jacket again boiled. If the substance dissolves readily, the solution quickly reaches its boiling-point and the thermometer reading becomes constant in a very short time. Usually only three or four minutes elapse between the time of reading the boiling point of the solvent and that of the solution. After the boiling-point of the solution is taken the tube *d* is again opened and the boiling stopped. The volume of the solution is read at once, after lifting the thermometer out of the solution.

To obtain further readings at greater dilution, the thermometer is replaced and a new determination of the boiling-point made. The corresponding volume is read off as before. In this way five, six, or even more determinations of the boiling-point may be made with the same amount of substance. Since, at each heating, some of the solvent will condense in the inner tube, the volume of the solution will be a little greater at each successive reading and the boiling-point of the solution will decrease accordingly. The volume that condenses in the graduated tube at each heating is small. It is greatest with benzene, where it amounts to only 2.5 cc. With water the increase was but a few tenths of a cubic centimeter, so that a little water was added each time in order to increase the dilution by larger increments.

The molecular weight is calculated from the formula

$$M = \frac{W \cdot T}{\varDelta \cdot V},$$

where W is the weight of the substance, $\varDelta$ the elevation of the boiling-point, and V the volume of the solution. T is a constant having a different value for each solvent. This formula is very similar to that used when the weight of the solvent instead of the volume of the solution is determined, the only difference being the replacement of the factor representing the weight by that indicating the volume. The values of T in the above formula are obtained from the corresponding values for the old formula by dividing the latter by the specific gravity of the solvent at its boiling-point.

The following are the values of T for a few common solvents :[1]

Alcohol	1560	Carbon bisulphide	1940
Ether	3030	Acetone	2220
Chloroform	2600	Aniline	3820
Benzene	3280	Water	540

The apparatus has been tested by determining the molecular weight of a number of substances, using four different solvents. The results have been very satisfactory. No tedious and troublesome precautions seem to be necessary to obtain fairly good results and the time required is very much less than is needed for a determination with the Beckmann apparatus. Frequently the apparatus has been set up, the substance weighed out, and a determination made at two dilutions in less than thirty minutes.

In the determinations here recorded the weighings were made on a simple balance, sensitive to milligrams, and the Beckmann differential thermometer was read by means of a hand lens. The substances whose molecular weights were determined were the so-called chemically pure preparations of

[1] Beckmann : Ztschr. phys. Chem., 6, 472.

C. A. F. Kahlbaum not further purified. The alcohol used was Kahlbaum's absolute, treated with anhydrous copper sulphate. The benzene was Kahlbaum's thiophene-free preparation, made from benzoic acid. It was dried with metallic sodium. The ether was of good quality. It was washed many times with water, dried with calcium chloride, and distilled over metallic sodium. The determinations were not made with the object of attaining the greatest possible accuracy, but rather to test the value of the apparatus for practical use in ordinary organic research. In the last column the values found by Beckmann, at about the same concentration, are given for comparison.

SOLVENT, ALCOHOL; T = 1560.

Naphthalene, 128.

Weight of substance.	Volume of solution.	Elevation of boiling-point.	Molecular weight found.	Beckmann found.
0.806	28.0	0.291	154	155
“	29.0	0.278	156	
		Benzoic Acid, 122.		
1.010	24.2	0.535	122	124
“	25.3	0.519	120	
		Salicylic Acid, 138.		
0.995	24.1	0.452	142	140
“	25.3	0.435	141	
		Benzanilid, 197.		
0.626	15.2	0.299	215	
“	17.9	0.262	208	

SOLVENT, BENZENE; T = 3280.

Benzil, 210.

Weight of substance.	Volume of solution.	Elevation of boiling-point.	Molecular weight found.	Beckmann found.
0.950	19.3	0.670	241	230
“	21.8	0.570	250	236
		Salicylic Acid, 138.		
0.985	22.5	0.549	261	234
1.000	24.0	0.538	256	

Naphthalene, 128.

0.981	19.1	1.301	130	144
"	21.6	1.141	131	

SOLVENT, ETHER ; T = 3030.

Naphthalene, 128.

Weight of substance.	Volume of solution.	Elevation of boiling-point.	Molecular weight found.	Beckmann found.
1.025	16.0	1.498	130	132

SOLVENT, WATER ; T = 540.

Boric Acid, 62.

Weight of substance.	Volume of solution.	Elevation of boiling-point.	Molecular weight found.	Beckmann found.
1.015	27.3	0.309	65.0	66.8
"	28.6	0.297	64.5	
"	31.1	0.282	62.5	
"	33 4	0.262	62.6	
"	36.0	0.247	61.7	
1.030	29.0	0.297	64.5	

Urea, 60.

1.203	18.2	0.542	66.2	73
"	21.2	0.465	66.3	
"	23.1	0.439	64.4	
"	25.4	0.396	64.9	
"	28.0	0.358	65.2	
"	30.4	0.343	62.7	
"	35.0	0.293	63.7	72

Mannite, 180.

2.044	18.8	0.294	199	
"	22.8	0.254	190	192
"	25.0	0.233	183	
"	30.5	0.200	181	

SALT LAKE CITY, Jan. 29, 1900.

REVIEWS.

ELEMENTARY CHEMISTRY. FOR HIGH SCHOOLS AND ACADEMIES. By ALBERT L. AREY, C.E., Rochester, New York, High School. New York: Macmillan & Co. London: Macmillan & Co. 1899.

The thought that has guided the author in the preparation of this book is expressed in his own words, thus: "It was decided to omit all reference to those properties of the substances studied in the laboratory, which can be learned by observation of the substances themselves; to render the work more complete than it would otherwise be by stating such properties as cannot be shown by experiments adapted to secondary schools." This assumes that the pupil at the outset is capable of making good observations. This does not accord with experience. It is the object of a laboratory course to train these powers of observation. It would certainly be interesting to read the note-books of pupils who, without directions from the teacher, should record the results of their first observations on chemical substances. Of course, the pupil should be led to use his own eyes and his own mind as much as possible, but it is only with the aid of a thoroughly conscientious teacher, who sees the needs of the pupil, that this power can be developed.

On page 4 an extremely dangerous experiment is described, thus: "Sulfur and potassium chlorate are mixed in a mortar with considerable friction." What the results would be of attempts by inexperienced persons to perform this experiment the writer of this notice shudders to think. Not a word of caution is given. It is all very well to say that this is an experiment to be performed by the instructor, but many instructors in chemistry have had very little experience, and they are as likely to go astray as the average pupil.

On page 5 are found directions for an experiment which is not clear, though it sounds learned. The pupil is directed to weigh a quantity of sulphuric acid and a solution of calcium chloride; then to pour them together and weigh the two vessels again. The pupil is then asked: "Does chemical action change the total quantity of matter in existence? Was the total quantity of sulphuric acid in the world increased or diminished by the above experiment? How was the total quantity of calcium chloride affected?" As a matter of fact, the total quantity of sulphuric acid in the world is diminished by such an experiment, but the pupil cannot possibly know this unless told. In the next question the pupil is asked to state his opinion as to why solution aids chemical action. If the pupil ventures to express an opinion at this stage of his work he ought to be reprimanded very promptly.

Instances of this kind are frequent throughout the book and are characteristic of it. They show clearly that the writer of the book is not a well-trained chemist. He may be an excellent teacher, but he has not shown that he is by the book that he has written; and this book, in the hands of inexperienced teachers, would not be helpful. An experienced teacher, on the other hand, might detect these defects, but it would be necessary for him to be on the alert at every stage. I. R.

VICTOR VON RICHTER'S ORGANIC CHEMISTRY, OR CHEMISTRY OF THE CARBON COMPOUNDS. Edited by PROF. R. ANSCHÜTZ, University of Bonn (Assisted by DR. G. SCHROETTER). Authorized translation by EDGAR F. SMITH, Professor of Chemistry, University of Pennsylvania. Third American from the Eighth German Edition. Volume II. Carbocyclic and Heterocyclic Series. Philadelphia: P. Blakiston's Son & Co., 1012 Walnut St. 1900. pp. 671+xvi. Price, $3.00.

Last year attention was called to the first volume of this book that had then just been published. Now we have presented the "aromatic" and related compounds, or the "carbocyclic and heterocyclic series." The book has been so long known and so favorably known that comments upon it are superfluous. The work of editing and of translating has been in most competent hands, so that we may be sure that no pains have been spared to bring it up-to-date in every respect. As remarked in the earlier notice, it is not adapted to the use of the beginner, who would surely be drowned if he should plunge in or even wade in too far. It is a shorter book of reference, a good thing to have on the study table, whether the table belongs to a student or a teacher. It is not, of course, a substitute for Beilstein—nothing could play that part successfully—but still it will be found helpful in many cases if Beilstein is lacking or if completeness is not aimed at. It is condensed to an extent rarely met with, and to such an extent as to make it hard to follow in places. Take, for example, the treatment of the "Constitution of the Benzene Nucleus," which covers not quite two pages of small type. All that is said is no doubt correct, but either the reader must understand the subject beforehand, or his efforts to find out what this means will surely end in a bad headache. It may, however, serve a useful purpose as a reminder to the old stager. I. R.

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PREPARATION AND PROPERTIES OF THE SO-CALLED "NITROGEN IODIDE."

BY F. D. CHATTAWAY AND K. J. P. ORTON.

Nitrogen iodide was originally obtained by Courtois[1] in 1813 by the direct action of ammonia on solid iodine. Solutions of iodine in alcohol, chloroform, carbon tetrachloride, or aqueous potassium iodide were substituted for solid iodine by later observers, and both alcoholic and aqueous solutions of ammonia have been employed. In all cases a black or dark-brown amorphous solution was obtained.

Sérullas[2] prepared the substance by the interaction of iodine monochloride and a solution of ammonia, a method which was afterwards employed by Bunsen[3]. We have prepared nitrotrogen iodide by these various methods, and have compared the products which we find to be identical when proper precautions are taken to ensure the removal of all free iodine and ammonia and to prevent decomposition.

Whenever iodine itself is used, whether in solution or as a solid, less than half appears as nitrogen iodide. Exact experiments showed that at ordinary laboratory temperatures the nitrogen iodide formed contains about 47.5 per cent of the iodine used. Of the remainder 51.6 per cent appears as ammonium iodide and 0.8 per cent as ammonium iodate.

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[1] Ann. Chim., **88**, 304.

[2] Ann. chim. phys. [2], **22**, 172 (1825); and **42**, 200 (1829).

[3] Ann. Chem. (Liebig), **84**, 1 (1852).

The use of alcoholic solutions of iodine or ammonia decreases largely the yield because the nitrogen iodide reacts rapidly with the alcohol to form iodoform, which, moreover, can never be wholly removed from the product. Bunsen, however, used this method and obtained a substance, analysis of which led him to the formula $N_2H_3I_3$ for nitrogen iodide. All our analyses of nitrogen iodide prepared in various ways agree absolutely with this formula.[1]

Preparation of Nitrogen Iodide by the Action of Iodine Monochloride on a Solution of Ammonia.

When iodine monochloride is used, 95 per cent of the iodine appears as nitrogen iodide. The remainder is converted into ammonium iodide and iodate, while the chlorine appears as ammonium chloride. We have carefully investigated this method and consider it the most suitable for preparing pure nitrogen iodide in large quantities. The best procedure for the preparation of the iodine monochloride and of the nitrogen iodide is as follows:

One hundred grams of finely powdered iodine are placed in 300 cc. of hydrochloric acid of sp. gr. 1.15 in a porcelain basin and 28 cc. of nitric acid of sp. gr. 1.41 are added. This quantity of nitric acid provides just sufficient chlorine to convert the iodine into iodine monochloride. The mixture is warmed on a water-bath to about 40° and continuously stirred, the beginning of the reaction being marked by the color of the liquid changing from brown to pale-yellow. The iodine gradually dissolves and the solution becomes orange in color. If the mixture be well stirred and the temperature not allowed to rise above 40°, no chlorine escapes. After the whole of the iodine has dissolved, the water in the bath is boiled for some time in order to expel the nitrosyl chloride. With the excess of hydrochloric acid used, the solution of iodine monochloride is perfectly stable and undergoes no decomposition even when boiled. To prepare nitrogen iodide it is cooled and diluted by adding about three times its bulk of crushed ice.

For every 10 grams of iodine 100 cc. of strong commercial

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[1] Bunsen determines the relation of nitrogen to iodine only, and in his method of analysis any trace of iodoform present would not cause error.

ammonia (sp. gr. 0.880) are poured over about three times their weight of crushed ice and the cold solution of iodine monochloride slowly run in, the mixture being vigorously stirred during the addition.[1] The black precipitate of nitrogen iodide which at once separates, is filtered off by a pump through asbestos and washed with dilute ammonia, and finally, if required free from ammonia, three or four times with water. In this way a kilogram of nitrogen iodide can be obtained as a compact cake with perfect safety. It is best, if possible, to leave the solid mass damp with strong ammonia, for then filter-paper can be used instead of asbestos, and the slight decompositions which take place in the total absence of ammonia, and may give rise to local explosions, is prevented.[2]

Preparation of Crystalline Nitrogen Iodide.

In the course of this investigation it became obvious that nitrogen iodide is not formed by a direct substitution of iodine for hydrogen in ammonia, but that the iodine reacts with ammonium hydroxide as with other alkalies to form ammonium iodide and hypoiodite, and that the latter then decomposes, forming nitrogen iodide. This view was originally offered by Schönbein[3] as a suggestion, which has been endorsed by Seliwanow.[4] The addition of ammonia to an alkaline solution of potassium hypoiodite should, therefore, lead to the formation of NH_4OI, ammonium hypoiodite, which should then decompose, producing nitrogen iodide. This we have found to be the case; and, further, under certain conditions of concentration the nitrogen iodide separates in a crystalline form.

The following method gives good results: A decinormal solution of iodine monochloride is prepared by diluting with water to 1 liter a solution of iodine monochloride, ICl, made as above, from 12.7 grams of iodine. This dilute solution is

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[1] The solution of ammonia should not be added to the solution of iodine monochloride, for then iodine is liberated and the yield much reduced.

[2] André (Jour. Pharm., **22**, 137 (1836)) obtained nitrogen iodide by the addition of ammonia to a solution of iodic acid in hydrochloric acid. Such a solution contains iodine monochloride after it has been heated, for, as is well known, iodic and hydrochloric acids then react according to the equation: $HIO_3 + 5HCl = ICl + 2Cl_2 + 3H_2O$.

[3] J. prakt. Chem., **84**, 385 (1861).

[4] Ber. d. chem. Ges., **27**, 1012 (1894).

unstable and should only be prepared immediately before use. Fifteen cc. of this solution are added to 100 cc. of a half-normal solution of potassium hydroxide (3 per cent), and then, as rapidly as possible, 10 cc. of ammonia (sp. gr. 0.880) are run in while the solution is gently shaken. The pale-yellow liquid remains clear for a short time, but within a minute glittering copper-colored crystals of nitrogen iodide begin to separate, and after a few minutes the crystallization is complete. The yield is satisfactory, being from 65–70 grams per 100 grams of iodine. When larger quantities than those indicated are used the yield is not so good owing to the difficulty of mixing the solutions sufficiently rapidly. Under the microscope very minute needles first become visible, which steadily grow to the usual crystals. The large excess of potassium hydroxide used prevents any setting free of iodine when the acid solution of iodine monochloride is added to it. If more than 15 cc. of $\frac{\mathrm{ICl}}{10}$ be added to 100 cc. $\frac{\mathrm{KOH}}{2}$, the crystals separate more rapidly and are smaller. With further increased concentration the crystals become mixed with amorphous nitrogen iodide, which finally forms the chief product.

Replacement of ammonia by a dilute solution of an ammonium salt also causes a deposition of crystalline nitrogen iodide, if the ammonium salt be added very cautiously. An amorphous precipitate is obtained if the solution of ammonium salt be added rapidly or if it be concentrated.

Amorphous nitrogen iodide can be converted into the crystalline variety by an apparent recrystallization from a hot solution of ammonia. The conversion is, however, really due to the occurrence of a reversible reaction in the system (nitrogen iodide + ammonium hypoiodite + ammonium hydroxide). In this system, at the state of equilibrium, the concentration of ammonium hypoiodite is greater at a high than at a low temperature with a given concentration of ammonia. To obtain crystalline nitrogen iodide by this method about 0.5 gram of the amorphous substance is heated with 100 cc. of thrice-normal ammonia solution, in which it partially dissolves, producing a pale-yellow solution, and this, after filtration through asbestos, deposits crystals when rapidly cooled. With larger quantities the time required to cool the bulk of hot liquid leads to the conversion of so large a proportion of the ammonium hypoiodite into iodate and iodide that little nitrogen iodide separates.

Crystals can also be obtained by the direct addition of a solution of iodine monochloride to ammonia. For this purpose the solution of ICl must be about one-fiftieth normal and must be added very slowly to a fairly concentrated solution of ammonia.[1]

Properties of Nitrogen Iodide.

Crystals of nitrogen iodide suspended in water look like splinters of burnished copper, and when dry have a ruby-red color and a fine luster. Ordinary amorphous nitrogen iodide shows no trace of crystalline structure and appears quite black when suspended in water, but if filtered off and dried is seen somewhat to resemble the crystalline substance in color.

Pure nitrogen iodide is without effect on a neutral solution of litmus and gives no reaction of iodine when shaken with chloroform. In contact with water it soon shows signs of decomposition, the amorphous more rapidly than the crystalline variety. The crystals lose their lustre and under the microscope are seen to be etched and corroded. Too prolonged washing with water on the filter will cause this decomposition to take place. Free iodine is then always found by the chloroform test in the solid residue while free ammonia can be detected in the filtrate.[2]

Nitrogen iodide can be dried over lime or baryta in an atmosphere of ammonia, if light be absolutely excluded, without any decomposition taking place. When dry it can be safely detached from a porous tile with a spatula, but slight percussion, pressure between hard surfaces, or rapid heating

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[1] The formation of nitrogen iodide has been observed in the action of bleaching powder on a solution of ammonium iodide. [Playfair in discussion on Gladstone's paper (Chem. Soc. J., **4**, 34 (1852)]. In this case undoubtedly ammonium hypoiodite is first produced and from it the nitrogen iodide is formed. The product separating is always mixed with calcium iodate, which can only with difficulty be removed by prolonged washing with ammonia. In the electrolysis of an ammoniacal solution of potassium iodide Losanitsch and Jowitschitsch (Ber. d. chem. Ges., **29**, 2430) noticed that at the positive pole nitrogen iodide was deposited and that hypoiodite could be recognized in the solution.

[2] Pure nitrogen iodide consequently cannot be obtained, as many observers have stated, by washing the product until the filtrate becomes neutral.

cause it to detonate with violence. The whole mass explodes at once without scattering, but the explosion is never communicated to any of the substance lying only a few centimeters away. A puff of violet vapor surrounded by a cloud of white fumes is seen, and in a dark room a green flash of light is noticed, resembling in color the flame of burning ammonia. Nitrogen iodide is remarkably sensitive to light. Bubbles of nitrogen are slowly given off in diffused light from the compound suspended in water while in direct sunlight rapid effervescence takes place. The dry substance in diffused light becomes gradually covered with minute crystals of iodine, which appear more quickly and grow more rapidly in sunlight.

Partially decomposed nitrogen iodide is very unstable and explodes at the slightest touch.

The following description of the crystals of nitrogen iodide has been given us by Mr. W. J. Pope, who very kindly undertook their examination: The crystals are small, flattened needles of a bright ruby color in transmitted light. The extinction through all faces in the zone of the long edge is straight and the crystals are probably orthorhombic; the forms would then be }001{.}101{ and }110{ and the crystals are lengthened in the direction of the axis b. The plane angle between the edges 001 : 101 and 001 : 110 is 140° and very frequently only one face of }110{ is present at one end. An optic axis can be sometimes just discerned at the edge of the field, emerging in the plane }010{.

The crystals are dichroic. On looking through }001{ using light polarized in the plane }100{ light of a beetle-green color is transmitted, but if the plane of polarization be }010{ light of a ruby-red color comes through.

The specific gravity of crystalline nitrogen iodide is about 3.5. This number has been obtained by drying a quantity of the substance in an atmosphere of ammonia in a specific gravity bottle and weighing it first in air and then under water.

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THE ACTION OF REDUCING AGENTS UPON NITROGEN IODIDE.

By F. D. Chattaway and H. P. Stevens.

All ordinary reducing agents when brought into contact with nitrogen iodide, suspended in water, rapidly decompose it. In these reactions the different reducing agents are invariably oxidized while hydriodic acid and ammonia are produced. The quantity of reducing agent oxidized is found in every case to be exactly double the amount equivalent to the hydriodic acid produced, using nitrogen iodide obtained by any method. The action of sodium sulphite, sulphurous acid, arsenious oxide, antimonious oxide, stannous chloride, and hydrogen sulphide has been investigated with the following results:

Amount of reducing agent oxidized	Na_2SO_3	H_2SO_3	As_2S_3	Sb_2O_3	$SnCl_2$	H_2S
Amount of hydriodic acid simultaneously produced	HI	HI	2HI	2HI	HI	HI

All the iodine contained in nitrogen iodide, therefore, behaves towards reducing agents like the chlorine contained in a hypochlorite and exerts twice its normal oxidizing action.

Action of Sodium Sulphite on Nitrogen Iodide.

When a solution of sodium sulphite in excess is added to nitrogen iodide suspended in water, rapid interaction ensues and a colorless solution, somewhat acid from the presence of hydriodic acid, results.

If the sulphite be added slowly from a burette a liquid colored brown by free iodine is obtained when the solid has entirely disappeared; the end-point of the reaction is then easily seen by the disappearance of the color, or starch paste may be used as an indicator. The hydriodic acid produced can afterwards be estimated in one of several ways; the most convenient and the one usually adopted is to titrate the clear solution with standard silver nitrate, using the blue so-called "iodide of starch" as indicator.[1] The actual operation is car-

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[1] Pisani: Annal. d. Min., **10**, 83.

ried out as follows: Nitrogen iodide prepared in any one of the ways previously described is rapidly filtered off through asbestos by the aid of a pump, and thoroughly washed with decinormal ammonia, and finally once with water. A number of 250 cc. flasks having been prepared, about 0.2–0.5 gram of the moist iodide is placed in each with about 25 cc. of water, and titrated as rapidly as possible with decinormal sodium sulphite, shaking gently the while. The estimation of hydriodic acid by silver nitrate is then carried out in the ordinary way. Light must be rigorously excluded while washing and transferring the nitrogen iodide to the flask and during the titration until all solid particles have disappeared.

In the tables where the results are recorded the amount of reducing agent oxidized is stated in the second line, that of the hydriodic acid produced in the third, while in the fourth is the ratio between the reducing agent oxidized and the hydriodic acid produced, calculated to the third decinormal place.

The Roman numerals in the first column refer to the mode in which the nitrogen iodide used was prepared. The experiments numbered I were made with amorphous nitrogen iodide prepared by adding a decinormal solution of iodine in potassium iodide to a strong solution of ammonia; those marked II with material prepared similarly but using a normal solution of iodine. In those numbered III the nitrogen iodide was made by treating finely powdered iodine with a strong solution of ammonia; in those numbered IV iodine, precipitated by diluting a saturated solution of iodine in potassium iodide, was used. In preparing the material for those numbered V an alcoholic solution of iodine,[1] and for those marked VI a solution of iodine monochloride was added to a saturated solution of ammonia. In experiments VII and VIII crystalline nitrogen iodide was employed, prepared respectively by adding ammonium hydroxide to a solution of potassium hypoiodite and by heating amorphous nitrogen iodide with ammonia and rapidly cooling. In those numbered IX the nitrogen iodide was prepared by adding an excess of a solution of bleaching powder to a solution of ammonium iodide.

[1] In these cases a small residue of iodoform was left in the flask after titration.

Although in the tables one result only with each specimen of nitrogen iodide is given, this has in every case been confirmed by from 22 to 30 concordant experiments :

Number of experiment.	$\frac{N}{10}\,\frac{Na_2SO_3}{2}$ oxidized. cc.	$\frac{N}{10}$ HI produced. cc.	Ratio.
I	87.1	43.6	2 : 1.001
II	68.2	34.1	2 : 1
III	47.1	23.6	2 : 1.002
IV	70.5	35.3	2 : 1.001
V	86.2	43.2	2 : 1.002
VI	138.2	69.1	2 : 1
VII	60.8	30.4	2 : 1
VIII	98.1	49.1	2 : 1.001
IX	80.7	40.3	2 : 0.999

In order to establish beyond question this ratio between the sodium sulphite oxidized and the hydriodic acid produced, series of experiments have been made in which the latter was estimated by other methods.

In the following series, after the decomposition of sodium sulphite, the hydriodic acid was oxidized by iron-alum and sulphuric acid, and the liberated iodine distilled off and titrated by the same sulphite solution. The distillation was carried out in a special form of apparatus,[1] in which only ground glass joints are employed, and to prevent bumping, a very slow stream of carbon dioxide is led in by a capillary tube to the bottom of the boiling liquid :

Number of experiment.	$\frac{N}{10}\,\frac{Na_2SO_3}{2}$ oxidized by nitrogen iodide used. cc.	$\frac{N}{10}\,\frac{Na_2SO_3}{2}$ oxidized by iodine liberated from hydriodic acid produced. cc.	Ratio.
I	46	23	2 : 1
II	42.1	21.1	2 : 1.002
III	52.7	26.3	2 : 0.998
IV	65.6	32.7	2 : 0.997
V	45	22.5	2 : 1
VI	48.6	24.3	2 : 1

Exactly similar results were obtained when the hydriodic acid formed was estimated by adding an excess of silver nitrate

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[1] Chem. News, 1899, 85.

and then determining the excess by a standard solution of potassium thiocyanate.

In connection with the action of reducing agents a number of experiments were made to show the necessity for the exclusion even of the diffused light of a laboratory when working with nitrogen iodide. Some amorphous nitrogen iodide prepared by adding a solution of iodine monochloride to ammonia was taken and carefully washed with decinormal ammonia. Approximately equal quantities were then placed in 4 flasks; that in flask *A* was titrated immediately with sodium sulphite; that in flask *B* was exposed to the diffused light of the laboratory on a dull winter afternoon for five minutes and then titrated; that in *C* was similarly exposed for ten minutes; that in *D* for twenty minutes. The hydriodic acid formed in each case was afterwards estimated by silver nitrate, and the ratio calculated between this and the sulphite oxidized.

Number of experiment.	$\frac{N}{10}\frac{Na_2SO_3}{2}$ oxidized. cc.	$\frac{N}{10}$ HI present. cc.	Ratio.
A	74.8	37.4	2 : 1
B	71.5	39.2	2 : 1.100
C	65	38.2	2 : 1.17
D	73.2	49.1	2 : 1.34

It is seen that the ratio diminishes as the time of exposure increases. This is due to a decomposition of some of the nitrogen iodide into nitrogen and hydriodic acid, a change which occurs whenever the substance is exposed to light.

A solution of sulphurous acid behaves toward nitrogen iodide as sodium sulphite does; a further action, however, accompanies this, similar to the one occurring when nitrogen iodide is exposed to light, whereby a small portion breaks up into nitrogen and hydriodic acid. This latter, as it is estimated with that produced by the reducing agent, causes the ratio to appear too low. If, however, the amount due to the reaction with the sulphurous acid be calculated from the ammonia formed, as can easily be done when the composition of the substance is known, the quantity of sulphurous acid oxidized is found to be exactly double that equivalent to the hydriodic acid produced.

Action of Arsenious Oxide on Nitrogen Iodide.

When a solution of arsenious oxide is slowly added to nitrogen iodide suspended in excess of a solution of sodium bicarbonate until the particles disappear, ammonia, arsenic acid, and hydriodic acid are produced, and the amount of arsenious acid oxidized is found to be exactly double that which is equivalent to the hydriodic acid formed. The experiments were carried out much as before, the hydriodic acid, however, being estimated by making the liquid acid, adding silver nitrate in slight excess, and estimating the excess added by potassium thiocyanate.

Number of experiment.	$\frac{N}{10}$ $\frac{As_2O_3}{4}$ oxidized. cc.	$\frac{N}{10}$ HI produced. cc.	Ratio.
I	42.3	21.1	2 : 0.997
II	45.9	22.9	2 : 0.997
III	37.9	18.9	2 : 0.997
IV	44.5	22.3	2 : 1.002
VI	43.8	21.9	2 : 1
VII	33.2	16.6	2 : 1

Similar results were obtained when the hydriodic acid was estimated by determining the amount of a standard solution of potassium permanganate required to oxidize it to iodic acid.

Action of Antimonious Oxide on Nitrogen Iodide.

The action of antimonious oxide on nitrogen iodide is exactly similar to that of arsenious oxide, the compound being converted into the higher oxide, while ammonia and hydriodic acid are produced. Similarly the quantity oxidized is double the amount equivalent to the hydriodic acid formed. The experiments were carried out as with arsenious oxide, a decinormal solution of tartar emetic being used and sodium bicarbonate added in larger excess.

Number of experiment.	$\frac{N}{10}$ $\frac{Sb_2O_3}{4}$ oxidized. cc.	$\frac{N}{10}$ HI produced. cc.	Ratio.
I	31.3	15.7	2 : 1.003
II	39.4	19.8	2 : 1.005
III	32.6	16.4	2 : 1.006
IV	26.1	13.1	2 : 1.003
VI	38.2	19.1	2 : 1
VII	34.7	17.4	2 : 1.002

Action of Stannous Chloride upon Nitrogen Iodide.

Stannous chloride, dissolved in the least possible quantity of dilute hydrochloric acid, readily reacts with nitrogen iodide, and if it be added slowly a little iodine is liberated. If the addition be continued till this liberated iodine just disappears, stannic chloride, ammonium chloride, and hydriodic acid alone are formed. The latter can be estimated by converting it into iodic acid by a solution of potassium permanganate, the ammonium being first expelled by a slight excess of caustic soda. The quantity of hydriodic acid formed is found to be half the amount equivalent to the stannous chloride oxidized.

Number of experiment.	$\frac{N}{10}$ $SnCl_2$ oxidized. cc.	$\frac{N}{10}$ HI produced. cc.	Ratio.
I	32.5	16.6	2 : 1.009
II	31.4	15.8	2 : 1.006
III	40.2	20.1	2 : 1
IV	30.7	15.5	2 : 1.009
VI	30.1	15.1	2 : 1.003
VII	27.9	14	2 : 1.003

The ratio usually comes out slightly too high. This, as in the case of sulphurous acid, is due to a small quantity of the nitrogen iodide breaking down into nitrogen and hydriodic acid under the influence of the hydrochloric acid which must be present to keep the stannous chloride in solution.

Action of Hydrogen Sulphide on Nitrogen Iodide.

On a solution of hydrogen sulphide being added to nitrogen iodide suspended in water the solid particles rapidly disappear, sulphur is precipitated, and ammonia and hydriodic acid are produced as in other cases. If the solution of hydrogen sulphide be very slowly added, iodine is set free, and the end of the reaction can be recognized easily by its disappearance. The investigation of this action is complicated by the circumstance that during it a considerable portion of the nitrogen iodide decomposes into nitrogen and hydriodic acid, and thus the ratio between the hydrogen sulphide oxidized and the hydriodic acid produced appears too great if the latter is directly estimated.

The following estimations show that the ratio thus obtained is variable but approximately 2 : 1.2.[1] The hydriodic acid was determined by adding a small excess of silver nitrate and estimating this excess by potassium thiocyanate.

Number of experiment.	$\frac{N}{10}\ \frac{H_2S}{2}$ oxidized. cc.	$\frac{N}{10}$ HI produced. cc.	Ratio.
I	28.4	16.7	2 : 1.18
II	31.2	18.9	2 : 1.21
III	27.3	16.8	2 : 1.23
IV	33	19.8	2 : 1.2
VI	31.6	19.5	2 : 1.23
VII	35.8	22.5	2 : 1.26

As, however, the composition of nitrogen iodide has been definitely determined, the amount which actually reacts with the hydrogen sulphide and consequently the quantity of hydriodic acid liberated can be calculated from the ammonia formed. In the following experiments this was done, the nitrogen iodide which breaks up into nitrogen and hydriodic acid being neglected :

Number of experiment.	$\frac{N}{10}\ \frac{H_2S}{2}$ oxidized. cc.	$\frac{N}{10}$ HI produced. cc.	Ratio.
I	30.8	15.4	2 : 1
II	24.7	12.3	2 : 0.995
III	32.2	16.2	2 : 1.006
IV	40.4	20.3	2 : 1.005
VI	26.8	13.4	2 : 1
VII	20.9	10.5	2 : 1.004

It is seen that the action of hydrogen sulphide upon nitrogen iodide is perfectly normal and that the amount of hydrogen sulphide oxidized is twice that equivalent to the hydriodic acid produced.

The close agreement between all the results obtained with such very different reducing agents places it beyond doubt that, when nitrogen iodide reacts with any reducing agent, the ratio between the amount of the latter oxidized and that of the hydriodic acid produced is as 2 : 1 ; in other words,

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[1] Compare Bineau's (Ann. chim. phys. [3], **15**, 71 (1845)) and Gladstone's (Chem. Soc. J., **4**, 34 (1852), and **7**, 51 (1854)) analytical results obtained by this method. They differ among themselves, and this accompanying decomposition was not observed.

that the iodine contained in nitrogen iodide behaves in these reactions like the chlorine contained in a hypochlorite and exerts twice its normal oxidizing action.

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COLLEGE, LONDON.

Contributions from the Chemical Laboratory of Harvard College.

CXVII.—ON CERTAIN COLORED SUBSTANCES DERIVED FROM NITRO COMPOUNDS.

[THIRD PAPER.[1]]

BY C. LORING JACKSON AND F. H. GAZZOLO.

The colored substances formed by the action of sodic alcoholates and certain nitro compounds have been studied by Victor Meyer,[2] Lobry de Bruyn,[3] and in this laboratory,[4] but as yet no satisfactory constitutional formula has been assigned to them.

In continuing this investigation we tried first to replace the sodic alcoholates by other similar reagents, and succeeded in obtaining colored products from trinitranisol or trinitrobenzol by the action of sodic malonic ester, sodic acetacetic ester, sodic phenylate, the sodium compound of benzyl cyanide, and perhaps the sodium compound of phloroglucine, although in this last case the action was not well marked. As it has been shown already that similar compounds are formed with various sodic alcoholates,[5] and even with sodic hydrate,[6] it appears that this behavior with nitro compounds is a very general reaction of alkaline substances.

Of these new colored products only those with sodic malonic ester or sodic acetacetic ester were stable enough to be prepared for analysis, but they were unusually stable for bodies of this class. All four of the substances formed from trinitranisol or trinitrobenzol, and these two sodium esters were analyzed and were proved to consist of 3 molecules of the

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[1] Presented to the American Academy of Arts and Sciences, December 13, 1899.

[2] Ber. d. chem. Ges., **27**, 3153; **29**, 848.

[3] Rec. Trav. Chim. Pays-Bas., **14**, 89, 150; **15**, 848.

[4] Jackson and Ittner: This JOURNAL, **19**, 199, where a historical account of the previous work is given; Jackson and Boos: *Ibid.*, **20**, 444.

[5] *Ibid.*, **20**, 444.

[6] Hepp: Ann. Chem. (Liebig), **215**, 359.

sodium ester combined with 1 of the trinitro compound; for instance, the malonic ester trinitrobenzol compound has this formula, $C_6H_3(NO_2)_3[CHNa(COOC_2H_5)_2]_3$. The formation of compounds with 3 molecules of the sodium constituent is noteworthy, since all the compounds analyzed heretofore have contained the two constituents in the proportion of 1 molecule of each. Similar experiments with sodic methylate, ethylate, or amylate and trinitrobenzol also led to products apparently containing 3 molecules of the alcoholate to each molecule of the nitro compound[1]—a surprising result, since Lobry de Bruyn and Van Leent[2] obtained from trinitrobenzol a substance with the following formula, $C_6H_3(NO_2)_3KOCH_3\frac{1}{2}H_2O$. The difference in the result is unquestionably due to differences in the method of preparation. Lobry de Bruyn and Van Leent's compound was obtained by crystallization, whereas all our products with 3 molecules of the alkaline material were precipitated from an alcoholic solution with benzol. Experiments are now in progress to test this explanation of the phenomena.

The discovery of these sodic malonic or acetacetic compounds would furnish a strong argument, if that were needed, against the only theory of these colored substances as yet published—that of Victor Meyer,[3] who supposed they were formed by the replacement of atoms of hydrogen on the benzol ring by atoms of sodium. This theory has been disproved by the observations of Lobry de Bruyn,[4] supported by those made in this laboratory;[5] and among other arguments the point was made that Victor Meyer's theory necessitated the assumption of alcohol of crystallization in every compound of this class which had been analyzed. In these malonic and acetacetic compounds the presence of malonic ester or acetacetic ester of crystallization must be assumed, if this theory is

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[1] The ethyl and methyl compounds seemed to contain alcohol of crystallization, to judge from the percentages of sodium obtained. The publication of these results will, therefore, be postponed until further analytical data have been collected. The amyl compound, on the other hand, gave a percentage of sodium corresponding to $C_6H_3(NO_2)_3(NaOC_5H_{11})_3$.

[2] Rec. Trav. Chim. Pays-Bas., **14**, 150.

[3] Ber. d. chem. Ges., **27**, 3153.

[4] Rec. Trav. Chim. Pays-Bas., **14**, 89.

[5] This Journal, **20**, 445.

adopted; and, further, the number of molecules of "ester of crystallization" corresponds in each case to the number of atoms of sodium; the view, therefore, that the colored bodies are addition and not substitution compounds is confirmed by these observations.

Other experiments were tried to study the effect on the formation of the colors of increasing or diminishing the negative nature of the aromatic constituent. That there is some effect of this sort has been shown already, since certain substituted toluols give less stable colored derivatives than the corresponding benzoic acids.[1] Picramide, the first substance selected for this work, gave colored compounds with sodic methylate or sodic malonic ester, but too unstable to analyze, whereas trinitranisol or trinitrobenzol, in which the negative character of the nitro groups is not weakened by the presence of a positive radical like NH_2, gave stable, well-marked colors. Dinitroxylol $((CH_3)_2 1.3.(NO_2)_2 4.6)$ also gave a slight and evanescent coloration with sodic methylate, and no reaction with sodic malonic ester, whereas trinitroxylol $((CH_3)_2 1.3.(NO_2)_3 2.4.6)$ gave colored compounds with both these reagents, which, although much more stable, could not be prepared for analysis. These results, therefore, as far as they go, show that an increase in the negative nature of the aromatic constituent increases the tendency to form colored compounds.

The next subject considered by us was the effect of the presence of methyl groups attached to the benzol ring on the formation of colors. Dinitrotoluol $((NO_2)_2 2.4)$ gave colored compounds with sodic methylate or sodic malonic ester; dinitroxylol $((CH_3)_2 1.3.(NO_2)_2 4.6)$ gave only a passing coloration[2] with sodic methylate, none at all with sodic malonic ester; and dinitromesitylene gave no color with either reagent. Trinitroxylol gave strong color reactions with both reagents; trinitromesitylene none whatever. It is evident, therefore, that the presence of methyl groups on the benzol ring diminishes the tendency to form these colored compounds. Whether

[1] This JOURNAL, 19, 201.

[2] This may have been due to a small quantity of a thiophene compound. As a rule we have not considered that a colored product belonged to the class we are studying unless we could obtain a copious precipitate of it with benzol.

this effect is due to a specific action[1] of the methyl group, or to the fact that these groups stand in the ortho position to the nitro groups, or to both these causes, cannot be determined from the facts at present at our disposal.

In consideration of the complete absence of a color reaction with trinitromesitylene and sodic methylate, it is interesting to note that M. Konowalow[2] obtained red salts from nitromesitylenes in which one of the nitro groups stands in the side chain. We cannot find that he analyzed these salts to determine whether they were true salts or addition-products with sodic hydrate. If the latter, they would have a strong bearing on the discussion given above.

Another series of experiments was tried with aromatic bodies rich in negative radicals by containing no nitro groups; for, if colors of the same class could be obtained from these, it would prove that the addition of the alkaline substance took place on the benzol ring and not on the nitro group. We were encouraged to undertake these experiments by the striking resemblance in properties[3] between our colored products and the green bodies made by Astre[4] from the action of sodic alcoholates on quinone. In the quinones, however, the formation of hemiacetals[5] is possible, and it may be that the green bodies belonged to this class; we accordingly used for our new experiments substances in which the formation of hemiacetals could not occur, such as trimesic triethylester, which is especially fit for these experiments, since it has a still stronger resemblance to trinitrobenzol than quinone has, because it contains three negative radicals symmetrically disposed. We have not succeeded in obtaining any colored or other addition-products from this substance, or from the free trimesic acid, although the attempts have been repeated often and under varying conditions. Nor did we have better success with other bodies free from nitro groups, such as phloroglucine, or resorcine; pyrocatechine, it is true, gave a temporary coloration with sodic methylate, but we think this re-

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[1] Lobry de Bruyn: Rec. Trav. Chim. Pays-Bas., **14**, 95.

[2] Ber. d. chem. Ges., **29**, 2204.

[3] This JOURNAL, **20**, 446.

[4] Compt. rend., **121**, 530 (1895).

[5] This JOURNAL, **17**, 579, 633.

action does not belong to the series under discussion. These experiments, as they have given negative results, throw no light on the constitution of our colored compounds.

It has been shown earlier in this paper that the only theory as yet proposed for these colored compounds (that of Victor Meyer) is inadmissible, because they are addition-, not substitution-products. The facts now at our disposal are not sufficient to furnish an absolute proof of the structure of these compounds, but it is possible to show that certain constitutional formulas explain these facts better than others, and it seems to us that the work has arrived at a point where such a discussion of the possible formulas will be useful. In this discussion the following properties must be considered, as they seem to be characteristic of all the members of this group: (1) The very marked color. (2) The ease with which they are decomposed even by dilute acids, giving the aromatic constitution unaltered. (3) Their behavior with alcohols, which we describe here in some detail, because the principal observations are new. When the methyl compound, $C_6H_2(NO_2)_3OCH_3NaOCH_3$, is allowed to stand for some time with benzyl alcohol, both the methyls are replaced by benzyls, and the compound $C_6H_2(NO_2)_3OC_7H_7NaOC_7H_7$ is formed. Conversely this benzyl compound is converted into the corresponding methyl compound if boiled with methyl alcohol. In the same way[1] the methyl is converted into the ethyl compound by crystallization from common alcohol.[2]

There are three possible ways in which these compounds can be formed: *First*, The addition of the sodic methylate (or other alkaline substance) may take place upon the carbon atoms of the benzol ring. *Second*, It may take place on the nitro group alone. *Third*, It may take place partly on the nitro group and partly on the carbon of the benzol ring.

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[1] This JOURNAL, **20**, 449.

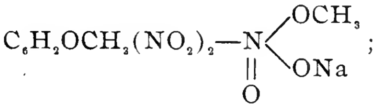
[2] Some experiments of less importance may be mentioned here, with the remark that they are not incompatible with the formula adopted later as giving the best explanation of the observed facts. Bromine decomposes the salt

$$C_6H_3(NO_2)_3[CHNa(COOC_2H_5)_2]_3,$$

giving trinitrobenzol as one of the products of the reaction. No salts with other basic radicals could be obtained from $C_6H_2(NO_2)_3OCH_3NaOCH_3$. No sodic iodide was formed by heating $C_6H_3(NO_2)_3[CHNa(COOC_2H_5)_2]_3$ with ethyl iodide to 140°. On the other hand, it looked as if benzoyl chloride acted on these bodies, but the end of the college year prevented us from studying this reaction.

The first method of addition, that on the carbon alone, seems to us much less probable than the second or third, in which a nitro group takes part, especially since the work of Nef and others has shown that the sodium is attached to the nitro group in the sodium salt of nitromethane. As we have succeeded in finding no analogous case in which an alkaline substance is added to carbon atoms with the formation of a strongly colored product, we think that this first hypothesis is not worthy of a detailed discussion.

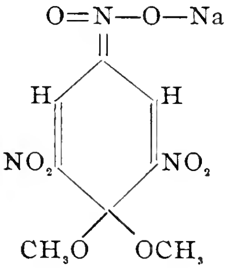
Turning to the formulas in which the nitro group is affected, we have the second method of addition, in which the sodic methylate is attached to the nitro group only; this would give rise to a structure such as the following :[1]



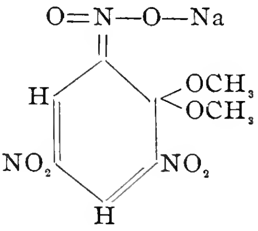
$$C_6H_2OCH_3(NO_2)_2-\underset{\underset{\displaystyle O}{\|}}{N}\begin{matrix}\diagup OCH_3\\ \diagdown ONa\end{matrix};$$

I.

while the third hypothesis, according to which both the nitro group and the carbon of the phenol ring take part in the addition, would be represented by the formulas given below, in which it is supposed that an isonitro[2] compound is formed with the development of a quinoid structure in the benzol ring. The difference between the two formulas is that in II the quinoid structure is developed in the para position, in III in the ortho position :



II.



III.

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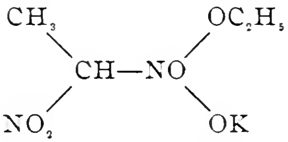
[1] This is analogous to that given by Hantzsch and Rinckenberger (Ber. d. chem. Ges., **32**, 628) for their dinitroethanester acid.

[2] Compare Hantzsch (Ber. d. chem. Ges., **32**, 575-651) and also the orthobenzoldioxime of Zincke and Schwarz (Ann. Chem. (Liebig), **307**, 28).

We have used the formula of the addition-product from sodic methylate and trinitranisol, as it is the simplest that will serve in the argument which follows. In applying these formulas to the malonic ester compounds it must be assumed that the malonic ester radical which is added to the benzol ring has the constitution $—OC(OC_2H_5)=CHCOOC_2H_5$, as, if it is assumed to be $—CH(COOC_2H_5)_2$, we should have an attachment of carbon to carbon incompatible with the instability of these compounds.

In applying formulas I, II, and III to the explanation of the observed properties of these compounds, we consider first the strong color, their most marked characteristic; this is explained by the quinoid structure in formulas II or III, but is not accounted for by formula I, since, according to Hantzsch and Rinckenberger,[1] their subsubstance



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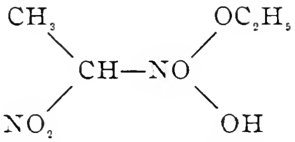
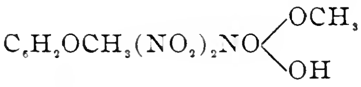
which contains the group characteristic of formula I, has only a pale-yellow color.

The easy decomposition of the colored body by hydrochloric acid with regeneration of the trinitranisol, from which it was formed, is accounted for by either of the three formulas, I, II, or III, but the preference should be given to II or III, since Hantzsch and Rinckberger[2] state that their compound



is a true stable acid ten times as strong as acetic acid, and it is fair to suppose, therefore, that the substance



$$C_6H_2OCH_3(NO_2)_2NO\begin{cases}OCH_3\\OH\end{cases}$$

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[1] Ber. d. chem. Ges., **32**, 628.

[2] *Ibid.*

(formed by hydrochloric acid on our sodium salt, if it has formula I) would also be comparatively stable, and not drop at once into the trinitranisol, which, as a matter of fact, is formed immediately by the action of hydrochloric acid on the colored compound. On the other hand, this rapid decomposition by acid would be explained according to formula II or III by the strong tendency of quinoid bodies to pass into the hydroquinoid form, which might easily cause the splitting off of methyl alcohol as soon as the atom of sodium was replaced by hydrogen. This rapid decomposition with removal of methyl alcohol when the colored bodies are treated with dilute hydrochlyric acid recalls the similar behavior of the dichlordimethoxyquinonedimethylhemiacetal ;[1] and the similarity of these phenomena may tell in favor of classing the colored salts with quinone derivatives, although the two reactions are not strictly analogous.

The third point in favor of formula II or III is the replacement of the two methyls in $C_6H_2(NO_2)_3OCH_3NaOCH_3$ by benzyls when the compound is soaked in benzyl alcohol, and the reverse change when the benzyl compound is boiled with methyl alcohol. As under the same conditions benzyl alcohol has no action on methyl picrate, or methyl alcohol on benzyl picrate, it is obvious that the complete replacement of one radical by the other here depends on the structure of the addition-product ; and, whereas formula I gives no reason why the change should proceed beyond the methyl attached to the nitro group, it is easy to see that in a substance constituted like formula II or III any reagent which affected one methyl would act in a similar way on the other, so that the methyl compound would be completely converted into

$$C_6H_2(NO_2)_3OC_7H_7NaOC_7H_7.$$

The inferences drawn in the foregoing discussion may be briefly recapitulated as follows : It is improbable that the sodic methylate is added to the carbon of the benzol ring only. A quinoid formula (II or III) explains the observed facts better than one in which the sodic methylate is added to the nitro group alone (I), but this latter structure is not definitely ex-

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[1] This JOURNAL, **17**, 604.

cluded. Under these circumstances we think it would be premature to contrive names for these colored bodies, or to give structural formulas in the experimental part of this paper. We hope that a continuation of the work, now in progress in this laboratory, will definitely settle the constitution of these colored substances.

EXPERIMENTAL PART.

Preparation of Picryl Chloride.

As the method of making picryl chloride used by us in this work is an improvement on that given by Pisani,[1] we describe it. Twenty-five grams of dry picric acid were mixed with 50 grams of phosphoric pentachloride in a large Erlenmeyer flask provided with an air condenser, and heated on the water-bath until the violent reaction had ceased, and the contents had assumed a very dark-brown color. When cold, the flask was surrounded with ice, and its contents treated with ice-water, care being taken to avoid any considerable rise of temperature. The precipitate formed in this way was filtered out, dried, washed with ether, and crystallized from a mixture of benzol and alcohol to purify it. The advantages in our method are that there is a considerable saving of time, and there is much less danger that the substance will be converted into a tarry decomposition-product, as happens in Pisani's method if the heat runs too high in either the preparation or the removal of the phosphoric oxychloride by distillation.

Action of Sodic Acetacetic Ester with Trinitranisol.

In our first experiment in this direction we prepared our sodic acetacetic ester with sodic methylate, and obtained a red precipitate which gave the following result on analysis:

0.2438 gram substance gave 0.0576 gram Na_2SO_4.

	Calculated for $C_6H_2(NO_2)_3OCH_3NaOCH_3$.	Found.
Na	7.69	7.66

It was evident, therefore, that we had only the color formed from sodic methylate, and that the acetacetic ester took no part in the reaction. In order, then, to obtain an acetacetic ester

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[1] Ann. Chem. (Liebig), **92**, 326.

addition, it was obviously necessary to exclude all alcohol and alcoholates; we accordingly proceeded as follows: To an excess of acetacetic ester mixed with benzol a quantity of sodium in the form of ribbon was added (in our later preparation the amount of sodium used provided 3 atoms of it to each molecule of trinitranisol). After the sodium had disappeared, the liquid thus obtained was added drop by drop to a benzol solution of trinitranisol. It is unnecessary to say that absolute benzol was used in all this work. The first drop imparted a deep vermilion color to the solution, and this color became more and more intense as the reaction proceeded. During the process the mixture was kept cool by surrounding the beaker with ice. After all the sodic acetacetic ester had been added, the liquid was mixed with an excess of anhydrous benzol, which threw down a semi-gelatinous or oily precipitate. This was filtered out, washed with benzol, and pressed upon a porous plate, all these operations being carried on as quickly as possible. The dark-colored dried product crumbled easily into a red amorphous powder of a much darker color than the addition-product from sodic methylate. It was dried *in vacuo* and analyzed with the following results:

I. 0.2376 gram substance gave 0.0740 gram Na_2SO_4.

II. 0.2196 gram substance gave 0.0697 gram Na_2SO_4.

III. 0.1928 gram substance gave 0.0700 gram Na_2SO_4.

IV. 0.2596 gram substance gave on combustion 0.4028 gam CO_2 and 0.1148 gram H_2O. In this combustion the substance was mixed with chromic oxide to drive out carbonic dioxide from the carbonate formed, and was spread out in a long copper boat, which was heated gently and gradually to avoid explosions.

	Calculated for $C_6H_2(NO_2)_3OCH_3(CH_3COCHNaCOOC_2H_5)_3$.	Found.			
		I.	II.	III.	IV.
Na	9.87	10.10	10.28	11.75	....
C	42.91	....	....	....	42.32
H	4.57	....	....	....	4.91

There can be no doubt, therefore, as each analysis is of the product of a separate preparation, that the substance is a definite compound, and is formed by the addition of 3 molecules of sodic acetacetic ester to 1 of trinitranisol. The variation in the percentages of sodium in the different specimens is no more than would be expected, when it is remembered that the product was purified only by washing with benzol.

Properties of the Addition-product of Trinitranisol and Sodic Acetacetic Ester,

$$C_6H_2(NO_2)_3OCH_3(CH_3COCHNaCOOC_2H_5)_3.$$

This substance forms a deep crimson powder, which we have not succeeded in bringing into a crystalline state. It is decidedly stable for a body of this class, keeping for several days in a desiccator, but finally decomposing into a black tar. When heated it is slightly explosive. It dissolves completely in water without decomposition, to judge from the color; is soluble in common alcohol, but gives a turbid solution; on the other hand, it dissolves, forming a clear solution, in methyl alcohol; soluble in acetone; insoluble in benzol, ether, chloroform, carbonic disulphide, or ligroin. Acids decompose it instantly, as was shown by the destruction of the color.

Action of Sodic Malonic Ester on Trinitranisol.

Two grams of trinitranisol dissolved in absolute benzol were mixed with a benzol solution of 4.5 grams of sodic malonic ester prepared by the direct action of sodium on the malonic ester,—that is, 3 molecules of the sodium ester to each molecule of trinitranisol. As the two solutions came together, an intense cherry-red color appeared, with the formation of a thick gelatinous precipitate of the same color, which increased in volume and deepened in color as the reaction continued. After the mixture had stood some time at ordinary temperatures, a large enough quantity of benzol was added to produce complete precipitation, the product was then filtered rapidly, washed with benzol till the filtrate was colorless, pressed quickly on the porous plate, and dried *in vacuo*. This reaction seemed to run more quickly and clearly than the corresponding one with sodic acetacetic ester, giving a purer product, which was very easily handled and washed.

I. 0.2028 gram substance gave 0.0536 gram Na_2SO_4.

II. 0.3027 gram substance gave 0.0796 gram Na_2SO_4.

	Calculated for $C_6H_2(NO_2)_3OCH_3[CHNa(COOC_2H_5)_2]_3$.	Found. I.	II.
Na	8.74	8.56	8.52

Properties of the Addition-product of Trinitranisol and Sodic Malonic Ester,

$$C_6H_2(NO_2)_3OCH_3[CHNa(COOC_2H_5)_2]_3.$$

This substance is an amorphous powder with a deep maroon color. We have not succeeded in crystallizing it. It is one of the most stable bodies of its class, as when exposed to the air it usually remains unaltered for nearly five days; at the end of this time it begins to grow moist, then turns black, and is finally converted into a black powder with a somewhat tarry consistency. When heated it explodes with a slight puff, but with little or no noise; it is, however, apparently stable at as high a temperature as 140°. It dissolves completely in water, forming a clear cherry-red solution; soluble, although more slowly, in ethyl alcohol; completely and quickly soluble in methyl alcohol, but this solution seems to be attended by some decomposition, as a fading of the color was observed; soluble in acetone; insoluble in ether, benzol, chloroform, carbonic disulphide, or ligroin. A few drops of hydrochloric acid added to its aqueous solution changes the red color to yellow instantly, and causes a precipitate which, on filtration, solution in alcohol, and evaporation of the solvent, proves to be a reddish oil containing malonic ester, to judge from the smell, and trinitranisol, since this substance crystallizes out on standing.

As this substance was more stable than most others of its class, we tried the action of ethyl iodide upon it in the hope of replacing the atoms of sodium with ethyl. For this purpose 0.5 gram of the addition-product was heated in a sealed tube with ethyl iodide, at first to 100°, but, as this produced no apparent effect, later to 140° for an hour and a half, and then it was kept at 100° for two days. The contents of the tube were treated with benzol, after the ethyl iodide had evaporated, which gave a red solution and a black residue; the residue was extracted with water, and the extract gave no test for an iodide. It is obvious, therefore, that the ethyl iodide had not acted at all, but that the unmanageable black product was produced by the decomposition of the addition compound.

Action of Sodic Malonic Ester with Trinitrobenzol.

The sodic malonic ester was prepared with sodium alone, benzol was used as the solvent, and the proportions were 3 molecules of the ester to 1 of the trinitrobenzol. As soon as the solutions were mixed, a deep-scarlet, lumpy precipitate was formed ; it was found best, therefore, to add the solution of the sodic malonic ester in small portions at a time with constant stirring. The beaker was cooled by immersing it in ice. The precipitate was washed with benzol until the filtrate was colorless, and then dried on a porous plate and *in vacuo*. Analyses I and II are of 2 different products prepared in this way. As in these preparations and the other similar one described in this paper we had used 3 molecules of the sodium compound to one of the nitro body, there seemed some danger that our products might not be definite compounds, but mixtures of an addition compound containing only 1 atom of sodium, with the two additional molecules of the sodic malonic ester (or the corresponding reagent) precipitated by the large excess of the benzol. This objection to our results did not seem a very important one, because they agreed better with the theoretical numbers than would be probable if this theory were true, but we felt that it was necessary to test it by experiment, and for this purpose repeated the preparation, using 2 molecules of sodic malonic ester to each molecule of trinitrobenzol (1 gram of trinitrobenzol and 1.7 grams of the sodic malonic ester). Analysis III was made with the specimen prepared in this way, and proves that our substances are definite compounds and not mixtures, since it agrees with those prepared with 3 molecules of the sodium ester.

I. 0.2038 gram substance gave 0.0544 gram Na_2SO_4.
II. 0.2154 gram substance gave 0.0590 gram Na_2SO_4.
III. 0.2630 gram substance gave 0.0756 gram Na_2SO_4.

	Calculated for $C_6H_3(NO_2)_3[CHNa(COOC_2H_5)_2]_3$.	Found. I.	II.	III.
Na	9.09	8.66	8.87	9.31

Properties of the Addition-product of Trinitrobenzol and Sodic Malonic Ester,

$C_6H_3(NO_2)_3[CHNa(COOC_2H_5)_2]_3$.

This body has a rich maroon color brighter than that of the corresponding compound of trinitranisol and sodic malonic ester. It is stable for some time if kept dry and cool, otherwise it gradually undergoes decomposition, as shown by its change of color and becoming gummy. In its other properties it resembles the corresponding trinitranisol compound most closely. When treated with hydrochloric acid the color is destroyed, and a thick brownish-yellow precipitate is formed ; by washing this with small quantities of alcohol to remove the malonic ester the trinitrobenzol was recovered in quantity, and recognized by its melting-point, 121°–122°, after crystallization from benzol. As soon, therefore, as the three atoms of sodium are replaced by hydrogen the addition-product splits into its constituents.

Action of Bromine on the Addition-product of Trinitrobenzol and Sodic Malonic Ester.

The addition-product, $C_6H_3(NO_2)_3[CHNa(COOC_2H_5)_2]_3$, was added in small successive portions to a chloroform solution of bromine cooled by immersing the vessel in ice. The color of the solid changed instantly from maroon to white. After the mixture had stood over night, the solid was filtered out and the filtrate allowed to evaporate spontaneously, when it left a thick brownish-red oil, which, after standing two days, deposited crystals identified as trinitrobenzol by their melting-point, 221°, the form of the crystals, and the formation of the characteristic red color with sodic alcoholates. The portion insoluble in chloroform, after thorough washing with chloroform and boiling benzol, proved to be sodic bromide. This experiment does not absolutely disprove the formation of some bromtrinitrobenzol, since a small amount of it might have remained dissolved in the oil from which the trinitrobenzol was deposited, but it shows that trinitrobenzol is one of the principal products of the reaction ; and as this separated from the oil in a nearly pure state, it is very probable at least that no bromtrinitrobenzol was formed.

Action of Acetacetic Ester on Trinitrobenzol.

The product was prepared in the same way as the corresponding addition compound of trinitrobenzol and sodic malonic ester. In this case the precipitate had a deeper red color than that produced with sodic malonic ester, and the reaction ran less neatly. Analyses of three different preparations dried *in vacuo* gave the following results :

I. 0.1865 gram substance gave 0.0623 gram Na_2SO_4.
II. 0.2017 gram substance gave 0.0658 gram Na_2SO_4.
III. 0.2104 gram substance gave 0.0680 gram Na_2SO_4.

	Calculated for $C_6H_3(NO_2)_3[CH_3COCHNaCOOC_2H_5]_3$.	Found. I.	II.	III.
Na	10.32	10.82	10.56	10.47

The addition-product of trinitrobenzol and sodic acetacetic ester is a rich brownish-red amorphous powder darker than the corresponding product from trinitrobenzol and sodic malonic ester. It is fairly stable if kept dry. In its other properties it is exactly similar to the colored substances already described in this paper.

Preparation of the Trisodic Amylate Addition-product of Trinitrobenzol.

To a benzol solution of 1 gram of trinitrobenzol 1.5 grams of sodic amylate were added gradually, care being taken to keep the mixture cool. The proportions are 3 molecules of the amylate to each molecule of trinitrobenzol. A heavy scarlet precipitate was formed as soon as the substances came together ; this was filtered quickly, thoroughly washed with benzol, and dried on a porous plate, after which it was analyzed, with the following results :

I. 0.2596 gram substance gave 0.1070 gram Na_2SO_4.
II. 0.1700 gram substance gave 0.0680 gram Na_2SO_4.
III. 0.3190 gram substance gave 0.1288 gram Na_2SO_4.

	Calculated for $C_6H_3(NO_2)_3(C_5H_{11}ONa)_3$.	Found. I.	II.	III.
Na	12.71	13.36	12.96	13.07

Properties of Trisodic Amylate Addition Compound of Trinitrobenzol, $C_6H_3(NO_2)_3(C_5H_{11}ONa)_3$.

The dry substance is a dark-crimson amorphous powder.

It is remarkably stable for bodies of this class, since it did not change in color, or show any tendency to become moist, even after standing for two weeks in contact with the air. It is soluble in ethyl or methyl alcohol or acetone; very soluble in water; insoluble in benzol, chloroform, carbonic disulphide, or ligroin. The strong acids decompose it at once, giving trinitrobenzol as one of the decomposition-products.

Upon treating trinitrobenzol with sodic methylate or sodic ethylate under the same conditions, products were obtained with the following formulas, if we may judge from the sodium determinations:

$$C_6H_3(NO_2)_3(CH_3ONa)_3CH_3OH,$$

and

$$C_6H_3(NO_2)_3(C_2H_5ONa)_3C_2H_5OH,$$

but as these seem an insufficient foundation for such formulas, we shall postpone the description of these substances until we have collected sufficient analytical data to establish their composition. They are both red, but decompose more rapidly than the amylate, becoming moist and discolored after exposure to the air for a few hours. Heating also decomposes the methylate body, so that the presence of methyl alcohol of crystallization could not be established in this way. The discussion of the conditions under which these tri bodies are formed instead of the mono compounds will also be postponed until it has been thoroughly settled by further experiments.

Attempts to obtain Colored Compounds with other Reagents.

Sodic phenylate, made by adding sodium to an excess of phenol, gave with trinitrobenzol a clear red color, but no precipitate. A similar result was obtained when an alcoholic solution of sodic phenylate was added to a benzol solution of trinitranisol; but this latter coloration does not necessarily proceed from the sodic phenylate, as part of it may have been converted into sodic ethylate by the alcohol.

Sodic hydrate also gives a red color with trinitrobenzol, as was observed by Hepp,[1] but as there seemed little chance of isolating this in a state fit for analysis, we did not attempt to study it.

[1] Ann. Chem. (Liebig), **215**, 359.

The sodium salt of phloroglucine, made by treating an excess of it with sodic hydrate, gave a light-reddish color when treated with a benzol solution of trinitrobenzol, and upon adding an excess of benzol a most uninviting sticky precipitate was formed which it would have been foolish to try to analyze. We doubt whether this colored substance was really a phloroglucine compound, as it is very possible that it was formed from a little sodic hydrate produced by the decomposition of the sodium salt of the phloroglucine.

Benzyl cyanide, treated with metallic sodium, after the slight action with the sodium was finished, was mixed with trinitrobenzol. Upon stirring for a few seconds a deep blood-red precipitate appeared in large quantity; but it was so unstable that even the addition of benzol to wash out the excess of benzyl cyanide converted it into a black, tarry mass, so that we were obliged to give up all idea of analyzing it.

Attempts to obtain Colored Compounds from other Nitro Bodies.

Picramide, $C_6H_2(NO_2)_3NH_2$, treated with a mixture of sodic methylate, methyl alcohol, and anhydrous benzol, gave at once a strongly colored, dark-crimson solution, which deposited a brick-red precipitate; but in collecting it for analysis the substance decomposed as soon as it dried on the porous plate, forming a brownish mass, which later became tarry. We were unable, therefore, to make an analysis.

Trichlorbromdinitrobenzol ($Cl_3 1.3.5.Br 2 (NO_2)_2 4.6$) gives a strong vermilion color with an alcoholic solution of sodic ethylate, as already stated by us in a previous paper.[1]

Dinitrotoluol ($(NO_2)_2 2.4$) melting at 70°.5, gave with sodic methylate a deep vermilion-colored solution, from which a precipitate was obtained with an excess of benzol. A benzol solution of the dinitrotoluol gave with sodic malonic ester a crimson-red solution and a colored precipitate, but both this and the precipitate of the methylate compound decomposed while drying on the porous plate.

Symmetrical dinitroxylol, melting at 93°,

$$((CH_3)_2 1.3.(NO_2)_2 4.6),$$

gave with sodic methylate, after a few seconds, a faint green-

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[1] This Journal, **22**, 58.

ish color, which turned rapidly to a deep purple, and finally became brownish-black. It was evidently, therefore, very unstable. Neither sodic malonic ester nor sodic acetacetic ester gave any trace of color.

Trinitroxylol ($(CH_3)_2 1.3.(NO_2)_3 2.4.6$) gave a deep cherry-red solution with either sodic methylate or a benzol solution of sodic malonic ester or of sodic acetacetic ester. An excess of benzol precipitated from each of these solutions a gummy, reddish body, which decomposed before it could be prepared for analysis. In these cases the decomposition-product had a pinkish-white color.

Neither dinitromesitylene nor trinitromesitylene gave a trace of color after standing with sodic methylate. At the moment the trinitromesitylene was mixed with the sodic methylate we thought in one or two cases we perceived a very faint coloration, but it was so indistinct that we felt doubtful of its existence, and at best it was very evanescent. Sodic malonic ester and sodic acetacetic ester also gave negative results with both these bodies.

Dinitrophloroglucinetriethyl ether, $C_6H(OC_2H_5)_3(NO_4)_2$, gave no color with sodic methylate, sodic malonic ester, or sodic acetacetic ester.

Attempts to Obtain Colored Compounds from Bodies which Contain no Nitro Group.

Pyrocatechin gave no color with sodic malonic ester, but with sodic methylate a bright-green color was formed along the edges, which soon darkened, and finally gave a black oil. This coloration is probably similar to those observed by Kunz Krause[1] on treating various phenols with sodium and alcohol, but we do not feel sure that these colors are related to those obtained from nitro compounds.

Resorcine gave no color with either sodic methylate, sodic malonic ester, or sodic acetacetic ester. The same negative results were obtained with phloroglucine.

Neither trimesic acid, ($(COOH)_2 1.3.5$), nor its ester, $C_6H_3(COOC_2H_5)_3$, gave any sign of sodic methylate, although the experiments were tried with great care, and under condi-

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[1] Arch. Pharm., **236**, 542.

tions which gave colors even with some of the less reactive nitro compounds.

Experiments on the Replacement of the Allyl Radical in the Colored Compounds.

Action of Methyl Alcohol on the Benzyl Compound.—The addition product of benzyl picrate and sodic benzylate, discovered by W. F. Boos and one of us,[1] was heated with methyl alcohol for about half an hour, and the methyl alcohol was then allowed to evaporate at ordinary temperatures. The product consisted of glistening scarlet crystals, which were at once decolorized by hydrochloric acid, yielding a substance melting at 64°, and crystallizing in yellow rhombic plates from benzol. It was therefore trinitranisol, and the methyl alcohol had replaced the benzyl groups in the original addition-compound by two methyls.

Action of Methyl Alcohol on Benzyl Picrate.—Benzyl picrate was prepared according to the method given by Boos and one of us.[2] The melting-point of this substance is 145°, not 115° as given in the paper just cited ; the number 115° was due to a mistake in copying the melting-point from the note-book. A quantity of the benzyl picrate was recrystallized four times from boiling methyl alcohol, and after each crystallization the melting-point remained constant at 145°, thus showing that the benzyl picrate is not converted into methyl picrate by methyl alcohol at its boiling-point.

Action of Benzyl Alcohol on the Addition-product of Trinitranisol and Sodic Methylate.—The colored compound was dissolved in benzyl alcohol with the aid of gentle heat, and the mixture was allowed to stand at ordinary temperatures until crystals separated. The red substance obtained in this way was decomposed with hydrochloric acid, when the product, after crystallization, showed the constant melting-point 145°, and was therefore benzyl picrate. In this case, therefore, the benzyl alcohol had converted the colored methyl compound into the corresponding benzyl compound.

Action of Benzyl Alcohol on Trinitranisol.—A solution of

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[1] This JOURNAL, **20**, 452.

[2] *Ibid.*, 453.

trinitranisol in benzyl alcohol was allowed to stand in a paraffin desiccator until all the benzyl alcohol had evaporated; the residue showed the melting-point of trinitranisol, 64°.

Benzyl alcohol, therefore, does not affect trinitranisol under the conditions used in the experiment described in the last paragraph.

Attempts to Prepare Derivatives from the Addition Compound of Trinitranisol and Sodic Methylate.

Salts.—The sodium salt, $C_6H_2(NO_2)_3OCH_3NaOCH_3$, was treated with the salts of various metals in the hope of obtaining other salts. The chlorides of calcium, barium, mercury, and zinc, in mixed methyla lcohol and aqueous solutions, produced no change. Cupric chloride, on the other hand, formed a brown precipitate, from which trinitranisol was isolated, and tests were obtained for copper and picric acid. We decided, therefore, that the cupric chloride had decomposed the colored compound, and neither this nor any of the other experiments we tried seemed to point to the formation of salts of the colored compounds by metathetical reactions.

Treatment with Benzoyl Chloride.—The addition compound $C_6H_2(NO_2)_3OCH_3NaOCH_3$, if dissolved in methyl alcohol and treated with benzoyl chloride, was at once decolorized, even when sodic methylate was also present. Upon treating the dry compound with benzoyl chloride, and allowing the mixture to stand over night, the amorphous powder had become converted into masses resembling cauliflower, with an even more intense scarlet color than at first. An attempt to introduce the benzoyl group by the Baumann-Schotten method led to a similar result. One gram of the addition-product was added to 25 grams of an 18 per cent solution of sodic hydrate, and then 5 grams of benzoyl chloride were gradually poured into the mixture; the granular red powder was gradually converted into masses resembling cauliflowers, most of which dissolved in the alkaline liquid with a distinct intensification of the red color. On acidifying with hydrochloric acid, the color was discharged and a white precipitate of benzoic acid was formed. The filtrate apparently contained picric acid. Unfortunately we had not time to study this reaction more carefully, but we hope it will be investigated in this laboratory during the coming year, and also that the behavior of this compound with methyl iodide may be studied then.

Postscript.—The manuscript of the foregoing paper was ready for the press, when I received an article[1] on colored compounds of this class by Hantzsch and Kissel, in which they ascribe to them formulas with the sodic alcoholate added to the nitro group only (I). I cannot find any reason in their article for changing the conclusion to which I had already come, that a quinoid formula (II or III) explains all the observed facts better than the formula (I) adopted by them. Their most important new facts are the isolation of the free acid from the addition-product of potassic methylate and trinitrotoluol, and the formation of the corresponding acetyl compound, both of which are explained better by the quinoid formula than by theirs. They also call attention to the fact that the free acid is a weak one instead of being a strong one, as it should be, if derived from a salt with their formula, and that the marked color of the compounds would not be expected from this structure; both of these anomalies disappear if the quinoid formula is adopted. It seems, therefore, that their observations tend to confirm this quinoid formula.

The authors also claim to have disproved definitely the theory of Victor Meyer that these bodies are substitution-products, but neglect to mention that Lobry de Bruyn,[2] in 1895, proved the incorrectness of this theory by treating trinitrobenzol in boiling xylol with sodium. Therefore all subsequent arguments against Victor Meyer's theory (of which I have furnished three) must be considered as only confirmatory of Lobry de Bruyn's work.

It may not be out of place to repeat here that work on this subject is still in active progress in this laboratory.

C. LORING JACKSON.

DECEMBER 27, 1899.

[1] Ber. d. chem. Ges., **32**, 3137 (1899).

[2] Rec. Trav. Chim. Pays-Bas., **14**, 89.

THE SOLUTION-TENSION OF ZINC IN ETHYL ALCOHOL.

BY HARRY C. JONES AND ARTHUR W. SMITH.

The conception of solution-tension of metals was first made use of by Nernst[1] to explain the action of primary cells. The chief seat of the electromotive force of such cells was shown to be at the surfaces of contact of the electrodes with the electrolytes. The magnitude of the potential which is produced when a bar of metal is immersed in a solution of one of its salts, is a function of two quantities: The osmotic pressure of the cations of the dissolved salt, and the solution-tension of the metal in question. These two forces act in opposition to each other; the osmotic pressure of the cations tending to drive these ions out of solution on to the metal, while the solution-tension of the metal tends to drive the metallic atoms off from the bar as ions, which would then remain in the solution.

The result of the reaction of these two opposing forces is to produce around the bar of metal the well-known Helmholtz[2] double layer. The metal atoms passing off into the solution as ions, take positive electricity from the bar of metal which thus becomes negative; the solution into which these cations pass, since it now contains an excess of cations, becomes positive.

The osmotic pressure of the cations, on the other hand, drives cations out of the solution on to the metal, the metal becoming positive due to the charge which it has received from these cations when they passed over into metallic atoms; the solution, having lost some of its cations, becomes negatively charged.

The action which will result in any given case depends upon the relative values of the solution-tension of the metal and the osmotic pressure of the cations of the salt.

There are three conditions possible. If we represent the solution-tension of the metal by P, and the osmotic pressure of the cations of the salt by p, we may have: (1) $P > p$; (2)

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[1] Ztschr. phys. Chem., 4, 129.

[2] Ann. der Phys. (Wied.), 7, 337.

$P = p$; (3) $P < p$. In the first case, where the solution-tension of the metal is greater than the osmotic pressure of the cations, a small part of the metal will pass over into ions, or as we generally say, will dissolve. These ions carry positive electricity from the metal into the solution—the former becoming negative, the latter positive. The negative electricity on the metal would attract, electrostatically, the positive ions in the solution, and a double layer would be formed which would tend to drive the metallic ions out of the solution on to the metal. The attraction between the two parts of this double layer, which tends to drive the metallic ions out of the solution, acts against the solution-tension of the metal, and equilibrium will be established when these two opposing forces are equal.

If $P < p$, the above condition will be exactly reversed. Cations will separate from the solution upon the metal, which thus becomes positive with respect to the solution. The positive charge on the metal attracts, electrostatically, the negative ions in the liquid, and an electrical double layer is formed, but the reverse of the above. Metallic ions will separate from the solution until the electrostatic repulsion of these ions by the positive metal is equal to the osmotic pressure tending to force them out of solution.

In the second case, where $P = p$, nothing will happen. The formula which has been deduced[1] for calculating the potential between a metal and a solution of one of its salts is:

$$\pi = \frac{0.058}{v} \log \frac{P}{p},$$

in which π is the potential, v the valence of the metal, P the solution-tension of the metal, and p the osmotic pressure of the cations in the solution.

It is obvious that this equation can be used to calculate the solution-tension of the metal. It is only necessary to solve for log. P, and determine π and p.

It was supposed for a time that the solution-tension of a metal is a constant, independent of the nature of the solvent

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[1] Nernst: Ztschr. phys. Chem., 4, 129; Ostwald: Lehr. d. allg. Chem., II, p. 851; Le Blanc: Lehrb. d. Elektrochemie, p. 123; Jones: Theory of Electrolytic Dissociation, p. 236.

in which it is immersed. Ostwald states[1] that "The solution-tension of a metal is a constant peculiar to the metal, which depends only on the temperature and generally increases with rise in temperature."

On the assumption that the solution-tension of a metal is a constant, Jones[2] studied the following cell:

$$Ag—\underset{\text{(Aqueous)}}{AgNO_3}—\underset{\text{(Alcoholic)}}{AgNO_3}—Ag.$$

The electromotive force of such an element can be calculated from the following equation:

$$\pi = 0.058 \left(\log \frac{p_1}{P_1} - \log \frac{p_2}{P_2} \right),$$

where p_2 is the osmotic pressure of the silver ions in the aqueous solution, P_2 the solution-tension of the silver in this solution, p_1 the osmotic pressure of the silver ions in the alcoholic solution, and P_1 the solution-tension of the silver in this solution. But since the solution-tension of a metal is a constant, $P_1 = P_2$, everything in the above equation is already known or could be measured, except p_1, the osmotic pressure in the alcoholic solution. It seemed very probable to Jones that he had a general method for measuring dissociation in solvents other than water. It was only necessary to construct a cell using an aqueous solution of a salt of the electrode on one side, and a solution in some other solvent upon the other, in order to measure the dissociation of the salt in the other solvent. But these hopes were soon abandoned.

If the solution-tension of silver is the same in the alcoholic as in the aqueous solution, then the electrode immersed in the aqueous solution must be positive against the electrode in the alcoholic solution, since it was well known that p_2 is greater than p_1. The first point discovered by Jones was that the alcoholic solution was positive against the aqueous. From this it was at once evident that the solution-tension of silver in the alcoholic solution was much less than in the aqueous solution. He then determined the value of the solution-ten-

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[1] Lehr. der. allg. Chem., II, 852.

[2] Ztschr. phys. Chem., **14**, 346.

sion in alcohol as compared with the solution-tension in water. The above equation,

$$\pi = 0.058 \left(\log \frac{p_1}{P_1} - \log \frac{p_2}{P_2} \right),$$

when solved for P_1 becomes :

$$\log P_1 = -\frac{\pi}{0.058} + \log \frac{p_1}{p_2} + \log P_2,$$

if $P_2 = 1$, $\log P_2 = 0$.

Jones measured the electromotive force of a number of cells containing an aqueous solution of silver nitrate on the one side and an alcoholic solution on the other. He calculated the solution-tension of silver in alcohol, using the approximate values for the dissociation of silver nitrate in alcohol which had been furnished by Völlmer.[1] He found that the solution-tension of silver in the alcoholic solution of its salt is about *one-twentieth* of that in the aqueous solution.

Jones has recently attempted to measure more accurately the dissociation of silver nitrate in ethyl alcohol, by means of the improved boiling-point method,[2] which has proved so efficient in other cases. He has, however, not been successful, since silver nitrate in boiling ethyl alcohol always undergoes more or less reduction.

The problem of the solution-tension of metals rested here until quite recently.

Kahlenberg[3] has very greatly extended the work which was begun by Jones. He has used a number of metals as electrodes, and a number of solvents in which the salts of these metals were dissolved, and has entirely substantiated the conclusion reached by Jones, that the solution-tension of a metal is not a constant but varies for every solvent used.

He has not been able to calculate the absolute value of the solution-tension of many of the metals in the different solvents, because he had no means of measuring the dissociation of the salts of these metals in the several solvents. He has calculated the approximate solution-tension of silver in aceto-

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[1] Ann. der. Phys. (Wied.), **52**, 328.

[2] This Journal, **19**, 581; Ztschr. phys. Chem., **31**, 114.

[3] J. Phys. Chem., **3**, 379.

nitrile, and finds that it is greater than in water. Similar results were obtained with silver in pyridine.

Kahlenberg[1] adds that "further attempts to calculate solution-tensions will not be made, seeing that the requisite values of p are not available;" p being the dissociation of the salts in the non-aqueous solutions.

It will be seen from the above that all that has been done, even up to the present, is to determine the relative solution-tensions of one metal—silver—in a very few solvents. Now it so happens that silver stands at one of the extremes of the tension series. It is the metal with the very smallest solution-tension. This will be seen from the following table of metals arranged in the order of their solution-tensions in aqueous solutions of their salts.

	Atmos.		Atmos.
Magnesium	10^{44}	Lead	10^{-2}
Zinc	10^{18}	Copper	10^{-9}
Aluminum	10^{13}	Mercury	10^{-15}
Cadmium	10^{7}	Silver	10^{-15}
Iron	10^{3}		

The relations which obtain for silver with its infinitesimal solution-tension, might not exist for metals with a high solution-tension, and especially for metals with such enormous solution-tensions as those which stand near the head of the first column. It is, therefore, very desirable to determine the solution-tension of some metal high in the tension series, in different solvents, and see what variations obtain.

We have succeeded in doing this in the case of zinc immersed in an alcoholic solution of zinc chloride. The electromotive force of the element,

$$\mathrm{Zn}—\underset{\text{(Alcoholic)}}{\overset{\frac{N}{10}}{\mathrm{ZnCl_2}}}—\underset{\text{(Aqueous)}}{\overset{\frac{N}{10}}{\mathrm{ZnCl_2}}}—\mathrm{Zn},$$

was measured by Kahlenberg[2] and found to be 0.195 volt, the alcoholic pole being positive. To determine the solution-tension of the zinc in the alcoholic solution, we must know the dissociation of the one-tenth normal solution of zinc chlo-

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[1] J. Phys. Chem., 3, 400.

[2] *Ibid.*, 3, 389.

ride in ethyl alcohol. This will be seen from the following equation for the electromotive force of the above cell :

$$-\pi = \frac{0.058}{2}\left(\log\frac{P_1}{p_1} - \log\frac{P_2}{p_2}\right),$$

in which P_1 and P_2 are the solution-tensions of zinc in the alcoholic and aqueous solutions, respectively, and p_1 and p_2 the osmotic pressures of the zinc ions in the alcoholic and aqueous solutions.

In the above equation P_2 and p_2 are known, π was measured, and we must therefore know p_1 before we can calculate P_1.

We have a method for measuring approximately p_1—the dissociation of zinc chloride in ethyl alcohol—at a concentration of one-tenth normal. The boiling-point method which has been improved and used by one of us[1] to measure dissociation, was employed.

The zinc chloride which we used was prepared by distilling a fine sample of zinc chloride in a hard-glass tube through which a stream of hydrochloric acid was passed. This was done to remove any oxychloride which might be present, or which might be formed when the last traces of water were being removed from the zinc chloride. The redistilled zinc chloride was allowed to cool in the glass tube in the stream of hydrochloric acid gas, and was then removed to a desiccator and kept over phosphorus pentoxide. The salt thus quickly lost every trace of the acid gas which clung to it when it was removed from the glass tube.

The ethyl alcohol used was dried first over lime, and after distillation was kept over copper sulphate for several months. A solution of zinc chloride in ethyl alcohol of the strength desired ($\frac{N}{10}$) was prepared, and with this the dissociation of the solution was measured.

The mean of six determination showed that a tenth-normal solution of zinc chloride (by volume) in ethyl alcohol is dissociated 6.5 per cent. It seems probable from our determinations that this is correct to within 1 per cent. Substituting this value of p_1 in the equation :

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[1] *Loc. cit.*

$$-\pi = 0.029\left(\log\frac{P_1}{p_1} - \log\frac{P_2}{p_2}\right),$$

and solving for log P_1, we have :

$$\log P_1 = -\frac{\pi}{0.029} + \log P_2 + \log p_1 - \log p_2.$$

$$P_1 = 1.9 \times 10^{10}.$$

We have calculated the solution-tension of zinc in an alcoholic solution of zinc chloride by a second method. Kahlenberg[1] measured also the absolute electromotive force of the alcoholic side of the above element, by means of a standard electrode, and found it to be 0.327 volt.

The equation for the potential upon the alcoholic side of the cell is :

$$\pi = 0.029 \log\frac{P_1}{p_1},$$

the symbols having the same significance as in the last equation.

$$\log P_1 = \frac{0.327}{0.029} + \log p_1.$$

$$P_1 = 2.7 \times 10^{10}.$$

The values of P_1, calculated by the two methods, agree as well as could be expected. *Hence the solution-tension of zinc in ethyl alcohol equals, approximately, the solution-tension in water divided by* 10^9.

In determining the value of p_1 by the boiling-point method, the assumption is made that zinc chloride in ethyl alcohol is dissociated to the same extent at the boiling-point of the alcohol, as at ordinary temperatures. This assumption cannot be far from true, since it was shown several years ago[2] that dissociation in water, as measured by the freezing-point method at 0° C., agrees very closely with the dissociation as measured by the conductivity method at 18° C.

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[1] *Loc. cit.*

[2] Ztschr. phys. Chem., **11**, 529; **12**, 639.

Contribution from the Kent Chemical Laboratory of the University of Chicago.

NOTES ON LECTURE EXPERIMENTS TO ILLUSTRATE EQUILIBRIUM AND DISSOCIATION.

By Julius Stieglitz.

I. Equilibrium and Gaseous Dissociation.

The prominent rôle played by conditions of ionic equilibrium in solutions of electrolytes makes a thorough presentation of the subject desirable in college courses on general chemistry, and a still more exhaustive study necessary in analytical chemistry. The relative size of the dissociation constants and the influence exerted on the condition of equilibrium by increasing the concentration of one of the dissociation-products are the points most emphasized. It seems desirable to impress these two points on the mind of the student at the stage where the general subject of equilibrium and dissociation is first dealt with, which may, perhaps, be done best in connection with the question of gaseous dissociation, raised, for instance, by the vapor-density determinations of phosphorus pentachloride, ammonium chloride, etc. The following two lecture experiments with phosphorus pentabromide and phosphorus trichlordibromide[1] were developed to illustrate the second of the two points mentioned, the effect of an increase of the concentration of one of the products of gaseous dissociation. The contrast of the tubes showing the dissociation of the pentabromide and the trichlordibromide at 50° may also serve to demonstrate the first point, the influence of the relative size of the dissociation constant or the relative ease of dissociation, in default of substances for which the constants for gaseous dissociation have actually been determined and which could at the same time be used for lecture experiments in general chemistry.

Phosphorus Pentabromide and Phosphorus Tribromide.

The effect of an excess of phosphorus tribromide on the dissociation of the pentabromide is shown by comparing the in-

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[1] Vide Wurtz's work on phosphorus pentachloride, Ber. d. chem. Ges., 3, 572.

tensity of the color of the bromine vapor in two tubes charged as follows :[1]

Sealed bulbs containing 0.029 gram bromine (1 molecule) and 0.058 gram phosphorus tribromide (a little more than 1 molecule) were placed in a piece of thick-walled tubing[2] closed at one end, the tube drawn out to a capillary, the air exhausted to 30 mm. pressure, and the capillary sealed rather close to the tube, the rest of the capillary being bent into a loop. The tube charged in that way was 18 cm. long and had a capacity of 40 cc. By vigorous shaking the bulbs containing the bromine and tribromide were broken. A second tube of the same size was charged with 0.029 gram bromine (1 molecule) and 0.45 gram tribromide (9 molecules). A few coils of lead or fuse wire were wound around the lower part of the tubes.

The tubes, thus prepared, are suspended side by side in a tall beaker of water by means of the glass loops at the upper ends. A glazed white porcelain tile placed in a slightly slanting position behind the beaker makes the comparison of the colors easier. On heating, at 50° only a very slight color appears in the first tube (see below, phosphorus trichlordibromide), none in the second tube. From 80° to 90° the dissociation has progressed to the most favorable stage for comparison ; the first tube shows a more intense color than the second one, which contains the excess of the tribromide, the color of the former being reddish-brown and opaque while that of the latter is reddish-yellow, through which the white of the tile can still be seen.

Phosphorus Trichlordibromide and Phosphorus Trichloride.

The difference in color between the two tubes in the above experiment will be sufficiently evident to most students, but perhaps not quite marked enough for the student whose judgment is still to be developed. By using phosphorus trichlor-

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[1] Instead of using phosphorus pentabromide it was found more convenient to use the tribromide and bromine in molecular proportions, weighed in small bulbs blown at the end of capillaries. The weighing out of the exact quantities required was rapidly accomplished by weighing a bulb both on an analytical balance and on rougher scales. When by means of the latter the amount required in the bulb was very nearly adjusted, the final weighings were made on the sensitive balance, the bulb being placed in a pair of weighing tubes fitting closely over each other.

[2] The ordinary tubing used for heating solutions under pressure.

dibromide[1] with and without an excess of the trichloride greater differences in color were obtained, putting the student in question out of temptation to rely less on his own judgment than on the demands of theory.

Tubes of the same size (40 cc. capacity) were charged as above, respectively with 0.029 gram bromine (1 molecule) and 0.029 gram phosphorus trichloride (0.004 gram more than 1 molecule) and with 0.029 gram bromine (1 molecule) and 0.155 gram phosphorus trichloride (6 molecules); the air pressure in the tubes was reduced to 27 mm. At 40°–55° the difference in the colors of the two tubes is most marked, the first one being dark-brown and the second one yellow.

The influence of the relative size of the dissociation constants or the relative ease of dissociation of phosphorus pentabromide and of phosphorus trichlordibromide is shown by comparing, at 50°, the colors of the tubes containing these substances (the first tube in each series); the former is found to be nearly colorless, while the latter is dark-brown, showing the greater tendency of the trichlordibromide to dissociate.

II. Equilibrium and Electrolytic Dissociation. Ammonium Hydroxide and Solutions of Ammonium Salts (Ammonium Ions).

Lovén[2] has shown that the characteristic action of ammonium salts in preventing the precipitation of magnesium hydroxide by ammonium hydroxide is simply the result of equilibrium changes. The most important of these is the gradual suppression of the hydroxyl ions of the ammonium hydroxide by greatly increasing the concentration of the ammonium ions on adding the easily dissociating ammonium salts, equilibrium being established according to

$$NH_4 \times OH' = k \times NH_4OH.^3$$

This important action of ammonium salts can be demonstrated

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[1] Phosphorus trichlordibromide dissociates at 35° into phosphorus trichloride and bromine (Michaelis: Ber. d. chem. Ges., **5**, 9).

[2] Ztschr. anorg. Chem., **11**, 404.

[3] At the same time $NH_4OH = k' \times NH_3 \times H_2O$; the symbols are used to designate concentrations.

very simply by the following experiment[1] with phenolphthalein; after producing a brilliant red color by adding a drop or two of dilute ammonia to each of two beakers containing water and a little phenolphthalein, a few drops of a rather concentrated solution of ammonium chloride are added to the contents of one of the beakers. The color fades to a scarcely perceptible pink and then disappears.

As ammonium chloride is liable to have an acid reaction ammonia may be added to its concentrated solution until a little of it can be shown to give a faint but distinct pink color to a solution of phenolphthalein—proving that it certainly contains no free acid. On adding a few drops of this somewhat *alkaline* ammonium chloride solution to the crimson solution produced by a drop of ammonia, the red color instantly gives way to a faint pink. This form of the experiment seems to be the most convincing and striking one: the adoption of either form must depend on the advancement of the class.

It may be added that ammonium chloride solutions which react distinctly *alkaline* to litmus (see below) make the red color produced by the action of ammonia on phenolphthalein disappear completely. These experiments are, of course, based on the well-known lack of sensitiveness of phenolphtalein towards hydroxyl ions.

With analytical students the experiment just described may well be followed by a parallel experiment with litmus solution: it is best to use four beakers containing neutral litmus solution; the first is used to preserve the original tint; to the second 5 to 10 cc. of a concentrated ammonium chloride solution are added, which, to avoid the suspicion of acidity, has been made very slightly alkaline; the color in this second beaker changes distinctly towards a bluer violet. The other two beakers are each treated with a drop of quite dilute ammonia, which gives to each a pure-blue tint, and to one of them 5–10 cc. of the solution of ammonium chloride are added,

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[1] The experiment may serve as a particularly simple and pretty illustration of ionic equilibrium in general and as a basis for the discussion of the use of ammonium salts with ammonia in many important reactions of analytical chemistry, *e. g.*, in preventing the precipitation of magnesium hydroxide and many analogous hydroxides, in facilitating the quantitative precipitation of aluminium hydroxide, etc. The simpler form is preferable for general chemistry classes, the use of the slightly alkaline ammonium chloride is more instructive for advanced students.

the color reverting to violet. The change is perfectly plain; but, as litmus is more sensitive to hydroxyl ions than phenolphthalein, the change is not as pronounced as when the latter is used.

Küster[1] has described a lecture experiment to show, by means of methyl orange, the analogous suppression of the hydrogen ions of acetic acid by adding acetate ions in the form of an acetate (*e. g.* sodium acetate), according to

$$CH_3CO_2' \times H = k \times CH_3CO_2H.$$

In consequence of hydrolysis sodium acetate reacts alkaline and the experiment in its original form is, perhaps, open to this objection. A convincing and striking proof of its correctness may be given by using a solution of sodium acetate which, to prevent the suspicion of alkalinity, has been made very slightly acid, giving with methyl orange the well-known reddish-brown hue of beginning acidity. On adding even 2 or 3 drops of this slightly acid solution to a beaker of a methyl orange solution, colored an intense red by a drop or two of acetic acid, the red color is at once replaced by the brown hue of lesser acidity.

CHICAGO, February 19, 1900.

A CONTRIBUTION TO THE KNOWLEDGE OF TELLURIUM.

BY F. D. CRANE.[2]

The rise of the electric refining industry has placed within reach the dross which is produced in large quantities in the final purification of the precious metals, and it is with tellurium from this source that the work here described was done. The process by which the by-product is obtained has been described by C. Whitehead.[3] It contains much silica, tellurium mostly as tellurite, with a little tellurate due to the drying, and some selenium, antimony, arsenic, copper, and

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[1] Ztschr. Elektrochem., **4**, 110.

[2] From the Author's dissertation for the degree of Doctor of Philosophy, submitted to the Board of University Studies of the Johns Hopkins University, June, 1898. The work described was undertaken at the suggestion of Professor Remsen and carried on under his supervision.

[3] J. Am. Chem. Soc., **17**, 849.

other metals. Varying quantities of iron and aluminium and a relatively large quantity of potassium are present.

Extraction of Tellurium.

From this white substance the tellurium is readily extracted by repeated leaching of the powdered material with strong commercial hydrochloric acid. Heating the acid does not appear to be of much advantage. The best results are obtained when large quantities of it are used.

In order to filter the slimy mud at all rapidly, a good pump and as large a filtering surface as possible, should be used. To make such a surface a 3.5 cm. Witte plate is put in a large funnel and covered with a rather thick layer of glass beads. On this is placed a layer of asbestos in the usual manner. This device allows lateral passage of the filtrate, and gives a much larger effective surface than the combined area of the holes of a plate alone.

The bright-yellow hydrochloric acid solution which is obtained is evaporated to a convenient consistency, depending on the use to which it is to be put. It contains considerable quantities of the metals which occur as impurities as well as the tellurium and selenium.

Precipitation of Tellurium.

Since the work of Berzelius the use of sulphur dioxide as a precipitant of tellurium has ordinarily been advised, although it has been known equally long that the action is never quite complete and that traces of other metals, as well as all the selenium, come down also. Its exceeding convenience, however, was a strong reason for its use in the present instance for at least the preliminary precipitation. It was found that, in all probability, the main reason for the incompleteness of its action is the very rapid increase in the ratio of acid to unprecipitated tellurium in the solution, two-thirds of this being due to the hydrochloric acid set free, and one-third to the sulphuric acid formed.

If these could be removed the precipitation should go on. Evaporation sufficed for the hydrochloric acid, and an additional quantity of tellurium was obtained, but the increase of the sulphuric acid soon stopped the reaction.

The practical removal of the acids by neutralization was then tried, and it was found that the addition of an alkali or alkali carbonate resulted in a renewed precipitation. At this point Mr. R. L. Whitehead advised the use of acid sodium (or potassium) sulphite; and his suggestion was thenceforward followed.

But even with this very efficient reagent the action in the cold is never quite complete. It was found that, if a solution in which neither more acid sulphite nor more hydrochloric acid, added to decompose some of the excess of acid sulphite already present, will produce a further precipitate, is heated to boiling, there is then a further precipitation without any addition of reagents.

It is better to remove the first precipitate before boiling, as the action is then more readily seen. This new precipitate gives the qualitative reactions for tellurium, and differs from the first precipitate only slightly in tint. Its formation is probably due to the decomposition of some alkali tellurate at first formed through mass action. By this means, then, the tellurium was obtained, mixed with selenium and a little of the other impurities.

Precipitation of Tellurium by Magnesium.

In devising a method for the more accurate estimation of tellurium it was found that metallic magnesium would completely precipitate tellurium from a solution of the tetrachloride in hydrochloric acid. The excess of hydrochloric acid should be as small as possible, and a slight excess of magnesium should be added. This latter may be destroyed by vigorous boiling, when it decomposes the water; the magnesium hydroxide is then removed by acidifying very slightly with acetic acid. The well-washed tellurium precipitated by this method seems to be less easily oxidized.

Detection of Tellurium.

The apparent completeness of the action of acid sodium sulphite led to the idea that it would detect small quantities of tellurium and do this more rapidly and efficiently than former methods. To test this, a weighed portion (0.107 gram) of tellurium was dissolved in hydrochloric acid by the aid of as little chlorine gas as possible, and the solution gently heated to expel any excess of chlorine. It was then diluted with a little hydrochloric acid and finally with water to 500 cc. Ten cc. of this solution gave a marked precipitate. Ten cc. were diluted to 110 cc., and as the same quantity of this also gave a strong reaction, the dilution was repeated in a similar manner. An effective surface of about one-half a square centimeter of white filter-paper was used to collect the precipitate, and on this the layer of black tellurium was plainly visible ; the amount present per cubic centimeter of solution being 0.00000214 gram, and the total quantity used being 0.0000214 gram. The presence of tellurium was still discernible when the dilute solution contained only 0.000000214 gram per cubic centimeter and there was present but 0.00000214 gram.

It appears probable that this limit is due simply to the fact that we have here nearly reached the physiological limit of seeing black on white.

Detection of Selenium.

Mr. Edward Keller has recently called attention to the precipitation of selenium by ferrous sulphate,[1] and this reaction was tested in like manner, 0.1139 gram of selenium being weighed out, dissolved, and diluted. The precipitated selenium colored the paper the bright, characteristic red when the dilution was 0.00000207 gram per cubic centimeter, ten times that quantity being used. And at a dilution of 0.000000207 gram per cubic centimeter the precipitate from 10 cc. was more easily seen than that of tellurium at about the same dilution.

Furthermore, the precipitation of selenium at a dilution of 0.00000207 gram per cubic centimeter is independent of the presence of a little more than one hundred times as much tellurium as tetrachloride.

Precipitation of Tellurium by Ferrous Sulphate.

Mr. Keller[2] states that ferrous sulphate does not precipitate

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[1] J. Am. Chem. Soc., **19**, 771.

[2] Keller : *Loc. cit.*

tellurium. The statement is evidently made with respect to a solution of the tetrachloride in hydrochloric acid, and, if only the tetrachloride is present, it is quite true. Ferrous sulphate, however, precipitates tellurium from a solution of the tetrachloride in hydrochloric acid if it has been boiled vigorously for some time, the evaporating acid being replenished; or if it is boiled, heated, or remains for some time in contact, with tellurium.

This seems to be due to the presence of tellurium dichloride. But tellurium dichloride, according to Rose,[1] breaks down in the presence of acids into tellurous acid and tellurium. To test this the two chlorides of tellurium were made, first by the direct action of chlorine on tellurium, and then by the action of this tetrachloride on the proper amount of tellurium. The solution which was obtained by treating the dichloride in the cold with hydrochloric acid gave, to a slight extent, a black precipitate with ferrous sulphate, and a solution made with the hot acid gave it much more markedly.

A mixture of the two chlorides treated with the acid gave a very decided precipitate, and a solution of the dichloride in a strong solution of the tetrachloride in hydrochloric acid, gave it most strongly of all. In all these experiments the known decomposition of the dichloride into free tellurium was prominent and evidently nearly in theoretical quantity, so all the solutions were well filtered before the ferrous sulphate was added.

The actual mass of the precipitated tellurium is small in comparison with the quantity present as chloride, but the deep black color and the very fine state of division produce a very marked effect. The black precipitate collects and settles after a time, and seems to diminish in bulk.

This is no doubt the same sort of change as that which occurs in tellurium precipitated by sulphurous acid or acid sulphite, and that is probably akin to the changes in precipitated selenium and tellurium when heated.

Furthermore, a boiling solution of tetrachloride in hydrochloric acid will dissolve a little tellurium. In order to have the action complete, there must be but little of it, and that in

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[1] Rose: Pogg. Ann., **21**, 443.

a state of fine division. This action may account in part for the apparent diminution of the precipitate just mentioned.

It is hard to keep a concentrated solution of the chloride in a condition in which it gives no precipitate with ferrous sulphate, but it may be quickly brought to such a condition by passing through it a few bubbles of chlorine, the excess of which is soon lost by allowing the solution to stand open a short time.

Purification of Tellurium.

The purification of tellurium in quantity appeared to be a question of getting rid of selenium on the one hand, and of various more metallic elements on the other. And it seemed advisable to do this as simply as possible in view of the uncertainty as to the individuality of the substance.

Suspicion has been cast, at various times, on all methods which require repeated evaporations, distillations, or crystallizations, or in which nitric acid must be removed by prolonged heating. Further, it has been directly alleged that distillation in hydrogen gave a product with a lower relative weight.[1]

The method of Keller works well for selenium, if precaution is taken to prevent a reversal of the action through the mass action of the tellurium tetrachloride on the precipitated selenium, which will be referred to below. But it has the great disadvantage of burdening the solution with iron salts and sulphuric acid, which latter always makes the precipitation of tellurium more difficult.

The method of Stolba,[2] which depends on the reduction of a tellurate in alkaline solution by boiling with glucose, which reduction is claimed to begin and be completed before a similar action with any selenite present, appears to work as described. But in the presence of the excess of glucose and its decomposition products it is very hard to determine the limits of the reactions. Pure tellurium is unquestionably formed at first, but the uniformity of the reaction remained in doubt. This process could doubtless be made to work well, but it was not used, since that to be described seemed simpler.

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[1] Bauner: J. Chem. Soc., **55**, 392.

[2] Stolba: Jahresbericht, 1873, 214.

As only a small fraction of the more metallic elements was carried down by the tellurium, it seemed probable that several precipitations would remove practically all of these. Consequently, it was required to repeatedly convert the precipitated tellurium into the tetrachloride. The direct action of gaseous chlorine on dry tellurium is very rapid, but much heat is evolved, enough, in fact, to volatilize a part of the chloride unless the process is carried on quite slowly. The action of gaseous chlorine on tellurium suspended in strong hydrochloric acid is, on the other hand, quite slow; and rapidly becomes slower as the quantity of dissolved chloride increases, and is very slow if the tellurium is at all compact.

It has long been known that tellurium is much more metallic than selenium, and that selenium is the first to be precipitated by sulphur dioxide. In fact this method has been suggested for their separation. Now it seemed probable that, if the mixed precipitate could be subjected to the action of nascent chlorine, by being made the positive pole of an electrolytic cell containing hydrochloric acid, not only would the tellurium be rapidly converted into the chloride at a low temperature, but also the more metallic tellurium would be first attacked, to the practical if not total exclusion of the selenium.

Preliminary trials on a small scale having shown the rapid action of the nascent chlorine, a larger apparatus was made. This consisted of a 750 cc. funnel with the stem ground square off. In the bottom of the funnel portion was placed a button of commutator carbon about 2.5 cm. in diameter, to which was soldered a small brass nut.

The button was sloped to fit the funnel and jacketed with a doubled rubber tube. Through the stem of the funnel was passed a heavy copper wire, threaded at both ends, and having on the lower end a small nut. The upper end of this wire was screwed into the nut on the button, and the button then drawn down tight by the lower nut acting against the lower end of the funnel stem. This formed the positive pole, the current being taken in on the wire.

The negative pole was formed of a sheet of thin copper of some 30 sq. cm., which was soldered to a convenient wire.

This pole was never in the acid but a moment before the current was on, and was removed at once when it was off, so that it was not attacked by the acid. To prevent the deposition of tellurium, it was inclosed in a little porous cell which was hung on the edge of the funnel. A small automatic drip supplied pure hydrochloric acid just fast enough to keep the surface of the liquid in the cell about 0.5 cm. above that in the funnel, so that there was always a flow of pure acid through the cell away from the negative pole. It was expected that the sloping sides of the funnel would keep the unattacked tellurium always at the bottom, but as the specific gravity of the solution increased, the solid did not sink rapidly enough, so a glass rod, mechanically turned, was put in to act as a stirrer. When somewhat heated from the passage of the current, this arrangement had a very constant resistance of a little more than half an ohm, and, with the current employed, used about 9 amperes.

Practically, every trace of the chlorine liberated was absorbed, and consequently the speed of solution depended directly on the current. The first charge of the cell was not quite all dissolved when it became necessary to stop the action over night, and the entire contents of the cell were removed to another vessel. At the same time a portion of the liquid was taken out and tested for selenium, which was found to be present. Evidently the tellurium was not exclusively or primarily attacked, as some of it visibly remained. The next morning this test was repeated, and no selenium was found. And the reddish color of the selenium indicated that it had been precipitated. This electrolytic chlorine method of solution is very efficient and has the marked advantage of adding no foreign substance. It is the more rapid, of course, the more finely divided the tellurium.

Separation of Selenium by Tellurium.

Further experiments showed that if to a mixture of selenium dichloride, and tellurium tetrachloride dissolved in hydrochloric acid, tellurium is added, or a portion of the tellurium precipitated, and the mixture allowed to stand for some time, or better and much more expeditiously, boiled, all the selenium will disappear from the solution, and will be found in the sediment, with the excess of tellurium. If the action takes place at the ordinary room temperature, the selenium can easily be seen on account of its color, but if heat is used the well-known change to the black form will occur, and it cannot be distinguished from the tellurium.

It can be readily detected, however, by filtering off the black residue and dissolving it in a little hydrochloric acid by the aid of chlorine, when the selenium may be again precipitated. If this reaction is carried on upon a microscope slide, it can be well seen and makes a very pretty effect when magnified to about 80 diameters.

On the large scale it is preferable to heat the solution of mixed chlorides gently just below the boiling-point, and to have the tellurium in as fine a state of division as possible and well mixed with the fluid. To attain both these ends it is advisable to precipitate some of the tellurium, either by leading in a little sulphur dioxide, or adding a little acid sulphite. The turbid liquid which results does not clear for some time by settling.

That this process is complete is shown by the fact that it not only removed selenium from tellurium tetrachloride solutions so completely that none could be detected by the ferrous sulphate test, but also removed selenium completely from a solution of selenium dichloride in hydrochloric acid, previously precipitated tellurium being employed. In this experiment tellurium is found in solution which shows conclusively a replacement or an exchange.

If, on the other hand, selenium is gently heated in a solution of tellurium tetrachloride for some hours, the addition of ferrous sulphate to the filtered fluid will show that a very small part of the selenium has gone into solution. This minute amount may be entirely removed by the treatment with tellurium. This seems to explain the observation that in working with quite large quantities of the mixed chlorides in solution, the action of ferrous sulphate even in excess did not seem to be quite complete if a few hours elapsed before the precipitated selenium was filtered off. But the solution could not be made to take up selenium if there was a little tellurium present, and it was kept well stirred. The phenomenon appears to be, to some extent at least, one of mass action.

In using this process for the removal of selenium, the precipitate, containing the excess of tellurium, is filtered off and redissolved, either by nascent chlorine or by conducting into it, suspended in hydrochloric acid, a stream of that gas. The selenium is then easily removed by ferrous sulphate and the tellurium by acid sulphite. It is well to avoid the use of nitric acid.

The Further Purification of Tellurium.

The logical sequence to boiling the mixed chlorides with tellurium in order to precipitate selenium or any less metallic elements was to boil the precipitated tellurium with a reserved portion of that solution from which it had been obtained, so that any more metallic elements which might have been carried down would be dissolved, and precipitate an equivalent quantity of tellurium. This was done, although several precipitations in the ordinary manner seemed to have already removed those traces of metals which have been previously noted as occurring in the crude material.

The tellurium prepared in this manner has the usual appearance and reactions, and could be completely distilled in a current of hydrogen, leaving only a slight residue of carbonaceous material probably derived from the filter-papers. It was noted that there was very little tendency to form hydrogen telluride with pure, dry hydrogen.

This process should tend to separate the suspected homologue of tellurium of greater relative weight, and although no definite indications of such a substance have been met with up to the present, work will be continued along this line if time and opportunity are found.

Determination of Tellurium.

There has never been any sure method of determining tellurium. Most observers have either determined other elements in the tellurium compounds, or precipitated the tellurium, treated it with nitric acid, and converted the compound thus formed into the dioxide by heat. This has been the most exact method.

But Brauner[1] notes the brown decomposition which Staudenmaier[2] had observed, and further claims that the nitric acid is not wholly driven off before a part of the dioxide is volatilized. A method of avoiding the brown color has lately been given by Norris and Fay,[3] but nothing is said as to the removal of the nitric acid, and there is visible volatilization. But gravimetric determinations by the method about to be described showed that the dioxide prepared by that method was quite pure. However, it is doubtful if nitric acid can be removed without some volatilization.

No volumetric method which does not require a correction term, with the exception of that of Norris and Fay, has been devised. The objections to the direct precipitation and weighing of the tellurium were alleged to be two; that it was not possible to precipitate all the tellurium from an acid solution, and that after precipitation it was oxidized so much in drying that the results were variable.[4]

In view of the extreme delicacy of the acid sodium sulphite as a test for tellurium, it seemed advisable to try it as a precipitating agent in quantitative work. There is no doubt that free acid does prevent the complete action of sulphur dioxide, but there is no evidence that neutral alkali salts in solution do this, if the solution is heated; at least qualitative experiments failed to show such an action. So it is only necessary to add enough acid sulphite to give up soda to the acids present and set free. A slight excess of sulphite does no harm, and an excess of sulphur dioxide is readily removed. After the acid sulphite has been added, it is advisable to let the mixture stand for a time, usually, for convenience, over night, as the precipitate seems to be in better mechanical form when this is done. But the action may be completed at once by heating. At any rate, the liquid with the precipitate still in it should be raised to the boiling-point for a short time. This is to gain two ends: to insure the total

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[1] Brauner: *Loc. cit.*

[2] Staudenmaier: Ztschr. anorg. Chem., **10**, 206.

[3] Norris and Fay: This JOURNAL, **20**, 278.

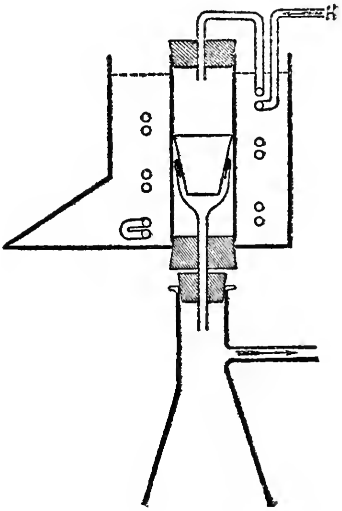
[4] Brauner: *Loc. cit.*; Norris and Fay: *Loc. cit.*

precipitation of the tellurium, which is never quite complete in the cold when large amounts are being handled (as has been noted) ; and to cause some definite but undetermined change in the precipitate. As a result of this it becomes much easier to filter and wash, and less liable to oxidation. This change, as has been said, seems to be like the long-known change in selenium. It is hard to describe, but easily recognized, although it consists only of the merest change in tint and a difference in the manner in which the precipitate settles. The precipitate is then collected on a Gooch filter and very thoroughly washed, care being taken that it always shall be covered with water. If speed is more requisite than exactness, it may now be pumped as dry as possible, quickly dried in an air-bath, and weighed. It will oxidize to some extent, but by no means seriously. The oxidation can easily be detected and the extent of it quite accurately judged by removing the precipitate with the filter surface, after weighing, and putting it in a beaker on a white surface, or in an evaporating dish and moistening it with a few drops of strong hydrochloric acid. A yellow tint of dissolved chloride appears at once only if oxidation has occurred, as unoxidized tellurium does not color hydrochloric acid. But if this preparation is allowed to stand, a color will appear, as the air acts readily on the acid mud. To determine how far this color could be used as a criterion of the presence of oxide and its amount, a weighed portion, 0.0068 gram, of pure tellurium tetrachloride was dissolved in strong hydrochloric acid and diluted. The yellow color of a layer 0.25 cm. thick was plainly visible when 0.00013 gram of tetrachloride was present in each cc.

To see if the method without special precautions in drying was even nearly correct, portions of a pure precipitated tellurium in which very little oxidation had occurred were weighed out, dissolved in a little hydrochloric acid by the aid of chlorine gas and treated as stated above.

Taken. Gram.	Found. Gram.	Gain. Gram.	Recovered. Per cent.
0.1768	0.1779	0.0011	100.6
0.1285	0.1289	0.0004	100.3

Probably practice in its use would make this method exact enough for all practical purposes. From the article by Mr. Keller already referred to, it appears that no special precautions in drying are used at the works of the Baltimore Electric Refining Company.



Device for Filtering.

To prevent, if possible, any oxidation, the filtering crucible was enclosed in a cylinder through which dry, pure hydrogen which had just been passed over hot platinized asbestos was slowly drawn under slightly diminished pressure. The device was so arranged that it was not necessary to remove it from the filter flask, and a T-tube in the pump connection was joined to a mercury safety-valve by which both the pressure and flow were regulated. The cylinder and its contents were heated by jacketing them with a strong solution of calcium chloride, after the manner of a hot-water funnel, and this bath was also used to warm the entering stream of hydrogen.

This arrangement prevents oxidation as far as can be detected by the coloration of hydrochloric acid, and as the results seem quite constant, it probably does not occur to a measurable extent. There is no evidence to show that tellurium, which has been boiled with water, can decompose water in the presence of hydrogen, so that the essential thing is to have pure hydrogen.

The Method.—The entire process is as follows: The given compound is so treated that the tellurium is in the form of the tetrachloride, avoiding, if possible, the use of nitric acid, and as little hydrochloric acid as possible being used. The solution is now diluted with water, but not to such an extent that a white substance appears, although a little of this seems to do no harm. The objection to a larger quantity is mechanical, the interior of the flocculent masses seeming sometimes to be unattacked by the sulphuric acid. A solution of acid sodium or potassium sulphite is now added. It should be moderately concentrated, and the quantity should be such as to neutralize nearly exactly the acids present and set free by the base of the reagent. The excess of sulphur dioxide will escape harmlessly, but anything more than a slight excess of the acid sulphite is detrimental. The mixture, which has turned dark, has been gently agitated during these manipulations; it is now diluted to about 50–75 cc. and allowed to stand for a time as the precipitate thus seems to form more evenly. But it may be warmed at once.

If too much sulphite has inadvertently been added, the precipitate should be decanted and reserved, and the precipitate washed once or twice and the decanted wash-water added to the other, and all this passed through the weighed filter later. The reason for this is that it is very hard to decant without getting some of the precipitate over, although it may remain invisible until it blackens the filter. If time is not a consideration, this decantation process may well be employed in all cases.

The precipitate, in about 75 cc. of water, is now gently warmed, being stirred with a glass rod tipped with a bit of rubber tube, both to prevent "bumping" and to detach those portions which at times form a very marked "mirror" on the sides of the vessel; it is allowed to boil rapidly for a moment or two, and then set aside. A little water may be added, as it aids the settling. The tellurium, which has changed in appearance, should settle very quickly. If it does not, it may be boiled a little more, but it is to be noted that differences in the concentration of the solution in which the precipitation took place may markedly influence the character of the precipitate.

The amount of material taken should be such that the tellurium will form a rather thin layer in the filter even while still wet. The precipitate is now filtered through a weighed filter, care being taken to keep it always covered with water, and well washed, and since there is no reason to suspect any action of the water, the washing should be thorough.

After the washing is completed, the hydrogen supply is connected at once, the last water being followed through the filter by the hydrogen. But no effort need be made to displace the small amount of air in the cylinder.

The temperature of the calcium-chloride bath is now quickly raised to about 110° and kept there till the tellurium is dry. This must be judged from its appearance.

The filter is then removed to a desiccator, and, when cool, weighed. There is no tendency to oxidize rapidly in the air if thoroughly dry. The main danger to be avoided is the accidental access of air to the wet tellurium.

Some of the results obtained by this method are as follows:

Tellurium Dioxide from the Nitrate, $Te = 127.6$; $O = 16$.

Taken. Gram.	Found. Gram.	Required. Per cent.	Found. Per cent.
0.1047	0.0838	79.95	80.03
0.1130	0.0904	79.95	80.00

Tellurium Tetrachloride Distilled in Carbon Dioxide, $Cl = 35.5$.

Taken. Gram.	Found. Gram.	Required. Per cent.	Found. Per cent.
0.3879	0.1857	47.33	47.87
0.5678	0.2717	47.33	47.85

Tellurium Oxychloride, Fused.

Taken. Gram.	Found. Gram.	Required. Per cent.	Fouud. Per cent.
0.62075	0.3689	59.46	59.43

Tellurous Acid, from the Chloride.

Taken. Gram.	Found. Gram.	Required. Per cent.	Found. Per cent.
0.11985	0.0862	71.84	71.92

A Yellow Form of the Dioxide.

If a solution of tellurium tetrachloride in hydrochloric acid which has stood for some time after the selenium has been precipitated by ferrous sulphate and removed, or a similar solution to which ferrous or ferric chloride has been added, is diluted with water, a white precipitate is formed. If this is now allowed to stand for a time, the excess of water being decanted and replaced till it is not colored by the iron, a heavy yellow precipitate will appear. Or if the solution is poured directly into boiling water, the whole mass or precipitate will be colored yellow. The difference in specific gravity is so great that the remaining white substance may be almost completely removed by washing.

This substance is easily soluble in hydrochloric acid, and more difficultly in nitric and sulphuric acids. It is readily and completely dissolved by alkalies and forms a colorless solution without residue. Under the microscope it is seen to consist of more or less regular yellow crystals, of the isometric system, octahedrons, sometimes modified by cubic faces. Among these were traces of a white substance which seemed to cling to the crystals. It appears to be a form of tellurium dioxide, analyses giving the following percentages of tellurium: 79.46, 79.52, 79.51, 79.58, 79.46; calculated for TeO_2, 79.95. The discrepancy may be due to the adherent white substance, or to a little iron, of which a trace may be found by the ferrocyanide and sulphocyanide tests. To this also may be due the yellow color, which is very persistent, not yielding to nitric acid till the substance is all in solution, but the solution is colorless and deposits white crystals.

Decomposition of the Tetrachloride.

If water is added to a portion of the distilled tetrachloride of tellurium, considerable heat is evolved and it passes into solution as a yellow liquid. If more water is added a curdy white substance is formed, which settles and after a time forms the crystalline dioxide. The white substance is tellurous acid, but the wash-water from it constantly contains a trace of chlorine, and there may be a little of some sort of oxychloride present. But if there is also present another metal, as iron, and particularly if antimony or arsenic is present, there is a marked change in the character of the white substance. It remains unchanged in water for days, and may be washed, dried, and redissolved and reprecipitated several times without forming the dioxide ; and no fixed amount of tellurium was found in various samples. It appears to be a double oxychloride, and will be the subject of further investigation, if possible.

Failure to Form Analogues of Thiosulphate.

The attempt was made to form substances analogous to thiosulphates by boiling sodium tellurite with sulphur, selenium, and tellurium, but after several hours no trace of any action could be found.

Instability of the Chlorides.

Many minor observations, as well as those already noted, show that the chlorides of tellurium tend to pass to a slight extent from one to the other. This is especially true of the tetrachloride, which darkens when distilled in dry carbon dioxide. It is to this that the high percentage of tellurium noted above is probably due. And even that distilled in chlorine will give a slight cloud with ferrous sulphate if it has been kept for a time.

Conclusions.

Tellurium may be easily obtained from certain wastes of electric refineries by extracting with hydrochloric acid and precipitating with acid sodium sulphite. Magnesium will also precipitate tellurium, and has some advantages for qualitative work, and also for quantitative. Tellurium may be detected in very dilute solutions by acid sulphite, and ferrous sulphate is equally sensitive with selenium, and is independent of tellurium tetrachloride. But ferrous sulphate precipitates tellurium under some circumstances, probably because some tellurium dichloride is present in the solution.

In order to avoid certain sources of suspected error, and to add nothing but hydrochloric acid as reagent, a method of dissolving tellurium by electrolytic chlorine was devised, and was found to work rapidly and well.

While using this it was found that tellurium would remove selenium. The use of tellurium for this purpose rather than any other reagent is of advantage because it does not add any other elements to the solution, or permit the escape of any portion of the tellurium beyond control. This replacement method may be extended to remove elements that are more metallic.

Tellurium can be estimated by precipitating with magnesium or acid sodium sulphite, boiling, drying in hydrogen, and weighing as tellurium.

The decomposition of the tetrachloride by water is not a simple matter, and becomes much more complex if other metals are present. The pure tetrachloride gives tellurous acid which decomposes to tellurium dioxide.

Contributions from the Chemical Laboratory of Cornell University.

THE CONSTITUTION OF GALLEÏN AND COERULEÏN.

[PRELIMINARY ARTICLE.]

By W. R. Orndorff and C. E. Brewer.

Although galleïn was the first of the phthaleïns discovered by von Baeyer, comparatively little work has been done on it and its derivatives. Baeyer's work[1] established the fact that galleïn is the phthaleïn of pyrogallol, being formed from phthalic anhydride and pyrogallol in accordance with the following equation :

$$C_8H_4O_3 + 2C_6H_6O_3 = C_{20}H_{12}O_7 + 2H_2O.$$

To gallin, the reduction-product of galleïn, Baeyer gave the composition $C_{20}H_{18}O_7$, while to coeruleïn, the product formed from galleïn by the action of concentrated sulphuric acid, he gave the formula $C_{20}H_{10}O_7$, regarding it as formed from galleïn by the loss of hydrogen.

In 1881, after Baeyer had determined the constitution of fluoresceïn and phenolphthaleïn, Buchka,[2] at Baeyer's suggestion, took up the question of the constitution of galleïn

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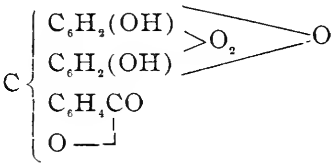
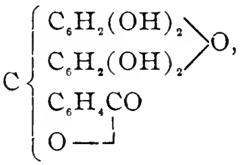
[1] Ber. d. chem. Ges., **4**, 457, 555, 663 (1871).

[2] *Ibid.*, **14**, 1326; Ann. Chem. (Liebig), **209**, 249 (1881).

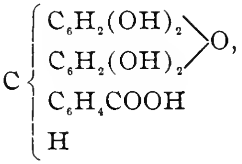
and coeruleïn. He states that galleïn, when reduced in alkaline solution in the cold with zinc dust, gives a product, which he called hydrogalleïn, having *no acid properties* and yielding a tetracetyl derivative *identical with that obtained from galleïn itself.* On further reduction this hydrogalleïn, according to Buchka, gives gallin, having acid properties and being easily converted into the phthalidin, coerulin, by the action of concentrated sulphuric acid. On the basis of this work Buchka asserts that galleïn contains a quinone group and assigns to it the following formula :



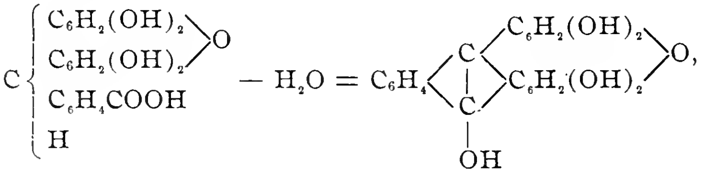
Hydrogalleïn formed by the reduction of the quinone group, according to him, has the following formula :



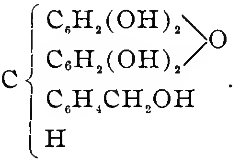
while gallin, the further reduction-product, is a true phthalin :



yielding the phthalidin, coerulin, with concentrated sulphuric acid, thus :

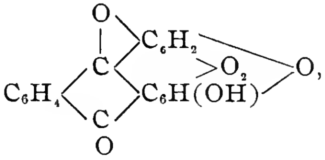


and gallol, on further reduction, to which he gives the formula :



$$C\left\{\begin{array}{l} \left.\begin{array}{l} C_6H_2(OH)_2 \\ C_6H_2(OH)_2 \end{array}\right\rangle O \\ C_6H_4CH_2OH \\ H \end{array}\right. .$$

For coeruleïn Buchka deduces the formula :



as it gives phenylanthracene, when heated with zinc dust, and a triacetyl derivative with acetic anhydride, just as galleïn gives a tetracetyl derivative, by the reduction of the quinone group. No direct evidence of a quinone group in galleïn is given by Buchka. It is assumed to be present, because, according to him, both galleïn and hydrogalleïn give the same tetracetyl derivative, the identity of these products being proved by the fact that they have the same melting-point and give similar results on combustion analyses.

Some three and a half years ago we attempted to make hydrogalleïn and hydrogalleïn acetate in this laboratory by Buchka's method, but to our surprise we found it impossible to obtain these products. We repeated the experiment a number of times, following Buchka's directions to the letter, but always with the same result. The products we obtained were those called by Buchka gallin and gallin acetate. We then found, on looking through the literature, that Herzig[1] records a similar experience. He first made galleïn acetate and found that it melted at 236°–237° C. Buchka gives the melting-point of his product at 247°–248° C. On reducing pure galleïn with caustic potash solution and zinc dust, in the cold, according to the directions of Buchka, he obtained a product having, to be sure, the properties assigned by Buchka to hy-

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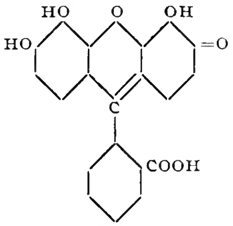
[1] Monatshefte für Chemie, **13**, 426 (1892).

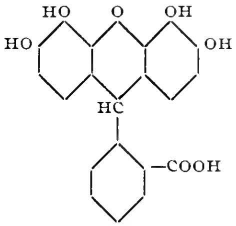
drogalleïn, but with acetic anhydride it gave *not galleïn acetate, but a product melting at 211°–213° C.*, and soluble in caustic potash solution without saponification, whereas galleïn acetate is only soluble in caustic potash solution after saponification. Herzig states that this product is tetracetylgallin, which, according to Buchka, melts at 220° C., though he did not make gallin acetate according to Buchka's method, for the purpose of comparing his product with it, but does call attention to the difference in the melting-points of the two products. Herzig was apparently not quite sure of his results, though realizing their importance for the determination of the constitution of galleïn and coeruleïn, for he goes on to say: "Buchka scheint nach seiner Beschreibung eine grössere Menge des Hydrogalleïns in der Hand gehabt zu haben, und es können daher meine beiden negativen Befunde vorläufig die Existenz desselben nicht in Frage stellen. Allerdings glaube ich, dass die Darstellung des Hydrogalleïns nicht so einfach ist, wie sie Buchka beschreibt und dass noch andere Vorsichtsmassregeln nothwendig sind, die der genannte Autor entweder nur unbewusst eingehalten oder in seiner Arbeit zu erwähnen vergessen hat. Ebenso halte ich es vorläufig nicht für ausgeschlossen, dass die Identität der Acetylproducte des Galleïns und Hydrogalleïns nur auf Grund der Schmelzpunkte ausgesprochen wurde, während sie sich in Bezug auf die Löslichkeit in Alkalien von einander so unterscheiden können wie Acetylfluoresceïn von Acetylfluorescin." With this he leaves the subject.

We had originally taken up the study of galleïn with the idea that we might be able to contribute something to our knowledge of the constitution of the phthaleïns. As, therefore, our results did not agree with those of Buchka on galleïn, we resolved to repeat this work with great care. The Badische Anilin und Soda Fabrik of Ludwigshafen am Rhein, Germany, very kindly supplied us with all the galleïn and coeruleïn which we used in this investigation, and we desire here to express our appreciation of their generosity and keen interest in our work. Our surprise may be imagined when we found that *not only did Buchka's hydrogalleïn and hydrogalleïn acetate not exist, but that the product which he calls gallol* *is in fact gallin.* His hydrogalleïn, gallin, and gallol acetates are absolutely identical in every respect.

By making very careful analyses of the esters and ethers of galleïn and gallin, we have found that the relations existing between these two substances are best expressed by the following structural formulas :

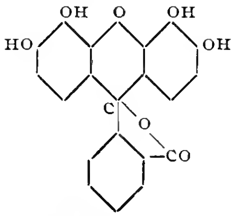


Galleïn.



Gallin.

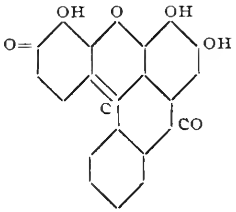
The hydrogalleïn, gallin, and gallol of Buchka are all the same and have the constitution given above for gallin. Galleïn thus appears as the phthaleïn of pyrogallol as originally stated by von Baeyer, while gallin is the corresponding phthalin. That galleïn has the above quinoid formula was shown by making a methyl and ethyl ester by boiling galleïn with the corresponding alcohol and a little sulphuric acid ; by making the galleïn triphenylcarbamate by heating galleïn with phenyl isocyanate; and by making the *colored* tetramethyl and tetraethyl ethers, which are easily saponified by sodium carbonate solution. Galleïn also reacts according to the tautomeric form (lactoid formula) :



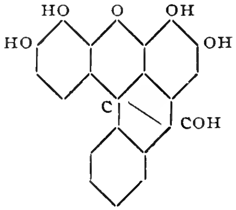
as it gives a *colorless* tetracetate, tetrabenzoate, and tetraphenylsulphonate. It also gives *colorless* tetramethyl and tetraethyl ethers. One particularly interesting derivative is the *colorless* trimethyl ether, which resembles phenolphthaleïn very closely. It dissolves in sodium carbonate or sodium hydroxide solution with a red color, and is precipitated out *colorless* by acids. With acetic anhydride it gives very readily a *colorless* acetate (trimethyl galleïn acetate), insoluble in alkalies. This same *colorless* trimethyl ether results from the saponification of the *colored* tetramethyl ether.

The constitution of gallin was proved by the fact that it gives a colorless tetracetate and pentamethyl ether. The gallin tetracetate has acid properties, as was shown by making a silver salt. The pentamethylether of gallin has no acid properties and is easily saponified.

We next took up the question of the constitution of coeruleïn and coerulin and found that they are best represented by the following structural formulas:



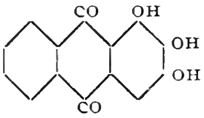
Coeruleïn.



Coerulin.

This was proved by showing that coeruleïn gives a triacetate, easily reduced in acetic acid solution with zinc dust, and coerulin, a pentacetate.

Buchka's statement that coerulin gives a tetracetate is incorrect. Coeruleïn thus appears as a derivative of anthragallol,



which, like coeruleïn, is soluble in alkalies with a green color. This will explain why coeruleïn resembles alizarin and anthragallol in its property of forming insoluble lakes with chromium, iron, and aluminium mordants. The name, alizarin green, by which coerulein is known, recalls this fact, which has been long known to the dyer. The above formula for coeruleïn also serves to recall the aurin group of dyestuffs to which it shows certain resemblances.

Full analytical data supporting the views expressed in this paper will be presented later.

CORNELL UNIVERSITY, ITHACA, N. Y.,
March, 1900.

PERMANGANIC ACID BY ELECTROLYSIS.

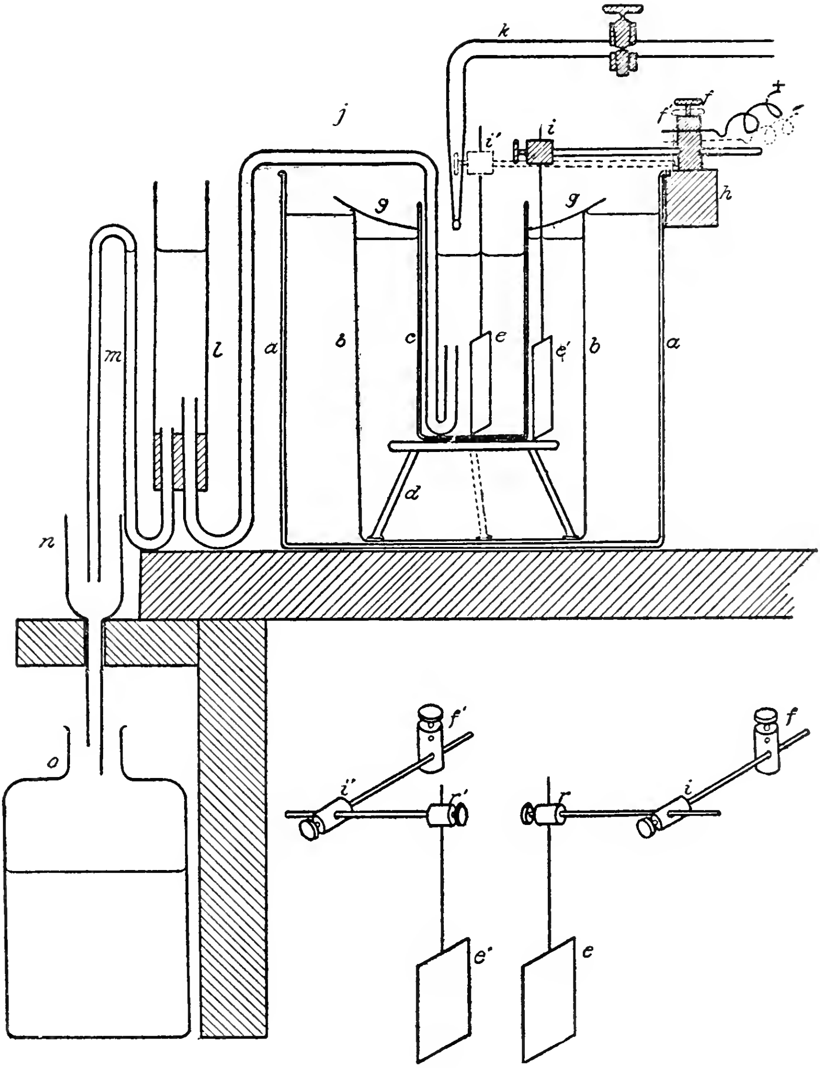
BY H. N. MORSE AND J. C. OLSEN.

In all of the work which has been done in this laboratory on the reduction of permanganic acid by manganese peroxide, the oxide has been prepared by partially reducing an acidified solution of potassium permanganate. But it is well known that the oxide, when precipitated in this manner, always contains a considerable quantity of potassium, and that it is not practicable to obtain an oxide free from alkali by increasing the excess of the acid which is added to the permanganate solution. The action of the oxide thus formed upon the unreduced permanganic acid, which has been the subject of our study, is doubtless influenced by the presence of potassium in the former. For this reason we desired to prepare an aqueous solution of pure permanganic acid, in order that we might obtain from it an oxide free from alkali or other bases. The need of such an acid was especially felt when we proposed to take up a study of the relative effects of equivalent quantities of sulphuric and nitric acids upon the evolution of oxygen which is produced by the oxide in solutions of the acid; for, if the oxide is made by the partial reduction of an acidified solution of the potassium salt, as has been our practice up to the present time, it is impossible to foretell in what proportions the potassium will distribute itself among the three acids; namely, that which is added, the permanganic acid, and the precipitated oxide. Nor is the case any clearer when the oxide is produced in neutral solutions to which an acid is afterwards added.

Two of the methods which have been employed hitherto appeared likely to yield a fairly pure acid. The first is by the decomposition of barium permanganate by sulphuric acid;

and the second, by the solution of the heptoxide in water. We decided to adopt the latter, and accordingly prepared a quantity of the anhydride by mixing potassium permanganate and concentrated sulphuric acid in vessels cooled by ice and salt. We soon learned, however, that something more than a low temperature is essential to safety in handling the product; for a minute quantity of the anhydride—certainly less than half a drop—which had been separated from the sulphuric acid, exploded with great violence and with disastrous consequences to one of us. We were unable to determine with certainty the cause of the explosion, but suppose it to have been occasioned either by accidental contact of the anhydride with some oxidizable matter or by slight friction between glass surfaces. Some idea of the force of the explosion may be gained from the fact that one of the flying fragments of glass passed entirely through a burette which was mounted in the vicinity, leaving holes over half the diameter of the burette, the edges of which were entirely free from cracks. After this experience, we decided to abandon the anhydride as a source of the acid, and to work out, if practicable, an electrolytic method of separating it from its salts. If a solution of a permanganate is electrolyzed in the usual manner, the acid is quickly reduced by the hydrogen which appears at the negative pole. This fact suggested the idea of placing the negative electrode in a porous cup filled with water, and of drawing off the accumulating alkali from time to time by means of a siphon. We pass over our earlier arrangements and preliminary experiments, and give at once the method which has already yielded us several kilograms of the acid in pure condition, and which appears to be adapted to its preparation in any desired quantity, whether for use in the free condition or for the manufacture of its salts.

The accompanying figure represents the apparatus which we employ: *a*,*a* is a galvanized iron tank through which hydrant water flows in order to prevent undue rise of temperature. We have in use two such tanks, each accommodating 5 cells. *b*,*b* is a beaker holding 1800 cc., in which are placed the permanganate solution, the positive electrode *e'*, and the porous cup *c*. The cup has a capacity of about 250 cc. and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rests upon the glass tripod *d*. It contains the negative electrode *e*, and one end of the siphon *j*. The open end of the siphon in the cup is on a level with the upper edge of the electrode. The electrodes are each 50 mm. square and are bent to conform to the sides of the cup ; *e* is of silver and *e'* of platinum. *g* is a large watch-glass with a hole in the center equal to the outside diameter of the cup. It serves to collect and return the spray from the permanganate solution and to protect the latter from the dust in the air. *n* is a square wooden strip which is clamped to the edge of the tank. Into this are screwed the binding posts *f*, *f'*, etc. The arrangement by means of which the electrodes are made adjustable in all directions is more clearly shown in the supplementary figure. *k* is a glass tube with stop-cock through which distilled water is made to flow into the cup at any required rate, the rate depending, of course, upon the frequency with which it is desired to dilute the alkali by emptying the cup to the upper edge of the electrode. *j* and *m* are siphons connected in an obvious manner in the tube *l*. Through this system the alkaline solution in the porous cup empties into the bottle *o*, whenever its level rises above the upper bend in *m*. *m* empties each time completely, while *j* remains always full. The internal diameters of *m* and *j* should be related to each other about as 2 to 3. If they are equal, *m* will empty *l* and itself before the required amount of liquid has passed out of the cup, and will not again act until the cup has been refilled.

The permanganate solution is made as concentrated as the temperature of the hydrant water which flows through the tank will permit. During the winter, the prevailing temperature of the water in the tanks has been from 10° to 11° ; we have, therefore, employed solutions containing 40 grams of the salt in a liter. Owing to the destructive effect of the peroxide on the acid, the solution of permanganate should be filtered through asbestos.

Usually 8 or 10 of the cells described were arranged in series. As the current at our disposal was one of 220 volts, it was necessary to insert additional resistance. For this purpose, we employed 6 110-volt lamps, which were so installed that the current could pass through any number of them in parallel; also so that any number could be thrown into series with any other number. On the average, about 40 per cent of the current was wasted in the lamps.

During the earlier part of the work, the current was broken at night and the cup removed from the permanganate solution. It was soon found, however, that when this was done the acid left in the walls was reduced in the interval, giving rise to a deposit of oxide, which greatly increased the resistance of the cup. In the later work, therefore, the current was uninterrupted from the beginning of an experiment to the end.

The resistance of the individual cells was determined twice daily; but, as it was subject to considerable temporary fluctuation—rising to a maximum whenever the cup was emptied by the siphon, and falling again as the refilling proceeded—the figures here given are to be regarded as having only a very general significance. As a rule, the cells were found to have a low resistance in the beginning, amounting to from 5 to 10 ohms on the first day. On the second day, it would rise to 25 or 30 ohms, only to decline through the third and fourth to perhaps from 10 to 14 ohms, after which the resistance remained fairly constant to the end. When the average of all the observations amounted to less than 13 ohms, the cup was regarded as a good one, though in some cases the average was below 9. The increase of resistance during the second day, and its subsequent decline to a minimum which was thereafter fairly well maintained, were characteristic of every experiment; but we could find no adequate cause for the phenomenon. Occasionally the resistance of a cell would rise much above 30 ohms, and would continue thereafter much higher than that of other cells in series with it. In such cases, the cups were replaced by others. On breaking them, their walls were found to contain a deposit of black oxide, which was always denser immediately between the electrodes than elsewhere.

The cup used by us was the ordinary porous battery cup; but, thinking that greater porosity might have the effect of diminishing resistance, and therefore of economizing current, we had made for us a number of new cups, in some of which the clay was mixed with sand, in others with ground flint, and in still others with pulverized charcoal which was afterwards burned out. All of these were found to be more porous than the battery cups with which they were compared, but, as regards average resistance, they proved to be no better than the latter; while, in respect to yield of acid, the most porous of them were distinctly inferior. Those made from clay mixed with sand were too porous. The alkaline solution which was drawn from them was constantly colored in consequence of the infiltration of permanganate during the time that the cups were only partly filled. Usually, the alkali drawn from the other, less porous, cups was colorless. At times, however, when the refilling of the cups was slow—after having been partially emptied by the siphons—the inner exposed walls of even the less porous cups would take on a pink color from infiltration of permanganate. This was afterwards reduced, giving rise to a deposit of oxide on the walls or on the bottoms of the cups.

To test the relative merits of the old and the new cups, cells containing one of each variety were connected in series and the electrolysis conducted in the usual manner. The results are tabulated below:

	Material of cup.	Degree of porosity.	Average of resistances.	Yield of acid. Per cent.
I	Clay and sand	2.3	16.1	83.8
II	" " "	1.9	13.0	87.9
III	" " charcoal	1.4	12.9	89.4
IV	" " flint	1.3	12.8	90.7
V	Battery cup	1.0	13.2	91.4

The small yield of acid in cells Nos. I and II is probably to be ascribed, in a great measure if not altogether, to infiltration of permanganate. In general, the yield increases as the porosity diminishes. As stated elsewhere, much uncertainty attaches to the figures representing resistance. They are significant only as averages of a considerable number of observations, any one or two of which would have but little value when standing alone. Nevertheless, it is safe to conclude from the values recorded above that the more porous cups are not to be preferred because of their smaller average resistance. As might be expected, there is a more copious deposit of oxide in their walls, in consequence of which their resistance soon becomes equal to, or even greater than, that of the less porous cups.

It is hardly necessary to add that the battery cups which were examined and used by us differed greatly among themselves in respect to porosity and resistance. Several of them were rejected because of the high resistance which they exhibited even in the fresh state.

To prepare the cups for a second experiment, they were immersed for a long time in warm, rather concentrated, hydrochloric acid, and then kept for several days under small jets of hydrant water. This treatment, when thorough, sufficed to put the cups in nearly as good condition as when new.

A 4 per cent solution of potassium permanganate would yield a very dilute solution of the acid; and, in order to obtain a more concentrated one, more of the salt must be added from time to time as the alkali is drawn into the cup and removed by the siphon. Fortunately for purposes of concentration, the electrolysis is attended in a very striking manner by the phenomenon of "electrical endosmose." With a current varying between 1 and 1.5 amperes, the water passes out of the permanganate solution into the cup; *i. e.*, in the direction of the current, at the rate of about 500 cc. per day of twenty-four hours. By replacing the water thus withdrawn from the beakers by equal volumes of the 4 per cent solution of the salt, we were able to introduce into each cell an additional 20 grams of the permanganate per day; and, accordingly, to increase the concentration of the acid to any required extent. We have not yet ascertained how far it is practicable or profitable to concentrate the acid in this manner. Up to the present time, our strongest acid has not exceeded a ten per cent solution. But apparently the limit of concentration has not been reached, since the percentage yield of the acid has not thus far shown any tendency to decline, as the strength of it increased.

Though the loss of acid during electrolysis is not relatively greater when the stronger solutions are made in the manner described, it appears to be unprofitable to concentrate a weak acid, free from alkali, by means of the "endosmose" referred to. In one experiment in which a 3 per cent acid was concentrated to one of 7 per cent in this way, 10 per cent of the entire amount of the acid was lost; *i. e.*, reduced to oxide.

After discontinuing the addition of permanganate to replace the water drawn inte the cup, two or three days are required to remove the remainder of the potassium. During this time the alkali enters the cup in constantly diminishing quantity and the endosmose becomes less and less marked. It is not necessary, however, to continue the electrolysis until no more alkali can be extracted, for a small quantity of it appears to enter the cup long after the solution without is free from potassium. This alkali is derived from the walls of the cup, where it is probably in combination with the peroxide which is always deposited to a greater or less extent both upon the surface and within the walls.

We employ the following expeditious method for determining at any time the amount of potassium still remaining in the acid, and, consequently, when to discontinue the electrolysis. A dilute filtered solution of potassium permanganate, and a dilute solution of oxalic acid *which is free from any base*, are made. It is not necessary to know the strength of either. Two equal portions of the oxalic acid are measured off and treated with equal volumes of very dilute sulphuric acid. One portion is then titrated with the solution of permanganate and the other with the filtered solution of acid which is to be tested for potassium. A drop of a neutral solution of hydrogen peroxide is added to each solution to destroy the faint rose color, and the excess of acid in both is determined by means of an alkali whose relation to the sulphuric acid is known. Or, the volumes of the permanganate and of permanganic acid which have been found equivalent, by titration against equal volumes of oxalic acid, are measured off, treated with equal volumes of the sulphuric acid, carefully reduced by a neutral solution of hydrogen peroxide, and the excess of the sulphuric acid determined as before. If the permanganic acid is free from potassium, it will, of course, on reduction, neutralize just two-thirds as much of the sulphuric acid as the equivalent quantity of permanganate, and any additional amount which is found to have been neutralized is equivalent to the potassium still in the permanganic acid. The electrolysis has also been followed by titrating from time to time the alkali delivered by the siphons; but it is not practicable to determine, in this way, when the liquid outside of the cup is free from potassium because it is not known how much of the acid has been reduced to oxide, or how much alkali the oxide has carried down with it. In general, however, the deficit of the extracted alkali has been found to be approximately equivalent to the loss of acid.

The yield of acid has usually been from 87 to 92 per cent of the theoretically possible amount. In two cases it reached 94 per cent. The loss is due to various causes, some of which will doubtless be partially remedied after further and closer study of the conditions which control them. The greatest source of loss is the reduction of the acid to oxide, which takes place within and upon the walls of the porous cups, and also inside of them. Of the two, the former is the more serious because of its effect on the resistance of the cups. Very little oxide is found on the bottoms of the beakers when care has been taken to protect the solutions from the dust of the air. Some of the acid spatters upon the covering glasses and works its way by capillary action to the upper side, where it is reduced to oxide in contact with the air, or by the oxide previously deposited upon the glass. Another source of loss is the retention of the acid by the walls of the cups when they are removed at the close of an experiment. In two instances this was extracted and determined, and found to amount to about 3 per cent of the acid left in the beakers.

When permanganic acid is made in the manner here described, several days must elapse before a moderately concentrated solution (9 or 10 per cent) can be obtained. The last of the alkali is extracted very slowly and with a large expenditure of current. These considerations led us to try the plan of placing both electrodes in porous cups. It was foreseen that such an arrangement would give us a fairly concentrated acid within a short time, and one which would probably be free from potassium; but it appeared to be doubtful whether the change would prove economical, inasmuch as the introduction of a second cup would increase the resistance of the cell. We have tried only one cell of this kind, but so far as we can judge from the results with it, the introduction of the second cup is advantageous. Both cups were filled with water and allowed to stand until the walls were thoroughly saturated. They were then placed in the 4 per cent solution of permanganate and the electrodes introduced. The endosmose affected only the cup containing the negative pole. Into this the water was forced at about the same rate as when one cup was used, while the level of the liquid in the acid cup remained very nearly constant. The water which passed from the outer vessel into the alkali cup was replaced, as usual, with fresh portions of the 4 per cent permanganate solution. At the end of each twenty-four-hour period, the liquid in the acid cup was withdrawn and titrated for permanganic acid and potassium, and the cup was refilled with water. This was continued for three days. The acid was found to be free from potassium and to contain no suspended oxide. The walls of the cup from which it was taken were also free from any deposit of oxide. The volume of the liquid withdrawn at the end of each day, its concentration, the weight of the acid, and also the average current are given below :

	Volume. cc.	Weight $HMnO_4$. Grams.	Concentration. Per cent.	Average current. Amperes.
1st day	235	14.280	5.95	1.44
2nd "	228	13.068	5.73	1.15
3rd "	230	16.491	7.17	1.73

The yield per ampere-hour was :

	Gram.
1st day	0.397
2nd "	0.473
3rd "	0.397
Three days	0.422

The average resistance of the cell for the three days was 14 ohms. At the close of the experiment, the free acid remaining in the liquid outside of the cups was approximately determined and found to be nearly equal to that which had entered the cup.

For purposes of comparison, we give the yield of acid per ampere-hour and the average resistance in several other experiments in which only one cup was employed :

Acid per ampere hour. Gram.	Average of resistance. Ohms.
0.332	9.6
0.335	10.5
0.340	9.9
0.253	10.7
0.266	10.0
0.271	9.7

A similar experiment was made on the electrolysis of a 5 per cent potassium dichromate solution in a cell with two porous cups. It was not, however, carried very far, and we have at hand only the data which were recorded during the first two days. For this time, with an average resistance of 18 ohms and an average current of 1.3 amperes, the yield was 0.551 gram of chromic acid per ampere hour. The concentration of the acid when the portions withdrawn at the end of each twenty-four hour period were mixed was 8.59 per cent. The absence of any considerable quantity of potassium was roughly demonstrated by evaporating a measured volume of the solution to dryness and heating the residue to constant weight at 150°. The weight of the residue differed only about 1 mg. from that calculated for the trioxide, CrO_3, which had been found by titration in an equal volume of the aqueous acid.

Our work up to the present time is to be regarded as preliminary only. Much remains to be done in order to ascertain the most economical conditions of the electrolysis—how far it is profitable to concentrate the alkali around the negative, and the acid around the positive pole, the effect of temperature on the decomposition of the acid, etc. Enough has been accomplished, however, to show that the electrolytic method is a practicable one for the preparation of permanganic acid in the laboratory. Potassium permanganate is the only salt of the acid which has hitherto been available in sufficient quantities for ordinary use in the laboratory ; and this, owing to its very moderate solubility, fails often to accomplish all that could be desired of it as an oxidizing agent ; and its use involves the introduction of potassium, from which it is frequently difficult to separate the products of the oxidation. Many of the other permanganates, however, like those of strontium, calcium, magnesium, zinc, and cadmium, are extremely soluble in water, and in their concentrated solutions they are violent oxidizing agents. It is to be hoped that by suitable dilution of these, any desired degree of efficiency may be secured. At 18°, the strontium salt is soluble in one-third its weight of water, giving a concentration of active oxygen in solution which has probably not been available up to the present time. The permanganates of calcium and magnesium appear to be still more soluble than that of strontium. Even the very dilute solutions of the acid act readily upon the carbonates and oxides of the metals, so that there is no difficulty in the preparation of solutions of the salts. Many of these, though not all of them, can be concentrated on the water-bath to the crystallizing-point without serious loss, provided the solutions are freed from oxide in the beginning by filtration, and are protected during evaporation from dust or other substances which can start the formation of oxide.

We are now engaged in an attempt to ascertain whether it may not be generally practicable to determine carbon in organic compounds by burning them in more or less concentrated solutions of the very soluble permanganates, and, perhaps, by use of moderate quantities of sulphuric acid, to combine the determination of nitrogen with that of carbon.

The Conductivity of Permanganic Acid.

The conductivity of permanganic acid has been determined by E. Franke[1] and J. M. Lovén.[2] The latter prepared his acid—which he states was free from sulphuric acid—by dissolving the anhydride in water; while that used by the former was apparently made by decomposing the barium salt with sulphuric acid. The results of the two observers appeared to differ to an extent which justified a redetermination with acid made by electrolysis. For the preparation of this we decided to electrolyze the silver, rather than the potassium, salt; because it is somewhat easier to detect a trace of silver than of potassium, and because we had observed that the acid derived

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[1] Ztschr. phys. Chem., **16**, 476.

[2] *Ibid.*, **17**, 374.

from the potassium salt, when reduced and evaporated, gave in the flame a slight reaction for the metal, even when the titration showed it to be free from alkali.

In order to avoid a possible contamination of the acid through contact with glass, we substituted a large platinum dish for the beaker which was used in other experiments, making this the anode. Silver permanganate is soluble in 183 parts of water at 0°, in 107.5 at 15°, and in 59.2 at 28°.5; hence our saturated solution contained but little of the salt, and the concentration of the acid proceeded very slowly, notwithstanding the fact that the electrical endosmose is much stronger in a case of a saturated solution of silver permanganate than in that of a saturated solution of the potassium salt. The water entered the porous cup at the rate of about 50 cc. per hour, and at the end of thirty-four hours we had 4.511 grams of the acid entirely free from silver. The volume of the solution was 585 cc. This was filtered through asbestos and used in the determination of conductivity. The measurements were made at 25°. The concentration of the acid was determined with great care by means of pure potassium tetroxalate and with calibrated apparatus; the cells were standardized with a specimen of potassium chloride which had been repeatedly crystallized and frequently used for the same purpose; and, in general, every reasonable precaution was taken to insure the correctness of the results. These, it will be seen by the table given below, agree very much more closely with the results of Lovén than with those of Franke:

	M. and O.	Lovén.	Franke.
v.	μ_v.	μ_v.	μ_v.
2	....	315	....
4	....	332	....
8	....	348	....
16	352.3	354	....
32	361.2	361	....
64	371.6	368	345.2
128	375.0	373	346.6
256	374.7	378	346.1
512	376.6	378	343.9
1024	377.3	376	342.8

ON CHLORINE HEPTOXIDE.

By Arthur Michael and Wallace T. Conn.

The marked increase in stability shown by non-metallic oxides and acids with increment of oxygen led us to reinvestigate perchloric acid, with a view of preparing its anhydride. For this purpose a pure acid is necessary, and as the product prepared according to the directions given by Roscoe[1] is somewhat impure, and can be obtained in this way only with a great loss of material, we modified the method by heating the perchlorate and sulphuric acid in a vacuum. Portions of 25 grams of salt and 100 grams of sulphuric acid (of about 1.839 specific gravity at 15° C.) were brought into a fractionating flask[2] whose low lateral tube is connected with a second flask placed in a freezing-mixture, and heated under 10–20 mm. pressure in a paraffin bath. The reaction starts at about 90° C., and perchloric acid begins to pass over when bubbles are noticeable. The heating should be gradual to prevent frothing. In about an hour the bath may be raised to 160°, and it is kept at that temperature until all the perchlorate is dissolved, the operation usually taking about two hours. It was found impossible to decompose all the perchlorate, as the process becomes reversible towards the end, and 1.5–2 grams of salt are easily regained from the cooled contents of the flask. The crude acid contained traces of sulphuric and hydrated perchloric acids, which were removed by a subsequent fractionation of the freshly prepared substance in a vacuum. The yield was 85–90 per cent of the theory, if allowance was made for the regained salt.

The acid was usually very slightly colored and differed in some of its properties from the substance described by Roscoe. Under 11 mm. pressure its vapor heated a thermometer to 19° C. In a glass-stoppered bottle the colorless oil colored on standing, even when kept from light, and after three weeks

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[1] J. Chem. Soc., **16**, 82.

[2] The neck of the flask was contracted and the air-tube fitted in tightly by means of asbestos paper, which was covered by a piece of rubber tubing; a similar joint was used between this flask and the receiver. Attached to the air-tube was a P_2O_5 drying-tube, and between the receiver and manometer a calcium soda lime tube.

was quite dark, but this sample did not explode, although it was kept several months. In contact with paper or wood it exploded with a slight blue flame, carbonizing but not igniting the material. In small amounts it could be mixed with well-cooled absolute alcohol without explosion, apparently with ester-formation, as was also the case when dry ether was used. To 5 grams dry benzene, placed in a freezing-mixture, 1 gram acid was added and the cooled tube sealed. The acid dissolved, forming a green solution, which soon deposited a carbonaceous substance, increasing in amount until the green color disappeared. The tube opened under slight pressure and no free acid could be detected in the solution. Iodine dissolved in the well-cooled acid, using the proportion of 0.5 atom to 1 molecule, to form a dark solution, which, exposed to bright light, gradually changed into an almost white substance. The tube opened under slight pressure, and the gas contained a little chlorine. On heating the substance gave off iodine, leaving a white body, which, after dissolving in water, showed tests for iodic acid.[1]

The most interesting behavior of perchloric acid is towards phosphorus pentoxide, and to perform this experiment successfully it is necessary to adhere strictly to the following directions: In a small, glass-stoppered retort, connected with a drying-tube filled with phosphorus pentoxide and placed in a freezing-mixture of ice and salt, 10 grams of phosphorus pentoxide are brought and, by means of a long tube which is bent inward and contracted at the delivering end and has a rubber ball attached to the other end, not more than 10 drops of perchloric acid are added, waiting ten minutes before adding a second portion. It is advisable to allow the acid to drop on the sides of the retort, and the temperature of the freezing-mixture should be kept below —10° C. The retort, left in the freezing-mixture, is allowed to stand for a day, then connected with a well-cooled receiver, and slowly warmed in a water-bath to 85° C., when the new oxide passes over. The product ob-

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[1] In the last number of the Annalen (**310**, 369), which we have just received, Vorländer and von Schilling describe a similar method of preparing the acid, although their yield is not as favorable as ours. Their acid also appears to be somewhat more explosive, which may be due to their using a perchlorate not entirely free from chlorate.

tained in this way is practically pure and may be used for the experiments described below, but the freshly prepared substance may be redistilled under ordinary pressure without danger, when it passes over at 82° C. (corr.). It should be well borne in mind that, even though the above directions for preparing the crude oxide are followed, the apparatus may be virtually pulverized by a violent explosion, and that the personal precautions necessary for work of this kind must be always observed.

Chlorine heptoxide is a colorless, very volatile oil, that on standing a day begins to turn yellow, after two or three days is greenish-yellow, with the liberation of a greenish gas. In comparison with the previously known oxides of chlorine it shows a remarkable stability and, although when brought in contact with a flame, or by a sharp percussion, it explodes with great violence, it may be poured on paper, wood, or similar organic matter with impunity, the oxide simply volatilizing in the air. Brought into a well-cooled tube with some stick sulphur and the tube corked, no reaction occurred, even after standing several days; and what is a more striking evidence of its stability, it may be poured on a cooled piece of phosphorus and remain for some days without being attacked. With cold water it sinks to the bottom of the vessel and passes slowly over into perchloric acid, but in a closed vessel it requires some days' standing before the peculiar odor of the oxide has disappeared. Dry and cooled benzene dissolves the oxide, and after a short time a reaction ensues. With iodine a reaction occurs slowly in the dark, more rapidly in the light, with liberation of chlorine and formation of a white solid. This substance begins to decompose at 380° C., forming iodine and oxygen, and apparently represents the heptoxide of iodine. Bromine, under similar conditions, is without action.[1]

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[1] It is proposed to examine the behavior of concentrated solutions of chloric and bromic acids towards P_2O_5. The stability of chlorine heptoxide may be explained on lines similar to those which I (J. prakt. Chem. [2], **60**, 328) have given for carbon tetrachloride. This subject, which has a very important bearing on chemical affinity and on valency will be more fully discussed in a later paper. A. M.

OBITUARY.

DR. GUILLAUME LOUIS JACQUES DE CHALMOT,

a former contributor to this JOURNAL, died October 9, 1899. Dr. de Chalmot was born in Holland. He studied chemistry at the Realschule and afterwards at the Agricultural College at Wageningen. He then went to Germany and in 1891 he received the degree of Ph.D. from the University at Göttingen. He came to America soon thereafter, and took up research work in the laboratory of the Johns Hopkins University. In a few months he accepted a position as assistant chemist in the Agricultural Department of the State of Virginia at Richmond. In 1895 he became chemist of the Willson Aluminum Co. and took up the problem of calcium carbide and acetylene. His work was markedly successful both in the technical and purely scientific directions. At the time of his death he was general manager of the Willson Company. I. R.

NOTES.

Gadolinium.

In the Zeitschrift für anorganische Chemie, Vol. **22**, Number 5, C. Benedicks presents a contribution to the knowledge of gadolinium. The author gives a brief historical sketch of this element with some remarks in regard to the doubts that have been expressed as to its elementary nature.

The oxide of gadolinium was first isolated from samarskite in 1880 by Marignac, who designated it temporarily by the letters *γα*. It was again obtained in pure condition in 1890 by Lecoq de Boisbaudran, who had previously, with Marignac's consent, named the element gadolinium. It was likewise obtained quite pure, in 1892, by Bittendorf during his researches upon the earths of the cerium and yttrium groups. In 1896, Demarcay obtained gadolinium nitrate from a mixture of the nitrates of gadolinium and samarium.

Some doubts have been expressed in regard to the right of gadolinium to be classed among the elements. In 1881, Delafontaine stated that Marignac's *γα* was a mixture of the oxides of terbium and decipium. In 1885, Cleve showed that this position was untenable.

In 1886, from a study of the phosphorescent spectrum of gadolinium oxide, Crookes concluded that this so-called element must be regarded as consisting of at least three components. A similar statement, however, was made in regard to yttrium, but this conclusion was proved later by Lecoq de Boisbaudran to be erroneous, he having shown that pure yttrium oxide gives no phosphorescent spectrum, but that such a spectrum is produced by the presence of a small quantity of kindred oxides. The author thinks that the same remarks can be applied to Crookes's conclusion as to gadolinium, since the manner of purifying the substance is not indicated.

In 1896, Demarcay isolated what he considered to be a new earth, designating the element Σ, and believing it to be one of the constituents of gadolinium. But the author states that the previous work of Lecoq de Boisbaudran on the spectrum of gadolinium and his own atomic weight determinations prove that the oxide of gadolinium can be obtained free from Demarcay's Σ.

The best method of preparing the oxide is as follows: The weaker bases are first removed by partial decomposition of the nitrates. The material is then subjected to fractional crystallization from concentrated nitric acid, thereupon to fractional precipitation with dilute ammonia, and afterwards to a final fractional crystallization from concentrated nitric acid. The nitrate is readily converted into the oxide.

The average of six atomic weight determinations, made by converting a weighed quantity of the oxide into the sulphate, gives for gadolinium the value 156.38. Bettendorf, who has also determined the atomic weight from very pure material, has formed for it the number 156.33.

By means of a Salet tube in connection with an induction coil with a long spiral wire, a beautiful spectrum consisting of bands and bright lines can be obtained without difficulty.

The salts are easily prepared from the oxide, which has the composition Gd_2O_3, many of them crystallizing in forms so large and perfect as to admit of exact measurement. The following is a list of those prepared by the author:

Gadolinium chloride, $GdCl_3 + 6H_2O$.
Gadolinium bromide, $GdBr_3 + 6H_2O$.
Gadolinium platinic chloride, $GdCl_3.PtCl_4 + 10H_2O$.
Gadolinium aurichloride, $GdCl_3.AuCl_3 + 10H_2O$.
Gadolinium platinocyanide, $2Gd(CN)_3.3Pt(CN)_2 + 18H_2O$.
Gadolinium nitrate, $Gd(NO_3)_3 + 6\frac{1}{2}H_2O$.
Gadolinium nitrate, $Gd(NO_3)_3 + 5H_2O$.
Gadolinium sulphate, $Gd_2(SO_4)_3 + 8H_2O$.
Gadolinium potassium sulphate, $Gd_2(SO_4)_3.K_2SO_4 + 2H_2O$.
Gadolinium selenate, $Gd_2(SeO_4)_3 + 10H_2O$.
Gadolinium selenate, $Gd_2(SeO_4)_3 + 8H_2O$.
Gadolinium potassium selenate, $Gd_2(SeO_4)_3.3K_2SO_4 + 4H_2O$.
Acid gadolinium selenite, $Gd_2(SeO_3)_3.H_2SeO_3 + 6H_2O$.

Gadolinium ethylsulphate, $Gd(C_2H_5SO_4)_3 + 9H_2O$.
Gadolinium vanadate, $Gd_2O_3.3V_2O_5 + 26H_2O$.
Basic gadolinium carbonate. $Gd.OH.CO_3 + H_2O$.
Neutral gadolinium carbonate, $Gd(CO_3)_3 + 13H_2O$(?).
Gadolinium oxalate, $Gd_2(C_2O_4)_3 + 10H_2O$.
Gadolinium acetate, $Gd(C_2H_3O_2)_3 + 4H_2O$.
Gadolinium propionate, $Gd(C_3H_5O_2)_3 + 3H_2O$.

Special attention is called to the fact that the double cyanide, $2Gd(CN)_3.3Pt(CN)_2 + 18H_2O$, is isomorphous with the corresponding double cyanides of yttrium and erbium, while the sulphate, $Gd_2(SO_4)_3$, is likewise isomorphous with the corresponding yttrium sulphate.

While nothing definite can be said in regard to the position of gadolinium in the periodic system, the author thinks it probable that it will find its place in the eighth horizontal series of Mendeléeff's scheme. W. M. B.

On Inorganic Ferments.

A paper has recently appeared by G. Bredig and R. Müller von Berneck[1] under the surprising title of "Inorganic Ferments." We have hitherto been accustomed to regard fermentation as peculiar to, and produced only by, organic living matter; but these authors point out very close analogies between the action of certain inorganic substances and the organic ferments. There are many reactions effected by organic ferments, which are also brought about by finely divided metals, oxides, etc. Take the following as an example, alcohol is oxidized to acetic acid by the oxygen of the air, not only by means of the ferment *mycoderma aceti*, but also by finely divided platinum.

To discover any relations which may exist between the action of ferments and inorganic substances, it is desirable to find some reaction which is effected by both classes of substances. The reaction must then be studied in every possible manner, when brought about on the one hand by the ferment, and on the other by the inorganic substance. Such a reaction is the following:

$$H_2O_2 = H_2O + O.$$

This reaction is produced by organic ferments in general, and also by finely divided metals and oxides. The authors study this reaction in detail as it takes place in the presence of finely divided platinum. To prepare the colloidal solutions, so-called, of the metals, the older method of reducing a salt of the metal is not used, but an electrical method is em-

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[1] Ztschr. phys. Chem., **31**, 1258 (Jubelband für van 't Hoff).

ployed. Pseudo solutions, generally called colloidal solutions of platinum, iridium, palladium, silver and gold can be prepared by making bars of the metal the poles of a current, immersing the poles in water, and bringing them sufficiently close to produce an electric light under the water. The metal is torn off in a very fine state of division and forms a dark-brown pseudo solution in the water. A pseudo solution of platinum was thus prepared in very pure water. When examined under a high-power microscope the solution appeared perfectly homogeneous, which shows the very fine state of division of the metal. The platinum in the solution could be determined by boiling with concentrated hydrochloric acid, when it clotted and settled to the bottom.

The action of the pseudo solution of platinum, above described, on hydrogen dioxide was then studied. It was found, from the velocity of the reaction, that it is of the first order in neutral or weakly acid solution, which means that it is a monomolecular reaction. This is analogous to the action of ferments.

The second point investigated was the amount of the platinum solution required to decompose the hydrogen dioxide. It is characteristic of the action of ferments that a very small quantity is capable of bringing about a large amount of decomposition. It was found that a gram-atomic weight of platinum in 70,000,000 liters of water accelerates the decomposition of hydrogen dioxide to an appreciable extent, and can decompose, relatively, an enormous amount of the dioxide. Other inorganic substances, such as manganese dioxide and lead dioxide have the same property.

The action of ferments can be modified by change of conditions such as temperature, presence of foreign substances, etc. The action of the platinum is affected by change in temperature, by the presence of electrolytes, by the concentration of the solution, etc.

But the most striking analogy between the action of ferments and that of the platinum is the following: It is well known that a very small quantity of certain substances is capable of poisoning the organic ferments and entirely destroying their activity. The poisonous action of hydrocyanic acid and other molecules and ions, on organic ferments, have been studied quantitatively, and the most striking result is the almost infinitesimal quantity of the poison required to destroy the characteristic action of the ferment, and even the ferment itself.

It is shown by Bredig and von Berneck that the platinum solution can also be poisoned by minute traces of certain substances, so that it will no longer have the same power to decompose hydrogen dioxide. Thus, a gram-molecular weight of hydrocyanic acid in 1,000,000 liters of water will retard, quite appreciably, the decomposition of the dioxide by the platinum solution. Hydrogen sulphide acts to nearly the same extent, and mercuric chloride also shows a marked power to poison the platinum solution.

These are some of the analogies pointed out between the action of organic ferments and of the finely divided metals and oxides of the metals. It is too early to draw any final conclusion as to how deep-seated these analogies are, but they are certainly interesting and promise much for the future. Should it be shown that these relations are fundamental, it will be of service in studying the action of organic ferments in general, since the metals and even the metallic oxides are simple substances in comparison with the organic enzymes. H. C. J.

REVIEWS.

A SYSTEM OF INSTRUCTION IN QUALITATIVE CHEMICAL ANALYSIS. By ARTHUR H. ELLIOTT, PH.D., Professor Emeritus of Chemistry and Physics in the College of Pharmacy in the City of New York, and GEORGE A. FERGUSON, PH.B., Professor of Analytical Chemistry and Director of the Chemical Laboratory in the College of Pharmacy of the City of New York. Third edition, revised and enlarged. 1899. Published by the authors. 155 pp.

As the first and second editions of this book have been favorably noticed in this JOURNAL,[1] it is only necessary to say that the revision is judicious, and that the manual will be found especially useful to those teachers who are compelled to instruct large classes without assistance, as the notes of analytical details are unusually full and minute. E. R.

DETERMINATION OF RADICLES IN CARBON COMPOUNDS. By DR. H. MEYER, Docent and Adjunct of the Imperial and Royal German University, Prague. Authorized translation. By J. BISHOP TINGLE, PH.D., F.C.S., Instructor of Chemistry at the Lewis Institute, Chicago, Ill. First Edition. First Thousand. New York: John Wiley & Sons; London: Chapman & Hall, Limited. 1899. pp. 133.

Dr. Meyer's book is favorably known to chemists in the original and its character is such as to lead to the belief that the English translation will be of service. No doubt some of the methods described could be made part of a laboratory course in organic chemistry to the great advantage of the course, and it is to be hoped that those who have charge of the work in organic preparations in our larger laboratories will avail themselves of some of the suggestions made in the book.

There are five chapters: The first treats of the determina-

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[1] Vol. **15**, 373; and **16**, 476.

tion of hydroxyl; the second of the determination of methoxyl, CH_3O—, ethoxyl, C_2H_5O—, and carboxyl, COOH; the third of the determination of carbonyl; the fourth of the determination of the amino group and of the imino group; the fifth of the determination of the diazo group, of the hydrazide group, of the nitro group, of the iodoso and iodoxy groups, and of the peroxide group.

The following quotation will indicate the object of the book: "The quantitative analysis of organic compounds, as usually performed, consists almost exclusively in the determination of ions, since in the present state of the science this generally suffices for the identification of the substance; but to attain the same end in the case of organic bodies the elementary analysis requires supplementing by other methods. The percentage composition gives no information about the relative arrangement of the atoms in the molecule, but the demand for methods of analysis which will yield such knowledge increases with our growing insight into the constitution of carbon compounds. * * * The successful methods hitherto proposed for the determination of organic radicles have been collected together in this work, and it is hoped that they may serve to indicate the direction in which research may be successfully prosecuted for the discovery of new ones applicable to hitherto unforeseen conditions."

The book is recommended to teachers and advanced students of chemistry. I. R.

ADDITIONS.

Vol. 23, pages 309, 310, and 311.

Under plate on page 309 add:

1. Metadinitrobenzene; 2. Orthonitrophenol; 3. Metamethoxybenzenesulphonamide; 4. Benzenesulphonamide; 5. Nitromethane; 6. Paramethoxybenzenesulphonamide; 7. Orthomethoxybenzenesulphonamide; 8. Trinitrotoluene.

Under plate on page 310 add:

1. Potassium Chloride; 2. Potassium Nitrate; 3. Ammonium Chloride; 4. Ammonium Nitrate; 5. Silver Iodide; 6. Strontium Nitrate.

Under plate on page 311 add:

1. Sodium Bromide; 2. Potassium Metanitrobenzenesulphonate; 3. Sodium Bromate; 4. Metanitrobenzenesulphonamide; 5. Benzoic Sulphinide.

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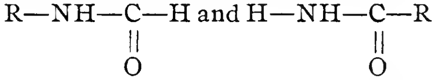
AMERICAN CHEMICAL JOURNAL

Contributions from the Sheffield Laboratory of Yale University.

LXXIV.—RESEARCHES ON THE SODIUM SALTS OF THE AMIDES.

BY HENRY L. WHEELER.

The work described in this paper was undertaken with the object of determining the relative ease with which certain acid amides yield sodium salts, and of determining whether a stereochemical interference is noticeable in this series, by comparing the velocity at which, under given conditions, metameric amides of the form  $R—NH—\underset{\underset{O}{\|}}{C}—H$ and $H—NH—\underset{\underset{O}{\|}}{C}—R$ form salts. Such a comparison, taken in connection with a similar examination of the disubstituted formamides,

$$RNHCOR' \quad \text{and} \quad R'NHCOR,$$

in which $R =$ aryl and $R' =$ alphyl, might be expected to throw new light on the disputed question of the structure of these salts. For example, which one of the above-mentioned isomeric forms is most favorable for the formation of sodium salts, or in other words, in what position does R have the more retarding effect? And is this effect general for one of these types? If the sodium attaches itself to nitrogen, then R should exert a greater interference when attached to the same atom than when further removed or attached to carbon; for example, formanilide, C_6H_5NHCOH, should then give a salt less easily than benzamide, $HNH—COC_6H_5$.

As regards the velocity of formation of the salts, the question of relative acidity or negative character of the molecules arises at once. Do the amides give salts in accordance with the strength of the acids from which they are derived? To what extent does the basic character of the amino group influence the velocity of formation of the salts?[1] The latter questions are evidently the first to be decided.

It was necessary at the outset to devise a new method for the preparation of the sodium salts. It was found that sodium amalgam answers the purpose better than metallic sodium; that in boiling benzene the former does not become covered with a coating, as the metal does; and that salts can be prepared by its use which cannot be obtained by any of the previously existing methods.

In order to determine whether acidity is the chief factor in determining the velocity of formation of the sodium salts, the following anilides in molecular proportions, taking 0.5 gram of acetanilide, were dissolved in 100 cc. of benzene and boiled for one hour with 9 grams of a 4.7 per cent amalgam. The solutions were then filtered as rapidly as possible, and the amount of anilide which had formed sodium salt was determined as described below. The following figures approximately show this amount in percentages, the affinity constants of the respective acids being given for comparison:

	Average of two experiments.		K.[2]
Formanilide, C_6H_5NHCHO,	1.00	Formic acid,	0.0214
Acetanilide, $C_6H_5NHCOCH_3$,	82	Acetic "	0.0018
Oxanilide, $(C_6H_5NHCO—)_2$,	63	Oxanilic "	1.21
Benzanilide, $C_6H_5NHCOC_6H_5$,	38	Benzoic "	0.006

From this it is evident that the results do not correspond with the strengths of the acids. Thus, oxanilide should give

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[1] It is well known that the presence of negative groups in the amides favors the formation of salts, dibenzamide, benzoylurethane, etc., are soluble in alkali, while benzamide is insoluble, and again, the acyl cyanamides have stronger acid properties than the acids from which they are derived. Bader: Ztschr. phys. Chem., 6, 305.

[2] Ostwald: *Ibid.*, 3, 241.

a salt more readily than formanilide and acetanilide, and benzanilide more readily than acetanilide.

That basicity does not exert the most important influence, the acyl radical being the same, is shown by the following results, which were obtained under the same conditions:

Benzamide, $H_2NCOC_6H_5$,	98
Benzanilide, $C_6H_5HNCOC_6H_5$,	38
Benzoylbenzylamine, $C_6H_5CH_2HNCOC_6H_5$,	1

	K.[1]
Ammonia,	0.0023
Benzylamine,	0.0024

Thus, if the positive character of the molecules determined the velocity of formation of the salts, benzanilide should react more readily than benzamide; and since benzylamine has practically the same basicity as ammonia, the benzoyl compounds should give salts with equal readiness.

It is interesting to note here that Hjelt[2] found that the rate of saponification of the alkyl malonic esters is not in agreement with the affinity constants of the corresponding acids, but that it agrees, rather, with what would be expected from the theory of stereochemical interference.

In order to determine which one of the two general forms, RNHCOH or HNHCOR, is more favorable for salt formation, the following amides were examined under the same conditions as described above, except that 23 grams of a 0.73 per cent amalgam were used. The figures represent the percentages of amide converted into sodium salt under these conditions:

	Average.
Formanilide, $C_6H_5.NHCO.H$,	57
Acetanilide, $C_6H_5.NHCO.CH_3$,	8
Propionanilide, $C_6H_6.NHCO.C_2H_6$,	12
Benzamide, $H.NHCO.C_6H_5$	51
Methylbenzamide, $CH_3.NHCO.C_6H_6$,	0
Ethylbenzamide, $C_2H_5.NHCO.C_6H_5$,	0

In the following cases the conditions were the same as in the first experiments, using a 4.7 per cent amalgam. In all

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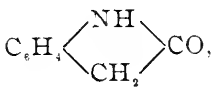
[1] Bredig: Ztschr. phys. Chem., **13**, 306.

[2] Ber. d. chem. Ges., **29**, 1866.

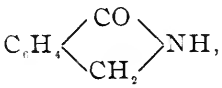
cases excepting formanilide and benzamide, however, 150 cc. of benzene were used :

	Average.
Formanilide, C_6H_5NHCOH,	100
Orthoformtoluide, $C_6H_4CH_3NHCOH$,	96
α-Formnaphthalide, $C_{10}H_7.NHCOH$,	99
2,4,6-Trimethylformanilide, $C_6H_2(C_6H_3)_3NHCOH$,	96
Benzamide, $HNHCOC_6H_5$,	98
Orthotoluamide, $HNHCOC_6H_4CH_3$,	91
α-Naphthamide, $HNHCOC_{10}H_7$,	76
2,4,6-Trimethylbenzamide, $HNHCOC_6H_2(CH_3)_3$,	88

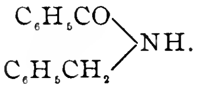
These results, thus far, show that a disubstituted formamide gives a salt less readily than one that is monosubstituted, which would be expected from the theory of stereochemical interference; and that when the larger or interfering radical is attached to nitrogen it has less effect in retarding the formation of sodium salts than when attached to the keto group. They, therefore, indicate that the sodium is attached to oxygen.[1] Although it is true that the results all point in this direction, nevertheless the interference which might be expected in certain cases does not exist, while in others an unexpected inertness is shown. An examination of the isomeric cycloamides, oxindol (I) and phthalimidine (II), under the same conditions as in the first experiments, showed that in both cases the amount of amide which had formed salt was practically 100 per cent, while benzoylbenzylamine (III), which has an acyclic structure corresponding to phthalimidine, as already stated, gave practically no salt under these conditions :


$C_6H_4{<}\begin{matrix}NH\\CH_2\end{matrix}{>}CO,$

I.


$C_6H_4{<}\begin{matrix}CO\\CH_2\end{matrix}{>}NH,$

II.


$\begin{matrix}C_6H_5CO\\C_6H_5CH_2\end{matrix}{>}NH.$

III.

The interesting results obtained by Remsen and Reid[2] on the saponification of the substituted benzamides show that substituents in the ortho position "exert a remarkable protective influence on the amide group." The order in which the various groups produce a retardation was found to be as fol-

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[1] Compare Michael : J. prakt. Chem., **60**, 322.

[2] This JOURNAL, **21**, 281.

lows, in order of decreasing influence: —NO_2, —I, —NH_2, —CH_3, —Cl, —OH, —$O.C_2H_5$, —$O.CH_3$. Unfortunately, for a comparison with the velocity of formation of the corresponding sodium salts, only —NH_2, —CH_3, and the least interfering groups, —$O.C_2H_5$ and —$O.CH_3$, are probably available for examination by the present method. The results with orthotoluamide indicate, however, that interference also plays a part in the formation of the sodium salt of that compound, although it is not shown in a very decided manner. On the other hand, it is curious that benzoylbenzylamine, and methyl- and ethylbenzamides are so inert, and that they give salts less readily than benzanilide, while the results with trimethylbenzamide are most unexpectedly high.

The derivatives of 2-4-6-trimethylbenzoic acid, like other diorthosubstituted acids, are notably inactive in reactions which are supposed to involve an addition to the keto group.[1] The acid is not converted into its ester by means of hydrogen chloride and alcohol.[2] The ester[3] and amide[4] are difficult to saponify, while the chloride is remarkably stable towards water and alkalies. Diorthosubstituted acid chlorides in general react readily with ammonia,[5] however, and the silver salt of trimethylbenzoic acid gives almost a quantitative yield of the ester with methyl iodide.[6] It is assumed that these latter reactions do not involve any addition to the keto group, but take place by direct substitution.[7] The fact now that 2,4,6-trimethylbenzamide forms a sodium salt practically as readily as orthotoluamide, and that no very decided stereochemical interference is found in this reaction, would suggest that here, also, direct substitution takes place, and that the sodium is attached to nitrogen. On the other hand, if the sodium is attached to oxygen, the reaction must be an

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[1] Henry: Ber. d. chem. Ges., **10**, 2041; Wegscheider: Monatshefte, **16**, 148; Angeli: Ber. d. chem. Ges., **29**, R, 591; Peckmann; *Ibid.*, **31**, 504.

[2] V. Meyer: *Ibid.*, **27**, 510.

[3] *Ibid.*, **27**, 1263.

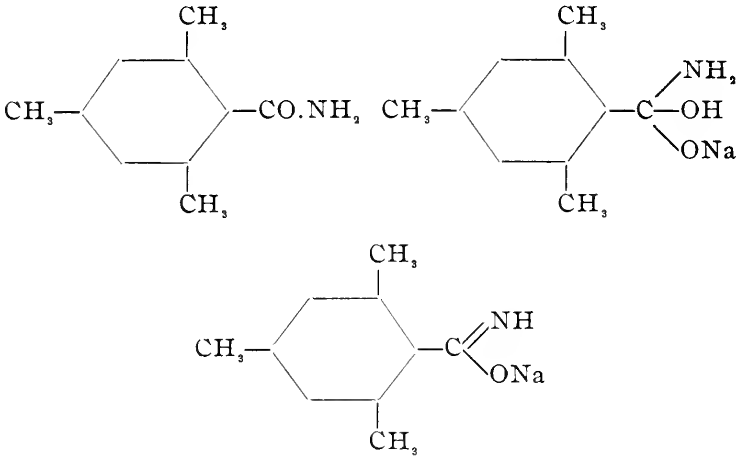
[4] Sudborough: J. Chem. Soc. (London), 1897, 229.

[5] Sudborough: *Ibid.*, 1897, 234.

[6] Meyer: Ber. d. chem. Ges., **27**, 1580.

[7] Max Scholtz: Der Einfluss d. Raumerfüllung d. Atomgruppen; Sudborough: *Loc. cit.*

addition of sodium hydrate to the keto group, and then a separation of water, as follows:[1]



If this is true, it follows that 2,4,6-trimethylbenzamide, out of all harmony with the theory of stereochemical interference, must readily form an addition-product with the alkali. This is precisely what takes place, not only in this case but also with the symmetrical 2,4,6-tribrombenzamide, which Sudborough states exhibits the greatest amount of stereochemical interference, as regards its hydrolysis, of any of the amides examined by him.

The ease with which 2,4,6-trimethylbenzamide forms a sodium salt is therefore in harmony with the theory that the metal in the sodium salts of the amides is attached to oxygen.

I have found that 2,4,6-trimethyl- and tribrombenzamides are readily removed from even their dilute solutions in ether by simply shaking with powdered potassium hydrate, the addition-product being absolutely insoluble in ether. On filtering and treating the residue with water, these compounds undergo dissociation and the unaltered amides are recovered.

In order to prepare the compound $C_6H_2Br_3CONH_2.NaOH$, it is simply necessary to pour an excess of the amide dissolved in benzene over finely powdered sodium hydrate, whereupon

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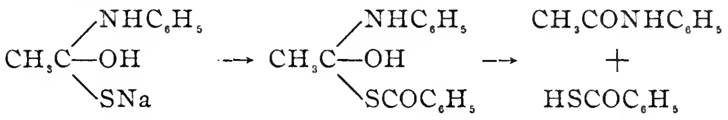
[1] Naturally a mere trace of moisture would be sufficient, since the water which separates would again react until all the amide is converted by the sodium into salt.

the latter is quantitatively converted into the addition-product.[1]

This is all the more surprising since Pechmann[2] found that 2,4,6-trimethylbenzoic ester does not form an addition-product with sodium alcoholate, which is one of the notable properties of ethyl benzoate, and I have found that 2,4,6-tribrombenzoyl chloride and methyl 2,4,6-tribrombenzoate do not give addition-products with potassium hydrate, and also that 2,4,6-tribrom-N-dimethylbenzamide yields no sodium hydrate compound under the same conditions that proved successful with the amide.

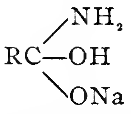
The readiness with which the diorthosubstituted amides form addition-products with the alkali, contrasted with their inertness as regards saponification, suggests that the processes involved in the formation of sodium salts and in saponification are not analogous. If we accept the addition theory of saponification the existence of these alkali addition-products shows that the stereochemical interference in regard to the saponification of these amides, at least with alkali, is not due to a protection from attack, but, for some other specific reason, they give up ammonia with difficulty.

That these alkali addition-products have the elements of the alkali attached to the keto group, and are not merely so-called molecular compounds, is shown by the behavior of the sodium hydrate addition-product of thioacetanilide with benzoyl chloride, which reaction yields acetanilide and thiobenzoic acid, as follows:



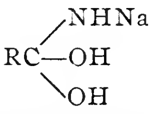
$$CH_3C\begin{array}{l}\diagup NHC_6H_5\\ -OH\\ \diagdown SNa\end{array} \longrightarrow CH_3C\begin{array}{l}\diagup NHC_6H_5\\ -OH\\ \diagdown SCOC_6H_5\end{array} \longrightarrow \begin{array}{c}CH_3CONHC_6H_5\\ +\\ HSCOC_6H_5\end{array}$$

That they have the formula



$$RC\begin{array}{l}\diagup NH_2\\ -OH\\ \diagdown ONa\end{array}$$

and not



$$RC\begin{array}{l}\diagup NHNa\\ -OH\\ \diagdown OH\end{array}$$

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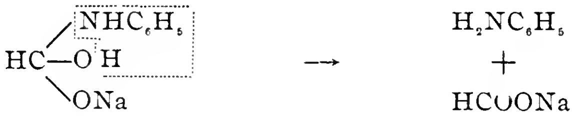
[1] Interesting also, in this connection, is the fact that Küster and Stallberg (Ann. Chem. (Liebig), **278**, 217) state that 3-nitro-2,4,6-trimethylbenzamide dissolves in aqueous alkali and even in carbonates.

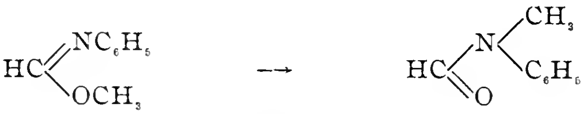
[2] *Loc. cit.*

is shown by the behavior[1] of the addition-products of formanilide, formtoluide, etc.

When heated, or, as found by Tobias,[2] when simply allowed to stand over sulphuric acid, these compounds decompose as follows :



This formula, as representing the structure of these addition-products is objected to by Cohen and Brittain,[3] since when heated the analogous sodium alcoholate addition-products[4] lose alcohol and yield sodium[5] acetanilide, which, with methyl iodide, gives methylacetanilide, methylaniline, etc. Their statement that this formula "would necessitate a molecular change of a very complex character which is scarcely justified by the facts" no longer holds true, since phenylformimidomethyl ester undergoes this rearrangement with methyl iodide, even in the cold, yielding methylacetanilide :



EXPERIMENTAL PART.

Experiments with a 0.73 Per Cent Amalgam.

Formanilide.—The method adopted in general for the determination of the ease with which the amides form salts was as follows : 0.4481 of a gram of formanilide and the equivalent of the other amides were dissolved in 100 cc. of benzene and heated, whereupon 23 grams of a 0.73 per cent amalgam were added. This is somewhat more than twice the calculated quantity of sodium. After boiling one hour, the solution was filtered and the residue of sodium salt was collected on the filter, while the heavier amalgam was allowed to remain in the flask.

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[1] See also Hantzsch: Ann. Chem. (Liebig), **296**, 91.

[2] Ber. d. chem. Ges., **15**, 2451.

[3] J. Chem. Soc. (London), 1898, 162.

[4] Cohen and Archdeacon: *Ibid.*, **69**, 91.

[5] Seifert: Ber. d. chem. Ges., **18**, 1358.

The whole was washed with somewhat over 50 cc. of warm benzene by means of a wash-bottle and the filtrate evaporated in a weighed flask, the residue being dried in a stream of air at ordinary temperature. In most cases the residue consisted of unaltered amide, which gave directly the weight of material not forming sodium salt. In all cases this residue, after weighing, was treated with water and titrated with a standard hydrochloric acid solution, using an aqueous solution of the sodium salt of orthonitrophenol as indicator, which recommended itself, since it gives a very sharp end-reaction by gaslight and carbonic acid does not interfere except in the cold.

In this manner the amount of sodium salt dissolved by the benzene was determined and the correction made. The amount of amide forming sodium salt was then determined by difference. In some of the experiments the amount of anilide recovered, after boiling with amalgam, was determined by saponifying the anilide with strong hydrochloric acid and then determining the amount of aniline volumetrically by means of a standardized solution of potassium bromate and bromide.[1]

Two experiments with formanilide, performed as above, gave 0.1963 and 0.1859 gram anilide not attacked, corresponding to 56 and 58 per cent as sodium salt. This sodium salt is insoluble in benzene.

It must be understood that the quantitative results given in this paper are merely approximate, and in certain cases it is difficult to get closely agreeing results. The first difficulty encountered is the fact that with the solid amalgam it is difficult to get the same state of division each time, although in each case the amalgam was freshly powdered and passed through a moderately fine sieve before it was used. A curious result was observed when two different preparations of a semisolid amalgam was used, both containing the same percentage of sodium as far as could be determined; *i. e.* 0.72 and 0.73 per cent. By means of the latter, when acetanilide was boiled for one hour, 8.7 and 8.0 per cent was found to have been converted into sodium salt; with the former preparation, however, on boiling for two hours three experiments each gave

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[1] Reinhardt: Ztschr. anal. Chem., **33**, 90; Compare Francois and Denigès: J. Soc. Chem. Ind., **28**, 866.

3.9 per cent as the amount of anilide that had been attacked.

It has previously been observed that certain preparations of sodium amalgam have given widely different results in reduction experiments[1] and Aschan [2]explains this by the assumption that impurities cause the evolution of hydrogen in the molecular form and not in an active state. This explanation fails in the above case. With these results, which fortunately occurred at the beginning of the work, all the comparisons were afterwards made with portions of the same preparations.

Other sources of error are as follows: The sodium salts are bulky, gelatinous, and difficult to wash when prepared in this way; therefore, the small quantities of amides used in the experiments, and, in some cases, the residues left on evaporating the benzene, are difficult to dry. In no case was any reduction of the amide observed, as is the case when the amides are acted on with amalgam in acid[3] or alkaline[4] solutions.

Acetanilide.—When two experiments with 0.5 gram of this anilide were performed as described above, 8.7 and 7.9 per cent of the anilide was found to have been converted into sodium salt. This quantity was all dissolved in the benzene solution. Experiments at 20°, the other conditions being exactly the same, gave peculiar results. It was found that 17.8 and 20.8 per cent of the acetanilide had been converted into sodium compound, or about two and one-half times as much as at the temperature of boiling benzene. The explanation of this was found on filtering the benzene solution, when before the washing was complete the sodium hydrate addition-product mentioned by Cohen and Brittain[5] began to separate. This owed its formation to the unavoidable presence of moisture absorbed by the amalgam and benzene during the manipulation. These authors state that the alkali addition-products are readily dissociated at the temperature of boiling ether; therefore, all other experiments described here were performed at the temperature of boiling benzene.

The sodium hydrate addition-product of acetanilide is sol-

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[1] Lassar-Cohn: Lab. Manual Org. Chem., p. 308.

[2] Ber. d. chem. Ges., **24**, 1866.

[3] Guareschi: *Ibid.*, **7**, 1462.

[4] Hutchinson: *Ibid.*, **24**, 173.

[5] *Loc. cit.*

uble in benzene, while that of formanilide is insoluble ; therefore, at temperatures at which the intermediate addition-products are stable, more sodium compound should be formed in the case of acetanilide than with formanilide, when treated with metallic sodium covered with a layer of sodium hydrate. The results of the following experiments proved this to be true. The anilides were dissolved in 100 cc. of benzene (0.4481 gram formanilide and 0.5 gram acetanilide) and shaken in a machine for one hour, with 0.5 gram of sodium, weighed in the air whereupon formanilide gave 5.3 and 5.9 per cent, and acetanilide 20.5 and 26.3 per cent anilide as sodium compound.

Propionanilide.—One experiment with 0.5518 gram of this anilide, which was performed in boiling benzene, gave no turbidity or separation of salt from the benzene solution, but on filtering and evaporating, 12.2 per cent was found to have been converted into salt.

Benzamide.—In this case two experiments with 0.4481 gram of material gave 1.4 per cent of amide as sodium compound dissolved in benzene and 49.1 and 50.2 undissolved ; total 50.5 and 51.6.

Methyl- and Ethylbenzamides gave no evidence of any salt formation under the above conditions. The benzene solution was found to be free from alkali and, on evaporating off the benzene, the weights of the residues came from 2 to 5 per cent too high, it being difficult to dry the material without loss.

Experiments with a 4.7 Per Cent Amalgam.

Formanilide.—In each of the following experiments 9 grams, or five times the calculated quantity of amalgam, was used. 0.4481 gram of this anilide, when treated as above, gave no residue on evaporating the benzene; hence the amount of salt formed was 100 per cent.

Acetanilide.—One-half gram gave, in two experiments, 29.6 per cent as salt dissolved in the benzene, and 48.1 per cent undissolved in one; and 29.6 and 56.8 per cent in another ; total 77.7 and 86.4 ; average 82. Lack of better agreement is due to the difficulty of drying, owing to the amount of salt dissolved by the benzene.

Oxanilide.—In two experiments 0.4444 gram gave 65.4 and 60.0 as monosodium salt. This salt is insoluble in benzene; it was separated from all but traces of the amalgam by decantation, and a sodium determination gave:

	Calculated for $C_6H_5NHCOCONaNC_6H_5$.	Found.
Na	8.8	9.1

Water decomposes the salt,[1] liberating anilide.

Benzanilide.—Attempts to prepare a sodium salt for synthetical purposes by boiling this anilide in benzene with sodium were unsuccessful. Quantitative experiments indicated that over 95 per cent of the anilide was unaltered. The use of xylene, as recommended by Hepp,[2] gave no better result. The method of Seifert[3] and Blacher[4] for the preparation of sodium salts also failed in this case. It was prepared, however, by boiling the concentrated benzene solution with an 8 per cent amalgam. Ten grams anilide gave about 7 grams of salt after boiling several hours. It was separated from the excess of amalgam by decantation. As the amalgam used was not freshly prepared and contained some sodium hydrate, the results on analysis came high. The percentage of sodium calculated is 10.5, found 11.7. In the experiments of Paal and Otten[5] on the action of acyl chloride on the sodium salts of the anilides, they invariably treated the salt of a lower anilide with a chloride of higher acid, benzoyl chloride with sodium acetanilide, sodium formanilide, etc., and obtained nothing but the anilide of the higher acid. The action proved to be abnormal as diacyl anilides were not obtained. It seemed of interest, therefore, to try the action of acetyl chloride on sodium benzanilide under the same conditions as described by the above authors, when it was found that the action was also abnormal in this case, and that nothing but benzanilide was obtained.

[1] In determining the amount of sodium in the following new salts, which was done volumetrically, a determination of the amount of mercury was also necessary in some cases; in others this was very small and was disregarded. The decanted precipitates always contain more or less mercury.

[2] Ber. d. chem. Ges., **10**, 328.

[3] *Ibid.*, **18**, 1357.

[4] *Ibid.*, **28**, 435.

[5] *Ibid.*, **23**, 2587.

Quantitative experiments with 0.7296 gram anilide, on the formation of sodium benzanilide, gave 35.3 as the amount of amide which had formed salt, in one, and 40.5 per cent in another; average, 37.9. The salt is insoluble in benzene; it is bulky and gelatinous, but when dried forms a white, amorphous powder.

Benzamide.—The amide (0.4481 gram) gave 98 per cent as the amount that had formed salt, while 1.4 per cent of the amide was in solution as sodium salt. After decanting the bulky, gelatinous salt and rapidly drying in a steam oven a sodium determination gave:

	Calculated for C_7H_6NONa.	Found.
Na	16.0	16.2

Ethylbenzamide.—Two experiments with 0.5518 gram each of this amide, again with the stronger amalgam, gave no evidence of any salt formation. On boiling the benzene solution it remained perfectly clear, and on examining the residue left on evaporating the benzene it was found that less than 0.7 per cent of the amide had formed salt.

Benzoylbenzylamine.—This was prepared by the Baumann-Schotten reaction. Two experiments with 0.7815 gram of material gave perfectly clear solutions on boiling with the amalgam, and an examination of the residue, on evaporating the benzene solution, indicated that in both cases 1.0 per cent of the amide had been converted into sodium salt. The recovered material melted sharply from 106° to 107°.

Oxindol.—This cycloamide (0.4926 gram) gave a bulky, gelatinous separation of salt immediately on warming and, on evaporating the filtered solution, the residue weighed 0.0050 gram. It was found to be free from alkali, and, therefore, 99 per cent of the amide was converted into salt. A sodium determination gave:

	Calculated for C_8H_6NONa.	Found.
Na	14.8	15.3

Phthalimidine.—This amide (0.4926 gram) gave a bulky, gelatinous salt, like the above, and the recovered residue of unaltered material weighed 0.0066 gram; hence 98.7 per cent of the amide formed salt. A sodium determination gave:

	Calculated for C_6H_6NONa.	Found.
Na	14.8	14.8

Phenyloxamide.—This amide (0.3037 gram) refused to dissolve completely in 100 cc. of benzene before adding the amalgam, so that the results are not directly comparable with the above. The amount of amide converted into salt was found to be 57.3 per cent.

Oxamide and *phthalamide* are insoluble in benzene. *Formamide*[1] immediately liberates ammonia, while *acetamide* appears to be less readily decomposed by the above treatment.

The following experiments required the use of 150 cc. of benzene, owing to the difficulty with which α-naphthamide dissolves in this solvent.

Orthoformtoluide.—This was one of the few cases in which the amalgam showed any tendency to "cake," or the salt to attach itself to the amalgam; nevertheless, 0.5 gram gave 95.7 per cent as the quantity of toluide forming sodium salt; 3 per cent of this was dissolved by the benzene. The salt separated by decantation gave:

	Calculated for C_8H_8NONa.	Found.
Na	14.6	14.2

Orthotoluamide.—This was prepared by the method suggested by Remsen and Reid. The amount used was 0.5 gram, and 90.6 per cent of this was found to have formed sodium salt. No salt was found in the benzene solution. A sodium determination gave:

	Calculated for C_8H_8NONa.	Found.
Na	14.6	15.1

α-Formnaphthalide.—Of this, 0.6333 gram gave 98.9 per cent as sodium salt. It is bulky and gelatinous, and therefore filters slowly. Less than 1 per cent of salt was found in the benzene. A sodium determination gave:

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[1] That this amide gives a sodium salt with great ease, by a less energetic reaction, is shown by the method used by Freer and Sherman (This JOURNAL, 18, 580).

	Calculated for $C_{11}H_8NONa$.	Found.
Na	11.8	12.2

α-Naphthamide.—The nitrile was prepared from α-naphthylamine by the Sandmeyer reaction. Of the amine 85.8 grams gave 13 grams of nitrile boiling at about 300°. When this was dissolved in an excess of alcoholic sodium hydrate and warmed for a few minutes, the first separation of crystals weighed 5 grams and were practically pure amide, melting at 202°.

The amide (0.6333 gram) gave 23.6 per cent unaltered material. After being heated as above, this melted sharply at 202°. The amount of amide as sodium salt was therefore 76.4 per cent. A sodium determination gave:

	Calculated for $C_{11}H_8NONa$.	Found.
Na	11.8	12.4

2,4,6-Trimethylformanilide.—The mesidine was prepared by heating trimethylphenylammonium iodide at 210° with a few drops of methyl alcohol. It is more readily obtained from mesitylene by nitration and reduction. The formyl compound melted at 177°. Of this, 0.6037 gram gave 95.9 per cent as sodium salt, which separated as a bulky, gelatinous mass. Less than 1 per cent of this was dissolved by the benzene. A sodium determination gave:

	Calculated for $C_{10}H_{12}NONa$.	Found.
Na	12.4	12.3

2,4,6-Trimethylbenzamide.—For the preparation of this amide mesitylene was nitrated according to the method of Schulz.[1] After distilling in steam, the oil obtained was distilled at 15–20 mm. pressure, when the fraction, 120°–130°, was collected. It boils for the most part at 150°–154° at about 50 mm. pressure. 131 grams of mesitylene gave 61 grams of crude nitro-compound. This, on reduction, gave 25.3 grams of mesidine boiling from 224°–226° (uncorr.). From this the nitrile was prepared according to Sandmeyer's reaction, using the conditions of Liebermann and Birukoff[2] for the prepara-

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[1] Ber. d. chem. Ges., **17**, 477.

[2] Ann. Chem. (Liebig), **240**, 286.

tion of the corresponding 2,4-xylylic nitrile. They obtained a yield of 50–60 per cent. In the present case the yield was far below this, about 8 grams of crude nitrile being obtained. On boiling this for seventy-two hours with alcoholic potash, the first separation of crystals, on cooling and crystallizing the product from benzene, weighed 2 grams and melted sharply from 187°–188°.

When 0.6037 gram of this amide was treated with the amalgam an immediate turbidity of the benzene solution resulted, and an extremely gelatinous precipitate separated which was difficult to wash. The salt is absolutely insoluble in benzene and 87.8 per cent of the amide was converted into salt. A sodium determination gave:

	Calculated for $C_{10}H_{12}NONa$.	Found.
Na	12.4	12.8

2,4,6-Trimethylbenzamide and Potassium Hydrate.—It was found that this amide readily unites with alkali in the following way: Potassium hydrate was used, as Cohen states that these addition-products, in the case of the substituted acetanilides, are more soluble than the sodium hydrate compounds. Of this amide 0.3003 gram was dissolved in 100 cc. of ether, in which it is readily soluble, and 2 grams of potassium hydrate were powdered under 40 cc. of ether and then the whole mixed together. The mixture was shaken for half an hour and then filtered into a weighed flask. It was washed with 100 cc. of ether and, on evaporating the ether and drying the residue in a stream of air for a few minutes, 0.0115 gram of unaltered amide was recovered; 96.2 per cent had, therefore, combined with the alkali. On treating the alkali with water the amide was recovered.

2,4,6-Tribrombenzamide.—This was prepared from metaminobenzoic acid. Tribrombenzoic acid was prepared by eliminating the amino group from this after brominating.[1] Twenty grams of aminobenzoic acid gave 52 grams of the tribromamino acid melting at 170°–172°, and this gave 43 grams of crude tribrombenzoic acid. This was converted into the chloride in the usual way, and, instead of attempting to

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[1] Volbrecht: Ber. d. chem. Ges., 10, 1708.

purify this by crystallizing from petroleum ether, in which the compound is readily soluble, it was distilled[1] under a pressure of 35–40 mm., when the chloride boiled from 200°–210°. On cooling the distillate, beautiful, four-sided tables separated, melting at about 47°. These were crystallized from petroleum ether. The yield was 25 grams. The amide separated immediately when this material was dissolved in alcoholic ammonia, and it melted sharply from 191°–192°.

This amide is the most difficult to saponify of any yet examined; nevertheless it unites with alkali to form addition-products with the greatest ease.

2,4,6-Tribrombenzamide and Potassium Hydrate.—1.0040 grams of the amide were dissolved in 100 cc. ether and 2 grams of potassium hydrate, powdered under 40 cc. of ether, were added. After shaking for half an hour the material was filtered and washed with 100 cc. of ether. On evaporating the filtrate only 0.0145 gram of residue was obtained. Therefore, 98.7 per cent of the amide had formed an addition-product with the alkali, and was filtered off.

2,4,6-Tribrombenzamide Sodium Hydrate, $C_6H_2Br_3CONH_2.NaOH$.—These addition-products can be isolated in a state of purity, as follows: 4 grams of the amide are dissolved in 150 cc. of benzene, and the solution poured on 0.3 gram of pure sodium hydrate in a mortar (calculated quantity 0.4 gram). The alkali is thoroughly powdered and then the mass is filtered and washed with benzene, in which the addition-product is insoluble. On drying rapidly in a steam-bath, a sample thus prepared gave the following result on determining sodium hydrate:

	Calculated for $C_6H_2Br_3CONH_2.NaOH$.	Found.
NaOH	10.0	10.3

Under the microscope the material appeared minutely crystalline, but no definite form could be observed. It was absolutely free from the characteristic needles of the free amide. Water immediately decomposes the compound.

2,4,6-Tribrom-N-dimethylbenzamide, $C_6H_2Br_3CO.N(CH_3)_2$. —This was prepared by treating the acid chloride with an ex-

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[1] Sudborough: *Loc. cit.*

cess of an aqueous 33 per cent solution of dimethylamine mixed with methyl alcohol. The product thus obtained was purified by crystallizing from a mixture of benzene and petroleum ether, whereupon well developed, colorless prisms separated melting from 85°–86°. A nitrogen determination gave:

	Calculated for $C_9H_8Br_3NO$.	Found.
N	3.61	3.57

When 2 grams of this amide were dissolved in 30 cc. of benzene and treated with 1.5 grams powdered sodium hydrate no addition took place. The alkali was free from amide, on filtering and washing, and the benzene solution contained no alkali.

2,4,6-Tribrombenzoyl Chloride and Potassium Hydrate.—1.1020 grams of the chloride were dissolved in 50 cc. of ether and 2 grams of potassium hydrate, powdered under 40 cc. of ether, were added. After twenty minutes the mixture was filtered, washed with 100 cc. of ether, and the ether evaporated, when the residue weighed 1.0620 grams. No alkali was found in this residue, hence 96.3 per cent of the chloride remained unaffected in this treatment.

2,4,6-Methyltribrombenzoate and Potassium Hydrate.—1.0055 grams of the ester were treated with 2 grams of powdered potassium hydrate, as above described, when 0.9841 gram of unaltered material was recovered, or 97.8 per cent.

Thioacetanilide Sodium Hydrate, $CH_3CS—NHC_6H_5.NaOH$.—1.2 grams of sodium hydrate (calculated 1.7) were powdered under a solution of 6.6 grams of thioacetanilide in 30 cc. of benzene. A finely divided precipitate formed at once, which was very slow in filtering. It was washed with a little ether and dried at about 55°, whereupon a sodium determination gave:

	Calculated for $C_8H_9NS.NaOH$.	Found.
Na	12.0	11.8

Thioacetanilide Sodium Hydrate and Benzoyl Chloride.—5.2 grams of the above were mixed with 3.5 grams of benzoyl chloride in 30 cc. of ether, whereupon reaction immediately set in with evolution of heat. On filtering and evaporating the ether a yellow oil was obtained, which, on standing over night, deposited a mass of needles or prisms. When these were washed with ether and crystallized from water broad, colorless plates of acetanilide were obtained melting at 114°. The yellow oil was easily recognized as thiobenzoic acid by its peculiar, disagreeable odor. It could not be distilled even under diminished pressure. When it was mixed with aniline in the cold it gave benzanilide.

The above sodium-hydrate addition-product appears to be formed when sodium alcoholate and thioacetanilide in alcohol are precipitated with moist ether. A portion prepared in this manner by Dr. P. T. Walden and treated with benzoyl chloride gave the same result as above. A determination of nitrogen in the crystals obtained proved that the material was acetanilide.

NEW HAVEN, CONN., February 28, 1900.

Contribution from the Division of Chemistry, U. S. Department of Agriculture.

ESTIMATION OF ALKALI CARBONATES IN THE PRESENCE OF BICARBONATES.

BY FRANK K. CAMERON.

Introduction.

In an aqueous solution sodium carbonate is hydrolyzed to a definite extent, depending upon the concentration and temperature conditions. This may be represented thus :

$$Na_2CO_3 + HOH \rightleftarrows NaHCO_3 + NaOH.$$

Of the four electrolytes then present in the solution only the sodium hydroxide is dissociated or ionized to any considerable extent, and in consequence the solution presents the characteristic features of a solution of this substance—it is markedly alkaline. Shields[1] has found the amount of this hydrolysis for a tenth-normal (N/10) solution of sodium carbonate at 25° C. to be about 3.17 per cent. For certain purposes it is desirable to determine the " alkalinity of such a solution, that is to say, the amount of sodium ions which may possibly result from this hydrolytic action, or one-half the sodium which

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[1] Ztschr. phys. Chem., **12**, 167 (1893).

has been brought into the solution as sodium carbonate. This may be done by titrating the solution with a standard acid solution. But this procedure usually requires that the solution should be heated to the boiling temperature. At the ordinary temperatures the acid reacts with the sodium carbonate to some extent to form the bicarbonate, thus:

$$Na_2CO_3 + HCl = NaCl + NaHCO_3,$$

and this formation of the bicarbonate may possibly be augmented by some of the liberated carbonic acid acting on the still undecomposed carbonate. Acid sodium carbonate is itself neutral towards indicators, and in consequence totally misleading results are inevitable. Furthermore, the presence of bicarbonates in the solution, other than that formed by the hydrolytic action of the water, will render an estimation of the sodium alone utterly valueless. The problem has been presented in this laboratory to estimate the amount of sodium carbonate in mixtures containing also the bicarbonate and, further, to do this without heating the material. Many attempts have been made by others to devise a method for this purpose. That proposed by Winkler has probably proved the most satisfactory. A good description of it has been given by Küster.[1] But this method was not adapted to our purposes for several reasons. The method of Sundstrom, described by Lunge,[2] as well as that devised by Lunge[3] himself, were also found to be impracticable under the conditions which confronted us. Without going into greater detail it may be said that no method of which a description could be found in the literature was free from serious objections. This appeared most surprising in view of the probable technical value of such a method in the manufacture of sodium carbonate. The problem has been satisfactorily solved and an account of the preliminary work on it may be found elsewhere.[4] It was deemed advisable, however, to give the method a more critical examination. The results are recorded in this paper.

Acid potassium sulphate is a well-characterized strong acid.

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[1] Ztschr. anorg. Chem., **13**, 127 (1896).

[2] Ztschr. angew. Chem., 41 (1897).

[3] *Ibid.*, 169 (1897).

[4] Report No. 64; U. S. Department of Agriculture, Division of Soils.

With sodium carbonate it has been shown to react as here indicated:

$$Na_2CO_3 + HKSO_4 = HNaCO_3 + NaKSO_4.$$

The reaction-products, sodium bicarbonate and sodium potassium sulphate, are neutral towards the ordinary indicators. Therefore, by titrating a solution containing sodium carbonate with a standard solution of sodium or potassium bisulphate, the amount of sodium carbonate present can be determined directly. Obviously the same statements may be made regarding potassium carbonate. Many indicators have been used with this method, but it may be said at once that, while good results can be obtained with others, phenolphthalein lends itself preeminently to the purposes here in view, and it alone is now used in this work in this laboratory. It is to be regretted that the reverse procedure from that just stated cannot be followed, for to the majority of analysts it would certainly be easier to titrate to the appearance of color rather than to its disappearance. But in this case such a procedure is entirely inadmissible because the sodium carbonate, on being brought in contact with an excess of the strong acid, is more or less decomposed, with the evolution of carbon dioxide, and misleading results that are not comparable are obtained.

It has become evident, in the course of the investigation, that acid sodium carbonate is a very unstable salt, especially in water solutions. The sodium carbonate solutions which had been titrated to loss of color, immediately began to color again on standing, the rate of this "inversion" being a function of the concentration and the temperature, as well as time. Some solutions which had been titrated just to loss of color at 1° C. had practically no color at the end of an hour, but on being gradually warmed over a Bunsen flame very soon became strongly colored from the reaction of the regenerated sodium carbonate on the phenolphthalein present. A tenth-normal solution, titrated just to loss of color, at the room temperature (about 25° C.) will show a marked pink color within five minutes and a strong color within half an hour.

A solution of sodium carbonate was divided into a number of portions in small Erlenmeyer flasks, and colored by the addition of phenolphthalein or litmus. Carbon dioxide was passed in until the solutions no longer showed any alkaline reaction with the indicators. They were then allowed to stand for several days. Some of the flasks were closed with rubber stoppers. The open flasks very soon showed a strong alkaline reaction. In the closed flasks, while a faint alkaline color appeared within a very short time, the color became more intense, but very slowly, showing the influence of the carbon dioxide in retarding the inversion. Nevertheless, it would appear that the inversion does take place, even though some carbonic acid must be present. This phase of the subject is now being studied in this laboratory, and the investigation will be continued as time and opportunity may permit.

In a qualitative sense precisely similar results were obtained with potassium carbonate and with sodium silicate, of which both yield acid salts which are unstable in water and at once invert to a greater or less extent. Sodium borate and disodium phosphate, being salts of weak acids, give an alkaline reaction in water solutions and can be very conveniently titrated to neutrality with acid potassium sulphate, but in neither case was any subsequent inversion observed.

Description of Experiments.

After some preliminary work it was deemed advisable to test the method by referring all solutions to a standard alkali solution, rather than by making the numerous gravimetric determinations which would otherwise be required. All the titrations were made from two burettes which previous experience had shown to be quite reliable. It was not thought necessary to calibrate them. The burettes were graduated to tenths (0.1 cc.) and smaller readings could be estimated. It was thought preferable, however, not to attempt readings closer than one-half a scale division (0.05 cc.) but to depend upon the average of a series of readings.

The standard for reference was a solution of potassium hydrate, accurately prepared and carefully freed from carbonates or other impurities. It was so prepared as to contain 18.17106 grams of potassium hydroxide per liter. A solution of approximately tenth-normal acid potassium sulphate was then made up and compared with the standard potassium hydrate solution. It was found, as a result of a satisfactory series of titrations, that 1 cc. of the potassium hydrate solution was equivalent to 6.764 cc. of the acid potassium sulphate solution. It follows that 1 cc. of the acid potassium sulphate solution contained 0.006518 gram of the acid salt, whereas a tenth-normal solution (N/10) would contain 0.006758 gram.

Reasonably pure potassium bisulphate is not difficult to obtain. But one cannot always be certain that an otherwise satisfactory sample contains precisely those proportions of the elements involved, which are required by the formula $HKSO_4$. A small excess of either sulphuric acid or the potassium sulphate will not materially alter the value of the reagent for the purposes under discussion, but it is obvious that for very accurate work it is safer to determine the concentration of the solution in the manner just described, rather than depend on either a gravimetric determination of the sulphuric acid alone or of the potassium it contains.

A solution of potassium carbonate (approximately tenth-normal) was then prepared and titrated with the results here given, the first column indicating quantity of potassium carbonate, the second column the quantity of potassium bisulphate, and the third column the ratio of the readings :

Table I.

10.00	12.70	1.270
15.00	18.90	1.260
15.00	18.90	1.260
20.00	25.20	1.260
20.00	25.20	1.260
		1.262

These titrations were made in the usual manner by adding a little of the acid solution, shaking, and waiting a few moments to see if color disappeared before proceeding.

The potassium carbonate was then analyzed in the following way : The solution was treated with an excess of hydrochloric acid, boiled to drive off all the carbon dioxide liberated, and the excess of acid determined by titration with the standard potassium hydrate solution. The figures follow. The first column represents amounts of potassium carbonate, the second column hydrochloric acid, and the third column potassium hydrate:

Table II.

40.00	20.00	7.15
40.00	20.00	7.15
40.00	20.00	7.20
		7.166

By a careful and satisfactory series of titrations 1 cc. of the hydrochloric acid solution was shown to be equivalent to 1.0464 cc. of the potassium hydroxide solution. Therefore:

20 cc. HCl solution = 20.928 cc. KOH solution.
Excess " " = 7.166 " " "

40 cc. Na_2CO_3 " = 13.762 " " "
1 " " " = 0.344 " " "

It has been shown that 1 cc. KOH solution was equivalent to 6.764 cc. $HKSO_4$ solution; therefore, 0.344 cc. KOH solution was equivalent to 2.327 cc. $HKSO_4$ solution. But since only one-half as much acid potassium sulphate is required to convert the potassium carbonate to bicarbonate it should have required 2.327 ÷ 2, or 1.163 cc., instead of 1.262 cc. as actually found. This disagreement was startling in view of the good results previously obtained with the method.

A sodium carbonate solution of about the same strength as the potassium carbonate solution just described was prepared and a long series of titrations made in the same manner as with the potassium carbonate solution. It was found that 1 cc. of the carbonate solution was equivalent to 1.137 cc. of the acid sulphate solution, though an analysis made in the same manner as in the case of the potassium carbonate showed that 1.035 cc. of the acid sulphate solution should have been required. The disagreement was practically the same in both cases.

Two series of titrations were then made with the potassium carbonate solution. In the first series the potassium carbonate solution was heated to boiling in each case before titrating. In the second series in each case the solution was filled with crushed ice and shaken until the temperature was lowered to less than 1° C. before titrating. The number of cubic centimeters of the acid sulphate solution required to neutralize 1 cc. of the potassium carbonate solution was:

	cc.
At 0°–1° C.	1.455
" room temperature (about 26° C.)	1.262
After boiling (about 97° C.)	1.210

From these results it would appear that the reaction was more complete at the higher temperature, in spite of the fact that the inversion of the acid potassium carbonate is more rapid at these higher temperatures and might be expected to produce exactly opposite results. For instance, the solutions which had been titrated at 97° were very strongly colored within five minutes after the titration was completed, while those which were titrated at 1° showed only a faint pink color after standing for upwards of an hour. The true explanation of the results, however, became apparent in the course of these titrations. It was found that it takes a measurable time for the reaction between the acid sulphate and carbonate to run to end, and that if the acid sulphate is delivered too rapidly from the burette a considerable excess may be run into the carbonate solution before the color of the indicator disappears so that, with these two effects of inversion of the acid carbonate and the relatively slow reaction velocity between the carbonate and acid working against each other, it would be possible to run in the solution at such a rate as to obtain any desired result within quite wide limits, and, in fact, beautifully comparable results were thus obtained. The value of the method would be very slight if the personal equation could not be eliminated in the titrations. That this can be done, however, was clearly demonstrated. If the acid potassium sulphate solution is delivered from the burette at about the rate of 2 drops per second, and the vessel containing the alkaline carbonate is *constantly* and *vigorously* shaken, markedly lower reading will be obtained than by any other procedure; furthermore, the readings thus obtained were found to be quite independent of the temperature at which the titrations were made. These facts were confirmed by several long and satisfactory series of titrations. This point having been clearly established, a solution of sodium carbonate was carefully prepared and boiled for some time to complete the inversion of any acid sodium carbonate which might be present. After being cooled to room temperature and made up to the desired volume, it was titrated with the following results: The first column represents the amount of carbonate, the second column the amount of acid sulphate, and the third column the ratio of the readings.

Table III.

20.00	21.50	1.075
20.00	21.60	1.080
30.00	32.30	1.076
30.00	32.30	1.076
		1.077

The sodium carbonate solution was then analyzed by boiling with an excess of acid potassium sulphate and titrating the excess of acid with a solution of potassium hydrate of known concentration. The results are here given; the first column indicating amounts of carbonate taken, the second column amounts of acid potassium sulphate, and the third amounts of potassium hydrate required to neutralize the excess of acid:

Table IV.

20.00	50.00	5.50
20.00	50.00	5.50
20.00	50.00	5.50
20.00	50.00	5.50
		5.50

1.00 cc. KOH solution = 1.352 cc. $HKSO_4$ solution.
5.50 “ “ “ = 7.436 “ “ “
20.00 “ Na_2CO_3 “ = 43.564 “ “ “
1.00 “ “ “ = 2.128 “ “ “

But since only one-half as much acid potassium sulphate would be required to convert the carbonate to acid carbonate, 1 cc. of the Na_2CO_3 was equivalent to 2.128 cc. ÷ 2 or 1.064

cc. of the $HKSO_4$ solution. Comparing the value found by direct titration, 1.077 cc., the error for 1 cc. was about 1.2 per cent. More accurate results have, however, been obtained for both sodium carbonate and potassium carbonate. This error would amount to 0.10 cc. in reading for 10 cc., about 0.25 cc. for 20 cc., or nearly 0.50 cc. in reading a titration of 30 cc. But it has been shown repeatedly that readings for this amount could be obtained by different observers agreeing to within less than 0.20 cc., and it may be said that the probable error for such an amount is certainly no greater than this. Considering the number and nature of the operations involved, the agreement obtained above was considered satisfactory, and it was not deemed worth while to repeat the work merely for the purpose of being able to present more refined figures.

In order to demonstrate that the presence of sodium bicarbonate in the salt analyzed does not affect the accuracy of the method, mixtures of the carbonate and bicarbonate were prepared. Before titrating these mixtures with the acid potassium sulphate solution, the solutions of the carbonate and bicarbonate were separately titrated with this reagent. In Table V the first column represents amounts of sodium carbonate taken, the second column the amounts of acid potassium sulphate required to neutralize them respectively, and the third column the ratio of the readings :

Table V.

10.00	8.90	0.890
20.00	17.50	0.875
30.00	26.30	0.876
15.00	13.29	0.886
10.00	8.90	0.890
20.00	17.60	0.880
20.00	17.60	0.880
30.00	26.45	0.882
30.00	26.45	0.882
30.00	26.45	0.882
		0.882

A solution of sodium bicarbonate was then prepared and allowed to stand until equilibrium had been reached with the inverted normal carbonate. It was then titrated with the results here given:

Table VI.

25.00	14.60	0.586
10.00	5.90	0.590
10.00	6.10	0.610
10.00	6.10	0.610
20.00	12.30	0.615
		0.602

Mixtures were then made by adding 10 cc. of the sodium bicarbonate solution to 20 cc. of the normal sodium carbonate solution and titrating as before. The first column represents the amount of acid potassium sulphate solution required, the second column gives the reading corrected for the sodium bicarbonate added, and the third column the corresponding amount of acid required to neutralize 1 cc. of the sodium carbonate solution taken:

Table VII.

23.70	17.68	0.884
23.75	17.73	0.886
23.70	17.68	0.884
		0.885

The agreement of this figure 0.885 with that found in Table V, 0.882, is very satisfactory, and may be regarded as establishing the point under investigation. It should be remembered, however, that when sodium carbonate is added to a solution containing sodium bicarbonate and consequently some inverted carbonate, the equilibrium between the two substances may well be materially altered. In solutions as dilute as those examined, this displacement was probably very small and so did not interfere with the demonstration of the fact that the presence of acid sodium carbonate does not interfere with the estimation of the hydrolyzed sodium in the solution. But when the concentrations are considerable, this equilibrium displacement may well become an important factor. Should this method ever commend itself to use in technical work, this displacement of the equilibrium corresponding to an apparent increase of the amount of normal carbonate present on dissolving mixtures must be considered.

An interesting extension of the method has been developed in the course of our work. It is frequently necessary to make a rapid determination of the chloride as well as the carbonates in solution. This may be done in the following way: As soon as the solution containing the carbonate has been titrated to neutral action with acid potassium sulphate, a drop or two of this reagent is added in excess to retard the inversion of the bicarbonate to the normal alkaline carbonate. A small amount of a solution of potassium or ammonium chromate is then added as an indicator, and the solution titrated at once with a standard solution of silver nitrate. Before titrating with the silver nitrate the solution may be boiled, in which case the inverted carbonate must again be neutralized before making the determination for the chloride. But little advantage is gained thereby, however, and results in every way satisfactory have been repeatedly obtained, working throughout at the room temperature. For instance, a solution (tenth-normal) of sodium carbonate was prepared by standardizing against a tenth-normal (N/10) solution of acid potassium sulphate; also a solution of sodium chloride, 1 cc. of which was equivalent to 1.734 cc. of a tenth-normal solution of silver nitrate. The following are the results obtained with the mixtures of the sodium carbonate and sodium chloride solutions: The first column represents amounts of sodium carbonate taken, the second column the amounts of sodium chloride taken, the third column the amounts of acid potassium sulphate required to neutralize the mixtures, and the fourth column the amounts of silver nitrate required to precipitate the chloride present.

Table VIII.

5.00	10.00	5.05	17.35
10.00	10.00	10.10	17.35
15.00	10.00	15.20	17.35

The agreement shown in these results leaves nothing to be desired, and many more equally satisfactory determinations have been made. An interesting theoretical point is involved in the operation just described. The presence of normal carbonates in the solution would, it is well known, interfere with a titration for chloride with silver nitrate, as insoluble silver carbonate would be formed to some extent and interfere with the desired precipitation of the chloride. The reaction is to be regarded as the result of the silver ions $\overset{+}{\mathrm{Ag}}'$ coming in contact with the carbonic acid ions $\overset{-}{\mathrm{CO}}_3'$. But no such reaction is to be observed in the case we have been discussing, where acid sodium carbonate is in the solution. Therefore it appears reasonable to assume that acid sodium carbonate does not yield a $\overset{-}{\mathrm{CO}}_3$ ion, but probably dissociates, thus

$$\mathrm{NaHCO_3} \rightleftarrows \overset{+}{\mathrm{Na}} + \overset{-}{\mathrm{HCO}}_3$$

and the ion $\overset{-}{\mathrm{HCO}}_3$ does not react with the silver ion to give an insoluble compound. There is further evidence to support this view.[1]

If a solution of acid sodium carbonate is added to a solution of a barium salt there is only a little precipitate formed at first, though the precipitation of the barium generally proceeds and is completed in time, more quickly if the solution be heated. It has been shown that acid sodium carbonate in water solution is unstable, some normal carbonate being formed at once, and it is to this small amount of normal carbonate that the first precipitation of the barium is due. But when this has taken place the equilibrium between the sodium carbonate and acid sodium carbonate is destroyed, more sodium carbonate is formed, and the precipitation of the barium again proceeds. This action is, of course, continuous. As the inversion of the acid sodium carbonate is more rapid at high temperatures, the formation of the normal carbonate and subsequent precipitation of the barium will proceed more rapidly on heating.

The use of ammonium carbonate in precipitating insoluble carbonates seems worthy of consideration in this connection. Unlike the corresponding sodium and potassium salts, ammonium carbonate is unstable in water solution, breaking down with the

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[1] Walker and Cormack: J. Chem. Soc., **47**, 5 (1900); Foundations of Analytical Chemistry; Ostwald and McGowan, pp. 193 and 207.

formation of the acid carbonate and the escape of some of the ammonia as such. But an equilibrium is established between the normal carbonate and the acid carbonate, which is destroyed when the solution is brought into contact with some salt which will precipitate an insoluble carbonate, such as calcium or barium. The inversion of the acid carbonate is measurably slow, however, and, as is well known, to obtain complete precipitation the solution must be allowed to stand for some time or be heated.

A statement of some of the preliminary experiments on the inversion phenomena referred to may be of interest in this connection. Three portions of a sodium carbonate solution were titrated with acid potassium sulphate to loss of color with phenolphthalein as indicator, allowed to stand for twenty-four hours, and then titrated a second time to loss of color. The results are here given, the first column being amounts of the carbonate solution, the second column amounts of acid sulphate added, and the third column amounts of acid sulphate required to neutralize the solution after standing.

Table IX.

10.00	8.90	1.00
20.00	17.50	1.85
30.00	26.30	2.55

It would appear that the inversion was approximately proportional to the initial amount of the bicarbonate, but as the concentrations were not quite the same and the sulphates present may have an influence, this conclusion can only be drawn tentatively. Some measurements, which have been made by Mr. Lyman J. Briggs, indicate that the inversion at first approaches a maximum quite rapidly, but, when equilibrium has been nearly reached, it becomes very slow and probably requires a long time before reaching final equilibrium.

Three portions of 20 cc. of a potassium carbonate solution were each titrated to disappearance of alkaline reaction with 24.2 cc. of the acid potassium sulphate solution and, after standing forty-eight hours, each required 3.1 cc. of the acid sulphate solution to neutralize them.

Ten cc. of a sodium silicate solution required 14.1 cc. of the acid sulphate solution to neutralize it. It was immediately boiled for three minutes, after which it required 1.1 cc. of the acid sulphate solution to neutralize it; another portion of 10 cc., to which 14.1 cc. of the acid sulphate had been added after the expiration of an hour, at the room temperature, required 0.9 cc. to neutralize it. The case of the sodium bisilicate differs essentially, however, from that of the sodium bicarbonate, in that no volatile component can be formed. So that this *apparent* inversion must be more limited in amount and is in reality a measure of the hydrolysis of the salt. It was not appreciable in the case of the borates or phosphates, as has already been noted.

An application of the method to a solution of sodium silicate was made. Table X gives the results of the titrations of the solution with the acid potassium sulphate, the first column indicating amounts of the silicate solution, the second column amounts of the acid sulphate, and the third column the corresponding ratios:

Table X.

20.00	31.00	1.550
20.00	31.00	1.550
10.00	15.70	1.570
10.00	15.80	1.580
10.00	15.50	1.550
10.00	15.70	1.570
15.00	23.60	1.573
15.00	23.60	1.573
20.00	31.40	1.570
20.00	31.45	1.572
		1.566

The solution was then analyzed by adding an excess of hydrochloric acid, boiling, and titrating the excess of the acid with a solution of potassium hydroxide. The first column of Table XI indicates the amounts of silicates taken, the second column the amounts of hydrochloric acid added, and the third column the amounts of potassium hydrate required to neutralize the excess of acid:

Table XI.

40.00	20.00	11.70
40.00	20.00	11.70
40.00	20.00	11.70
		11.70

Since in this case the silicic acid does not escape from the solution as does carbonic acid, when the hydrochloric acid is added to excess, enough potassium hydrate will be required not only to neutralize the excess of hydrochloric acid, but also to reconvert the silicic acid to potassium bisilicate before the solution will be alkaline.

20.00 cc. HCl solution = 20.928 cc. KOH solution.
Excess of " " = 11.700 " " "
40.00 cc. sodium silicate solution = 9.228 " " "
1.00 cc. sodium silicate solution = 0.231 " " "

It has been shown that 1 cc. KOH solution was equivalent to 6.764 cc. $HKSO_4$ solution, therefore 0.231 cc. KOH solution was equivalent to 1.562 cc. $HKSO_4$ solution. The agreement of this figure 1.562 cc. with that given in Table X, 1.566 cc., must be regarded as entirely satisfactory.

Summary.

The principal results of this investigation may be summarized as follows :

1. The amount of a soluble alkaline carbonate in a solution can be quickly and accurately determined whether the bicarbonates are present or not.

2. The method seems well adapted to the estimation of silicates, borates, phosphates, and the salts of weak acids in general.

3. The bicarbonates are unstable in water solution and are more or less completely converted into the normal salt.

4. Alkaline bicarbonates are themselves neutral in water solutions ; they do not yield a CO_3 ion by hydrolysis, or they do so only to a slight extent.

5. Therefore, an accurate volumetric determination of chlorides by means of a standard silver nitrate solution is feasible in the presence of alkaline bicarbonates, if the hydrolysis of these latter is prevented.

Contributions from the Chemical Laboratories of the Massachusetts Institute of Technology.

XXV.—ON THE ISOMORPHISM OF SELENIUM AND TELLURIUM.

BY JAMES F. NORRIS AND RICHARD MOMMERS.

The fact that the most trustworthy determinations of the atomic weight of tellurium have given results which place it in the eighth group in the periodic system of the elements, has led to a study of the analogies existing between tellurium and the platinum metals on the one hand, and sulphur and selenium on the other. Retgers,[1] in his work on isomorphism, studied carefully the relations between sulphur, selenium, and tellurium, and concluded that while sulphur and selenium showed complete crystallographic similarity in their compounds, tellurium was not isomorphous with either element. The only occurrence of isomorphism between tellurium and the elements of the oxygen family was in the case of the sulphides, selenides, and tellurides. These compounds crystallize in the cubic system and, consequently, according to Retgers, possess such a high state of crystallographic symmetry that their power to form mixed crystals should not be taken as a proof of the true isomorphism of their constituents. Potassium tellurate is not isomorphous with potassium selenate, but is isomorphous with potassium osmate.

Muthmann[2] showed later that the double bromide of potassium and tellurium is isomorphous with the corresponding salt containing selenium. Retgers[3] pointed out in reply, that the tellurium compound is also isomorphous with the analogous platinum salt and that, as is the case with the selenides and tellurides, the formation of mixed crystals is due to the fact that all of the compounds crystallize in the cubic system.

[1] Ztschr. phys. Chem., **8**, 70; **10**, 533.

[2] Ber. d. chem. Ges., **26**, 1011.

[3] Ztschr. anorg. Chem., **12**, 105.

As no case of true isomorphism between selenium and tellurium compounds has been proved, it seemed of interest to question further. The crystallography of the double bromide of platinum and dimethylamine has been studied carefully by Hjortdahl.[1] The salt crystallizes in the orthorhombic system, has the faces $\infty \breve{P}2$ and $\breve{P}\infty$, and the axial ratio 0.9903 : 1 : 0.9927. As the argument brought forward against the value of conclusions drawn from the formation of mixed crystals in the cubic system could not hold in this case, we compared this salt with the analogous selenium and tellurium compounds. The double bromide of selenium and dimethylamine had been prepared by one of us,[2] but its crystallography had not been studied. As the tellurium compound had not been made, it was prepared and was found on analysis to resemble in composition the other two salts.

The compound containing selenium crystallizes in stout, prismatic needles, terminated by domes, which closely resemble the platinum double bromide. The crystals of the tellurium salt are like those of the other two salts, with the exception that well-developed macropinacoids are present at times. The color of the compound, however, is different from that of the selenium and platinum salts; the latter are nearly alike, having a dark-red color resembling that of chromic acid, while the color of the tellurium salt is almost that of azobenzene.

As the facilities were not at hand for a complete crystallographic investigation, the isomorphism of the salts was studied by applying the test of the formation of mixed crystals in the manner devised by Retgers.[3] In using this method saturated solutions of two salts, which must differ in color, are placed side by side on a microscope slide and then are brought together with a glass rod. The crystals formed on evaporation are examined under a microscope. If the salts are isomorphous, the color of the crystals varies gradually from one side to the other, the crystals of the pure compounds being

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[1] Jsb. d. Chem., 1882, 474.

[2] This JOURNAL, **20**, 490.

[3] Ztschr. phys. Chem., **8**, 6.

visible on the extreme edges of the mass. If, however, the salts are not isomorphous, they do not mix, and in the center where the two solutions have been brought together, distinct crystals of each compound can be seen owing to their difference in color. In studying the isomorphism of two colored salts, Retgers made use of a third salt, which was colorless. If both of the colored salts formed mixed crystals with the colorless salt, the former were considered isomorphous with one another.

As the double salts which were to be investigated were somewhat alike in color, their isomorphism could be determined only by comparing each salt separately with a fourth salt having a different color. The double chloride of tellurium and dimethylamine was found to answer the purpose admirably. The compound crystallizes in light-yellow prisms, which have the same forms as the analogous bromide. The chloride formed mixed crystals of varying depths of color with the selenium and tellurium double bromides, but did not mix with the platinum compound. In the latter case the platinum salt crystallized in small, well-defined, dark-red crystals, which were at times overgrown with the tellurium salt. Solutions of the selenium, tellurium, and platinum bromides were mixed separately with a solution of the chloride and allowed to crystallize. The crystals obtained in the first two cases were uniform in color, whereas with the platinum salt two kinds of crystals were distinctly seen. It appears, then, that the double bromides containing selenium and tellurium are both isomorphous with the chloride, and are, therefore, isomorphous with one another. The platinum compound, however, does not form mixed crystals with the chloride and is not isomorphous with the analogous selenium and tellurium salts. The work has established the first case of isomorphism between selenium and tellurium compounds which is not open to the objections raised by Retgers.

The existence of isomorphism in the case of the double bromides appears to be inconsistent with the fact that potassium tellurate is not isomorphous with potassium selenate. The lack of crystallographic similarity in this case is not remarkable, inasmuch as one salt contains water of crystallization while the other is anhydrous. In order to get further evidence for or against the isomorphism of the two elements in their oxygen acids, the cesium, rubidium, and cerium salts of selenic and telluric acids are being prepared and studied.

In an investigation by one of us of the double chlorides and bromides of selenium and dimethyl- and trimethylamine a number of salts were obtained which possessed very unusual compositions for compounds of this class. With dimethylamine, compounds of the following formulæ were prepared :

$2SeOCl_2.3(CH_3)_2NH.HCl$,
$SeO_2.(CH_3)_2NH.HCl$,
$2SeBr_4.SeBr.3(CH_3)_2NH.HBr$,
$SeBr_4.2(CH_3)_2NH.HBr$,
$SeBr_4.2[(CH_3)_2NH.HBr_2]$,
$SeBr_4.2[(CH_3)_2NH.HBr_2].(CH_3)_2NH.HBr$.

In order to discover if tellurium resembled selenium in the power to form such oxysalts and perhalides, we undertook the preparation of all the possible double chlorides and bromides of tellurium and dimethylamine. The uncertainty about the relation of tellurium to the periodic law noted above, adds interest to any new facts brought to light and to any new analogies established. As a result of the work, compounds having the following formulæ were prepared :

$3TeCl_4.TeOCl_2.4(CH_3)_2NH.HCl.H_2O$,
$TeCl_4.TeOCl_2.2(CH_3)_2NH.HCl.H_2O$,
$TeCl_4.2TeOCl_2.3(CH_3)_2NH.HCl$,
$TeCl_4.2(CH_3)_2NH.HCl$,
$TeBr_4.2(CH_3)_2NH.HBr$.

A consideration of the above formulæ shows that tellurium, as well as selenium, forms double salts which contain the oxychloride of the metal. With the more basic tellurium, however, the tetrachloride enters into the compound. The first three salts in the list were obtained from solutions containing a large excess of tellurium. These salts, which at first appear to have very complicated formulæ, can be considered as derivatives of the salt $TeCl_4.(CH_3)_2NH.HCl$, in which a part of the tellurium tetrachloride has been converted into the oxychloride by the water present in the solvent from which the salts were crystallized. They all contain the tellurium and the amine in the molecular ratio of 1 : 1. In the first salt $\frac{1}{4}$ of the tetrachloride has been changed into oxychloride, in the second $\frac{1}{2}$, and in the third $\frac{2}{3}$. The formation of the various salts was determined by the amount of hydrochloric acid present during crystallization.

Double salts containing selenium and the perbromide of dimethylamine, $(CH_3)_2NH.HBr_2$, were readily prepared. The salts crystallized well from hydrobromic acid and dissolved in water with the evolution of bromine. With tellurium bromide analogous salts could not be formed. An unsuccessful attempt was made to prepare double salts containing the amine perbromide and platinum and lead. As far as our experiments go, selenium is the only element which forms salts of this class.

Wheeler[1] prepared two double bromides of tellurium and potassium, one of which contained water of crystallization. The double bromide of dimethylamine and tellurium was prepared under conditions favorable to the formation of a hydrated salt, but the resulting compound contained no water of crystallization.

The analogies in composition exhibited by the selenium and tellurium salts are as great as could be expected; the differences observed are well explained by the more metallic nature of tellurium.

Experimental.

The double salts were prepared by dissolving tellurium dioxide and dimethylamine hydrochloride or hydrobromide in the corresponding halogen acid and evaporating the solutions to crystallization. Seven different mixtures were prepared in each case in which the proportions of the constituents varied from 4 molecules of the oxide to 1 of the amine salt to 1 of the oxide to 4 of the salt.

In the analyses, tellurium, halogen, and the amine were determined. An attempt was made to estimate the water of crys-

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[1] Am. J. Sci. [3], **45**, 267.

tallization in the hydrated chlorides, but without success, for even at 80°–90° the salts could not be brought to a constant weight owing to the volatilization of a part of the tellurium tetrachloride. The presence of water was shown, however, qualitatively. The tellurium was determined volumetrically by the method of Norris and Fay[1] after the amine had been removed by heating with a solution of sodium hydroxide. In some of the compounds the halogen was estimated gravimetrically; in the analysis of the others the volumetric method of Volhard was used. The method was shown to be accurate in the presence of tellurium by an analysis of the double bromide of tellurium and potassium.

Salt of the Composition $TeCl_4.2(CH_3)_2NH.HCl$.—This compound is obtained readily by evaporating to crystallization a mixture of tellurium dioxide and dimethylamine hydrochloride, in the theoretical proportions, dissolved in dilute hydrochloric acid. The salt crystallizes in light-yellow, stout, lustrous needles from a hot solution. When obtained by spontaneous evaporation the crystals are well-developed prisms, which are probably orthorhombic, modified by brachydomes and macropinacoids. The salt is soluble in a small amount of water. Excess of the solvent causes decomposition into tellurous acid, which separates as a curdy, white precipitate. It dissolves readily in alcohol and is insoluble in ether. The results of the analyses follow:

I. 0.2634 gram salt gave 0.1293 gram Cl by the volumetric method.
0.3396 gram salt gave 0.0986 gram Te.
II. 0.2508 gram salt gave 0.1237 gram Cl.
0.3053 gram salt gave 0.0897 gram Te.
III. 0.3910 gram salt gave 0.0813 gram $(CH_3)_2NH$.

	Calculated for $TeCl_4.2(CH_3)_2NH.HCl$.	Found. I.	II.	III.
Cl	49.20	49.10	49.35	....
Te	29.43	29.41	29.38	....
$(CH_3)_2NH$	20.84	....	....	20.79

Salt of the Composition $TeCl_4.TeOCl_2.2(CH_3)_2NH.HCl.H_2O$.—When a solution containing tellurium dioxide and di-

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[1] This JOURNAL, **20**, 278.

methylamine hydrochloride, in the molecular ratio of three of the former to one of the latter, dissolved in dilute hydrochloric acid (sp. gr. 1.12), is allowed to evaporate slowly two well-crystallized compounds are formed. The salt of the above composition first separates in compact, almost colorless, crystals, which completely cover the bottom of the containing vessel. Stout, yellow needles are next formed. The two compounds can be separated mechanically without difficulty, as the yellow crystals are from 0.5–1 centimeter in length. The compound closely resembles in composition the bromide of selenium and trimethylamine, which has the formula $SeBr_4.SeOBr_2.2(CH_3)_3N.HBr$. An analysis gave the following results :

I. 0.2624 gram salt gave 0.4535 gram AgCl.
II. 0.3275 gram salt gave 0.1251 gram Te.
III. 0.3055 gram salt gave 0.0425 gram $(CH_3)_2NH$.

	Calculated for		Found.	
	$TeCl_4.TeOCl_2.2(CH_3)_2NH.HCl.H_2O$.	I.	II.	III.
Cl	42.74	42.79	....	....
Te	38.32	....	38.20	....
$(CH_3)_2NH$	13.58	....	....	13.90

Salt of the Composition $3TeCl_4.TeOCl_2.4(CH_3)_2NH.HCl.H_2O$.—This salt was always formed under the conditions made use of in the preparation of the compound described above. The crystals were so well developed and large that they could be obtained pure for analysis without difficulty. The salt forms stout, columnar, rectangular, yellow crystals, whose ends are truncated by a single plane at a sharp angle to the prismatic faces. It was not very stable in the air, readily losing its bright luster, and consequently its crystallography was not carefully studied. The analytical results follow :

I. 0.3056 gram salt gave 0.5767 gram AgCl.
0.3691 gram salt gave 0.1375 gram Te.
II. 0.2675 gram salt gave 0.5056 gram AgCl.
0.3151 gram salt gave 0.1169 gram Te.
III. 0.3334 gram salt gave 0.0447 gram $(CH_3)_2NH$.

	Calculated for		Found.	
	$3TeCl_4.TeOCl_2.4(CH_3)_2NH.HCl.H_2O$.	I.	II.	III.
Cl	46.77	46.71	46.79	....
Te	37.27	37.26	37.11	....
$(CH_3)_2NH$	13.20	....	....	13.41

Salt of the Composition $TeCl_4.2TeOCl_2.3(CH_3)_2NH.HCl$.—As two salts were obtained which were derivatives of the compound $TeCl_4.(CH_3)_2NH.HCl$, in which different proportions of the tetrachloride were converted into the oxychloride, the effect of varying the concentration of the hydrochloric acid from which the salts were crystallized, was investigated.

Tellurium dioxide and dimethylamine hydrochloride in the molecular ratio of three of the former to one of the latter were dissolved in the smallest quantity of concentrated hydrochloric acid possible. After standing two months in a desiccator the solution became very viscous and crystals separated slowly. These were removed, but it was found impossible to purify them for analysis. The crystals did not resemble any of the other chlorides which had been prepared and were probably a different compound.

To effect the greatest decomposition into the oxychloride, tellurium tetrachloride and the amine salt, in the proportions used in the experiment just described, were dissolved in water acidulated with just enough hydrochloric acid to keep the solution clear. After long standing a pale greenish-yellow salt separated in the form of stout prismatic crystals, truncated by domes. A careful study of the crystallography of the salt was impossible. It will be seen from the formula of the salt that complete decomposition of the tetrachloride did not take place.

The selenium compound prepared under the same conditions, however, contained no tetrachloride. The results of the analysis of the salt are as follows:

I. 0.2736 gram salt gave 0.4633 gram AgCl.
0.2987 gram salt gave 0.1213 gram Te.
II. 0.3096 gram salt gave 0.5227 gram AgCl.
0.3060 gram salt gave 0.1240 gram Te.

	Calculated for $TeCl_4.2TeOCl_2.3(CH_3)_2NH.HCl$.	Found. I.	II.
Cl	41.41	41.94	41.79
Te	40.52	40.63	40.52

Salt of the Composition $TeBr_4.2(CH_3)_2NH.HBr$.—A salt of this composition was the only bromide obtained as the result of a large number of experiments. Mixtures similar to those used in the preparation of the chlorides were made. From these, crystals were obtained by slow evaporation in a desiccator, by rapid concentration by heat, and in the presence of bromine. The salt is prepared most readily by dissolving the theoretical quantities of tellurium dioxide and dimethylamine hydrobromide in dilute hydrobromic acid and evaporating to crystallization. The compound can be crystallized from water, although it is decomposed by a large excess of the solvent. The crystallography of the salt has been described in the first part of the paper. The analytical results follow:

I. 0.2246 gram salt gave 0.1546 gram Br.
0.5012 gram salt gave 0.0925 gram Te.
II. 0.2279 gram salt gave 0.1559 gram Br.
0.4659 gram salt gave 0.0846 gram Te.

	Calculated for $TeBr_4.2(CH_3)_2NH.HBr$.	Found. I.	II.
Br	68.59	68.84	68.41
Te	18.24	18.46	18.15

Boston, March 9, 1900.

Contributions from the Chemical Laboratory of Harvard College.

CXVIII.—NOTE ON THE CONSTITUTION OF DIPARABROMBENZYLCYANAMIDE.[1]

By C. Loring Jackson and R. W. Fuller.

The work described in this paper consists of the conversion of the silver salt of cyanamide into a dialkylcyanamide, and the determination of the constitution of this body. Last summer (after this work was finished) a paper appeared in the "Berichte der deutschen chemischen Gesellschaft," in which Wallach[2] described a number of substituted cyanamides obtained by the action of bromide of cyanogen on secondary amines. For fear of approaching too near the field thus reserved by Wallach we shall abandon the further study of dialkylcyanamides, but the study of alkyl compounds of dicyandiamide and dicyanimide will be taken up in this laboratory; in fact, work on this latter substance is already in progress.

Theoretically, a dialkylcyanamide derived from the silver salt of cyanamide might have either of the following formulas:

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[1] Presented to the American Academy of Arts and Sciences, December 13, 1899.

[2] Ber. d. chem. Ges., **32**, 1872.

$R—N=C=N—R$ or $R_2=N—CN$, and it is easy to determine by experiment which of these two formulas is correct. So far as we can find, but a single experiment of this sort has been tried; this was published some years ago by Fileti and Robert Schiff,[1] who prepared diethylcyanamide by the action of ethyl iodide on argentic cyanamide at 100° for some hours. The product was extracted with ether, and divided into two portions; one was distilled, and gave a boiling-point of 186°, whereas Cloez and Cannizzaro,[2] who prepared it by the decomposition of ethylcyanamide, found a boiling-point of 190°. Fileti and R. Schiff analyzed their distillate, and obtained carbon 60.66 instead of 61.22, and hydrogen 10.11 instead of 10.30. The other portion of their product (which had not been distilled) was decomposed by means of hydrochloric acid on the water-bath; the chlorides obtained by evaporating the hydrochloric acid solution were converted into chlorplatinates and crystallized fractionally, when they obtained two end fractions in which the platinum was determined with the following results:

	Calculated for		Found.	
	$(NH_4)_2PtCl_6$.	$((C_2H_5)_2NH_2)_2PtCl_6$.	I.	II.
Pt	44.04[1]	35.30[1]	42.51	36.3

$(C_2H_5NH_3)_2PtCl_6$ requires 39.24[3] per cent of platinum.

In considering these results of Fileti and R. Schiff, it is to be observed that the diethylcyanamide was not purified, and that no very sharp criterion of purity was given (Wallach states that these substances are decomposed by distillation under ordinary pressure, so that the boiling-point is not of much value in this respect), further that their analyses of the platinum salts did not give numbers very near to those calculated. It seemed to us, therefore, worth while to try similar experiments with, if possible, a crystalline disubstituted cyanamide, which could, therefore, be obtained in a state of undoubted purity, and also with one which would yield amines more easily separated than ammonia and diethylamine. We selected for this purpose the diparabrombenzylcyanamide, since

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[1] Ber. d. chem. Ges., **10**, 425 (1877).

[2] Ann. Chem. (Liebig), **90**, 95.

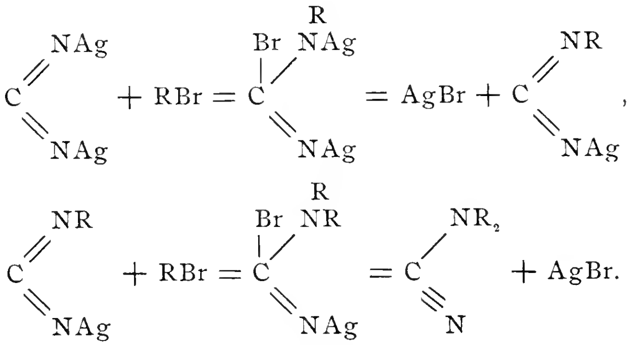
[3] These are the numbers given by Fileti and R. Schiff. They would be somewhat altered by using modern atomic weights.

the parabrombenzyl compounds show a great tendency to crystallize, and the diparabrombenzylamine, if formed, could be recognized by its melting-point, 50° (dibenzylamine is a liquid), while the parabrombenzylamine, if that were the product, gives a carbonate with a definite melting-point, and both these amines could be separated without difficulty from ammonia.

The diparabrombenzylcyanamide proved to be a well-crystallized solid, melting at 133°. On decomposition with dilute sulphuric acid it gave diparabrombenzylamine, ammonia, and carbonic dioxide by the following reaction :

$$(C_6H_4BrCH_2)_2NCN + 2H_2O = (C_6H_4BrCH_2)_2NH + NH_3 + CO_2.$$

Our results, therefore, confirm those of Fileti and R. Schiff, and leave no doubt that the dialkyl derivatives from argentic cyanamide are cyanamides and not carbodiimides. If they are formed by direct replacement of the silver in argentic cyanamide by the alkyl radicals, the same constitution (Ag_2NCN) must be ascribed to this substance and to cyanamide. If, on the other hand, these compounds are formed by successive additions of the alkyl bromide with splitting off of argentic bromide, the disubstituted cyanamides could be formed from a silver salt with a carbodiimide formula, as is shown by the following reactions :



Our results, therefore, prove nothing in regard to the true formula of cyanamide.

Preparation of Diparabrombenzylcyanamide, $(C_6H_4BrCH_2)_2NCN$.

The yellow silver salt of cyanamide, Ag_2NCN, prepared according to Walther,[1] was mixed with a benzol solution of parabrombenzyl bromide in the proportion of 2 molecules of bromide to 1 of the salt, which should be finely powdered. The mixture was heated in a flask with a return-condenser on the steam-bath, until after four or five hours the full yellow color of the argentic cyanamide had been completely replaced by the yellowish-white color of argentic bromide. The precipitate was then filtered out and washed thoroughly with hot benzol, and the filtrate and washings evaporated to dryness, when a thick reddish-yellow oil was left. To purify this it was dissolved in hot alcohol, and the strong solution allowed to cool slowly; a yellow oil was deposited, at first followed by a white crystalline substance, which was obtained by pouring the solution off from the oil as soon as the crystals began to appear. By repeated recrystallizations of this sort the melting-point of the substance was raised to 133°, where it remained constant. It was dried *in vacuo* and analyzed with the following results:

I. 0.1508 gram substance gave, by the method of Carius, 0.1494 gram argentic bromide.

II. 0.3041 gram substance gave 20.2 cc. nitrogen at 18°.6 and 760.4 mm. pressure.

	Calculated for $(C_7H_6Br)_2NCN$.	Found.	
		I.	II.
Br	42.11	42.18	....
N	7.37	....	7.64

In view of the great tendency of cyanamides to polymerize, it was thought safer to determine the molecular weight of the body[2] by the method of freezing a benzol solution, which gave the following results:

0.375 gram substance dissolved in 16.25 grams of benzol produced a depression of 0°.28 in the freezing-point.

	Calculated for $(C_7H_6Br)_2NCN$.	Found.
Mol. wt.	380	337

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[1] J. prakt. Chem., 1896, 510.

[2] This work was done before the appearance of Wallach's statement that disubstituted cyanamides show no tendency to polymerize.

There can be no doubt, therefore, that the substance is really $(C_6H_4BrCH_2)_2NCN$.

Properties of Diparabrombenzylcyanamide.

The substance crystallizes from benzol in sheaves of white crystals shaped like the blade of a lancet, sometimes united laterally into groups with comb ends. It melts at 133°. It is freely soluble in benzol, chloroform, acetone, or acetic ester; soluble in toluol; slightly soluble in cold ethyl or methyl alcohol or glacial acetic acid, freely soluble in these solvents when they are hot; slightly soluble in ether, carbonic disulphide, or in hot or cold water; essentially insoluble in ligroin. It is slowly decomposed by cold strong sulphuric acid; apparently unaffected by hydrochloric acid or nitric acid in the cold. The best solvent for it is hot alcohol.

In order to see if it could form a chloride, a portion of the diparabrombenzylcyanamide was dissolved in anhydrous benzol and saturated with dry hydrochloric acid gas. No precipitate was formed even after the mixture had stood for two weeks, and on evaporating off the benzol the original substance was recovered unaltered. It would seem from this experiment that the diparabrombenzylcyanamide cannot unite with hydrochloric acid.

A number of experiments were tried in the hope of obtaining polymers of the diparabrombenzylcyanamide. A dilute solution of sodic or potassic hydrate produced no effect on the substance, either by long standing in the cold or by boiling the mixture. The substance was boiled for two weeks with a solution of ammonic hydrate, care being taken to replace the ammonia which escaped, but the only change observed was that the color turned from white to pale-brown, evidently due to a slight decomposition, since the melting-point of the substituted cyanamide was essentially unaltered. Water alone was also tried at the boiling-point, but produced no change. Upon heating the substance above its melting-point it remained unaltered to 160°; above this point it turned first yellow, and at higher temperatures red, and on cooling gave an oily product, which we could not bring into a fit state for analysis. A similar viscous product was obtained when the substance was heated with sodic acetate. In both these cases it seemed evident that a decomposition had taken place rather than a polymerization, and our experiments, therefore, confirm the statement of Wallach that these dialkylcyanamides show no tendency to polymerize.

Decomposition of Diparabrombenzylcyanamide.

As some preliminary experiments showed that the substituted cyanamide was decomposed with difficulty by hydrochloric acid in open vessels, we adopted a dilute sulphuric acid having a specific gravity of 1.44, which has frequently given good results in this laboratory. Several grams of the diparabrombenzylcyanamide were boiled with a large excess of this acid in a flask with a return-condenser. Soon after the substance melted in the hot acid an effervescence was observed, and upon testing the gas given off with baryta water it proved to be carbonic dioxide. As the oily drops did not disappear, the heating was continued for ten hours, which reduced the amount of oil, but did not entirely remove it. On cooling, the whole liquid became filled with a voluminous white crystalline precipitate; we determined, therefore, to stop the process at this point and isolate this crystalline substance, which could be easily separated from the portion undissolved in the hot sulphuric acid. This latter substance, which solidified on cooling, seemed to consist of undecomposed diparabrombenzylcyanamide, as it gave a fresh quantity of the crystalline product on boiling again with sulphuric acid; its amount was insignificant. To obtain the crystalline product it was filtered from the acid liquid, washed with a little cold water to free it from adhering acid, and then dissolved in hot water, which left behind the few black lumps of undecomposed cyanamide. The solution was then filtered, and the sulphate decomposed by the addition of a strong solution of sodic hydrate, which set free the base as a pasty mass, solidifying on cooling. This base, after purification by crystallization from alcohol, showed the constant melting-point 50°, which is that of the diparabrombenzylamine,[1]

$$(C_6H_4BrCH_2)_2NH.$$

[1] Jackson: This Journal, 3, 251.

For greater security the chlorplatinate was prepared and analyzed. Chlorplatinic acid added to an alcoholic solution of the base gave a yellow precipitate, which was purified by washing with alcohol, and dried *in vacuo*.

0.1783 gram salt gave, on ignition, 0.0309 gram Pt.

	Calculated for $[(C_7H_6Br)_2NH_2]_2PtCl_6$.	Found.
Pt	17.58	17.34

The sulphuric acid filtrate from the crystals of the diparabrombenzylamine sulphate was treated at first with sodic carbonate, and finally with a large excess of sodic hydrate, and distilled with steam, the distillate being collected in a series of flasks containing hydrochloric acid. After the distillation was finished, the contents of the flasks were evaporated to dryness on the steam-bath, and the white residue dissolved in a little water and converted into the chlorplatinate; this was a yellow precipitate crystallizing in octahedra, which was washed with water and alcohol, dried *in vacuo*, and analyzed with the following results:

0.2061 gram chlorplatinate gave, on ignition, 0.0903 gram Pt.

	Calculated for $(NH_4)_2PtCl_6$.	Found.
Pt	43.91	43.81

It is evident from the experiment described above that the products of the decomposition of diparabrombenzylcyanamide, when boiled with dilute sulphuric acid, are carbonic dioxide, diparabrombenzylamine, and ammonia. The reaction, therefore, runs as follows:

$$(C_6H_4BrCH_2)_2NCN + 2H_2O = (C_6H_4BrCH_2)_2NH + NH_3 + CO_2.$$

ON THE EFFECT OF VERY LOW TEMPERATURES ON THE COLOR OF COMPOUNDS OF BROMINE AND IODINE.

BY J. H. KASTLE.

Some time ago the writer called attention to the fact that the characteristic red, orange, or yellow color of bromine and iodine compounds could probably be accounted for on the supposition that the halogen compounds exhibiting such colors are slightly dissociated even in the solid state; and that the characteristic color, therefore, is simply that of the halogen itself. The following facts were cited in support of this conclusion:

1. The color intensity of the halogens is in inverse ratio to their chemical activity, and may be represented roughly at least by $F < I$. Similarly, the color intensity of their compounds by $MF < MI$. Further, the color of bromine and iodine compounds is altogether similar to that exhibited by certain solutions of these two elements.

2. The perfect continuity exhibited in the color changes of such easily dissociable substances as phosphorus pentabromide in passing through the solid, liquid, and gaseous states.

3. Those halogen compounds are the most highly colored which are the least stable, and whose elements are held in combination by the weakest affinities.

4. On heating, the color of halogen compounds becomes darker and deeper in tint.

It also follows that, if the characteristic color of bromine and iodine compounds is due to dissociation, the color of these compounds ought to become lighter in tint, if not altogether white, on cooling to very low temperatures. At the time of my first communication on this subject, no opportunity was afforded for trying the effect of very low temperatures on the color of the compounds in question. Through the kindness of Dr. Freer, of the University of Michigan, and Dr. Simon, of the College of Physicians and Surgeons, Baltimore, I have recently been able to try the effect of very low temperatures (the boiling-point of liquid air —190°) on the color of certain of these halogen compounds. On the 9th of March, Dr. Freer lectured on liquid air in the city of Louisville, and on the 22nd of March Dr. Simon lectured in Cincinnati on the same subject. At the close of the lecture both of these gentlemen kindly placed at my disposal a quantity of the liquid. The following compounds were selected for experiment: Lead iodide, phosphorus pentabromide, phosphorus heptabromide, mercuric iodide,[1] iodoform, mercuric

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[1] Other observers have found this compound to become yellow in boiling oxygen.

bromiodide, benzene dibromsulphonamide, and tribromphenol bromide. Small amounts of these compounds in pure condition were placed in sealed tubes. These were then immersed in liquid air in a Dewar tube and allowed to remain in the liquid until no further alteration of color was observable. The color of these compounds before and after cooling in liquid air was observed to be as follows :

Substance.	Color at ordinary temperatures.	Color a' the temperature of liquid air.
Lead iodide	golden yellow	pale sulphur-yellow
Phosphorus pentabromide	citron-yellow	white, or very pale yellow
Phosphorus heptabromide[1]	red	yellow
Mercuric bromiodide	pale yellow	white
Iodoform	yellow	white, or nearly so
Benzene dibromsulphonanide	orange	pale sulphur-yellow
Tribromphenol bromide	yellow	very pale yellow.
Mercuric iodide	red	orange-yellow

It will be observed that all of these compounds became markedly lighter in color on cooling to —190° C., and in some cases the change of color was most striking. It would seem, therefore, that these results tend to confirm the idea that the color of halogen compounds is due to dissociation.

Before leaving this phase of the subject, it might be well to call attention to an observation by Van 't Hoff. In his "Études de Dynamique Chimique," Eng. Trans., p. 273, he points out that at 60° C. *in vacuo*, silver bromide dissociates in the sense of the equation :

$$2AgBr \rightleftarrows 2Ag + Br_2,$$

and that silver bromide at 60° C. *in vacuo* will decompose until the bromine vapor evolved has reached a pressure of 2.9×10^{-53} mm.

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[1] This compound has hitherto been regarded as the red modification of phosphorus pentabromide. Kastle and Beatty have recently shown, however, that the substance is in reality a higher bromide of phosphorus, probably the heptabromide, PBr_7.

It would seem to be generally, if not universally true, that colored substances become lighter in color on cooling to very low temperatures. That such is the case may be seen from the following :

Substance.	Color at ordinary temperature.	Color at —190°.
Bromine	dark red, opaque	orange-red
Iodine, solid	steel-gray	steel-gray
Iodine, in alcoholic solution	brown	very light yellowish brown
Iodine, in carbon disulphide solution	pink	very light pink
Sulphur, rhombic	sulphur yellow	nearly colorless
Phosphorus, red modification	dark crimson	ferruginous-brown
Copper sulphate	dark blue	dark blue
Chrome alum	dark plum color	pinkish violet
Manganous chloride	pink	very light pink
Chromic chloride	violet	pink
Phenolphthalein (alcoholic solution, alkaline)	pink	colorless
p-Nitrophenol (alcoholic solution, alkaline)	yellow	lighter yellow

At the temperature of liquid air fluorescein and eosin in alkaline alcoholic solutions retained their characteristic colors, but became considerably lighter in tint.

From these few observations it would scarcely be logical to conclude that the lightening of color produced by cooling to very low temperatures is in all cases due to the same cause as that which operates in the case of bromides and iodides. On the other hand, it is an interesting and suggestive fact that any increase in the depth of color produced by rise of temperature is usually accompanied by a corresponding increase in the chemical activity of the substance, and with such facts before one, it is almost impossible to keep out of mind such reversible processes as the following :

$$N_2O_4 \text{ (colorless)} \rightleftarrows 2NO_2 \text{ (reddish-brown)},$$

and

$$2HI \text{ (colorless)} \rightleftarrows H_2 + I_2 \text{ (violet)}.$$

In the light of the electrolytic-dissociation theory regarding the action of indicators, the effect of very low temperatures on the color of an alcoholic solution of phenolphthalein which has been rendered alkaline with caustic soda, is certainly most remarkable and interesting.

There is still another point of interest connected with this subject. This is regarding the effect of very low temperatures on the color of allotropic modifications of the same substance. It is well known that the red modification of mercuric iodide becomes orange-yellow when cooled in liquid oxygen, and that on removal from the bath of liquid oxygen, it quickly changes to red again. By some chemists this has been construed to mean that at very low temperatures the yellow variety of this compound is more stable than at ordinary temperature and that the yellow form of the iodide obtained by great cooling is identical with that produced by heating above 128°.[1] There can be little doubt regarding the correctness of the first of these conclusions, namely, that the yellow modification of mercuric iodide is more stable at these very low than at ordinary temperatures. It has been shown, for example, that at —35° monoclinic sulphur changes to orthorhombic about five hundred times more slowly than at ordinary temperature.[2] To conclude, however, that the yellow form of mercuric iodide obtained by cooling the red to —190° C. is identical with the yellow variety obtained by heating the red to 128° is certainly incorrect, as may be seen from the following:

Small amounts of mercuric iodide were sublimed in test-tubes. These tubes were then allowed to stand until a certain amount of the yellow had changed to red. Both the red and yellow varieties of this compound were thus obtained side by side in the same tube. On placing such tubes in liquid air, it was observed repeatedly that the red variety of the compound became orange-yellow, and that the yellow variety became white, or very pale-yellow. Above the level of the liquid air the yellow modification of the compound retained its ordinary yellow color, thereby rendering these differences

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[1] Newth's "Inorganic Chemistry," 5th edition, p. 558.

[2] See also "The Phase Rule," Bancroft, 32-34.

in color the more pronounced by contrast. The difference in color between the red and yellow modifications of mercuric iodide at —190° C. was thus rendered plainly visible. The effect, therefore, of these very low temperatures on the red modification of mercuric iodide is not to convert it into the yellow variety stable above 128°, but simply to lighten its color in a manner characteristic of other colored bromides and iodides. Therefore, at all temperatures below 128°, the red and yellow modifications of mercuric iodide are distintly different substances.

In conclusion, I desire to thank Professors Freer and Simon for their kindness in furnishing the liquid air necessary for these experiments.

STATE COLLEGE OF KENTUCKY,
LEXINGTON, March, 1900.

ON THE SUPPOSED ALLOTROPISM OF PHOSPHORUS PENTABROMIDE.

BY J. H. KASTLE AND L. O. BEATTY.

Phosphorus pentabromide has been described as existing in two forms. One of these is yellow and crystallizes in rhombs; the other is red and crystallizes in long prisms. In the preparation of phosphorus pentabromide by adding bromine in theoretical amount to phosphorus tribromide, both the yellow and red bromides are obtained, the former, however, in much the larger quantity. In the same way both varieties are obtained by crystallizing the compound from low-boiling solvents, such as carbon disulphide, etc., and also by subliming the yellow modification in sealed tubes. It has been stated by Baudrimont[1] that the red variety passes into the yellow by rubbing. Beyond this, however, but little seems to be known concerning these substances. It was in the hope of learning something more concerning them that this investigation was undertaken. Phosphorus pentabromide was prepared by adding gradually the theoretical quantity of bromine to phosphorus tribromide. The resulting product consisting mostly of the yellow compound, but mixed with some little of the red, was then sublimed in sealed tubes. Under these cir-

[1] Bull. Soc. Chim. de Paris, 1861, 118.

cumstances both varieties of the compound were usually obtained. By subliming at 90° C., in an oil-bath, the yield of the red compound could be considerably increased. The attempt was then made to determine the transition temperature of phosphorus pentabromide without success. On long standing the red compound was observed to change to yellow, but at just what temperature and under exactly what conditions it seemed at first almost impossible to determine. The first thing to furnish a clue to the nature and relation of these two substances was their conduct towards water. When the yellow phosphorus pentabromide is brought in contact with water it can be observed to change to the white oxybromide. This then dissolves in water, and ultimately a colorless solution is obtained. On the other hand, the red bromide dissolves in water apparently without the production of the intermediate oxybromide, and gives a solution which has the color of bromine water. Further, the reddish-yellow color of this solution is permanent. In fact, some of it was heated in a closed tube to 100° C. for several hours without any perceptible alteration in color. On shaking the reddish-yellow solution with carbon disulphide, bromine is removed and a colorless aqueous solution is obtained. It is difficult to see how two allotropic modifications of phosphorus pentabromide could so conduct themselves towards water. It occurred to us, therefore, that about the only way in which to account for a modification of phosphorus pentabromide yielding free bromine on solution in water would be to suppose it to have something of a perbromide nature, such as might possibly be represented by the formula $PBr_3.Br_2$, in which event the compound would also yield phosphorous acid instead of phosphoric acid on decomposition by water. Thus,

$$PBr_3.Br_2 + 3H_2O = H_3PO_3 + 3HBr + 2Br,$$

whereas,

$$PBr_5 + H_2O = POBr_3 + 2HBr,$$

and $$POBr_3 + 3H_2O = H_3PO_4 + 3HBr.$$

In order to test this point, small quantities of the red bromide were dissolved in water. The cold solution thus obtained was shaken with a small amount of zinc dust, in order to remove free bromine. It was then filtered, and the colorless filtrate tested for phosphorous acid by the phosphine test, and also by warming some of it with mercuric chloride. In neither case was any evidence of phosphorous acid obtained. It then occurred to us that the red substance might possibly be a higher bromide of phosphorus than the pentabromide. That this is the case would seem to derive support from the following facts: First, heat is evolved when bromine is added to phosphorus pentabromide; secondly, on adding a very small quantity of phosphorus tribromide to the red compound, the latter changes to the yellow pentabromide. This change takes place slowly, even in the cold, and very rapidly on warming; thirdly, in contact with bromine vapor, crystals of pure phosphorus pentabromide are changed to the red compound with absorption of bromine; fourthly, on sublimation, especially at 90° C., the crude phosphorus pentabromide gives a sublimate consisting of both the yellow and red compounds, and a small quantity of liquid, probably phosphorus tribromide, is often seen in the bottom of the tubes. On the other hand, the yellow crystals of phosphorus pentabromide which have been purified by sublimation, yield chiefly the yellow compound on resublimation in sealed tubes. Small quantities of the red compound, however, have always been obtained, along with the yellow, under all circumstances. On the other hand, the red compound has been found to yield chiefly red crystals on resublimation, only a few of the yellow crystals being obtained towards the end of the process. On the supposition that a higher bromide of phosphorus, such as the heptabromide, really exists, these changes become readily intelligible. First, the reaction

$$PBr_5 + 2Br = PBr_7$$

would probably be exothermic; secondly, the formation of a higher red bromide of phosphorus would explain the change of color produced by the action of bromine on the yellow phosphorus pentabromide,

$$PBr_5 + 2Br = PBr_7,$$

and, conversely, if phosphorus tribromide were to act upon phosphorus heptabromide, it would be natural to suppose that phosphorus pentabromide would be formed. Thus:

$$PBr_7 + PBr_3 = 2PBr_5.$$

This would account for the change from red to yellow on adding a small quantity of phosphorus tribromide to the red compound. Fourthly, from its mode of formation from phosphorus tribromide and bromine, crude phosphorus pentabromide might be expected to consist largely of the pentabromide, together with smaller amounts of a higher bromide, such as phosphorus heptabromide, and also phosphorus tribromide. On subliming such a mixture in sealed tubes, a separation of these constituents might be effected. Such, indeed, has been observed to be the case. Then again, phosphorus pentabromide and phosphorus heptabromide both undergo dissociation readily when heated. Hence, such changes as the following would be possible, even on subliming the pure compounds:

$$PBr_5 = PBr_3 + 2Br,$$

and

$$PBr_5 + 2Br = PBr_7,$$

and in case of the red compound,

$$PBr_7 = PBr_5 + 2Br.$$

These facts would certainly seem to indicate the existence of a higher bromide of phosphorus having a red color. The attempt, therefore, has been made to isolate this higher bromide in a state of purity. A small quantity of phosphorus pentabromide, together with the theoretical amount of bromine to form phosphorus heptabromide, were heated in a sealed tube. On keeping this mixture at 90° for some time, a sublimate consisting of prismatic red crystals was obtained. This compound gave the following numbers on analysis:

	Calculated for PBr_7.	Found.
P	5.25	5.40
Br	94.75	96.20
Total	100.00	101.60

Considering the difficulties in the way of handling the compound, it will be observed that these figures agree fairly well with those required by the theory for phosphorus heptabromide. Phosphorus heptabromide has usually been obtained in the form of bright-red, transparent, prismatic crystals. Under some circumstances it has been found to resemble chromium trioxide, or arsenic triiodide in general appearance. It is very unstable and seems to undergo dissociation even at ordinary temperatures. Hence, it is best preserved in sealed tubes. On standing in contact with bromine absorbents, it gradually loses its red color and passes to the yellow pentabromide. On rubbing, it also loses bromine and becomes yellow. This would explain the apparent change of the allotropic red modification of phosphorus pentabromide into the yellow, as described by Baudrimont. In our work on this substance we have seen certain indications of still other higher bromides of phosphorus. It is our intention to investigate these substances more fully.

STATE COLLEGE OF KENTUCKY,
LEXINGTON, April, 1900.

Contribution from the Chemical Laboratory of Hobart College.

ON THE ACTION OF NITROUS ACID ON ETHYL ANILINOMALONATE.

[PRELIMINARY REPORT.]

BY RICHARD SYDNEY CURTISS.

In a former paper[1] I described a peculiar oxidation of ethyl anilinomalonate, which was effected by treating the substance dissolved in ligroin with mercuric oxide. This resulted in the formation of ethyl dianilinomalonate. This same change can be brought about with other oxidizing agents. The mechanism of this reaction I will report upon later.

Of especial interest is the behavior of ethyl anilinomalonate with nitrous acid. I will give a brief account, at this time, of experiments now under way, in order to be allowed to continue this line of research undisturbed, and will report results in full in this JOURNAL in the near future.

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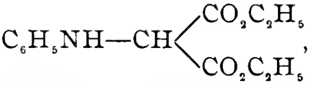
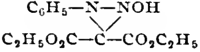
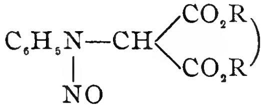
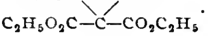
[1] This JOURNAL, **19**, 691.

If ethyl anilinomalonate,  $C_6H_5NH—CH\Big\langle\begin{array}{l}CO_2C_2H_5\\CO_2C_2H_5\end{array}$, in suspension in water, is carefully treated with sodium nitrite and sulphuric acid, a thick, clear, amber-colored oil is obtained.

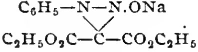
A molecular weight determination made with a carefully prepared sample of the oil gives, by the freezing-point method, in pure benzene :

		Molecular weight found.	Theory for  $\begin{array}{c}C_6H_5—N—NOH\\ \diagdown\ \diagup\\ C_2H_5O_2C—C—CO_2C_2H_5\end{array}$
(1)	1st det.	259	280
	2nd det.	264	
	3rd det.	268	
(2)	1st det.	253	

This body is extremely unstable, and, if not carefully freed from traces of impurity, it quickly dissociates on standing, even by contact with traces of pipe-water residue on the flask, or with bits of broken glass. Even when pure it loses nitric oxide gas on standing in the sunlight, or when slightly warmed. It does not give Liebermann's nitroso reaction (for  $\underset{\displaystyle NO}{\overset{}{C_6H_5N}}—CH\Big\langle\begin{array}{l}CO_2R\\CO_2R\end{array}$). It has, moreover, marked acid properties, giving a well-crystallized, but unstable, sulphur-yellow potassium salt when treated with a solution of potassium hydrate. This salt decomposes near 118° with evolution of gas.

	Theory for  $\begin{array}{c}C_6H_5—N—NOK\\ \diagdown\ \diagup\\ C_2H_5O_2C—C—CO_2C_2H_5\end{array}$.	Found.
K	12.26	11.60

Sodium hydrate yields an equally well defined and unstable canary-yellow sodium salt, which decomposes, when quickly heated, at 118°–122° with evolution of gas.

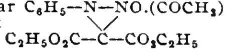
	Theory for  $\begin{array}{c}C_6H_5—N—N.ONa\\ \diagdown\ \diagup\\ C_2H_5O_2C—C—CO_2C_2H_5\end{array}$.	Found.
Na	7.28	7.41

From the sodium salt an insoluble white silver salt can be made with silver nitrate. The clear, yellow, aqueous solutions of the sodium and potassium salts decompose, even in the cold, in an hour or two, and a clear yellow oil separates, having a marked odor like an isonitrile. From this oily emulsion, white needles separate in a few days.

Metallic sodium gives a light-yellow sodium salt with evolution of hydrogen. A solution of sodium carbonate is quickly colored yellow but appears to act but slightly on the oil. Ammonium hydrate gives a still less stable crystalline salt, which is entirely decomposed to ammonia and a clear yellow oil at 35°–37° in ether solution.

Ferric chloride, in alcoholic solution of the acid oil, gives a deep-red color. Concentrated mineral acids turn it red. Sulphuric acid liberates oxides of nitrogen. Hot concentrated hydrochloric acid causes an evolution of gas and gives a marked odor of phenol.

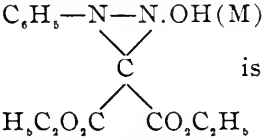
Treated with acetic anhydride at 100°–140°, 4 grams of the clear amber oil gave 1 gram of white needles (m. p. 114°); 2–3 grams of clear, neutral, thick oil, and 120 cc. of a colorless gas, which is in large part nitric oxide, turning red in the air with formation of nitrogen peroxide. A molecular weight determination made with this body (constant m. p. 114°) gave in pure benzene by Beckmann's boiling-point method:

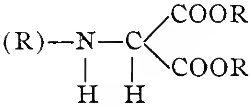
	Substance. Gram.	Molecular weight found.	Molecular weight for 
1st det.	0.0593	264	322
2nd det.	0.1003	334	
3rd det.	0.1383	346	

Operating in apparently the same way on another sample of the oil, a crystalline body was obtained of constant m. p. 111° on recrystallization from alcohol, and none of the 114° m. p. crystals. The average of four closely agreeing molecular weight determinations made with this substance (m. p. 111°) gave 222 as the molecular weight found.

These two neutral products, obtained by the action of acetic anhydride are quite stable, decomposing near 200°.

Reduction of the acid oil in dilute alcoholic solution by sodium amalgam results in loss of nitrogen in the form of ammonia and formation of a small amount of an orange-colored crystallized body. As a quantity remained, insufficient for analysis, of the substances on which the molecular weight determinations were made, no definite conclusions are drawn from the above results at this time.

The formula  is suggested as possibly the correct one for the amber-colored oil and its salts.

I shall make a thorough study of this interesting substance and its derivatives, as well as of the behavior of other negatively substituted derivatives , with oxidizing agents, and report the results in this JOURNAL.

HOBART COLLEGE, GENEVA, N. Y.,
April 18, 1900.

ON A MINIMUM IN THE MOLECULAR LOWERING OF THE FREEZING-POINT OF WATER, PRODUCED BY CERTAIN ACIDS AND SALTS.

BY VICTOR J. CHAMBERS AND JOSEPH C. W. FRAZER.

The molecular lowering of the freezing-point of water by dissolved substances, would be expected to remain constant as with non-electrolytes, or to increase with increase in dilution as with electrolytes. With non-electrolytes the molecular lowering does remain very nearly constant with increase in the dilution of the solution, after a certain dilution is reached, but it has long been known[1] that the molecular lowering of substances like cane sugar increases very considerably with increase in concentration from a certain point. In a word, there is a well-defined minimum in the molecular lowering produced by such substances.

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[1] Arrhenius : Ztschr. phys. Chem., **2**, 495 ; Jones : *Ibid.*, **12**, 642.

In the case of electrolytes, there were, until very recently, but few substances[1] with which such a minimum was suspected. Jones and Chambers[2] have, however, pointed out a number of substances in which a minimum in the molecular lowering of the freezing-point undoubtedly exists. They studied in this connection the chlorides and bromides of magnesium, calcium, strontium, and barium, and plotted the results obtained in curves. These showed very clearly the presence of the minimum in the molecular lowering, and this minimum occurred for the different compounds at approximately the same dilution—from one-tenth to two-tenths normal.

The conductivities of the same solutions of these compounds were measured and the results likewise plotted in curves. The conductivity curves, unlike the freezing-point curves, were perfectly regular, showing no sign of any minimum at any concentration. The dissociation of these substances thus continued to increase with increase in dilution, with perfect regularity, as is shown by the regular increase in the conductivity. Taking into account all of these facts, and, further, that the chlorides and bromides of the alkaline earths are, in general, very hygroscopic substances, Jones and Chambers offered the following suggestion as a possible explanation of the abnormally great lowering of freezing-point produced by the above compounds in concentrated solutions. "In concentrated solutions these chlorides and bromides must take up a part of the water forming complex compounds with it, and thus removing it from the field of action as far as freezing-point lowering is concerned. The compound, which is probably very unstable, formed by the union of a molecule of the chloride or bromide with a large number of molecules of water, acts as a unit or as one molecule in lowering the freezing-point of the remaining water. But the total amount of water present, which is now acting as solvent, is diminished by the amount taken up by the chloride or bromide molecules. The lowering of the freezing-point is thus abnormally great, because a part of the water is no longer present as solvent, but is in combination with the chloride or bromide molecules.

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[1] Arrhenius: Ztschr. phys. Chem., **2**, 496.

[2] This JOURNAL, **23**, 89.

But the conductivity results must also be taken into account. These show, unmistakably, a marked degree of dissociation even in the most concentrated solutions employed. There must, therefore, be a certain number of the molecules broken down into ions, either by the water acting as solvent or by the water in combination with the molecules, just as salts are probably dissociated in their water of crystallization."

Jones and Chambers point out, further, that there are unquestionably hygroscopic substances known which combine with water in concentrated solution. This is especially true in the case of sulphuric acid, where well-defined compounds are known.

The object of the present investigation is to study other hygroscopic substances, to see whether very different classes of compounds show this abnormally great freezing-point lowering in concentrated solutions. The compounds with which we have worked are hydrochloric acid, phosphoric acid, sodium acetate, zinc chloride, strontium iodide, cadmium iodide, and copper sulphate. These substances were purified by the methods best adapted to each case, and solutions prepared and standardized. In standardizing the solutions that constituent was chosen which could be most accurately and readily determined. From the standard solution the remaining dilutions in each case were directly prepared.

The method employed in measuring the freezing-point lowering was essentially the Beckmann method. We were careful to keep the temperature of the freezing-bath only a little below the freezing-temperature of the solution. The results which we obtained are given in the following tables. Column I gives the concentration in terms of normal, column II the freezing-point lowering observed, column III the correction to be introduced for the separation of ice, which concentrates the solution, column IV. the corrected freezing-point lowering, and column V the molecular lowering of the freezing-point :

Table I.

$CuSO_4$.

I.	II.	III.	IV.	V.
0.476	0°.722	0°.008	0°.714	1.50
0.595	0°.885	0°.019	0°.866	1.45
0.890	1°.300	0°.025	1°.275	1.43
1.190	1.°795	0°.055	1°.740	1.46

Table II.

H_3PO_4.

I.	II.	III.	IV.	V.
0.118	0°.282	0°.008	0°.274	2.32
0.236	0°.545	0°.010	0°.535	2.26
0.472	1°.065	0°.026	1°.039	2.20
0.944	2°.176	0°.033	2°.143	2.27
1.41	3°.410	0°.061	3°.349	2.37
1.62	4°.270	0°.057	4°.213	2.60

Table III.

HCl.

I.	II.	III.	IV.	V.
0.051	0°.187	0°.002	0°.185	3.63
0.102	0°.360	0°.007	0°.353	3.46
0.204	0°.755	0°.010	0°.745	3.65
0.408	1°.565	0°.030	1°.535	3.76
0.516	2°.003	0°.047	1°.956	3.79
1.032	4°.330	0°.092	4°.238	4.10

Table IV.

CH_3COONa.

I.	II.	III.	IV.	V.
0.058	0°.216	0°.005	0°.211	3.64
0.116	0°.421	0°.008	0°.413	3.55
0.174	0°.650	0°.022	0°.628	3.61
0.232	0°.861	0°.016	0°.845	3.64
0.348	1°.312	0°.033	1°.279	3.67
0.464	1°.774	0°.038	1°.736	3.74

Table V.

CdI_2.

I.	II.	III.	IV.	V.
0.133	0°.315	0°.001	0°.314	2.36
0.222	0°.480	0°.001	0°.479	2.16
0.333	0°.720	0°.010	0°.710	2.13
0.444	1°.005	0°.008	0°.997	2.24
0.666	1°.575	0°.011	1°.564	2.35
0.888	2°.245	0°.018	2°.227	2.51

Table VI.

SrI_2.

I.	II.	III.	IV.	V.
0.027	0°.143	0°.003	0°.140	5.18
0.054	0°.280	0°.005	0°.275	5.09
0.081	0°.425	0°.010	0°.415	5.12
0.108	0°.572	0°.014	0°.558	5.17
0.162	0°.863	0°.019	0°.844	5.21
0.216	1°.180	0°.024	1°.156	5.35
0.327	1°.855	0°.051	1°.804	5.51

Table VII.

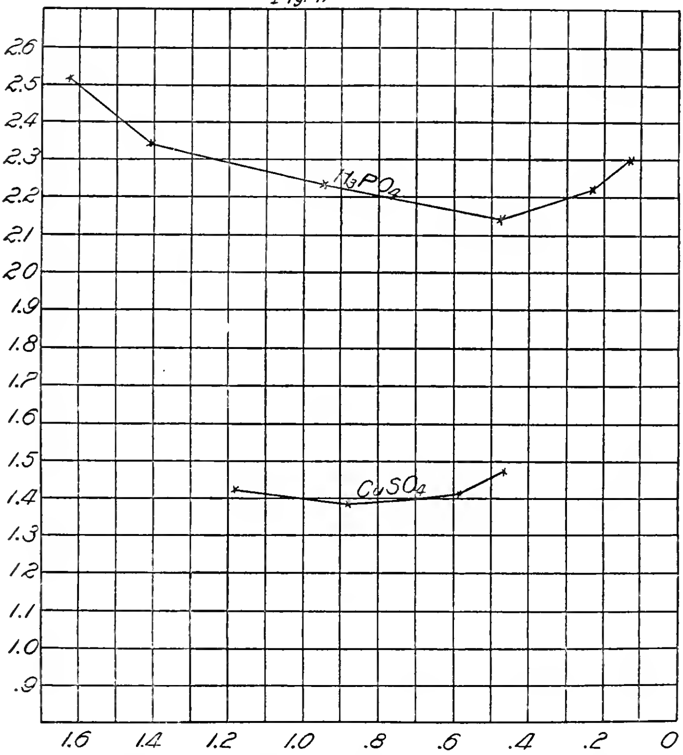
$ZnCl_2$.

I.	II.	III.	IV.	V.
0.0493	0°.270	0.°007	0°.263	5.33
0.0986	0°.521	0.°012	0°.509	5.16
0.197	1°.045	0.°025	1°.020	5.17
0.296	1°.585	0.°042	1°.543	5.21
0.394	2°.138	0.°040	2°.098	5.32
0.592	3°.272	0.°051	3°.221	5.44

These results are plotted in curves (Figs. I-III). The abscissae are concentrations, the ordinates molecular lowerings of the freezing-point. The more dilute solutions were not investigated in this work, since it is well known from previous work that the molecular lowering increases with the dilution in dilute solutions. We have, therefore, carried our measurements only a little beyond the minimum in the molecular lowering.

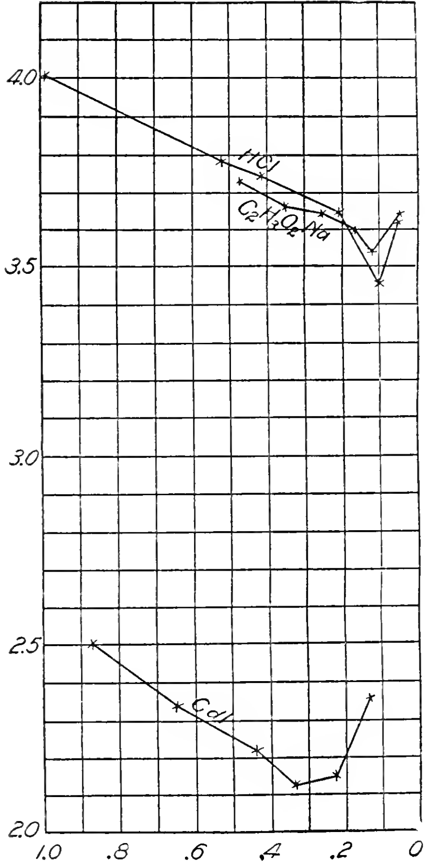
There is no very pronounced minimum in the case of copper sulphate, but the minimum for phosphoric acid comes out very sharply at about five-tenths normal. The minimum appears for hydrochloric acid and sodium acetate between one-tenth and two-tenths normal, while for cadmium iodide it exists at a slightly greater concentration. The minimum occurs for strontium iodide and zinc chloride in the region of a one-tenth normal solution.

Fig. 1.



In all the cases above described, with the possible exception of copper sulphate, there is an unmistakable minimum in the molecular lowering of the freezing-point, and from this minimum the molecular lowering increases with increase in concentration. Nearly all of these substances have a considerable attraction for water. This is shown by a number of these substances in the strong tendency to unite with water when

Fig. II.

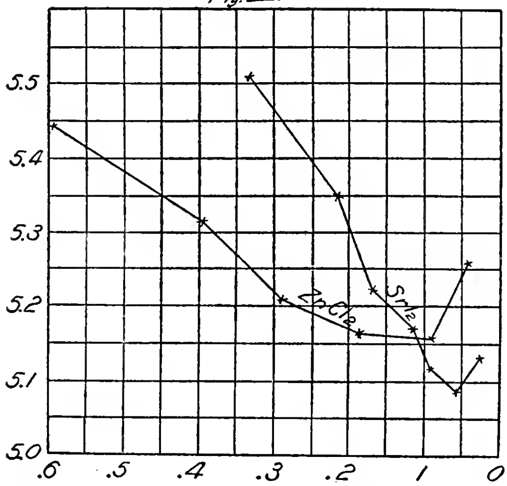


they have been freed from it. This is especially true with hydrochloric and phosphoric acids, and sodium acetate and zinc chloride. In other cases, as with copper sulphate, the attraction for water expresses itself in the water of crystallization in the salt.

We attempted to study disodium phosphate in the same way that we have investigated the above salts, but we were compelled to abandon the attempt because of the comparative insolubility of this compound at low temperatures.

It seems from the above results that the suggestion of Jones and Chambers to account for the minimum in the molecular

Fig. III.



lowering of the freezing-point of water produced by a number of electrolytes, is in the main substantiated by the facts. Indeed, it seems to be the only explanation possible up to the present, if we take into account both the freezing-point lowering and conductivity of these concentrated solutions. At present we seem forced to the conclusion, that in the very concentrated solutions of certain electrolytes there is some kind of union between the molecules of the dissolved substance and of the solvent. This view put forward by Jones and Chambers to account for the abnormal freezing-point lowerings which they had discovered, should be carefully distinguished from the attempt which was made a few years ago to account for all solutions on the basis of a combination taking place between the solvent and the dissolved substance. This latter view was meant to apply to all solutions, dilute as well as concentrated. In dilute solutions we have not the slightest reason to suppose that there is any union between the solvent and dissolved substance, but, on the contrary, the very best evidence that no such union exists. In this connection we have but to refer to the fact that dissociation, as measured by the freezing-point method, agrees with dissociation as measured by the conductivity method; or to the general applicability of the law of Kohlrausch to all solutions of all electrolytes.

Whether the view of Jones and Chambers should prove to be the final expression of the truth, in connection with concentrated solutions of electrolytes which show a minimum in the molecular lowering of the freezing-point, can be decided only by further work. But it is quite certain that any general theory of solutions must take into account such results as those previously described by Jones and Chambers,[1] and as recorded in this paper.

It was early pointed out that the laws of gas pressure do not apply to the osmotic pressure of concentrated solutions, and for this reason, if for no other, comparatively little progress has been made in the study of concentrated solutions from the physical-chemical standpoint. It seems to us quite possible that work of the kind here described may help, if only a little, towards the understanding of concentrated solutions, and we may thus be able to find out why it is that the laws which obtain for dilute solutions do not hold in the more concentrated. It is with this hope in mind that further work along the above line will be done.

In conclusion we wish to express our thanks to Dr. H. C. Jones, at whose suggestion the above investigation was undertaken, and under whose guidance it has been carried out.

CHEMICAL LABORATORY,
JOHNS HOPKINS UNIVERSITY,
January, 1900.

REPORT.

The Year's Advance in Technical Chemistry.

The year just passed has been perhaps the most important of the whole century in the advance made in all manufacturing industries, especially those having a chemical basis. This advance has been brought about, in a few instances, by the application of radically new methods, but more often by a wonderful enlargement of the scale of operations of well-tried processes, and by the general introduction of automatic mechanical devices and labor-saving machinery. Everywhere the striving for increased tonnage and for getting the very largest possible yield out of each piece of apparatus employed, has been more intense than ever before.

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[1] *Loc. cit.*

Considering first the industry which is of greatest commercial and economical importance in the United States, the metallurgy of iron and steel, the most striking change is the practical doubling in capacity of most of the newly designed blast-furnaces. The daily output of the coming furnace must approach 600 tons of pig-metal, while the maximum for most furnaces heretofore has been a daily average of from 200–300 tons. When we consider that only a decade ago an output of 100–150 tons daily was considered good practice, we can appreciate the magnitude of the change and wonder where the limit of the future is to be. The greater part of this increase has been caused by doubling, or more than doubling, blast pressures and blast quantity, thereby increasing the yield of existing furnaces and rendering possible larger hearth diameters.

A considerable increase of economy in the use of fuel for making pig-iron seems to have been accomplished abroad by the direct use of furnace gases in gas-motors for producing the air-blast, instead of burning this gas to generate steam and using steam-engines to operate the blast pumps. The solution of this problem is cause for congratulation, because of the numerous difficulties connected with it. The gas from iron-furnaces available for such motors contains only about 25 per cent of carbonic oxide, as almost its whole source of heat value, besides carrying large quantities of fine dust of coke, ore, etc., which greatly increases the difficulty of use in any mechanism where corrosion must be avoided. Any one who has seen the valves of a hot-blast stove cut through and worn out in a few months by the action of this dust will appreciate its cutting power.

In Scotland, furnaces using raw coal have made as a by-product about a tenth of all the ammonia produced in Great Britain during the year. Certain localities in the United States possessing abundant non-coking coal in proximity to cheap and good ore, might profitably adopt this method of iron manufacture, notably the new Michigan coal district of the Saginaw Valley, which, by this means, could easily supply the whole of the iron used in Michigan districts and all of the ammonia needed in the newly developing alkali industries of that locality.

Another important factor in the great increase of furnace capacity for the production of pig-iron has been the installation of automatic labor-saving devices for handling furnace-charges and removing furnace products. The most important of these are the car and ore-loading machines of Brown, McMyler, Lindsey, and Hulett, the casting machine of Uehling for handling the metal, and the various methods for carrying charges to the furnace top, with automatic dumping and distributing devices. These latter have removed the necessity for charging men or any laborers continuously at the charging level, where the work is exhausting and dangerous. By the use of a double bell they effect a thorough mixture of the charge and prevent the loss of furnace-gases.

The successful conversion of blast-furnace slag into a fair quality of hydraulic cement at a number of furnaces is a long step toward the economical solution of the troublesome problem of the disposal of this vast by-product. It has been found that certain grades of basic slag in which the proportion of magnesia and sulphur is not too high, by simply being granulated with water as they flow from the furnace, ground extremely fine and intimately mixed with the proper proportion of lime, are converted into a hydraulic cement which forms a cheap and, under certain conditions, an excellent substitute for Portland cement, and for which a permanent demand has been created.

In the production of steel the gap between the cost of producing Bessemer and open-hearth metal has been further lessened, mainly by the general introduction of basic open-hearth furnaces of greatly increased capacity and of labor-saving devices in charging metal and fluxes. Most important of these latter is the charging machine of Wellman. In this connection, too, the large introduction of the Wellman tilting open-hearth furnace during 1899 is worthy of mention, and a probable further economy of operation will be secured by their use. Several large plants using these tilting furnaces have been installed during the past year, and, while they have been used in a number of places heretofore, the record of their efficiency has not as yet been made public and is awaited with great interest. While their cost of construction is about 25 per cent more than that of the older stationary type, the complete removal of all metal and slag from the furnace hearth at each operation, with the resulting saving of metal, the saving of the time necessary for tapping, the small amount of repair necessary to the bed after the removal of each charge, and the facility with which this can be accomplished are factors which will probably cause this to become the standard type of steel furnace of this decade.

In Bessemer practice the most noticeable improvement is the general introduction of the Jones mixer for receiving the molten pig-metal direct from the furnace, thus saving its contained heat and doing away with cupolas for melting the iron previous to its treatment in the converter. This method effects not only a saving in heat or fuel, but a greater gain in the cost of handling the iron. It has been found that only about one laborer in a hundred can endure the strain of continuously handling the heavy pigs of metal at the blast-furnace in their removal from the sand molds and loading on cars. The doing away with this severe labor by the direct use of hot metal in the Bessemer plant and by the use of the Uehling casting machine seems, therefore, a gain to humanity as well as in the money value saved. The basic converter still fails to gain a permanent foothold in this country, and, because of our immense deposits of pure ore and beds of phosphate rock, and of the continued encroachments of the open-hearth process, probably never will.

The metallurgy of copper has undergone changes similar to those of iron, only in a much smaller degree. The most important of these are the increased use of the Bessemer converter in refining mattes, and an increased output of electrolytically refined metal. The general use of a gold-bearing material as a lining for the converter in matte Bessemerizing has effected a material economy. In roasters for copper sulphide ores, several new devices have gained general use. A Denver-made modification of the old Spence furnace, with its numerous beds and automatic plow rakes, in which the operating chains are placed upon the exterior of the hearth, and the Herreshoff furnace, consisting of a vertical cylinder with horizontal diaphragms or beds and rakes operated by a central shaft, have perhaps received the largest installment during the year. A plant of considerable size to operate the Hoepfner process of refining copper has been in operation for some time, but reliable cost data are not at hand. This process depends upon dissolving the oxidized metals with cupric chloride and electrolyzing the chloride solution. The process was tried at the Brooklyn experimental plant of a copper-nickel refining company some years ago, but was abandoned.

In the metallurgy of nickel the principal event has been the installation in England of a considerable plant to use the Mond process of refining by carbonic oxide, and of a plant in this country utilizing a new but unpublished process. Storer's method proposed, but not yet installed on a commercial basis, applies the old Hunt and Douglass copper method to nickel ores, treating nickel oxide at high temperature with a strong solution of ferrous chloride.

In the treatment of lead, tin, silver, mercury, and zinc ores, changes during the year seem to have been unimportant. Several methods have been proposed for treating the low-grade argentiferous blende-galena ores, so common in Colorado, but none has as yet stood the test of successful commercial application.

The output of gold has been further increased by the installation of many new cyanide works, much of the material treated in these mills being the tailings from old amalgamation plants or of abandoned dump heaps. Electrolyzing the cyanide solutions in this process is becoming more common. The Sulman-Teed method of adding a small quantity of cyanogen bromide to the lixiviating solution is claimed to effect increased gold extraction, especially in arsenic-bearing ores, but it is also asserted by many that the loss of cyanogen by this method is too great for success, and more time must be allowed for further evidence. A method of assisting the free access of the oxygen probably necessary to the solution of gold by cyanide solutions, which consists in violently agitating the ore with the solution by means of air introduced into the mixture under considerable pressure has been patented and is now being largely advertised under the name of the "Pneumatic Process." A possible serious objection to the use of this method is that an increased loss of cyanide may occur from excessive oxidation and decomposition by carbonic dioxide. During the years immediately following the marked success of the cyanide process in South Africa, the tendency was to introduce this method for all sorts of ores and under all sorts of conditions, whether adapted to success in this way or not. Now, the proper limitations of the use of cyanide solutions are better understood, and the chlorination process is again receiving more attention, so that the two methods are now beginning to assume their proper and normal relation to each other. Increasing amounts of gold and silver are being recovered by matting the ores with copper- and sulphur-bearing material, Bessemerizing this matte to blister copper, and electrolyzing the product.

In several industries the year has been marked by the beginning of that vast shifting of location from coal to water-power situations, which is to mark the coming decade. In several cases this shifting has already been nearly completed, notably in the production of chlorate. Norway, Scotland, Switzerland, and the mountain regions of France and the United States, where water-falls abound, are destined to become centers of manufacturing activities fully as great in many industries as the older coal localities, and with the advantage, that the coal fields once exhausted are gone forever, while water powers last for all time. This recent great development of the uses of water-power is due to new electrolytic processes, to material improvements in the transmission of high-tension currents, to improvements of dynamos, and to the development of water-turbines to utilize extreme pressures. This transference of many old industries to water-power districts will be limited only by the cost of carriage of the raw material to the plant, and of the finished product to its market. The competition with coal-generated power thus occasioned must result in a more and more economical use of fuel, and the year has shown material progress here. The previously mentioned use of blast-furnace gases in gas-motors is of this nature, but the very large year's increase of by-product coke-oven plants is of greater significance. In America new ovens of the Semet-Solvay or the Hoffman type have been started during the year at Halifax, Boston, Glassport, Pa., Benwood, W. Va., and Ensley, Ala. This is a satisfactory improvement, because the wasteful use of coal in bee-hive ovens will always remain a reproach of the 19th century, especially in American and English practice. These by-product coke ovens effect an increase of from 10 to 15 per cent in the amount of coke produced, with a saving of 3–4 per cent of the weight of coal tar, 0.4–0.8 per cent ammonium sulphate, and 7–10 per cent gas in excess of that required for coking. These last three items almost equal in value the coke produced.

The skill and care required in operating the Mond gas-producer, considerable fluctuations in the price of tar and ammonia, and the high cost of construction and depreciation of plant have restricted the introduction of this most valuable invention to a few localities, but a number of such plants have been started during the year and with considerable success. Probably the most important progress in the use of fuel and our greatest present hope of delivery from the smoke domination in soft coal districts, lies in the success of the Dellwick water-gas process which the past year has shown. In this device the fuel is burned directly to carbonic dioxide during the heating, or air-blast period, by using extra high blast pressure, and skillfully distributing its contact with the fuel. This increases the gas yield by nearly 100 per cent, and reduces the total loss of the heat value of the fuel from 55 to only 18 per cent. During the past year a plant has been installed in Pittsburg for the conversion of coal into fuel gas, utilizing a radically new method, which also bids fair to solve this important fuel question, and the result of this experiment is awaited with intense interest.

In many instances, where petroleum has been used as fuel, its recent increased cost has forced its abandonment. This has made the discovery of an equally convenient and efficient fuel a great desideratum. Fortunately such a substitute for oil has been found in the use of finely-powdered bituminous coal, injected into the furnace with an air-blast just as oil is used. The coal is thoroughly dried and ground very fine. Its only drawback seems to be almost explosive combustibility, rendering its storage unsafe. The temperature attainable by this means seems to be almost equal to that with oil, and in respect to cost and some other considerations it is more advantageous.

During the year a wonderful growth in the manufacture of Portland cement has taken place in the United States, so that within the coming decade we may reasonably expect to supply all of the home consumption and probably a great part of that used in other countries. The principal improvement in methods has been the general introduction of the automatic rotary kiln or burning furnace. These consist of inclined steel cylindrical shells about 60 feet long, mounted on rolls and lined with magnesia brick. The cement mixture is pumped with water or fed dry by a screw into the upper end and falls out as burned clinkers continuously at the lower end. The fuel used is oil, gas, or powdered coal, the process is continuous and requires a minimum of manual labor. The success of this invention, which has been brought about commercially in the United States first, has been so pronounced that American experts have been called to the oldest and best cement-producing districts in the world, to reconstruct their plants on the new lines.

In the manufacture of sulphuric acid, 1899 has seen the successful beginning of the greatest revolution since this acid began to be produced on a large scale, namely, the production of sulphuric trioxide, SO_3, by the contact power of finely-divided platinum on a mixture of sulphurous oxide and air. This reaction was long ago discovered by Winkler and utilized for making dry sulphuric trioxide and fuming acid, but the heat produced soon checked the reaction, and the converting power of the platinum soon gave out. The experts of the Badische Anilin and Soda Mfg. Co., a few years ago discovered the cause of the latter trouble to be the presence of dust and foreign gases, principally arsenic and phosphorus compounds, and much moisture. By using purified gas and providing a way of escape for the excess of heat generated by the reaction, the process became quantitative, even with dilute sulphurous anhydride and hence commercially possible for making all kinds of sulphuric acid. Many German acid makers are reported to be rapidly eliminating their lead chambers and using platinized asbestos or pumice-stone instead. The new method is especially economical for the strongest acids, the stronger the acid to be made the greater the economy over the niter method. Weaker acids, up to chamber acid strength, are probably still made much more cheaply by present methods. The new process is best also for making the purer grades, for, by using pure sulphurous gas, chemically pure acid can be made as cheaply as any other.

The latest antagonist by which the old salt-cake and muriatic acid soda and bleach industry has been assailed, namely, the electrolytic process of chlorine and soda production, has, during the past year, developed into such a giant that, with its older competitor, the ammonia-soda process ever enlarging, the death of the LeBlanc process cannot be postponed many years. Only in Great Britain does the process, by virtue of the retaining energy of immense capital invested, survive to any considerable extent. On the European continent ammonia soda had practically expelled it without the assistance of electrolytic methods. In this country it never had a foothold. In England it has survived mainly because of the profit on the chlorine industries. Now, electrolytic methods have removed this last prop, producing bleach as cheaply as the value of the hydrochloric acid used in the older processes. No competition is really ever likely to exist between the ammonia soda and electrolytic processes, because the soda produced by electrolysis is of little worth compared with the value of the halogen. The electrolytic production from salt of all the bleach used would produce only an eighth of the soda required for the world's consumption. There is even some possibility that hydrochloric acid may be made eventually by uniting electrolytic chlorine and hydrogen. The principal electrolytic processes so far successfully installed are the Kastner-Kellner mercury method with large plants at Niagara Falls and in England, the Hargreaves-Bird process using an asbestos diaphragm, with a considerable plant at Liverpool, and the large works at Leopoldschall. The plant at Rumford Falls, Maine, using platinum electrodes, went out of operation during the year. Probably the momentum of large capital invested in the chamber-acid plants and in the LeBlanc soda process will maintain for both a more or less profitable existence for a number of years to come, in spite of all competition.

The great change in the chlorate industry has already been referred to. Practically all that in use is now made by electrolysis. There has been a marked decrease during the year in American imports of chlorate, soda and caustic, due to the installation of large ammonia-soda works at Syracuse, Detroit, and Bay City, and another large works is now under construction at Barberton.

The manufacture of calcium carbide has grown during the year to immense proportions, but with a maintenance of prices, showing a large increase in its use. In Germany nearly all of the railway coaches are now lighted by a mixture of one-third acetylene and two-thirds Pintsch gas, resulting in both an increase of light and decrease of cost.

Another product of the electrical arc furnace which has been largely manufactured during the past year and has found an even larger demand, is graphitized electrolytic carbons. It is found that when ordinary pressed carbons are packed in charcoal and placed in the path of a large electrical current so as to be intensely heated for a considerable time, the carbon of which they are composed is practically converted into graphite. Such graphitized carbons, owing to the uniform texture which they are given, and to the higher power to resist oxidation, are found to have two or three times the life of ordinary carbons for all electrolytic purposes, and their use is rapidly growing.

In the manufacture of wood spirits a greater purity of product has been brought about by greater care in fractioning. Also many new externally heated retort plants are replacing old kiln-furnaces with internal firing for making charcoal, and greater economy is being attained in acetate production.

In the way of rubber products, the new substitute, Reid's "velvril" is claimed to have had a successful year's trial in England, and to have gained a large use. Velvril is a drying oil which has been nitrated, mixed by a common solvent with nitrocellulose, and the solvent subsequently removed. Castor oil is said to be used and, after nitration, contains 4–5 per cent of nitrogen. This, with nitrocellulose, forms a clear, homogeneous, rubber-like mass, its hardness being wholly under control by varying the relative proportions of the two ingredients, from a consistency like vulcanite to that of the softest rubber. The article to be made may be shaped from the mixture while softened by a solvent, or formed into shape by high pressure and heat somewhat above 100° C. In spite of its nitrated character, it is not explosive, but burns slowly and quietly. Numerous uses are claimed for the new compound by its inventors, including insulating material, clothing, belting, varnish, paint, enameling of leather, cement for wood, glass, metal, etc., hose and tubing, and even as a modifier of the explosive rate and power of guncotton and nitroglycerin. If only a small proportion of these claims stand the test of continued use, a most valuable discovery has been made and a substance of the widest applicability and use found at an exceedingly opportune time, because of the enormously increased demand for rubber in so many industries.

Not even a few of the inventions and processes described above were actually begun or perfected during 1899, but all for the first time last year stood the test of continued practical use. Inventions almost without number are recorded every year, but it would take an omnipotent judge to select those that are destined to work industrial revolutions, and their description or bare enumeration would be of little interest and less value here. The record given has therefore been confined to those inventions and changes which the year has recorded as of permanent value and which have proved themselves commercially successful.

ALBERT W. SMITH.

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REVIEWS.

THE THEORY OF ELECTROLYTIC DISSOCIATION AND SOME OF ITS APPLICATIONS. By HARRY C. JONES. The Macmillan Co. 1900.

In preparing this little book the author has had particularly those readers in mind who desire to keep in touch with the recent progress of physical chemistry, but who have not the time and opportunity to consult the original literature or larger German treatises on the subject. Until the recent and very timely appearance of Dr. Walker's excellent work on physical chemistry, there has been, in fact, no English source to which the reader could be unqualifiedly referred, so that the present work will be welcome to a large circle of readers. As the author states in his preface, an attempt is made to answer the questions: "What was physical chemistry before the theory of electrolytic dissociation arose? How did the theory arise? Is it true? What is its scientific use?" and the chapters into which the book is divided correspond to the divisions thus indicated.

Chapter I contains an outline of work done prior to 1885, when modern physical chemistry may be said to have had its beginning; all work which in any way touches on the relations between properties of bodies and their composition and their constitution as well as that on thermochemistry and electrochemistry is here considered: and the characteristic feature of the "old physical chemistry"—namely, its empirical inductive nature is pointed out. This chapter, which takes up a quarter of the whole book might, in the opinion of the reviewer, have been considerably abbreviated to advantage.

The second chapter on the origin of the theory of electrolytic dissociation is admirable and is thoroughly enjoyable reading. The essential parts of Pfeffer's, Van 't Hoff's, and Arrhenius' epoch-making papers are given in their authors' own words, all being clearly knit together in historical sequence. A feature of this chapter is the introduction of extracts from Van 't Hoff's Berlin lecture in 1894 on "How the Theory of Solutions Arose" which gives the reader a feeling of almost personal acquaintance with the working of this master mind. Chapter III, "Evidence Bearing upon the Theory," is devoted to a discussion of the numerous physical and chemical phenomena which have found a satisfactory explanation in the light of the dissociation theory. The illustrations are numerous and well chosen, but the general impression left on one unacquainted with the history of the theory is that the dissociation theory has been accepted almost without a question and that it will ultimately take its place among the so-called "laws of nature." This seems unfortunate to the reviewer, although himself a warm supporter of the theory; for, while it is unquestionably true that the hypothesis of Arrhenius, and the theory since built upon it as a foundation, has done more than any previous theory to explain the correlated phenomena of physics and chemistry, yet it is equally true that it still fails to account at all for some unquestionable facts and has had, and still has, some weighty opponents. A short chapter on the objections which have been raised to the theory and the arguments with which they have, for the most part, been satisfactorily answered, would have added to the value of the book and not left the reader with the impression that the theory has attained its present position without a struggle.

The concluding chapter is devoted to applications of the theory. The various methods of determining electrolytic dissociation are considered, and also certain applications to biological and toxic problems. Nernst's theory of the voltaic cell, liquid cells, gas batteries, etc., is gone into at considerable length, this being of particular interest to the physicist. The reviewer would point out that the question of the true seat of electromotive force in the voltaic cell was pretty definitely settled prior to the dissociation theory in an admirable paper by Lodge, in 1885, although no satisfactory theory to account for it was given until the appearance of Nernst's paper.

The work before us is a welcome addition to our literature, and will, no doubt, contribute its part in winning new disciples to the present large (in this country at least) following of the Van't Hoff-Ostwald-Arrhenius school.

H. M. GOODWIN.

TRAITÉ ÉLÉMENTAIRE DE MÉCANIQUE CHIMIQUE FONDÉE SUR LA THERMODYNAMIQUE. Par P. DUHEM, Professeur de Physique Théorique a La Faculté des Sciences de Bordeau. Tome IV, Les Mélanges Doubles. Statique Chimique Générale des Systèmes Hétérogènes. Paris, Librairie Scientifique A. Hermann. pp. 381. 1899.

The appearance of the earlier volumes of Duhem's work has already been noticed in this Journal (**19**, 621). The nature of the fourth volume can best be seen from a brief account of its contents. This volume contains two books, 8 and 9. Book 8 deals with double mixtures and is divided into nine chapters. Chapter I, General Theory of Liquid Mixtures; Chapter II, Theory of Distillation; Chapter III, Critical Conditions of a Mixture; Chapter IV, Liquefaction of a Gaseous Mixture; Chapter V, Liquid Double Mixtures; Chapter VI, Gaseous Solutions; Chapter VII, Mixtures of Volatile Liquids; Chapter VIII, Dissociation; and Chapter IX, Isomorphous Mixtures. The amount of material treated in book 8 is very great, indeed, and it will be noticed that it includes much that is usually treated in works on physical chemistry under the head of solutions.

Book 9, on Chemical Statics of Heterogeneous Systems, deals with the general principles of statics at a given pressure, general principles at a given volume, and general theorems of univariant and bivariant systems.

The whole work is written from the mathematical and theoretical standpoint rather than from the experimental and, therefore, appeals only to those who are well advanced in the subjects treated. A larger number of references to the literature might have made the work a little more useful to the investigator. The book is very clear, and will doubtless prove of great service in this important branch of science. H. C. J.

LEÇONS DE CHIMIE PHYSIQUE. PROFESSÉES A L'UNIVERSITÉ DE BERLIN. Par J. H. VAN'T HOFF. Membre de L'Académie des Sciences de Berlin. Professeur ordinaire a L'Université et directeur de L'Institut de Physique de Charlottenbourg. Ouvrage traduit de l'allemand par M. Carvisy, Professeur agrégé au Lycée de Saint-Omer, Deuxième Partie. La Statique Chimique. Paris, Libraire Scientifique A. Hermann. pp. 162. 1899.

The translation of the second part of Van't Hoff's book into French has thus appeared shortly after the German edition. This shows that the work of the great leader in modern physical chemistry is appreciated and valued in France as well as in his adopted country—Germany. The appearance of the first part of this book has already been noticed in this Journal (**20**, p. 610). The second part on chemical statics deals with: I. Molecular Weight and Polymerism, including determination of the molecular weights of rarefied gases, and determination of molecular weights in dilute solutions; II. Molecular Structure (Isomerism, Tautomerism), and as subdivisions, determination of constitution, determination of configuration (stereochemistry) and tautomerism ; III. Molecular Grouping (Polymorphism), comprising the laws which govern the reciprocal transformation of polymorphous substances, and molecular grouping properly so-called.

As is well known this work is, in a certain sense, a reproduction of the course of lectures given by Van 't Hoff in the University of Berlin on selected topics in physical chemistry. As far as it goes it contains, of course, what is newest and best in the subjects treated. It cannot, however, be regarded as a systematic and comprehensive text-book, covering the whole field of modern physical chemistry, and it is not adapted to the beginner in this branch of science. For those who are well grounded in the fundamental principles of the subject, this book is invaluable and needs no other recommendation than the name of its author. H. C. J.

ERRATA.

Page 296, line 17 from below, for "ammonia" read "ammonia at —38°."

Page 297, line 8 from above, for "water" read "water at 18°," and for "ammonia" read "ammonia at —38°."

Page 298, line 18 from below, for "a" read "α."

Page 299, lines 3 and 19 from above, for "a" read "α."

Page 306, line 5 from above, insert "or" after "salt."

Page 306, line 15 from below, for "investigators" read "investigations."

Page 306, line 6 from below, for "1856" read "18.56."

Page 307, line 12 from above, insert "coefficient" after "temperature."

Page 452, line 7 from below, for "potassium chloride" read "potassium bromide."

INDEX VOL. XXIII.

AUTHORS.

SUBJECTS.