REACTION BETWEEN NITRIC ACID AND COPPER

by

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Table of Contents

THE REACTION BETWEEN NITRIC ACID AND COPPER

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The work to be described is the outcome of an observation made some time ago while carrying out an investigation for Professor Rennie in the University of Adelaide. It was desired to measure the volume of nitric oxide produced by the action of dilute (five normal) nitric acid on copper under special conditions. For this purpose an apparatus was constructed consisting of a reaction vessel and a wash bottle containing caustic soda solution, the whole being connected to a Toepler pump. After exhaustion the nitric acid was run by means of a tap funnel onto the copper previously placed in the apparatus. It was intended that absorbable gases should be retained in the alkaline solution, the nitric oxide which ordinarily is produced in quantity being collected in the mercury pump. Under the conditions described where the gaseous products were immediately passed under very low pressure into the absorbing liquid it was found that there was no gaseous residue, the products being completely absorbed.

This reaction has been investigated in the hope of throwing further light on the nature of the reaction between nitric acid and copper. The fact that copper, in contradistinction to zinc and many other metals, will not dissolve in dilute acids such as sulphuric, is usually explained in terms of electro-chemical theory. A metal in contact with water will, according to Nernst's "Electrolytic solution pressure" theory, on account

of what is called its solution pressure, give off into solution positively charged metal ions, the metal at the same time acquiring a negative potential.

Owing to the opposite charges developed these ions are supposed to remain surrounding the metal and not to spread through the solution. The process of ionic solution will proceed until the metal has acquired a definite negative potential. This potential, characteristic for each metal, is such that, by electrostatic attraction, as many ions are withdrawn from solution in any time, as are given off by the metal through its "solution pressure" action. If metal ions in the form of a salt are already present in solution, they, by virtue of their osmotic pressure will oppose the solution pressure of the metal, fewer metal ions are given and a lower potential is reached. In some cases, copper for example, the osmotic pressure of any appreciable quantity of metal ions already in solution is greater than can be overcome by the solution pressure of the metal, and ions already in solution deposit on the metal conferring on it a positive potential, sufficient to oppose what may be called the "deposition pressure" of the ions. This positive potential will be greater, the greater the ionic concentration.

In acid solution there will exist also positive hydrogen ions and some of these will be taken up by the negatively charged metal, giving up their charge, and consequently lowering the potential of the metal. To restore the potential

more metal ions must pass into solution, such ions acting as
"partners" to the acid ions that have lost their hydrogen ion,
and thus being able to diffuse into solution. The hydrogen
liberated will be in extremely small quantity at first and will
collect as a layer on the surface of the metal. This film of
gas will now cause the metal to act also as a "hydrogen elect-
rode", which will endeavour to maintain its own equilibrium
potential with the hydrogen ions in solution. A system will
now exist where both metal ~~copper~~ and hydrogen are striving to estab-
lish electrical equilibrium with their ions.

To decide the final state of such a system it is necessary
to consider the potentials capable of being reached by the
different elements of the system, namely the metal electrode
and the hydrogen electrode.

The values for the electrode potentials of metals and
hydrogen against normal solutions of their ions may be found
in any work on electrochemistry. Zinc has a value -·5 volt,
copper +·6 volt and hydrogen, which behaves electrochemically
as a metal, + ·27 volt. It can be shown by application of the
ordinary concentration cell equation

$$E = \frac{057}{n} \log \frac{c_1}{c_2}$$

E = electromotive force
n = valance of metal
c_1 and c_2 = any two concen-
trations of the metal ion.

that even when the ionic concentrations are as low as 10^{-4}
normal or as great as can be reached by saturated solutions of
their salts, the zinc potential is still negative, and the

copper and hydrogen potentials positive, copper having the greater positive value and thus the smaller solution pressure.

It is now possible to explain why zinc evolves hydrogen by reaction with acid while copper does not. When zinc is immersed in the acid the system described is set up, the metal having a negative charge and having on its surface a minute film of hydrogen. This hydrogen film in the presence of an appreciable concentration of hydrogen ions, will be in equilibrium with the ions only when the potential is of the order + .27 volt. The metal acting as a zinc electrode will tend to a potential of the order of -.5 volt. The pressure of hydrogen ions in solution will continually force them on to the electrode until the potential has reached + .27 volt. As the metal as zinc electrode will continually give off ions to maintain a negative potential, it follows that hydrogen ions can continually deposit and give up their charge to the metal, their place in the solution being taken by the zinc ions given off by the metal in endeavouring to maintain the negative potential. Thus the hydrogen will accumulate in the metal and finally collect in sufficient quantity to form bubbles and escape from the system, leaving the zinc dissolved as a zinc salt of the acid.

In the copper system the metal will at first acquire a very small negative potential, (it has already been pointed out that even a very small copper ion concentration already in solution is sufficient to overcome the solution pressure of the copper and confer on the metal a positive charge). The "hydrogen electrode"

action as in the case of zinc will tend to cause the metal to
assume a potential of the order + ·27 volt. In order that there
shall be an equilibrium in this system and no evolution of hydrogen,
it is now only necessary that the copper shall, on account of the
positive charge conferred by the hydrogen, send into solution a
greater quantity of copper ions than it could by solution pressure
alone until the concentration of copper ions is such as to confer
on the system as copper electrode the same potential that it has
as a hydrogen electrode. These copper ions will of course replace
in solution the hydrogen ions deposited on the metal. The necessary
concentration of copper ions can be shown by application of the
concentration cell formula already stated, to be of the order of
10^{-10} normal. When, therefore, the copper ion concentration has
this value the copper and hydrogen "electrode potential" will be
the same, and there will be no further solution of copper or de-
position of hydrogen. If, however, by some means the hydrogen film
could be removed, this equilibrium would be disturbed, there now
being no hydrogen film to counterbalance the osmotic pressure of
the hydrogen ions, which will now tend to deposit on the metal
again, a corresponding quantity of copper again passing into solut-
ion and replacing the deposited hydrogen ions. By virtue of the
now greater copper ion concentration the metal will now have its
potential increased to more than ·27 volt. This seems at first to
be a contradiction of the statement that hydrogen "solution pressure"
would counterbalance the ionic deposition when the potential reached
+ ·27 volt. It must be considered, however, that it is possible for

hydrogen to form less than a complete molecular film, in which
case its solution pressure must be considered smaller and con-
sequently the positive potential necessary to prevent deposition of
hydrogen ions will be greater than in the case of a complete film.
Thus it is possible for a partial film of hydrogen to exist on the
copper even should the metal reach the potential $+ \cdot 6$ volt that it
has in the ~~pressure~~ presence of a large concentration of copper ions. The
continued removal of the hydrogen film will therefore have the
effect of causing ~~first~~ fresh deposition of hydrogen and solution of
copper, the final result being actual solution of the copper in
the acid.

It is possible to realise this process in practise. The
simplest means is to add to the solution a sufficiently strong
oxidising agent to oxidise the hydrogen, which may be considered
to be in a reactive state similar to hydrogen occluded in platinum.
Hydrogen peroxide is sufficient to accomplish this result, and copper
will be found to dissolve in dilute sulphuric or even acetic acid
to which hydrogen peroxide has been added.

The reaction may be formulated as follows:

$$Cu + 2H^+ + SO_4^= \rightleftharpoons Cu^{\pm} + SO_4^= + H_2 \xrightarrow{H_2O_2} Cu^{\pm} + SO_4^= + 2H_2O$$

As nitric acid is an oxidising agent the reaction between it and
copper might be ascribed to the oxidising action of the acid, but
Veley (Phil. Trans. 1891, 182, 279) has shewn that copper will not
dissolve in dilute nitric acid in the absence of nitrous acid, and
it must be concluded that nitric acid itself in dilute solution, is not a sufficiently
strong oxidising agent to effect the oxidation of the hydrogen.

Veley regarded the nitrous acid, which he showed to be present in any sample of even purified nitric acid, as the primary cause of solution. In ~~due~~ the course of his work Veley showed that various reagents that completely removed nitrous acid from the nitric acid, had the effect of preventing solution. Hydrogen peroxide was stated to achieve this purpose by oxidising the nitrous acid. This statement seems at variance with the theory of solution of copper just set out in detail. Although the nitrous acid was destroyed, the nitric acid should have acted as an acid still, and in the presence of the peroxide, the copper should have dissolved readily according to the scheme just set out for copper and sulphuric acid. The experiment was accordingly tried in the course of the present work, when it was found that copper readily dissolved in dilute nitric acid to which hydrogen peroxide was added, though, as would be expected, there was no evolution of oxides of nitrogen. The probable explanation of the fact that Veley found no evidence of solution is that he used a very small concentration of peroxide, and that after the oxidation of the nitrous acid there was not sufficient peroxide left to carry on the oxidation of the hydrogen to an appreciable extent.

Veley's explanation of the reaction between copper and dilute nitric acid is as follows:

(1) Solution of the copper in the nitrous acid

$$Cu + 4HNO_2 \rightarrow Cu(NO_2)_2 + 2NO + H_2O$$
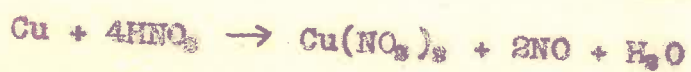
(2) Reaction between the copper nitrite and nitric acid with regeneration of nitrous acid

$$Cu(NO_2)_2 + 2HNO_3 \rightarrow Cu(NO_3)_2 + 2HNO_2$$

(3) Oxidation of nitric oxide by nitric acid with formation of nitrous acid

$$2NO + HNO_3 + H_2O \rightarrow 3HNO_2$$

The nitric ~~acid~~ *oxide* actually found in ~~the~~ practise was considered a decomposition product of the nitrous acid, which was shown to accumulate in solution up to a certain concentration, five molecules being formed finally as the result of reaction by four molecules. The increased nitrous acid concentration was considered to be the cause of the accelerated rate of solution usually found during the solution of copper in nitric acid.

In view of the work of Lewis and Edgar (J. Am. Chem. Soc. 1911, 33, 292) who have shown that there is an equilibrium in the system nitric oxide, nitric acid, nitrous acid, and further that this equilibrium is but slowly reached, it seemed that there might be a different possible explanation to that of Veley for this reaction. Donnan, in his article "Kupfer" in Abegg's Handbuch der Anorganische Chemie, refers to the action of the nitrous acid as catalytic.

The present work was undertaken in the hope of offering an alternative explanation of the mechanism of reaction between copper and dilute nitric acid.

The experiment described at the beginning of the paper where the products of reaction between dilute nitric acid and copper were distilled from the reaction vessel in vacuo almost as fast as formed, and completely absorbed by alkali, suggests that the first obtainable product of reaction is solely nitrous acid. ~~In view of~~ The fact that an equimolecular mixture of nitric oxide and nitrogen peroxide is absorbed by alkali as nitrite shows that an equilibrium

must exist

$$2 HNO_2 \rightleftharpoons H_2O + N_2O_3$$
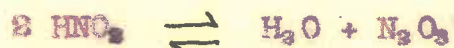
In vacuo the nitrogen trioxide would distil from the reaction solution and be absorbed in the alkali thus indirectly removing the nitrous acid from solution almost as fast as formed. In view of the work of Lewis and Edgar previously quoted it seems very unlikely that if nitric oxide would be instantly and completely oxidised to nitrous acid as would be necessary to secure complete absorption of product.

Consideration of ~~the~~ facts discussed presently/the suggestion ^(led to) of an alternative scheme of reaction, ^(to that of Veley) still, however, regarding nitrous acid as the primary source of reaction.

The mechanism proposed is as follows:

(1) Establishment of equilibrium between the copper and hydrogen ions of the nitric acid as already explained,

$$Cu + 2H^+ + 2NO_3^- \rightleftharpoons Cu^{++} + H_2 + 2NO_3^-$$
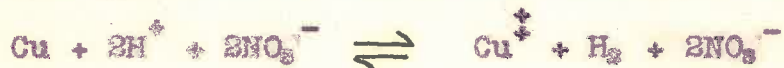
(2) Oxidation of the hydrogen by nitrous acid which itself is reduced to hyponitrous acid in unimolecular form,

$$2H + HNO_2 \longrightarrow HNO' + H_2O$$

The hypo nitrous acid at the moment of formation will be as shown in unimolecular form, and as Divers (I.C.S. 1899, **75**, 112) has shown that free hyponitrous acid has the double molecule $(HNO)_2$ it may be assumed that the unimolecular form at the moment of formation will be in a very reactive state corresponding to nascent hydrogen.

The third stage in the process will be the oxidation of the active hyponitrous acid by nitric acid with formation of

nitrous acid,

$$HNO' + HNO_3 \rightarrow 2HNO_2$$

The process so far as solution of the copper is concerned will follow the scheme already explained.

Each gram atom of copper dissolved should, according to this scheme, produce one gram molecule of fresh nitrous acid, neglecting the extremely small quantity in solution at the beginning of reaction, and it will be shown in the experimental section that this anticipation is realised.

If the reaction is carried out in such a manner that the products can accumulate in solution, decomposition of the nitrous acid will take place and nitric oxide will be produced, as is actually found to happen when copper is dissolved in nitric acid under atmospheric pressure, nitric oxide and nitrogen trioxide (nitrous acid) being the products described in published work. A table of such results from the work of Higley (Am. Chem. Journ. 1905, 17, 18) is reproduced here for reference. The products shown were obtained from 300 m.g. of copper.

Table I.

S.G. of acid	Normality of acid	Mg. of NO_2	Mg. of N_2O_3	C.C. of NO	C.C. of N_2O	Temp.	
1.05	1.5		6.45	58.5	2.6	65°	
1.10	3		16	54.3	3.36	65°	
1.20	6		60.5	45.9		20°	
1.25	8		74	39		20°	
1.30	10	76.7	141			20°	
1.40	15	328	44.7			50°	

If the explanation of the reaction suggested is correct it is to be expected that very dilute nitric acid would fail to oxidise completely the hyponitrous acid formed, and in such case, nitrous oxide, the well known decomposition product of hyponitrous acid should be produced. This has actually been found to be the case by Higley. It will be seen in the above table that small quantities of nitrous oxide were formed among the products of reaction with 3 normal and more dilute acid. It is not to be expected that much nitrous oxide should be formed, as if the nitric acid failed to oxidise most of the hyponitrous acid, the nitrous acid would be destroyed by reaction with the copper, and not re-generated, in which case reaction would come to an end.

This leads to the suggestion that ~~very~~ *still more* dilute nitric acid should fail to dissolve copper appreciably. Experiments were carried out to test the suggestion, when it was found that normal nitric acid took many hours to dissolve thin copper foil, while half normal acid showed no sign of reaction. Addition of a small quantity of sodium nitrite to either solution caused immediate reaction, but the reaction became slower, and in the case of the half normal acid came to a standstill when the nitrous acid was used up by reaction and decomposition. Addition of more nitrite started reaction again and by addition of sufficient nitrite the copper could be completely dissolved. Quantitative experiments are described in part B. of the experimental work to illustrate this point.

It is of course recognised that these solution experiments will fit with any scheme involving alternate reduction and regeneration

of nitrous acid, but as it is considered that the evidence
available thrown doubt on the nitric oxide theory of Veley, they
are included in the work as contributing evidence for the alter-
native course of reaction now suggested.

Veley has shown that copper will dissolve in nitrous acid in
the absence of nitric acid and it might be anticipated that nitrous
oxide should be the gaseous product of reaction, no nitric acid
being present to oxidise the hyponitrous acid, but Divers (loc.
cit) has shown that nitrous acid oxidises this substance with pro-
duction of nitric oxide and water, and it has been found in the
course of the present work that nitric oxide is the only gaseous
product of reaction with an excess of nitrous acid solution. The
experiments are described in detail later.

Just as nitric acid in very dilute solution fails to oxidise
hyponitrous acid completely, so it would be expected that nitrous
acid itself reacting with copper in very dilute solution, would
fail. In such case the hyponitrous acid formed, in part at least
should decompose yielding nitrous oxide, before coming into a
condition favourable to oxidation. This also has been verified,
the experiments being described in part C. of the experimental
work.

In view of the statements that nitrous acid accumulates in
solution when copper is dissolved in nitric acid under usual con-
ditions, and that nitrous acid will react with copper producing
nitric oxide, it is necessary to point out that it is unlikely that
direct formation of nitric oxide by this process will take place
in the presence of ~~considerable~~ any quantity of nitric acid. The nitrous acid in

the direct neighbourhood of the copper will be reacting with it
and thus nitrous acid is not likely to be present immediately
where the hyponitrous acid is being produced, while nitric acid,
if present in quantity, will be, and thus the conditions are
favourable for oxidation of the hyponitrous acid by the nitric
rathera than the nitrous acid.

Some recent work of Peters (Zeitsch. Anorg. Chem. 1919, 107,
313, see Abst. 1919, 11, 116, 413) may be mentioned as furnishing
further confirmation of the course of reaction proposed. Peters
states that in the presence of carbon dioxide a 5% sodium nitrite
solution will react with copper at 60° yielding as gaseous pro-
ducts nitric and nitrous oxides, while nitrate is formed in solution.
It can be calculated that in a sodium nitrite solution of the strength
mentioned, saturated with carbon dioxide at 60° the nitrite will be
converted to free nitrous acid to the extent of about •25%,* owing

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*

This value can be calculated from the following data. The formula
for calculating the distribution of a base between two competing
acids is given by Lewis, System of Physical Chemistry, 1916 ed.
page 285, as follows:

$$X = \frac{(\frac{K_1}{K_2} - 1)b + \frac{k_1}{k_2}c_1 + c_2 \pm \sqrt{[(\frac{k_1}{k_2} -1)b+ \frac{k_1}{k_2}c_1 +c_2]^2 -4(\frac{k_1}{k_2} -1)\frac{K_1}{K_2}bc_1}}{2(\frac{K_1}{K_2} - 1)b}$$

X = fraction of base combined with the nitrous acid.
K_2 for nitrous acid = 6×10^{-4}. Ray, Dey and Ghos (Trans. 1917, 111, 413)
K_2 for carbonic acid = 3×10^{-7}. Walker and Cormack (Trans. 1900, 77, 51)
b = conc. of base. = conc. of sodium nitrite = •7 gram. mol. per
                                     litre (5% sol.)
c_1 = conc. of nitrous acid = conc. of nitrite = .7 gram mol.
c_2 = conc. of carbonic acid = 1.01 gr. mol.
      (calculated from the solubility in water at 60° = •57 gr.
        per litre. (Landolt Bornstein) = .013 gr. mol.)

to the distribution of its base between the nitrous and carbonic
acids. The presence of this nitrous acid is sufficient to account

for the observed phenomena, as it would react with copper, forming,

on account of its small concentration nitrous oxide with perhaps

some nitric oxide, in the manner already explained. Nitrous acid

would also be expected to react in the solution not in contact with

the copper according to the well known equation

$$3HNO_2 = HNO_3 + 2NO + H_2O$$

forming nitric acid and nitric oxide, and thus the observed products

are all accounted for. The equilibrium between the carbonic acid

and the nitrite will lead to the formation of fresh nitrous acid as

that in solution is destroyed and the reaction can thus proceed.

This experiment has been repeated in the course of the present

work using copper in fine granular form with the result stated by

Peters, gas being evolved and copper passing into solution. The

experiment was then repeated substituting a hydrogen stream for the

carbon dioxide. In this case no sign of action was visible even

after a number of hours, thus showing that the carbon dioxide is a

necessary factor in the reaction, as suggested in the above discuss-

ion.

The arguments and evidence advanced all seem to confirm the

scheme of reaction suggested where the primary oxidising agent,

nitrous acid, is by reaction with the hydrogen film on the copper

reduced to hyponitrous acid, which is then oxidised to nitrous acid

again by the nitric acid, the nitric acid at the same time being

reduced to nitrous acid.

It is desirable now to consider in more detail the conditions
under which nitrous oxide can be produced by reaction between
nitric acid and copper. It has already been pointed out that Higley
obtained this gas when working with very dilute acid. Examination of
Higley's original paper shows that his reaction products were removed
from the reaction vessel by a stream of carbon dioxide, the nitrogen
trioxide found being collected in the absorption train. It is not
likely that any considerable quantity of *nitrous acid* could accumulate in the
nitric acid at $65°$ (the temperature of the experiment) owing to
decomposition, and the conditions would be favourable for the
production of nitrous oxide in the manner already explained. When
nitrous acid could accumulate in solution it would not be expected
in view of previous discussion that nitrous oxide would be produced
except under the special conditions to be discussed next. These
conditions appear to have existed in the early work of Ackworth and
Armstrong(J.C.S. 1877,32,54) These workers appear to have found
small quantities of nitrous oxide when working with acid of
different concentrations. In some cases the quantity was very small
and the results seem of doubtful value in view of modern work, but
there seems no doubt that they obtained the gas when working with
dilute acid. A constant small volume of acid was used for reaction
so that the actual quantity of acid would be small when using
dilute solution. In such case it is likely that the strength of the
acid would fall to a value where it would cease ~~completely~~ to
oxidise completely the hyponitrous acid, as already explained. The
products of reaction, which was carried out at room temperature

would accumulate to some extent in solution and finally as the
nitric acid became too dilute, the nitrous acid would take part in
the reaction without ~~regeneration~~ complete regeneration, and would
thus itself ^finally become very dilute, the condition necessary for the
production of nitrous oxide thus arising. It was also stated that the
presence of copper salts in the solution gave rise to an increased
yield of nitrous oxide. The explanation offered by the authors
involved the formation and subsequent decomposition of cuprous
nitrate. Experiments carried out during the present work mentioned
already and described fully later show that this explanation is not
sufficient. Nitrous oxide has been obtained by reaction between very
dilute nitrous acid solution and copper where the amount of nitrogen
acids present was very small and the total amount of copper dissolved
not more than .5 gram per litre.

Observation made in the course of the present work suggests an
alternative explanation. It was noticed that a deep blue colour
characteristic of copper complex salts was produced when copper
was dissolved in nitrous acid solutions. The colour was developed
in the absence of salts other than copper, when using nitrous acid
prepared from silver nitrite and dilute hydrochloric acid. The
colour disappeared when the nitrous acid decomposed. The ~~compound~~ colour
was formed in the presence of nitrous acid by even a small concen-
tration of copper and it is likely therefore that when a large
concentration of copper salts was present a small concentration
of nitrous acid would be largely combined in the complex. This *

Ray (J.C.S. 1907. 91 , 1405) has shown that cupric nitrite in solution
has a green colour.

effect in the case of Ackworth and Armstrong's experiments carried out under the conditions described already,would lead to a m much smaller concentration of free nitrous acid ,with consequent production of a greater quantity of nitrous oxide,than in the absence of copper salts.

Thus far discussion has been confined to reaction with dilute nitric acid.It has been shown that above a certain strength nitric acid will react in with copper in the absence of nitrous acid.The critical strength has been shown by Ihle (Zeit.Phys.Chem.1895. 19.577) to be about 35 % by volume.This strenghh is equivalent to just below 8 normal.

In the course of the present work experiments were also carried out with this stronger acid under the conditions already described,to determine in what manner the products differed from those previously published.It is well known that equilibrium is but slowly established amongst the oxides of nitrogen and in view of the result with dilute acid the results *shown later in the summary following table 2, for strong acid may be considered to more nearly represent the primary products of reaction than those quoted in table 1(these latter of course are not claimed by Bigley to be other than final products.)

It would be expected that with strong nitric acid a definite mechanism of reaction would exist and the production of nitrogen peroxide from 14.5normal acid in large quantity from 14.5 normal acid in the present work suggests that the direct reaction yields this substance.

* Page 25.

Considering for the moment only the oxidation of the hydrogen film
the reaction will be

$$H_2 + 2HNO_3 \rightarrow 2H_2O + N_2O_4$$

The process of solution of the copper will follow the scheme
already described. Inspection of the summary just referred to shows
that 8 and 10 normal acid yield a product consisting largely of
nitrous acid. This may be regarded as due to the simultaneous progress
of both types of reaction, the nitrous acid type still predominating.
with still stronger acid the direct nitric acid oxidation will
proceed at a greater rate and nitrogen peroxide will be the chief
product as is found with 14.5 normal acid.

A comparison of the results obtained with those in table 1 is of
interest. It will be seen that Migley obtained no nitrogen peroxide
from 8 normal acid, while with 10 normal he found a greater quantity
than was obtained during the present work. Secondary reaction with
water will explain the absence of peroxide in the first case, while
oxidation of trioxide by nitric acid will account for the greater
quantity of peroxide in the second case.
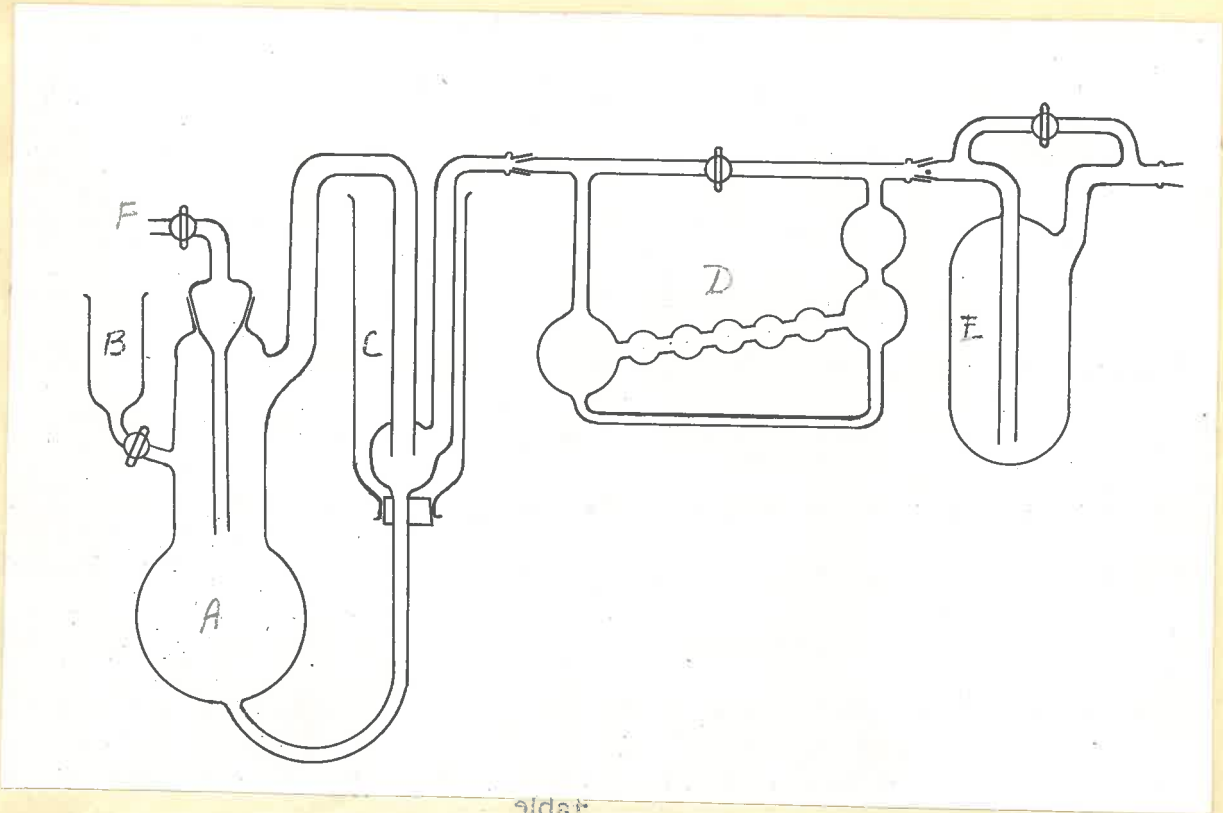
EXPERIMENTAL WORK

Part A.

Quantitative determination of the reaction products.
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As stated at the beginning of this paper it was found possible to carry out the reaction between dilute nitric acid and copper in vacuo in such a manner that the gaseous products of reaction were completely absorbed in alkali. Titration of the absorbing solutions with permanganate in such cases showed the presence of nitrite corresponding to form 310 to 320 cc. of tenth normal permanganate for every gram of copper dissolved. This result was obtained with acid of strength from 5 normal (S.G. 1·17) to about 15 normal (S.G. 1·40). The theoretical quantity of permanganate corresponding to the scheme of reaction suggested earlier is 318 cc. This determination is not sufficient to decide whether the product is nitrogen trioxide, however. A given amount of reducing agent will reduce twice as much nitric acid to peroxide as to trioxide, but only half of the peroxide forms nitrite in the absorber, so that the amount of nitrite formed is the same in either case, thus

$$2N_2O_5 - 2O = 2N_2O_4 \rightarrow 2HNO_2 + 2HNO_3$$
$$N_2O_5 - 2O = N_2O_3 \rightarrow 2HNO_2$$

In view of the nature of the reactions discussed earlier it seemed very unlikely that the product obtained in the course of the experiments with dilute acid could be nitrogen peroxide, nitrogen trioxide (nitrous anhydride) being considered more likely. To be quite certain on this point, however, and to determine the

nature of the products obtained by reaction with stronger acid
it was considered necessary to be able to determine the exact
nature of the products absorbed by the alkali. To do this it was
necessary to be able to estimate the total nitrogen collected in
the absorption liquid apart from that distilled there directly as
nitric acid from the reaction vessel. Attention was directed
towards devising some method for fractionally condensing the nitric
acid while allowing the reaction products to pass to the absorbing
system. The apparatus shown in the figure was finally adopted, the
various parts being either sealed together or connected by ground
joints as shown. Nitric acid was admitted after washing out the
apparatus with carbon dioxide and exhaustion, to the reaction
vessel A. containing the copper, by means of the tap funnel B.
Nitric acid was condensed in the condenser C. (which was cooled
with ice water as necessary) and returned to the reaction vessel.
The gaseous products were absorbed in the vessels D. and E. which
contained sodium hydroxide solution. From E. connection was made
to the mercury pump by means of a flexible coil of glass tubing,
the connection being closed by a tap during reaction. The bulb of
the reaction vessel A. had a capacity of about 50 cc. The con-
denser had a length of about 16 cm. giving the gases a length of
passage of about 30 cm.; the tubing had an internal diameter of
about 7 mm. The vessel E. had just sufficient liquid placed in it
to close the bottom of the inlet tube, its chief use being to act
as a reservoir if any small quantity of gas passed unabsorbed
through D. This apparatus was used for all the experiments except

those with the acid of S.G. 1·40 where a double surface reflux
condenser was used. Later work showed that with a large condenser
surface there was a slight tendency for the products to decompose
and the condenser shown in the diagram was adopted. As any small
decomposition in the case of the strong acid would merely give a
slightly lower value for the amount of nitrogen peroxide, it was
not considered necessary, in view of the large amount present, to
repeat this part of the work. Tests in the absence of copper showed
that no appreciable quantity of nitric acid distilled into the
absorption train when the condenser was cooled to about $10°$ with
cold water. In these tests the place of the oxides of nitrogen
passing through the condenser was taken by a slow stream of carbon
dioxide. In the course of preliminary tests with the above apparatus
using 10 normal and more dilute acid, it was found that when the con-
denser was not cooled there was no unabsorbed gas produced, but
that as soon as the condenser was cooled to $0°$ considerable nitric
oxide was collected in the pump at the end of an experiment. With
the 5 and 8 normal acid this effect was somewhat apparent at $10°$
and experiments were carried out with a condenser temperature of
$15°-17°$. A possible explanation of this effect is that, gaseous
trioxide being a mixture, at the lower temperatures the nitrogen
peroxide is slightly condensed, thus allowing the nitric oxide to
pass on, and through the alkali unabsorbed; the effect would then at
once be apparent in the case of the gas consisting of the trioxide;
if excess nitrogen peroxide were also present greater condensation
would have to take place before the composition fell below that
corresponding to the trioxide, when it would be expected that

complete absorption would cease and that nitric oxide would appear. This production of nitric oxides will lead to collection of a diminished quantity of "nitrous" and "total nitrogen" in the absorption liquid.

In carrying out an experiment the acid was kept gently boiling during the solution of the copper. If this were not done some nitrous acid was left in the nitric acid and the products collected in the absorption apparatus were consequently small in quantity. When using dilute acid a slow stream of carbon dioxide was passed through the tube F. to sweep the gaseous products from the condenser rapidly after condensation of the acid vapours.

The copper was used in the form of thin foil; the nitric acid was prepared from different brands of "chemically pure" and was practically free from oxides of nitrogen, one or two drops of tenth normal permanganate being sufficient to oxidise the nitrous acid/ present in the quantity of even the strongest acid used, after dilution. For analysis the solution in the absorption apparatus was made up to a standard volume, the nitrite in portion being determined by titration with permanganate,* and the total nitrogen estimated in the residue by distillation with Devarda's alloy, the ammonia produced being absorbed in standard acid. A series of results obtained is shown in the following table.

* For this determination permanganate was added in excess to the solution after dilution. The solution was then acidified with sulphuric acid and the excess permanganate titrated with oxalic acid.

In all the experiments detailed in table 2, .250 gram of copper was used.

TABLE 2.

	S.G. of acid	Normality of acid	Temp.	Gr. of N. as N_2O_3	Gr. of N. Total	% of N_2O_4	Gr. of N. as NO	Temp. of Condenser
1	1.40	14.5	60	.0553	.0980	77	---	10
2	1.40	14.5	60	.0546	.1001	80	---	10
3	1.30	10	45-50	.0557	.0616	10.2	---	10
4	1.30	10	45-50	.0560	.0630	11	---	10
5	1.30	10	45-50	.0542	.0600	10.5	---	5
6	1.25	8	35-40	.0542	.0582	7.2	---	10
7	1.20	6	30	.0550	.0610	(10.8)	---	16
8	1.20	6	30	.0490	.0490	---	.0045	10
9	1.20	6	30	.0420	.0423	---	.0090	7
10	1.17	5	30	.0546	.0595	(9)	---	20

The theoretical quantity of nitrogen as nitrogen trioxide required to satisfy the mechanism of reaction suggested for dilute acid is .0555 gram, the "total" nitrogen being the same.

This applies to experiments 7 to 10. In the case of the stronger acid capable of direct reaction with copper, where nitrogen peroxide is suggested as a product, the "nitrogen trioxide, found should be the same as before, but the total nitrogen will be greater according to the amount of peroxide, being double the above quantity when peroxide is the sole product.

In view of the blank tests the values given for the experiments down to number 6 are considered accurate. In the case of the 5 and 6

The blank tests mentioned show that the "total nitrogen" values of

experiments 1 to 6,8 and 10 will not include any appreciable

quantity of nitric acid collected by direct distillation from the

reaction vessel. It is necessary however to consider the fact that

when carrying out reaction with 6 normal acid and a condenser

temperature of 10° small volumes of nitric oxide were obtained .The

volume was about 4 to 5 cc. corresponding to about 5 mg. of

nitrogen as shown in experiment 8. It must be considered that a

similar action ta kes place with the stronger acid, but as already

explained a small effect in such case will not produce an excess of

nitric oxide. An allowance is made for this effect in the summary of

table 2 that follows this discussion. In the case of experiments 7 and

10 the blank test affords less certainty as to the absence of nitric

acid. Five normal acid required about an hour and 6 normal acid about

20 minutes on an average to dissolve the copper. The (The reason for

the slow reaction is discussed later.) During the solution of the

copper in the dilute acid the acid occasionally "boiled with bumping"

and unless the condenser temperature was at least as low as 10°

a small amount of vapour would blow through the condenser and a

momentary film of moisture would be seen on the tube leading to the

absorbers. It is almost certain that from this cause the nitric

acid would reach the absorption system and the values for the nitrogen

peroxide in experiments 7 and 10 will be high on this account.

Results of the nature shown in table 2 were repeatedly obtained

but it was not possible to secure more definite results. The fact

already discussed, that the reaction product from the dilute acid more

readily forms nitric oxide than that from the 8 and 10 normal acid in passing through the condenser is evidence that it contains at most a small quantity of nitrogen peroxide.The low values for the "nitrous" and " total nitrogen" in experiments 8 and 9 will be brought to nearly the theoretical value when correction is applied for the loss due to nitric oxide formation.Experiments such as the one detailed presently show that the less nitric oxide represents about two thirds of the loss.The corrected value for experiment 8 becomes .055 gr. and for experiment 9 it is .054 gr.

As a result of the discussion on the results shown it may be concluded that the product of reaction between copper and

14.5 normal acid	is about 10 % nitrous anhydride and 90 % nitrogen peroxide
10 normal acid	80 % nitrous anhydride 20 % nitrogen peroxide
8 normal acid	15 % nitrous anhydride 85 % nitrogen peroxide
5 and 6 normal acid	Almost entirely nitrous anhydride.

In all cases the amount of nitrous anhydride is of the order required to satisfy the mechanism of reaction discussed.

A typical result of an experiment where a cold condenser was used may be quoted as an example of the result obtained under such conditions.

Copper used .250 gram   Acid 6 normal.
Condenser cooled with ice and salt.
Nitrogen as trioxide .015 gr.
Nitrogen as nitric oxide .028 gr. = 44 cc at N.T.P.

The nitrogen peroxide removed by the condenser would be converted

finally to nitric and nitrous acids or to nitric acid and nitric
oxide and in either case the would nitric acid would be retained
in the condenser or returned to the reaction vessel ∧thus making
the nitrogen products collected less in quantity than required by
theory. This loss is apparent in the above experiment and to a small
extent in experiments 8 and 9 of table 2.

Attention may be called here to a statement made in the discussion
on the experiments described, that the copper took a considerable time
to dissolve in the dilute acid. The quantity of foil that took an
hour to dissolve in the five normal acid would dissolve in the
same acid in a few minutes under ordinary conditions at atmospheric
pressure. The different behaviour is ascribed to the fact that the
nitrous acid was being continually removed from solution in the
present experiments and could not accumulate and exert the
"autocatalytic"effect usually shown. With acid

With acid of strength less than 5 normal the time required for
solution in vacuo was so long that experiments were not practicable.

Experimental Work

Part B.

Effect of nitrous acid on the rate of solution of the copper.

A series of quantitative tests was also carried out at 25° to illustrate the statements previously made regarding the effect of nitrous acid on the solution of copper in very dilute acid. For these tests pieces of thin copper foil were used, 2 cm. square, weighing about .175 gr. The foil was carefully cleaned before use by washing in acid, water, alcohol, and ether. The surface area remained practically constant during solution until the foil was almost dissolved, so that the quantity dissolved will be proportional to the rate of solution. The reaction was carried out in small beakers exposed to the air, the acid being kept stirred.

Experiment 1.

50 cc. of normal nitric acid + 1 cc. of 5 normal sodium nitrite
(345 gr. per litre)

	Time	Weight	Loss	During
	10.40 am.	.172		
Removed for weighing	11.43	.083	.089	68 mts.
	11.52	.083		
	1.0 p.m.	.042	.041	68 mts.

At 1.5 p.m. •5 cc. more nitrite solution was added and the remainder of the copper dissolved in 35 mts.

Experiment 2.

100 cc. of half normal nitric acid ⊹ 1 cc. of 5 normal
sodium nitrite.

	Time	Weight	Loss	During
	10.40 a.m.	.166		
Removed for weighing	12.10 p.m.	.140	.026	90 mts.
	12.15	.140		
	1.45	.126	.012	90 mts.

Experiment 3.

100 cc. of half normal nitric acid ⊹ 2 cc. of 5 normal
sodium nitrite.

In this experiment the nitric acid has the smaller concentration of experiment 2, the nitrous acid the greater concentration of experiment 1.

	Time	Weight	Loss	During
	1.52 p.m.	.175		
Removed for weighing	3.0	.087	.088	58 mts.
	3.5	.087		
Next day	10.0 a.m.	.060	.027	19 hours

The reaction in the case of this experiment had come to a practical standstill but the addition of more nitrite caused complete solution in the course of another hour.

Experiments 3 illustrates the statement made that copper will not dissolve appreciably in very dilute nitric acid and that if nitrous acid is added, solution takes place so long as that acid is present, but that the acid is decomposed by the reaction instead of being regenerated as it is with stronger nitric acid, and consequently the rest of solution falls off, reaction finally ceasing. Experiments 1 and 3, where the concentration of the nitrous acid is the same but the concentration of the nitric acid is different, illustrate the fact stated by previous workers that the rate of solution is proportional to the nitrous acid concentration; reference to the figures furnished shows that in the same time the two solutions dissolved almost the same quantity of copper. Experiments 1 and 2 illustrate the effect of dilution on the rate of solution, the rate being much greater in the more concentrated solution, though the same total quantity of acids is present in both solutions.

Experimental Work.

Part C.

Determination of the nature of the gaseous products of
the reaction between nitrous acid and copper.

Two series of experiments were carried out, namely, with fairly concentrated and with very dilute nitrous acid solutions. The stronger solution was prepared by mixing two volumes of five normal hydrochloric acid with one volume of 7% (normal) sodium nitrite solution, both solutions being carefully cooled. This solution in considerable excess ^(of what was necessary to dissolve the copper,) was run from a tap funnel on to copper foil contained in a flask which had been freed from air by washing out

with carbon dioxide. The gases evolved were collected in a gas analysis apparatus of the Elliott type, the reaction solution being finally boiled to expel any nitrous oxide. Nitric oxide was removed by adding oxygen and treating with alkali, excess oxygen being removed by phosphorus. The absence of residual gas was taken to denote the absence of nitrous oxide, which should either have remained as such after the treatment described, or have produced an equivalent volume of nitrogen if it reacted with the phosphorus during removal of the oxygen. The very dilute nitrous acid solution was prepared by adding 2 cc. of 7% sodium nitrite solution to 100 cc. of 2 normal hydrochloric acid. Reaction between this solution and excess of copper foil produced considerable nitric oxide. When reaction had ceased the gases in solution were boiled out, several cc. being obtained. This gas was found to consist chiefly of nitrous oxide, being tested by the introduction of a smouldering splinter of wood, which burst into vivid flame.

In another test carried out with the very dilute nitrous acid solution, 500 cc. of solution were used acting on a large excess of copper gauze, and the gas boiled out of solution was collected over mercury. Nitric oxide was removed by adding oxygen and removing the nitrogen peroxide by alkali. The oxygen was added in separate small volumes until no brown fume was produced. Phosphorus was then added and produced no appreciable reaction in the cold, but on momentarily heating the phosphorus an explosive reaction took place, while the residual gas occupied nearly the same volume as before combustion, the small contraction being due to removal of the small excess of oxygen. This reaction is characteristic of nitrous oxide,

the nitrogen produced occupying the same volume as the original gas. In this particular experiment 8 cc. of nitrous oxide were obtained calculated from the volume of the residual nitrogen.

In these experiments nitric oxide was rapidly evolved at first, and the nitrous oxide was probably formed when the nitrous acid was nearly exhausted, and very dilute. On account of the nitric oxide formed by direct decomposition of the nitrous acid it was not considered practicable to carry out quantitatively the experiments described in this section of the work.

Nitric acid will, of course, also be formed in these experiments by direct decomposition of nitrous acid but the conversion of even the whole of the nitrous acid into nitric will produce a concentration much less than that of the half normal solution already shown to be incapable of taking part in the reaction with copper so that it does not seem necessary to consider the small amount of nitric acid formed as taking any part in the reactions under discussion.

ELECTROLYSIS IN LIQUEFIED SULPHUR DIOXIDE.

By L. S. BAGSTER, B.Sc., and B. D. STEELE, D.Sc.

(A Paper to be read before the Faraday Society, Tuesday, March 26, 1912.)

Although considerable attention has been devoted in recent years to the study of the solvent properties of various inorganic and organic chemicals, most of the work that has been carried out has dealt only with the power possessed by various solvents to form conducting solutions and with the relation between this power and certain physical properties of the solvent. Of the large number of investigations of this character, reference may be made to the work of Franklin, Kraus, and others on liquefied ammonia, and especially to those of Walden and his collaborators on a very large number of solvents, both inorganic and organic, and to the investigations of the liquefied halogen hydrides by Steele, McIntosh, and Archibald.

The majority of the above-mentioned investigators have examined the conductivity of solutions in the various solvents, but the behaviour of these solutions during electrolysis has only been examined carefully in the case of solutions in ammonia.

The purpose of the present investigation was to extend our knowledge of some of the lesser-known inorganic solvents, and in particular to determine, if possible, the mechanism of electrolysis in solutions in these solvents. Liquefied sulphur dioxide has been selected as the most convenient solvent to use for two reasons. Firstly, that it is easily obtained in quantity and is liquid at the temperature of boiling ammonia ; and secondly, that as a compound containing no hydrogen it should present the greatest possible contrast in its general behaviour to that of water.

The fact that minute traces of moisture profoundly modify the nature of the reaction has interfered with the rapid progress of the investigation, and considerable difficulty has been experienced throughout in carrying out the manipulations on account of the difficulty of excluding moisture.

Ultimately it was found necessary to carry out certain of the experiments *in vacuo* with very carefully dried apparatus and materials.

The electrolysis of the following substances when dissolved in liquefied sulphur dioxide has been investigated :—

(a) Potassium iodide and sodium iodide.
(b) Trimethylsulphonium iodide.
(c) Tetramethylammonium iodide.
(d)   „   „   sulphate.
            „   „   sulphite.
(e) Hydrogen bromide.
(f) Mixture of hydrogen bromide and either water or an organic compound.

POTASSIUM IODIDE AND SODIUM IODIDE.

There appears to be no qualitative difference in the behaviour of these two substances when their solutions are electrolysed. A description of the behaviour of a solution of potassium iodide will therefore be sufficient.

Preliminary experiments were carried out in an apparatus consisting of two glass tubes about 1 cm. in diameter, which were joined together near the bottom by a somewhat narrower tube, the object of the latter being to minimise as far as possible the mixing of the cathode and anode solutions during the experiment.

It was soon found that the resistance of this system was variable and very high when small platinum electrodes were used. When the circuit was first closed, the current, which started at about 200 milliamperes, fell very rapidly to the value of about 1 milliampere. On reversing the current, it rose momentarily to the value of about 40 milliamperes, and again fell very rapidly to about 1 milliampere. On again reversing, the current rose, but never to its original high value. If this process of reversal was repeated a great number of times, it was found that after each reversal the maximum value to which the current rose became less and less, until finally practically no current passed at all at the original potential difference. If the latter was raised considerably, the resistance, which appeared to have been gradually built up, broke down, and the same behaviour could then be repeated at the new voltage. On substituting a fresh pair of platinum-wire electrodes the same behaviour could be repeated, thus indicating that the very high resistance was located at the surface of the electrodes. The cathode at the close of such an experiment was found to be coated with a minutely crystalline dark-coloured deposit, which, as the liquefied SO_2 evaporated, became white in colour.

The gradual cutting off of the current is therefore accompanied by the formation of a deposit on the cathode.

At the anode no changes were observed, but the changes which can occur during this experiment are of such a small magnitude, on account of the cutting off of the current, that in all probability iodine, if liberated at the anode, could not be detected.

When an e.m.f. of 40 to 80 volts is applied to the electrodes, it sometimes happens that if the current flowing is large for the first few seconds, gas appears to be evolved at both electrodes, and as long as this happens the current is erratic, but does not fall to the low value which it reaches when no gas is formed.

With larger platinum electrodes of about 1 to 3 cm. area, the changes are very similar, with the difference which might be anticipated that it takes longer for the current to fall from its initial high to its extremely low value, and that iodine is liberated at the anode and forms there a characteristic red solution in the sulphur dioxide. There is, moreover, little or no evidence of gas evolution.

When mercury electrodes were substituted for platinum, it was found that the general behaviour was the same as before. In this case, however, stirring the liquid electrode caused a rise in value of the current, and at the anode a green compound was formed as a scum on the surface of the mercury. This green substance was probably mercurous iodide.

Experiments with silver and copper cathodes showed that with these the current did not exhibit any of the erratic variations which were found with Pt and Hg cathodes ; the silver (or copper) became covered with a dark brown, almost black, deposit, in all probability silver (or copper) sulphide

which, since it is a conducting substance, does not cut off the current. Iodine is liberated both with silver and with copper anodes at the current densities employed.

Experiments with Anode of other Metal.

With a Zinc Anode.—No iodine is liberated except when a high current density is used ; with moderate current densities zinc is dissolved and is found afterwards in the solution surrounding the anode.

With an Anode of Iron Wire.—The behaviour of the solution appeared to depend on the previous history of the electrode ; thus in several experiments it was found that it sometimes happened that iodine was liberated from the anode, whilst at other times, with the same electrode, no iodine would be liberated, but a dark greenish-black solution would be formed in the immediate neighbourhood of the anode. This solution could be decolorised by reversing the current, and the presence of iron in the coloured solution was repeatedly demonstrated.

With iron the behaviour is therefore erratic, and suggests the ordinary behaviour of iron in aqueous solutions and the passivity of iron.

It is interesting to note that both zinc and iron iodides are only very slightly soluble in liquefied sulphur dioxide, and their solution in the experiments described must be accompanied by the formation of some soluble complex salt with the potassium iodide already in solution.

In the investigation of the electrolysis of potassium iodide in sulphur dioxide two series of quantitative experiments were carried out.

The first had for its object the examination of the properties of the deposit which is formed on the cathode when the solution is electrolysed, and the second the examination of the permanent gas which is liberated at the cathode when current densities of a sufficient magnitude to boil the solution are employed.

The Nature of the Solid Deposit.

In these experiments the electrolysis was carried out in an apparatus consisting of a pair of glass tubes of about 2 cm. internal diameter, connected by a narrower tube of about 8 mm. internal diameter. The wider tubes were closed at the top by means of carefully ground glass joints, through which the wires carrying the electrodes were sealed. To one of these ground glass attachments a side tube was sealed containing phosphoric anhydride. Before carrying out an experiment the potassium iodide which was to be dissolved was strongly heated and then placed at the bottom of one of the tubes of the apparatus, the phosphoric anhydride attachment inserted, and the apparatus exhausted. The exhausted apparatus was then heated to 95° C. for about twelve hours. It was then cooled and immersed in a bath of liquefied ammonia and the sulphur dioxide distilled in through a long column of phosphoric anhydride. This general method of procedure was adopted in all the experiments that were carried out, and the effect of dissolved water vapour was in this way eliminated.

The cathode consisted of a piece of platinum foil which could be suspended from the wire which passed through the ground-glass stopper, and could be removed and weighed before and after each experiment.

An examination of the cathode after the first experiment showed that the deposit was partially soluble in water, that the solution smelt strongly of sulphur dioxide, and that it contained suspended solid matter which proved to be sulphur, and a series of experiments was therefore carried out in which current was passed through the solution and through a silver voltameter in

series, the object being to determine the relation between the amount of silver deposited in an aqueous solution and the amount of sulphur deposited by the same current in the sulphur dioxide solution.

The results of the experiments are contained in the following table :—

TABLE I.

No. of Experiment.	No. of Milligram Equivalents deposited.			Ratios.	
	Of Ag in H_2O Solution.	Of K in SO_2.	Of S in SO_2.	K in SO_2. Ag in H_2O.	S in SO_2. Ag in H_2O.
1	0·58	—	0·33	—	0·57
2	1·06	—	0·70	—	0·65
3	1·15	—	0·64	—	0·56
4		Experiment lost.			
5	0·513	0·483	0·25	0·94	0·49
6	0·527	0·495	0·25	0·94	0·475

These experiments show conclusively that sulphur is always deposited on the cathode when a solution of potassium iodide is electrolysed, but that it is not possible to obtain quantities corresponding with those indicated by Faraday's law. This is sufficiently accounted for by the known solubility of sulphur in sulphur dioxide.

Qualitative experiments showed that the crystalline deposit on the cathode when dissolved in water and filtered from the separated sulphur, and treated with dilute acids, yielded sulphur dioxide and a very small quantity of sulphur, and that the solution contained potassium. This indicated that in addition to the sulphur the deposit contained some potassium sulphite and a small quantity of the potassium salt of an acid richer in sulphur, probably potassium thiosulphate. Experiments 5 and 6 of Table I. were therefore carried out to determine the ratio of the equivalent of potassium and silver.

Considering the difficulty of obtaining an adherent deposit on the cathode, these experiments may be taken as indicating the equivalence of the deposit value in the two solutions.

In several of the experiments that have been described a pair of platinum electrodes was placed in the neighbourhood of the cathode during the experiment, and the conductivity of the solution was measured from time to time during electrolysis. The conductivity fell in every case.

We may summarise the result of this series of experiments as follows :—

1. Sulphur is always deposited at the cathode, but the quantity cannot be accurately determined owing to its solubility in the solvent.

2. A salt deposit consisting largely of potassium sulphite is formed on the cathode in quantities which are equivalent in potassium content to the quantity of silver deposited from an aqueous solution of silver nitrate by the same current.

3. The conductivity of the solution in the immediate neighbourhood of the cathode is lowered during the changes which occur.

The explanation of these facts is immediately forthcoming if we consider them side by side with those which occur at the cathode during the electrolysis of the same salt (potassium iodide) in aqueous solution. This has been done in the following table :—

Changes at Cathode during Electrolysis of Potassium Iodide dissolved in—

(a) *Water.*	(b) SO_2.
1. Hydrogen liberated equivalent to Ag in voltameter.	Sulphur liberated.
2. Potassium hydroxide formed equivalent to Ag in voltameter.	Potassium sulphite (or thiosulphate) formed equivalent to Ag in voltameter.
3. Conductivity increased due to *increase* in salt concentration at cathode from formation of soluble potassium hydroxide.	Conductivity diminished due to *decrease* in salt concentration at cathode from formation of insoluble potassium sulphite (or thiosulphate).

From this it will be seen that if the liberation of gaseous hydrogen during the electrolysis of aqueous solutions furnishes any evidence for the existence of hydrogen ions in water, the corresponding evidence for the existence of sulphur cations in a solution in liquefied sulphur dioxide is furnished by the liberation of sulphur. Just as in aqueous solution we represent the formation of potassium hydroxide as a combination of the potassium ions which reach the cathode with the hydroxyl ions which have been formed from the water by the discharge of hydrogen ions, so also must we picture the formation of potassium sulphite in sulphur dioxide solutions as a combination of the potassium ions with the minute number of sulphite ions which are formed by the discharge of the sulphur ions.

From these considerations we see that potassium sulphite bears the same formal relation to the solvent sulphur dioxide as potassium hydroxide does to water, but that it is rather to be compared with the insoluble than with the soluble hydroxides, and a closer analogy would be obtained by comparing its formation with that of magnesium hydroxide when a magnesium salt is electrolysed.

The Nature of the Gas.

The gas that is evolved in small quantity at the cathode when moist solutions in sulphur dioxide are electrolysed was found to consist of an explosive mixture of hydrogen, oxygen, and nitrogen. When carefully dried materials are used no gas is evolved unless the current density at the cathode is so great that the liquid boils at this point. When this happens a small quantity of gas is evolved, which, after an examination which was prolonged by reason of the difficulty of obtaining and of analysing the small quantities obtained, was proved to consist of a mixture of nitrogen and oxygen considerably richer in nitrogen than ordinary air. It obviously consisted of dissolved air which was boiled out from the solution surrounding the cathode. The hydrogen of the earlier experiments was traced to the presence of traces of water.

ELECTROLYSIS OF TETRAMETHYLAMMONIUM IODIDE AND TRIMETHYLSULPHONIUM IODIDE.

The experiments with these two substances were approached with considerable interest, as it was thought possible that their electrolysis might result in the formation at the cathode of compounds such as ditetramethylammonium and ditrimethylsulphonium. As it was thought that these compounds, even if formed, would probably be unstable at high temperatures, easily decomposed by water, and readily oxidised by atmospheric air, experi-

ments were planned whereby all operations could be carried out at —35° and in a vacuum. As this latter condition involved the continuous pumping away of considerable quantities of SO_2 a special automatic mercury pump was designed and constructed.*

Preliminary experiments showed that in the case of each of these substances there is formed at the cathode a dark blood-red solution, the colour of which is very readily discharged. The conditions necessary for its discharge were first investigated, and it was found that—

(a) The colour is not discharged by dilution with sulphur dioxide.

(b) The colour is not discharged by prolonged standing.

(c) The colour is discharged immediately by the addition of moist liquid sulphur dioxide, and

(d) Slowly by contact with dry air.

(e) The colour is discharged and a yellow precipitate formed by mixing together the cathode and anode solutions.

Experiments were therefore planned and the necessary apparatus was designed and constructed to find out, if possible—

(a) What is the nature of the compound contained in the red solution.

(b) What is the nature of the yellow precipitate formed on mixing the cathode and anode solutions.

Investigation of the Nature of the Compound or Compounds contained in the Red Solution.

Several experiments were carried out, in all of which an apparatus was used which had been specially designed and constructed to admit of the following operations being carried out :—

1. The apparatus and previously heated tetramethylammonium iodide could be exhausted with a phosphorus pentoxide tube attached and left in this condition at 95° C. for twenty-four hours to ensure thorough drying of the materials.

2. The solution for electrolysis could be made in the dried apparatus by admitting sulphur dioxide gas through a stopcock and condensing it in the apparatus on to the dried tetramethylammonium iodide. In some of the experiments the sulphur dioxide was previously purified and dried by distilling it from the metal cylinder into a receiver containing phosphorus pentoxide, leaving it in contact with the latter overnight, and finally distilling it from this receiver through a long column of phosphorus pentoxide into the electrolysing apparatus.

3. The solution made as described, with complete exclusion of air and moisture, could be electrolysed in an atmosphere of sulphur dioxide at the vapour pressure of the solution, no air being admitted.

4. The red cathode solution, after electrolysis had been carried on for the desired time, could be transferred, without opening the apparatus, into a special receptacle, which could then be sealed off from the main apparatus. The solution in this receptacle then contained the compound or compounds which were to be investigated and the solution had at no time been subjected to a temperature higher than —33° C. (boiling-point of liquefied ammonia), nor had it been exposed to contact with any substance other than the glass of the containing vessel. It had not passed through any stopcocks and therefore could not contain anything but the original salt and the products of its electrolysis.

5. The next stage in the operation was the evaporation of the solution and

* Steele, *Phil. Mag.*, June, 1910.

the examination of the residue.   In order to effect the former, the receptacle had been provided with a tube and stopcock.   This tube was now attached to the automatic pump, and after the bulb and attachments of the latter had been thoroughly exhausted, the stopcock was opened and the sulphur dioxide removed through the pump, the receiver being kept immersed in a bath of liquefied ammonia.

Fig. 1 represents the type of apparatus used for the electrolysis experiments.   The portion B was added when it was desired to separate either
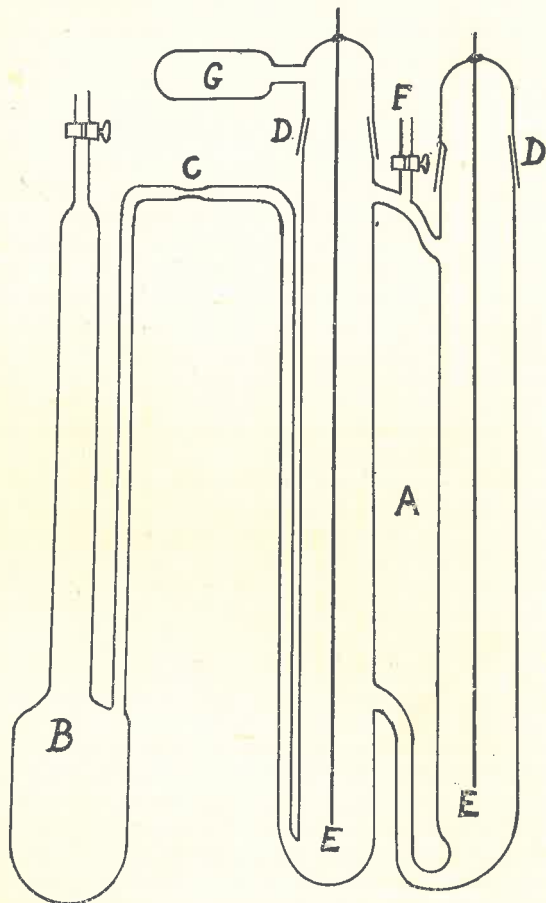
FIG. 1.

anode or cathode solution for examination.   The solution could be drawn over from A, which is the actual electrolysis vessel, into B, by slight variation of the temperature of the two vessels with consequent variation of vapour pressure. B could be sealed off at C by a small blow-pipe flame. EE represent the electrodes. DD are ground caps to allow of the insertion of solids and the removal of the electrodes.   Sulphur dioxide was distilled in through a tube containing phosphorus pentoxide, sealed to the tap F. G is a phosphoric oxide tube for drying the apparatus.

The possibility that a compound such as $(N(Me)_4)_2$, even if formed during electrolysis, might be decomposed during the subsequent evaporation was investigated. Should such a decomposition occur, it is almost certain that the products would include ethane, and accordingly the sulphur dioxide as it was pumped away was tested occasionally to see if any permanent gas could be detected, and in no case was even the smallest trace of such found. It is therefore concluded that no such decomposition occurs.

During the evaporation of the solution the dark red colour is retained until no liquid is left. If the exhaustion is stopped at this stage there remains a solid residue of a very dark brown, almost black substance. At the temperature of the bath the vapour pressure of this substance is about 3·5 mm. of mercury, and on continuing the exhaustion the pressure remains nearly constant at this value, but as the gas is removed from the vessel the colour of the solid substance gradually changes from dark brown to pale yellow. At this stage the gas that was removed was very carefully examined for permanent gases, but none were ever found.

The practical constancy of the sulphur dioxide vapour pressure during exhaustion pointed to the dark brown solid as being simply a compound of the yellow one with sulphur dioxide, and to test this assumption dry sulphur dioxide was admitted to the vessel containing the yellow solid to see if the dark brown substance could be reproduced. It was found that sulphur dioxide was absorbed, but the colour of the compound formed was a pale red. Whether another modification of the original compound or a fresh compound was formed was not determined.

This yellow residue was obtained in about eight experiments, and its properties were examined in various ways. It was found that it never contained more than a trace of iodide, thus showing that separation of the cathode solution had been efficiently carried out. The substance always smelt strongly of sulphur dioxide, was not hygroscopic, and in the case of samples from which the gas had not been continuously pumped away for a prolonged period, it evolved sulphur dioxide on adding to water.

All solutions of the substance were found to leave a residue of sulphur on standing and some samples rapidly deposited sulphur shortly after solution. The samples which behaved in this manner were found to be very strongly reducing and gave reactions very similar to those of thiosulphate. The reducing value of the substance was determined by titration with $\frac{N}{20}$ iodine solution, and the solution after titration was found to be strongly acid. This is the characteristic behaviour of sulphites when titrated with iodine. The amount of sulphite present was determined by combining the results of the iodine and acidity titrations, and the result of the analyses of the different samples is shown in the following summary :—

Experiment 1.—*Analysis carried out immediately after solution.* Iodine reducing value was due to sulphite 87 per cent. and thiosulphate or other reducing agent 13 per cent.

Experiment 2.—*Analysis made after the solution had stood some time.* Reducing action entirely due to sulphite.

Experiments 3 *and* 4.—*Analysis made before the deposition of sulphur was complete.*

Experiment 3.—Reduction due to sulphite 93 per cent. Other substances 7 per cent.

Experiment 4.—Reduction due to sulphite 94·5 per cent. and other substances 5·5 per cent.

The substance is obviously composed mainly of tetramethylammonium

sulphite, formed at the cathode, together with a small quantity of some extremely easily decomposed and highly reducing substance formed also at the cathode by the interaction of the discharged sulphur. It is probable that the red colour, which is characteristic of this cathode solution and which is so easily destroyed, is a property of this easily decomposed compound.

Similar experiments to those recorded in the foregoing summary were carried out with trimethylsulphonium iodine and the results, both qualitatively and quantitatively, were the same, namely, a blood-red liquid was formed at the cathode. From this a pale yellow solid was obtained by evaporating off the sulphur dioxide, and this solid, when treated with water, left a residue of sulphur, and the aqueous solution was found to contain sulphite and a very small proportion of a very highly reducing substance which rapidly decomposed with deposition of sulphur.

The Yellow Precipitate formed on mixing the Cathode and Anode Solutions.

The anode employed in the foregoing experiments was of zinc, which dissolved during the action, and it was therefore probable that the precipitate was a zinc compound. To test this, a solution of zinc bromide and tetramethylammonium iodide in sulphur dioxide was added to a small quantity of the cathode solution and an immediate yellow precipitation occurred.

The experiment, in which the compound was prepared, was carried out in an apparatus specially designed and constructed for the purpose of making the solutions by electrolysis, subsequently mixing the cathode and anode solutions and transferring the mixture of solution and suspended precipitate to another specially designed and constructed apparatus in which it could be washed repeatedly with fresh quantities of pure sulphur dioxide, all the operations being conducted in a dry exhausted atmosphere. The precipitate thus prepared was washed seven or eight times, or until the filtrate of sulphur dioxide came through colourless, and it was then dried whilst still in the apparatus, and finally removed for analysis.

The results of the analysis are as follows :—

Sulphur estimated as sulphur dioxide, 19·13 per cent.
Sulphur estimated as sulphate, 20·8 per cent.
Zinc estimated as oxide (two samples), 28·6 and 29·6 per cent.
Theory requires for $Zn_3(NMe_4)_2(So_3)_4$ S = 19·3 per cent.
$$Zn = 29·5 \text{ per cent.}$$

The high result of the sulphur estimation as sulphate might be due to the presence of a small amount of free sulphur in the precipitate, and is in accord with the general experience of the foregoing analyses.

It is interesting to observe the formation of this particular double salt as an insoluble precipitate in liquefied sulphur dioxide, corresponding potassium and ammonium salts having been prepared in aqueous solution and examined by Berglund.*

ELECTROLYSIS OF TETRAMETHYLAMMONIUM SULPHITE.

For these experiments a sample of tetramethylammonium sulphite was prepared from the iodide by first precipitating the latter with moist silver hydroxide, filtering off the silver iodide, and evaporating the bulk of the water from the filtrate.

The very concentrated solution of tetramethylammonium hydroxide was then placed in the apparatus in which the electrolysis was to be carried out and sulphur dioxide passed in in sufficient quantities to combine with all the

* Ber., 1874, **7**, 469.

tetramethylammonium hydroxide and to displace all the air. The apparatus was then exhausted, after being connected to a tube charged with phosphoric anhydride. When all the water had been removed sulphur dioxide was distilled into the apparatus so as to make with the dry sulphite a water-free solution for electrolysis.

The sulphite is freely soluble in sulphur dioxide, forming a deep yellowish red solution. On electrolysis, the characteristic blood-red solution containing sulphur is formed at the cathode.

Tetramethylammonium sulphate is also soluble in sulphur dioxide, forming a good conducting solution, which on electrolysis yields the same characteristic red cathode solution as is produced by the iodide and sulphite.

Electrolysis of Hydrogen Bromide.

Hydrogen bromide appears to be freely soluble in sulphur dioxide, but if quite dry the solution is almost non-conducting, in this respect presenting a great contrast to the corresponding solutions in water.

If the solution contains as an impurity either water or certain organic compounds, the current flows freely with any metal as electrode, the products of electrolysis being hydrogen at the cathode and bromine at the anode. This behaviour is probably to be attributed to interaction between the hydrogen bromide and the second solute resulting in the formation of an oxonium compound, which acts as a good electrolyte.

Oxonium compounds have been investigated by a number of investigators, and especially by Collie and Tickle, Baeyer and Williger, and Archibald and McIntosh.

The last-named workers, for example, have isolated and examined a number of compounds of hydrogen bromide or iodide with compounds such as ether, acetone, and generally with the alcohols, ethers, and ketones.

It has been already noted that hydrogen bromide when dissolved in liquefied sulphur dioxide does not form a highly conducting solution, and experiments have shown that the same may be said of the sulphur dioxide solutions of the following substances :—

| Dimethylpyrone, | Acetone, | Benzophenone, |
| Benzaldehyde, | Ether, | Water, |

and M. dinitrobenzene, but when small quantities of hydrogen bromide are added to solutions of either of the first six compounds enumerated above, good conducting solutions result ; with M. dinitrobenzene there is no appreciable change in conductivity.

The compound of dimethylpyrone and hydrogen bromide was isolated and examined by Collie and Tickle ; those of acetone and ether with hydrogen bromide were isolated and examined by Archibald and McIntosh, and there can be no doubt that the increase of conductivity in the case of these compounds and in the case of benzaphenone and benzaldehyde is due to the formation of these oxonium compounds. If this is granted, we must accept the same explanation for the case of water.

The view that combination of water and hydrogen bromide is an antecedent to conduction is strongly confirmed by the behaviour of mixed solutions of these substances when electrolysed. When water is added to a solution of hydrogen bromide in sulphur dioxide, a small quantity dissolves in the solution, the remainder dissolving some hydrogen bromide and sinking to the bottom as a heavy liquid, which may sometimes crystallise as a white solid which melts below the boiling-point of the sulphur dioxide. This solid is probably one of the hydrates of hydrogen bromide which are known to exist at low temperatures.

When a current is passed through such a saturated solution, small droplets appear on the cathode, increase in size, and fall to the bottom, producing a liquid similar in properties to the solution of hydrogen bromide in water previously mentioned.

If the scheme suggested below, in which water takes part in the conduction, be correct, water should be carried to the cathode, and in a saturated solution be precipitated there. At the same time the anode solution should lose water and become unsaturated. To test this an H-shaped electrolysis vessel was constructed, filled with solution, and an excess of water placed in the anode limb. A stopper was fitted in the tube connecting the two limbs. After passing the current for some time the anode and cathode solutions were separated by means of this stopper and the solutions stirred. The quantity of undissolved water in the anode limb was found to have decreased, that in the cathode limb to have increased.

On account of the many similarities between hydrogen sulphide and water it was considered possible that a solution of hydrogen sulphide in a mixture of sulphur dioxide and hydrogen sulphide might be conducting.

It was found that sulphur dioxide and hydrogen sulphide did not react in the gaseous state if even moderately dry. Passage rapidly through five or six cm. of phosphoric oxide dried the gases sufficiently. It was found possible to condense the liquids together at $-80°$ and to prepare solutions of hydrogen sulphide in sulphur dioxide at temperatures up to the boiling-point of that liquid without reaction taking place, in an apparatus dried in a water oven and cooled in air.

A solution so prepared was almost non-conducting, and the addition of hydrogen bromide caused practically no increase in the current.

These results are entirely consistent with the following representation of the reactions that take place :—

1. $H_2O + HBr \rightleftharpoons H_3OBr$, oxonium bromide.
2. $H_3OBr \rightleftharpoons H_3O\cdot + Br'$, and during electrolysis.
3. $2H_3O\cdot + 2\theta \longrightarrow H_2 + 2H_2O$ (at cathode).
4. $2Br' - 2\theta \longrightarrow Br_2$ (at anode).

This series of reactions is extremely interesting as indicating the probability that hydrogen bromide (and inferentially the other halogen hydrides) does not in itself act as an electrolyte, but must first enter into combination with water, or ammonia, or with some compound with which it can form oxonium or ammonium compounds.

Thus when hydrogen bromide dissolves in liquefied ammonia it would be readily conceded that the resulting solution contains ammonium bromide, and when it dissolves in water we must be prepared to recognise the similar formation of oxonium bromide, probably very much dissociated, at the ordinary temperature. The non-formation of a conducting solution when hydrogen bromide is dissolved in the other halogen hydrides or in liquefied sulphur dioxide is probably due, at least in part, to the non-formation of such compounds.

Measurements have been made of the conductivities of sulphur dioxide containing in solution various mixtures of hydrogen bromide and the substances enumerated above, a special apparatus having been made to permit of the preparation of solutions of known strength with carefully dried materials. All the sulphur dioxide used was distilled into the apparatus through a long column of phosphorus pentoxide. The conductivities were determined at a temperature of $-35°$ C.

The cell constant $= 0·059$.

The specific conductivity, K, of pure sulphur dioxide $= 1.5 \times 10$ mhos.

As stated previously, water is not very soluble in a mixture of hydrogen bromide and sulphur dioxide. As time did not permit of determinations of the solubility of the water, the value for the molecular conductivity only represents the minimum possible and is really too low, excess of water having been added.

TABLE II.

Molecular Conductivities.

Gram. Mols. HBr.	Of	Dissolved in x Gram. of SO_2.	Dilution.	Specific Conductivity.	Molecular Conductivity.
	Ether.				
0.0	0.0051	9.72	$1.25 \times 10^{+3}$	1.18×10^{-4}	1.47×10^{-1}
0.049	0.0051	19.5	2.5×10^3	1.4×10^{-3}	3.50
0.049	0.0051	9.72	1.25×10^3	$2.95 \times 10^{-}$	3.69
	Dimethylpyrone.				
0.0	0.0011	10.17	$6.1 \times 10^{+3}$	1.5×10^{-4}	9.15×10^{-1}
.011	0.0011	10.17	6.1×10^3	2.8×10^{-3}	1.74×10
0.011	0.0011	19.00	1.14×10^4	$1.47 \times 10^{-}$	1.67×10
0.011	0.0011	33.8	2.02×10^4	0.908×10^{-3}	1.83×10
	M. dinitrobenzene.				
0.0	0.00595	10.00	1.100×10^3	1.48×10^{-4}	1.63×10^{-1}
0.025	0.00595	10.00	1.100×10^3	$1.50 \times 10^{-}$	1.65×10^{-1}
	Acetone.				
0.0	0.007	9.5	9.0×10^2	5.9×10^{-5}	5.3×10^{-3}
0.016	0.007	9.5	9.0×10^2	$1.85 \times 10^{-}$	1.67×10
0.016	0.007	20.34	1.9×10^3	7.46×10^{-3}	1.43×10
	Benzophenone.				
0.00	0.00055	10.37	1.24×10^4	2.0×10^{-6}	3.72×10^{-2}
0.02	0.00055	10.37	1.24×10^4	3.75×10^{-4}	1.08×10
0.02	0.0033	24.67	4.92×10^3	2.04×10^{-3}	0.98×10
0.02	0.0033	10.37	2.06×10^3	4.62×10^{-3}	0.952×10
	Benzaldehyde.				
0.00	0.005	10.0	1.31×10^3	1.95×10^{-3}	2.54×10^{-2}
0.025	0.005	10.0	1.31×10^3	4.72×10^{-3}	6.17
0.025	0.005	21.9	2.88×10^3	2.42×10^{-3}	6.95
0.025	0.0283	21.9	(5.75×10^3)	1.25×10^{-2}	(7.15)
	Water.				
.035	0	9.8	1.86×10^2	1.5×10^{-4}	2.8×10^{-2}
0	.0083	9.8	7.83×10^2	1.5×10^{-5}	—
.035	.0083	9.8	7.83×10^2	4.2×10	> 3.3

The results of the measurements are collected in Table II., which shows the number of gram molecules of hydrogen bromide, of water, or other solute, or of both, which are dissolved in the stated weight of sulphur dioxide.

The fourth column contains the dilution of the solution expressed as the number of c.c.'s of solution containing one gram molecule of dissolved substance.

The fifth column contains the values of the specific conductivities of the various solutions, and the molecular conductivities are given in the last column.

The molecular conductivities which are given in the case of the mixed solutions are those of the water or other organic solvent, with the exception of the most concentrated solution of benzaldehyde, the concentration of which is greater than that of the hydrogen bromide. In this case the figures in brackets refer to the volume containing one gram mol of hydrogen bromide and the corresponding molecular conductivity.

TABLE III.

Some Molecular Conductivities Compared.

1. KCl in H_2O, 125.
2. HBr in SO_2, ·0405.
3. Acetone in SO_2, ·0053.
4. HBr Acetone in SO_2, 16·7.
5. HBr Ether in SO_2, 3·7.
6. HBr Dimethylpyrone in SO_2, 17·4.
7. HBr Benzaldehyde, 6·95.
8. HBr Benzophenone, 10·8.
9. $HBrH_2O$ in SO_2, > 3·3.

In order to convey a clear idea of the actual magnitude of the conductivities of these solutions a few molecular conductivities have been collected in Table III. It will be seen that the molecular conductivity of a mixture of water and hydrogen bromide in sulphur dioxide is of the same order of magnitude as that of a 1 per cent. solution of acetic acid in water (3·5), while the specific conductivity (4×10^{-3}) is several times greater than that of the acetic acid solution at 18° ($5·8 \times 10^{-4}$).

In all cases but one the quantity of hydrogen bromide is considerably in

TABLE IV.

Variation of Molecular Conductivity with Time.

Solution containing		Time in Minutes after Mixing.	Mol. Conductivity.
H_2O ·0083 gr. mols	} 780	0·0	3·31
HBr ·035 gr. mols in 6·5 c.c. of SO_2... ...		30	2·72
Ether ·0051 gr. mols	} 1,250	0	3·68
HBr ·049 gr. mols in 6·4 c.c. of SO_2 ...		90	4·56
Acetone ·007 gr. mols...	} 900	0	14·8
HBr ·010 gr. mols in 6·23 c.c. of SO_2 ...		25	16·5
Acetone ·007 gr. mols	} 1,900	0	14·2
HBr ·016 gr. mols in 13·4 c.c. of SO_2 ...		40	17·3

excess of that required for combination with the other solute, and the dilution has been calculated on the assumption that practically all of the water or organic solute has combined with the hydrogen bromide.

The figures for meta dinitrobenzene indicate that no combination of the two compounds is brought about. It has been found that the conductivity of certain solutions varies with time, and this variation is well shown by the following figures, Table IV., which refer to experiments with water, with ether, and with acetone,

When a water mixture was allowed to stand for several hours a heavy oily liquid appeared at the bottom. The fall in conductivity might be attributed to the slow formation of this substance, which in general properties corresponded with sulphur bromide. It is hoped to investigate the nature of the substance more fully at a later date.

The rise in molecular conductivity which occurs with the other substances is consistent with the supposition that the velocity of the formation of the oxonium compound is not instantaneous, the conductivity rising with the increase in concentration of the compound.

ELECTROLYSIS OF SOLUTIONS OF ETHER AND HBr IN SO_2.

With ether solutions current flowed freely, but at the start of the experiment very little hydrogen was evolved. After the current had passed for some time (an hour or two) much more gas could be collected. Quantities up to about two-thirds of the theoretical amount were collected from solutions which had previously been electrolysed for some time.

With water solutions more gas was evolved at the commencement of the electrolysis, approximately half the theoretical volume, but this quantity did not increase with continual passage of the current.

The fact that hydrogen is not evolved in theoretical volume may be explained by the suggestion that some is used up in the formation of reduction products.

In view of its possible bearing on the nature of the hydrogen ion and on the general theory of electrolysis, it is hoped to extend that portion of the work dealing with the conductivity and electrolysis of hydrogen bromide solutions at a later date.

ELECTROLYSIS OF POTASSIUM MERCURY IODIDE.

Qualitative attempts were made to electrolyse solutions of certain double salts, as, for example, the double compound of potassium and mercury iodides. It was found that this compound behaved very similarly to potassium iodide : a deposit containing sulphur being formed on the cathode, and the current falling very rapidly to the usual small value. In one experiment, in which the materials had not been carefully dried, it was found that mercury was deposited as a film on a strip of copper immersed in the solution, but when the experiment was repeated with carefully dried materials no such effect could be produced.

ELECTRODE POTENTIALS OF THE METALS.

The programme mapped out for the determination of the electrode potentials was as follows :—

1. To determine the electrode potentials of metals when immersed in saturated solutions of their salts.

2. To determine the solubility of these various salts, using for the purpose the microbalance recently described by Steele and Grant.*

3. To determine the conductivities of extremely dilute solutions of these salts, and so to ascertain the ionic concentrations of the various metallic ions.

From the data thus obtained it should be possible to calculate the normal electrode potentials of the metals when dissolved in a solvent such as sulphur dioxide, which contains no hydrogen, and to compare the values thus determined with those obtained in aqueous solutions.

Owing to the removal of one of us from Melbourne to Brisbane, and the

* *Proceedings of the Royal Society*, 1909, A 82, p. 580.

consequent temporary loss of facilities for experimental work, this programme has been interrupted, and the only part actually carried out is the measurement of the electrode potential of metals immersed in saturated solutions of their salts.

The choice of metals and salts was limited in the first place by the fact that the only freely soluble metallic salts are the bromides and iodides of the alkali metals, and that these are not capable of being used for electrodes on account of their rapid tarnishing in an atmosphere of dry sulphur dioxide.

On the other hand, the salts of other metals being extremely insoluble, cells prepared with saturated solutions of these salts have an extraordinarily small capacity. As a consequence of this, it was found to be impossible to determine the e.m.f. of these combinations by the usual potentiometer method, since the minute amount of current taken out of the cells during the measurement immediately lowered the e.m.f. to zero.

The measurements were therefore carried out with a quadrant electrometer, one pair of quadrants being earthed and the other connected with one electrode of the cell, the other electrode being earthed. The electrometer was one of very small capacity, and it was found that no polarisation was produced in the cell when its e.m.f. was measured by this method. It was not found possible to use the ordinary dipping electrode vessels, and therefore an apparatus was designed for the measurements. This apparatus consisted of two electrode vessels immersed in a wide test-tube. One of these vessels is shown in Fig. 2. It consists of an H-shaped tube, one limb of which, A, is closed at the bottom, the other, B, being open. The open limb is provided with a ground-in hollow glass stopper, C, with a hole drilled in it opposite the connecting tube, D, and by rotating this stopper the solution contained in the closed limb could be brought into communication with the liquid in the wide test-tube E.

The two electrode vessels were fitted in a rubber cork, F, which in its turn fitted the

FIG. 2.

test-tube, and the whole could be immersed in a Dewar flask containing liquefied ammonia.

In carrying out an experiment, the electrodes, G, which were composed of a wire of the metal under investigation, were placed in the closed limb of the H tube, a small portion of the selected salt of the metal having been first placed in the same limb. The upper end of the tube containing the wire was then sealed with sealing-wax and the apparatus exhausted and dried. When
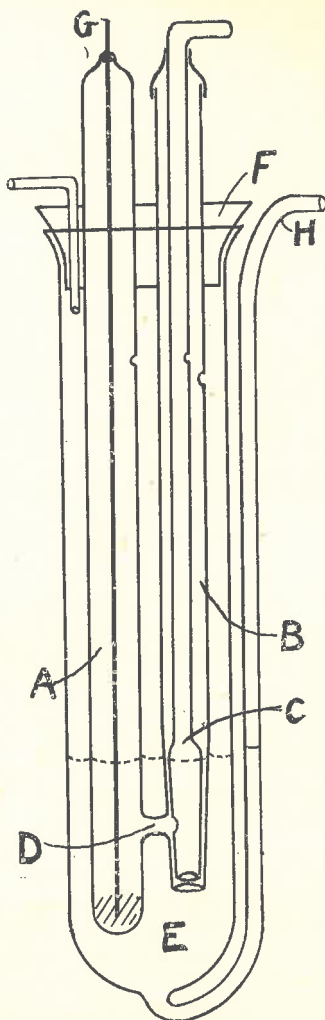
it was judged that the whole apparatus was thoroughly dry, it was immersed in a bath of liquefied ammonia, the electrode vessels placed in communication with the test-tube by turning the stopper, and sulphur dioxide distilled into the apparatus through H. The sulphur dioxide filled the test-tube to the required level and overflowed into the electrode vessels, forming there after the lapse of a few hours a saturated solution of the salt in question. It was usually found that the film of sulphur dioxide surrounding the stopper was sufficiently conducting to allow of readings being taken without polarisation effect being observed.

The materials employed were from various sources, and were subjected to various methods of purification, with the object of testing whether the effects measured were due to the presence of minute quantities of impurities.

A sufficient number of measurements have been made to indicate that each metal has a definite electrode potential when immersed in liquefied sulphur dioxide, and that the magnitude of the potential is affected by the concentration of the metallic ion in solution in the same manner and in the same direction as it is in aqueous solution.

The measurements that are described were made at a temperature of $-35°$ C. The deflections of the electrometer were standardised by means of a standard Clark cell. The standard electrode employed was one of mercury, covered with a layer of purified mercurous chloride, made into a paste with liquefied sulphur dioxide.

The following measurements of the e.m.f. of a typical cell are given as an example of the degree of constancy of e.m.f. which can be obtained with the extremely dilute solution which it was necessary to employ.

Cell Constancy of $Hg/HgCl$ *in* $SO_2/SO_2/PbCl_2$ *in* SO_2/Pb.

Time Measurement.						E.M.F.
H.	M.					
0	0	...	...	...	...	0·40
1	45	...	...	...	...	0·427
3	15	...	...	...	...	0·430
5	0	...	...	...	...	0·437
7	30	...	...	...	...	0·430
8	45	...	...	...	...	0·433

A. $Pb/PbCl_2/HgCl/Hg$. Mercury electrode negative.
    1. E.m.f. $= 0·435$ volt.
    2. Same cell, but freshly prepared and purified materials.
       E.m.f. $= 0·435$ volts.

B. $Zn/ZnBr_2/HgCl/Hg$. Mercury electrode negative.
    1. Pure zinc cast into rod.
       Zinc bromide distilled.
       E.m.f. 0·38 to 0·40 volt.
    2. Zinc bromide redistilled.
       E.m.f. 0·37 to 0·40 volt.

C. $Cd/CdI_2/HgCl/Hg$.
    1. Cd metal electrolytic, Schuchardt, cadmium iodide recrystallised.
       E.m.f. 0·42 to 0·445 volt.
    2. Freshly prepared and treated material from the same stock.
       E.m.f. 0·42 to 0·43 volt.

Addition of potassium iodide and of tetramethylammonium iodide to the solution surrounding the cadmium iodide instantly altered the e.m.f., and in all

cases tested the e.m.f. was sensitive to the addition of any salt having an anion common to the added and dissolved salt.

SUMMARY.

In the foregoing pages experiments are described which were designed to ascertain the mechanism of electrolysis in liquefied sulphur dioxide.

1. It has been shown that during the electrolysis of solutions of potassium or sodium iodides, tetramethylammonium iodide, trimethylsulphonium iodide, sulphur is deposited on the cathode, and that a sulphite is simultaneously formed.

2. That, at the anode, changes occur which are analogous to those occurring in aqueous solution. For instance, bromine and iodine are liberated from solutions of bromides and iodides.

3. That anodes of zinc and iron are attacked and pass into solution as complex iodides when iodides are electrolysed.

4. Evidence has been adduced to show that water and hydrogen bromide unite to form an oxonium compound which is electrolytic in character, and this evidence has been strengthened by comparison with the behaviour of several well-known oxonium compounds.

5. A few electrode potentials of metals immersed in saturated solution of their salts have been measured.

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PROPERTIES OF BINARY MIXTURES OF SOME LIQUEFIED GASES.

BY

LANCELOT SALISBURY BAGSTER
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CXXX.—*Properties of Binary Mixtures of Some Liquefied Gases.*

By LANCELOT SALISBURY BAGSTER (Victorian Government Research Scholar).

IN a previous paper (Trans., 1910, **97**, 2607) an account was given by the author, in conjunction with Dr. B. D. Steele, of the vapour pressure-concentration curves of binary mixtures of liquid hydrogen sulphide with liquid hydrogen bromide and with liquid hydrogen iodide. The hydrogen bromide curve showed a mixture of minimum vapour pressure, whilst the hydrogen iodide " curve " was a straight line.

It was pointed out that such a minimum was regarded as evidence for ionisation or combination or association, and that existing evidence was against the occurrence of ionisation or association in the case of the hydrogen bromide mixtures, whilst there was no other reason than the vapour pressure curve for assuming compound formation.

As hydrogen bromide and iodide usually show a general similarity in behaviour, it was considered of interest to examine further

these mixtures. The shape of the freezing-point curve of a binary
mixture being usually regarded as trustworthy evidence for or
against combination, an examination of these curves was under-
taken.

The curves obtained are shown in Fig. 1. It will be seen that
both are of the same general type, and that neither is of the
characteristic shape with two eutectic points and a maximum,
exhibited by a mixture in which compound formation is taking
place. There is no eutectic point in either curve, both being
continuous and of the form produced by a system in which the

FIG. 1.
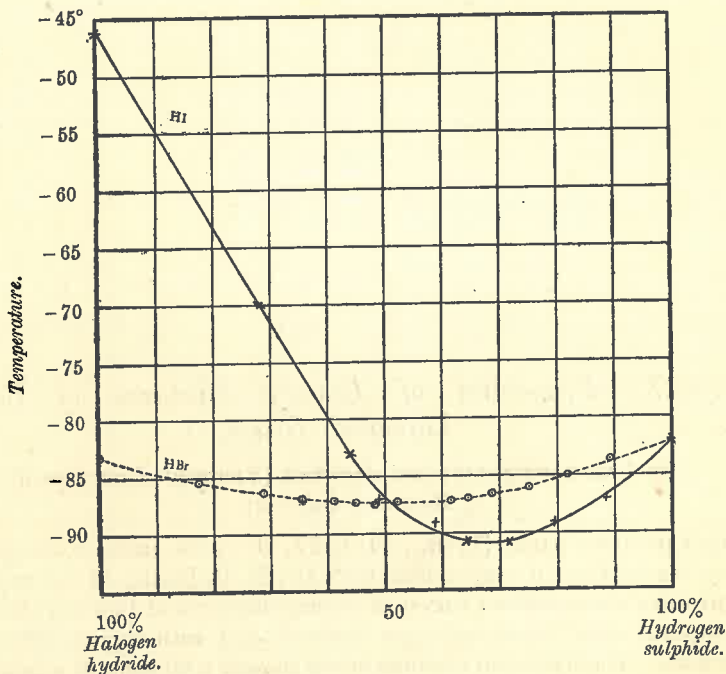
solid phase consists of mixed crystals. It will be seen that
hydrogen iodide has a much greater depressing effect on the
freezing point of hydrogen sulphide than has an equivalent amount
of hydrogen bromide.

Tsakalotos (*Zeitsch. physikal. Chem.*, 1910, **71**, 667) concludes
from the evidence of freezing-point curves and viscosity measure-
ments that a minimum in the vapour-pressure curve of a binary
mixture does not necessarily indicate the formation of compounds.
Apparently the hydrogen bromide system may be regarded as
adducing further evidence for this conclusion.

The apparatus used for the measurements is shown in Fig. 2. It consists of two parts, a burette A for measuring the liquids, the mixtures being made up by volume; and the actual freezing-point apparatus B. It was constructed wholly of glass, all joints being sealed together, and was so designed that a vacuum could be maintained, in order that, having once removed air, liquid could be quickly distilled from one vessel to the other without loss. All points where moisture could gain entrance were protected by

FIG. 2.
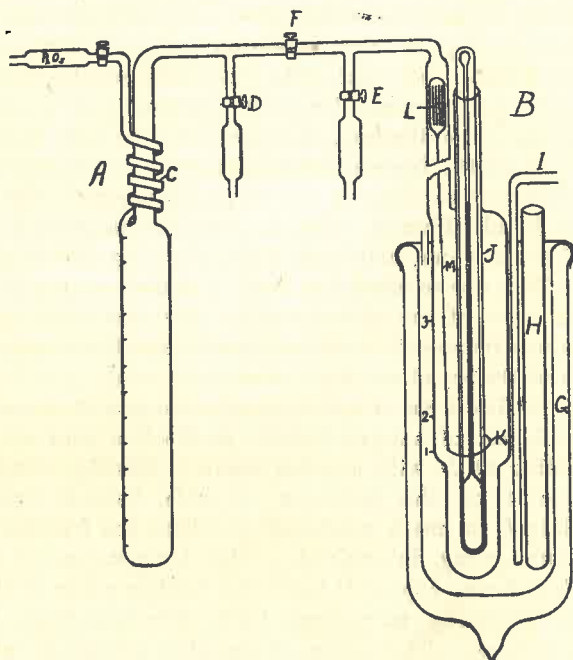
phosphoric oxide tubes. Taps were lubricated with a mixture of paraffins.

To perform an experiment, the burette A was immersed in a suitable refrigerant contained in a long narrow Dewar flask, and a little over 5 c.c. of one liquid, say, hydrogen sulphide, distilled in through the spiral C, which acted as a condenser, uncondensed gases passing out at D. Air was then removed by alternately exhausting at E with a water-pump, and admitting vapour through the tap F. The tube B was then immersed in an unsilvered Dewar flask G, containing light petroleum, the top of the flask being closed by a piece of sheet rubber with holes cut to admit the various

tubes, this being found to be practically air-tight and more convenient than a rubber cork when there is no great difference of pressure on the two sides. Liquid air was now blown into the tube H, where it boiled off, cooling the light petroleum in so doing. The petroleum bath was stirred by a current of dry air blown through the tube I. When the temperature, as indicated by a normal pentane thermometer contained in the tube J, had fallen sufficiently, an exactly measured volume of the liquid (about 5 c.c.) was distilled from A to B. The thermometer used was graduated in degrees to $-200°$. The column was only partly immersed, giving rise to a considerable immersion error. No attempt was made to correct the readings for this, attention being concentrated on an endeavour to keep it constant. The space between the thermometer bulb and the tube J was filled with petroleum, as shown by the black shading in the diagram, to ensure good thermal contact. The lower portion of the freezing-point tube was made narrow in order that the thermometer bulb should be well immersed with a small volume of liquid. Five c.c. filled it to about the point 1; the rest of the tube was wider, a further 5 c.c. changing the level only to about 2. This was to ensure as small a change as possible in the immersion error of the thermometer. For the same reason the apparatus was immersed in the petroleum bath to the point 3, well above 2, and the petroleum kept at constant level.

Having distilled 5 c.c. of hydrogen sulphide into B, A was cleaned out, about 11 c.c. of halogen hydride distilled in, and air removed by exhausting at D with a water pump. Having obtained the freezing point of the hydrogen sulphide, halogen hydride was distilled into B in small, measured quantities, the freezing point of each mixture being determined. The temperature of the bath surrounding B was kept well below the boiling point of the liquid in A when distilling, to prevent back diffusion from B. The solutions were mixed by means of the glass stirrer K, which was worked by a magnet acting on a bundle of iron wire sealed into the tube L. The glass stem of the stirrer was broken at M, and a piece of platinum wire inserted for the sake of flexibility. In order to obtain a freezing point, liquid air was blown into H in small quantities, keeping the bath well stirred by the air current through I, and the solution with the magnetic stirrer. The temperature was made to fall very slowly until crystallisation began. If much solid separated, the reading was considered doubtful. Having obtained a reading, the solid was allowed to melt, and the freezing repeated. When a total quantity of 5 c.c. of the second liquid (halogen hydride) had been added, the liquid was distilled out from B, and 5 c.c. of halogen hydride distilled in, its freezing

point being then determined. Finally, the burette A was emptied, and 5 c.c. of hydrogen sulphide were condensed in it. The curve was then begun from the halogen hydride end, finishing with the final mixture of the first series. This method was found to be the quickest and most economical for obtaining the entire range of concentrations.

The methods adopted for the preparation and purification of the liquids were similar to those described in the previous paper, except that hydrogen bromide was prepared by heating potassium bromide with phosphoric acid solution which had been concentrated to a thick syrup. Hydrogen sulphide and bromide were condensed by a mixture of solid carbon dioxide and ether, and measured at the temperature of that mixture, taken as $-80°$. Hydrogen iodide was condensed and measured in liquid ammonia kept at $-45°$ by blowing a current of air through it. The change in the volume of the burette A due to the temperature change from $-45°$ to $-80°$ was neglected. For the calculation of the molecular compositions of the mixtures, densities were taken from a paper by Steele, McIntosh, and Archibald (*Phil. Trans.*, 1905, A, **205**, 99). Knowing the relative volumes of both constituents of a mixture and the densities, it was easy to calculate the relative weights, and from these and the atomic weights the molecular percentage of each constituent was calculated. In the tables concentrations are expressed as percentage of molecules of halogen hydride.

Tables I and II give the experimental data for hydrogen bromide mixtures, table III for hydrogen iodide.

TABLE I.

Hydrogen Bromide—Hydrogen Sulphide.   First Experiment.

Molecular percentage of HBr.	Freezing point.	Molecular percentage of HBr.	Freezing point.	Molecular percentage of HBr.	Freezing point.
0·0	$-82°$	38·6	$-87·1°$	55·0	$-87·3°$
10·7	$-83·5$	42·0	$-87·9*$	58·5	$-87·2$
18·2	$-85·0$	45·5	$-88·0*$	64·4	$-86·9$
25·0	$-86·0$	48·5	$-88·0*$	71·2	$-86·2$
31·0	$-86·7$	48·0	$-87·3$	82·4	$-85·3$
35·7	$-87·0$	51·5	$-87·5$	100·0	$-83·1$

All the points in table I lie on a smooth curve, except the three marked with an asterisk at 42, 45·5, and 48·5 per cent. hydrogen bromide, which lie on a line nearly a degree too low. These readings were taken after about eighteen hours' almost continuous work. The method of reading the thermometer depended partly on the nearest ten mark; in the present case, $-90°$ was just invisible; consequently an error in reading the thermometer was suspected.

This was to some extent confirmed by the value at 48 per cent. hydrogen bromide obtained at the end of the second half of the experiment, which should have almost corresponded with the value for 48·5 per cent. in the first set. A fresh experiment was undertaken, the curve being carefully repeated from 35 to 55 per cent. hydrogen bromide. The results are given in table II. All the points lie on a smooth curve, which, however, is about 0·2° higher than for the first experiment. As the apparatus had been cut to pieces and cleaned between the two experiments, the exact conditions may not have been recovered, with consequent small change in the thermometer. error.

The curve has been drawn from the data contained in table I, rejecting the three doubtful readings. It is shown in Fig. 1.

TABLE II.

Hydrogen Bromide—Hydrogen Sulphide. Second Experiment.

Molecular percentage of HBr.	Freezing point.	Molecular percentage of HBr.	Freezing point.	Molecular percentage of HBr.	Freezing point.
35·0	− 87·0°	44·2	− 87·0°	55·5	−86·7°
39·8	− 87·0	49·0	− 87·0	100·0	− 83·0
		52·5	− 86·9		

Table III contains the data for hydrogen iodide. The curve is shown in Fig. 1.

TABLE III.

Hydrogen Iodide—Hydrogen Sulphide.

Molecular percentage of HI.	Freezing point.	Molecular percentage of HI.	Freezing point.	Molecular percentage of HI.	Freezing point.
0·0	− 82·0°	28·4	− 90·8°	56·0	− 83·0°
11·3	− 87·0	35·6	− 90·7	71·8	− 70·0
20·3	− 89·0	41·0	− 89·0	100·0	− 46·0
		51·0	− 87·0		

The author wishes to acknowledge indebtedness to Professor Masson for kind advice and for the interest he has taken in the work.

UNIVERSITY OF MELBOURNE.

ELECTROLYSIS OF HYDROGEN BROMIDE IN LIQUID SULPHUR DIOXIDE.

BY

LANCELOT SALISBURY BAGSTER

AND

GEORGE COOLING.

LXXIII.—*Electrolysis of Hydrogen Bromide in Liquid Sulphur Dioxide.*

By Lancelot Salisbury Bagster and George Cooling.

The work to be described in this paper was suggested by some results previously published by Bagster and Steele (*Trans. Faraday Soc.*, 1912, **8**, 51), who found that, although dry solutions of hydrogen bromide in liquid sulphur dioxide were practically non-conducting, the addition of water, which itself in solution is also non-conducting, allowed current to flow freely, hydrogen being discharged at the cathode and bromine at the anode, whilst water was carried from anode to cathode and deposited there. The conclusion drawn was that combination between the two solutes preceded conduction, and comparison with the similar behaviour of organic compounds led to the suggestion that the water and hydrogen bromide united to form an oxonium compound which was electrolytic in character.

The present work was undertaken in order to examine the nature of this phenomenon carefully, and in particular to obtain quantitative information regarding the products formed during electrolysis and regarding the compound from which the products are derived. As an alternative explanation to that already offered, it may be suggested that a simple hydrate type of compound is formed analogous to $CuSO_4,5H_2O$, and that the deposition of water at the cathode is brought about during electrolysis by the loss of the hydrogen bromide holding it in solution. The experimental evidence, however, renders this suggestion untenable.

The experiments to be described were carried out at the temperature of boiling liquid ammonia, which was used as

refrigerant. The solutions were prepared and the experiments carried out in large test-tubes immersed in the ammonia contained in Dewar flasks. The tubes were closed by rubber stoppers carrying the electrodes and tubes for introducing the gaseous sulphur dioxide, which condensed to liquid at the temperature of the ammonia. Water was placed in the tube before placing the latter in the ammonia. The water remained as a solid at the bottom of the test-tube after the introduction of the sulphur dioxide, but on passing gaseous hydrogen bromide into the liquid, two layers were formed, the lower one consisting of a solution of sulphur dioxide and hydrogen bromide in water, and the upper one of a solution of water and hydrogen bromide in sulphur dioxide.

In the course of preliminary experiments, it was found that if the upper layer were syphoned off and used for the electrolysis, the current soon fell in value, whilst no water was deposited at the cathode, sulphur being liberated there in quantity. When the lower layer was allowed to remain in the vessel during the electrolysis, the current maintained its initial value, whilst water appeared at the cathode, very little sulphur being deposited. The water deposited at the cathode collected as small drops, which fell to the bottom of the apparatus.

The probable explanation of the need for the presence of the second layer is that it serves to maintain a saturated solution, and that otherwise the solution near the electrodes becomes depleted of water and hydrogen bromide, a different type of reaction then setting in. In the electrolysis experiments to be described, the second layer was present, but the electrodes were so arranged that conduction and electrolysis took place in the upper solution with the sulphur dioxide as solvent.

Two series of quantitative investigations were carried out, namely, (1) solubility determinations, and (2) determination of the quantity of water deposited at the cathode. In both cases the following method of analysis was adopted for the mixtures and solutions obtained, which contained water, sulphur dioxide, and hydrogen bromide. The sample was introduced into a weighed vessel, and most of the sulphur dioxide and some of the hydrogen bromide boiled off at a temperature below $0°$, the gases being absorbed in sodium hydroxide solution. The bromide and sulphite in the hydroxide solution were determined by standard methods. Trial showed that the water was not appreciably distilled and could be estimated in the residue. For this purpose, a weighed quantity of concentrated sodium hydroxide solution was added to the already weighed vessel containing the water and residual sulphur dioxide and hydrogen bromide, the vessel then being re-

weighed. A determination of the bromide and sulphite in the solution enabled the water to be calculated by difference. Tests with known quantities of the constituents showed that the method was accurate to about 1 per cent.

For the solubility determinations, the solutions were prepared by adding excess of water to the sulphur dioxide and passing into the liquid varying amounts of hydrogen bromide. The solutions were well shaken and allowed to settle, the clear, upper layer being syphoned off for analysis. The results of the analyses are given in the following table:

Hydrogen bromide. Gram.	Water. Gram.	Gram-mol. of hydrogen bromide.	Gram-mol. of water.	Dissolved in x grams of sulphur dioxide.
0·568	0·126	0·0070	0·0070	10·2
0·970	0·214	0·0120	0·0119	15·6
0·435	0·096	0·0054	0·0053	11·0
0·650	0·145	0·0080	0·0080	9·7

It will be seen that the water and hydrogen bromide are found in the solutions in equimolecular proportion, and as water i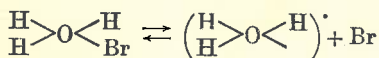tself is but sparingly soluble in sulphur dioxide, it may be concluded that a compound, H_2O,HBr, is formed. Whether this compound is an oxonium derivative or a simple hydrate can be decided from observation during electrolysis. If the deposit of water at the cathode were formed by precipitation of dissolved water as the hydrogen bromide holding it in solution was destroyed by electrolysis, a similar deposit should appear at the anode. In no case was the slightest indication of such deposit observed, and it may be concluded that a true oxonium compound is formed:

$$H_2O + HBr \rightleftharpoons \begin{matrix} H \\ H \end{matrix}\!\!>\!\!O\!\!<\!\!\begin{matrix} H \\ Br \end{matrix},$$
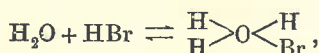
and as the hydrogen and water liberated during electrolysis both appear at the cathode, this compound must ionise as follows:

$$\begin{matrix} H \\ H \end{matrix}\!\!>\!\!O\!\!<\!\!\begin{matrix} H \\ Br \end{matrix} \rightleftharpoons \left(\begin{matrix} H \\ H \end{matrix}\!\!>\!\!O\!\!<\!\!H\right)^{\!\cdot} + Br$$

the H_3O' ion losing its charge at the electrode during electrolysis and forming hydrogen and water.

This formula and mechanism of reaction have been previously suggested by Bagster and Steele, but no quantitative evidence was available, and the formula adopted was based on speculation. It was also shown in the paper referred to that Faraday's law holds for solutions in sulphur dioxide, and it is to be expected that the water and hydrogen liberated will correspond with the quantity of silver deposited in a silver voltameter. It was shown, however,

that in the case of the hydrogen this expectation was not realised, and further careful experiments lately carried out gave no better result. As the solutions were always coloured yellow, probably by traces of bromine, it is probable that the hydrogen was destroyed by reaction at the electrode. The water deposited, however, has been estimated, and found to correspond closely with the quantity predicted by the theory put forward. For this determination, the cathode consisted of a platinum wire sealed through the bottom of a glass tube, the deposited water being collected in a small glass cup suspended underneath. At the end of the experiment, the cup was transferred to the weighed vessel and its contents analysed, as already described.

Two experiments were carried out, with the following results:

Silver in voltameter. Gram.	Water deposited. Gram.	Milligram equivalent of silver.	Milligram equivalent of water.
0·120	0·022	1·11	1·22
0·224	0·037	2·08	2·06

It will be seen from the results that one equivalent of water is liberated at the cathode in the sulphur dioxide solution for every equivalent of silver deposited in the voltameter. This is the result to be expected if the explanation offered as to the mechanism of reaction is correct.

This work has seemed of sufficient importance to publish, as it is probable that similar compounds exist in aqueous solutions of halogen hydrides, quite apart from hydrates of the ordinary type, and that they may take part in the electrolysis and reactions of such solutions.

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COMPOUNDS OF CALCIUM CHLORIDE AND ACETONE.

BY

LANCELOT SALISBURY BAGSTER.

XLIII.—*Compounds of Calcium Chloride and Acetone.*

By Lancelot Salisbury Bagster.

Attention was directed to these compounds while drying acetone with dehydrated calcium chloride, the liquid being treated with successive amounts of the chloride. The first quantity of chloride added had obviously taken up water, showing a moist appearance on the surface, whilst fresh amounts of calcium chloride added to the same acetone showed quite different behaviour, the lumps swelling considerably and becoming powdery in appearance. These lumps, when exposed to the air and apparently acetone "dry," continued to smell of acetone and to ignite on application of a flame, the burning continuing for a considerable time.

The existence of a compound similar to the magnesium compounds described by Menschutkin (*Zeitsch. anorg. Chem.*, 1907, **53**, 28) was suspected, although calcium chloride is practically insoluble in acetone, such compound being analogous to the hydrate of calcium sulphate. No description of such a compound could be found, and in view of the frequent reference in chemical papers to the use of calcium chloride for drying acetone, it was considered of interest to investigate the possible compound.

The behaviour already described indicated that the compound would not be formed so long as water was present to form hydrate, and it was assumed that acetone, when treated with several successive quantities of calcium chloride, would be practically anhydrous, liquid so treated being used in the experiments to be described.

Dry acetone was added in excess to powdered dehydrated calcium chloride, which process caused the development of considerable heat. The vessel containing the mixture was then attached to a mercury pump and manometer, and the pump set in action. So long as liquid was present the pressure remained constant at 18 cm. (the temperature being kept at 20°), which corresponds with the vapour pressure of acetone. After the liquid had disappeared, the pressure rapidly fell to 4 cm. and there remained constant during further pumping.

A sample of the substance was removed as soon as the pressure became constant. It had a strong odour of acetone and ignited on the approach of a flame. A sample was analysed by heating to constant weight, with the following result:

0·687 lost 0·349. $C_3H_6O = 50·8$.
$CaCl_2, 2C_3H_6O$ requires $C_3H_6O = 51·1$ per cent.

The vapour-pressure measurement confirms the existence of the substance as a definite compound. The results were repeated and confirmed with different samples of acetone and calcium chloride.

To search for the existence of a compound containing less acetone, pumping was continued after the pressure had fallen to 4 cm. The pressure remained constant at this value for some time and then fell rapidly to about 1 mm., at which value it again became constant. A sample removed at this stage still had a faint odour of acetone and ignited on the approach of a flame:

0·291 lost 0·100. $C_3H_6O = 34·4$.
$CaCl_2, C_3H_6O$ requires $C_3H_6O = 34·3$ per cent.

The vapour pressure again confirms the existence of the definite compound.

It was next considered of interest to determine the vapour pressure curves of these compounds as affording some indication of their stability. The material was placed in a tensimeter immersed in a water-bath, using mercury as liquid in the U-tube connecting to the manometer, etc., and balancing the vapour pressure by admitting air to the manometer side of the apparatus as necessary. By means of a side-tube and tap all air could be removed from over the substance. As a check the pressures of the acetone were determined in the same apparatus. The values obtained are shown in the

following table, the corresponding curves being shown in the accompanying figure.
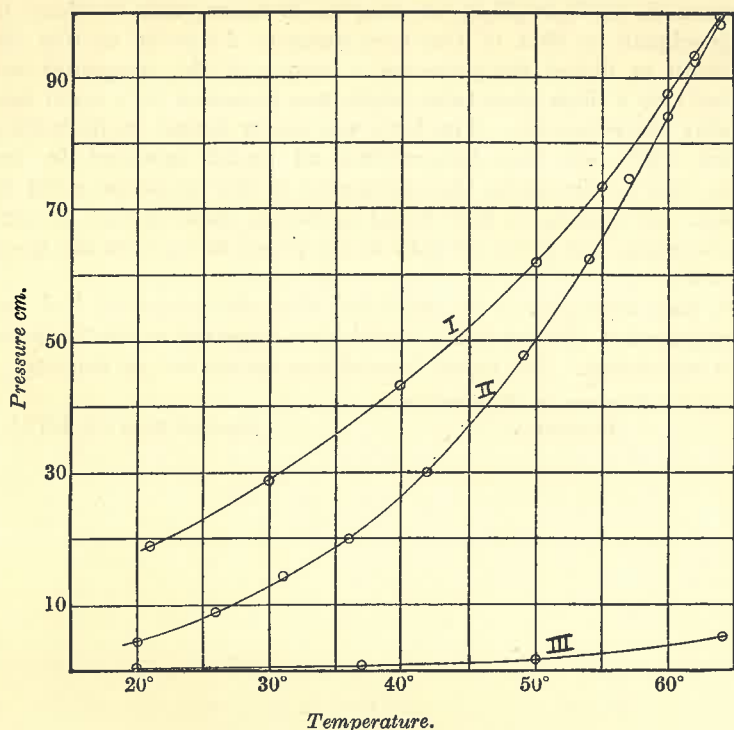
Temperature.

I. Acetone.　　II. $CaCl_2,2C_3H_6O$.　　1 I. $CaCl_2,C_3H_6O_2$.

Pressure in mm.

Temperature.	Acetone.	$CaCl_2,2C_3H_6O$.	$CaCl_2,C_3H_6O$.
20°	—	41	about 1.
21°	190	—	—
26°	—	87	—
30°	288	—	—
31°	—	139	—
36°	—	200	—
37°	—	—	5
40°	427	—	—
42°	—	300	—
49°	—	478	—
50°	617	—	15
54°	—	623	—
55°	731	—	—
57°	—	745	—
60°	876	840	—
62°	933	923	—
64°	997	983	50

As the apparatus would not withstand a pressure of more than 100 cm., readings were not taken at temperatures exceeding 64°. It is evident that at higher temperatures the pressure of the compound, $CaCl_2,2C_3H_6O$, so long as it exists, will continue to approximate to that of the free acetone. In order to test the stability at higher temperatures a sample of the compound was sealed into a thick glass tube, which was immersed in a vessel containing chlorobenzene. The bath was slowly heated to its boiling point, 132°. At this temperature no liquid appeared in the tube, and no change in the appearance of the substance could be noted. On cooling to 130° liquid appeared, showing that at 132° more acetone was given off than was required to saturate the space at 130°.

It may consequently be concluded that the compound had not decomposed at 130° or liquid would have appeared as the temperature was raised. The liquid formed was reabsorbed on keeping.

BINARY MIXTURES OF SOME LIQUEFIED GASES.

BY

BERTRAM DILLON STEELE

AND

L. S. BAGSTER.

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CCLXVII.—*Binary Mixtures of Some Liquefied Gases.*

By Bertram Dillon Steele and L. S. Bagster.

The work described in this paper was undertaken in the first place in connexion with the study of simple inorganic solvents.

Combination between solute and solvent is usually held to be a necessary antecedent to conduction, whilst the form of the vapour pressure-composition curve for mixtures of volatile substances is often accepted as evidence for or against combination in such solutions.

One of us (*Proc. Roy. Soc.*, 1904, **73**, 450) has found that mixtures of the halogen hydrides with hydrogen sulphide form solutions which do not conduct, whilst we have examined sulphur dioxide and hydrogen bromide, and found them to mix in all proportions, forming solutions which show but very slight conductivity. The hydrogen sulphide solutions are doubly interesting, owing to the analogy between hydrogen sulphide and water.

We therefore decided to examine the vapour pressure-composition curves of the solutions formed by sulphur dioxide and by hydrogen sulphide with the halogen hydrides. Hydrogen chloride solutions have not been systematically examined, owing to difficulties caused by the low boiling point of the hydrogen chloride, and to the absence of liquid air. We have, however, found from some rough experiments that sulphur dioxide at $-35°$ dissolves hydrogen chloride to form a solution approximately normal, and that all the hydride can be removed from such a solution by fractional distillation, and therefore no constant boiling mixture can be formed at this temperature. Judging from analogy, also, one would expect the curve obtained to be of a similar type to that given by sulphur dioxide and hydrogen bromide, which pair of liquids has been systematically examined.

Mixtures of hydrogen iodide and sulphur dioxide could not be formed, owing to the fact that these substances react in the gaseous state, depositing sulphur and iodine.

It will be convenient, first, to describe the apparatus used and the method of working, following this with an account of the results obtained. For the preparation of the various hydrides used, the methods described in the paper previously mentioned have been followed. The sulphur dioxide was obtained commercially in a steel cylinder, and fractionated before use. For the preparation of the liquid hydrogen sulphide and bromide, a mixture of solid carbon dioxide and ether was used as refrigerant, liquid ammonia

being used to condense the sulphur dioxide and hydrogen iodide. In the actual experiments, liquid ammonia was used for the low temperature bath, constant temperatures from $-35°$ to $-75°$ being easily obtained by varying the pressure over the ammonia by means of a water pump.

Ammonia and hydrogen iodide boil at about the same temperature, but it was found that if the top of the vacuum vessel containing ammonia were left open to the air and not plugged with cotton wool, as is usual, the diminution in the partial pressure of the ammonia, brought about by air convection currents, was sufficient to lower the temperature to $10°$ or $15°$ below the boiling point of the ammonia under atmospheric pressure. The temperature thus obtained was sufficiently low to condense the hydrogen iodide, and as the carbon dioxide mixture froze the liquid in the condenser, the above method of cooling was adopted. If the temperature rose owing to heat given out by the condensing hydride, an air current occasionally blown through the ammonia by means of a foot-bellows sufficed to reduce it again.

The difficulty of measuring the vapour pressure of substances, such as the halogen hydrides, which attack mercury was overcome by using the glass spiral manometer of Ladenburg and Lehmann (*Ber. Deut. physikal. Ges.*, 1906, **8**, 20), as modified by Johnson (*Zeitsch. physikal. Chem.*, 1908, **61**, 458).

It may be mentioned here that as the halogen hydrides are decomposed by organic matter, rubber tap grease was not used, being replaced by a mixture of pure paraffins. On account of the extremely hygroscopic nature of the halogen hydrides, every entrance to the apparatus by means of which moisture could gain access was protected by a phosphoric oxide tube, and as the oxide appeared to contain some impurity which slowly reacted with the halides, the tubes containing it were attached to the apparatus with taps interposed as shown in Fig. 1. The oxide was thus only exposed to the halides for short periods.

Fig. 1 shows the apparatus used. Glass was, of course, used for its construction, and all joints were sealed. The apparatus was fitted with a rubber cork A, selected to fit closely the mouth of an unsilvered, cylindrical Dewar flask. The various tubes were passed through holes in the cork, and sealed to the apparatus afterwards. In addition to the holes for the apparatus, the cork was bored to contain the thermometer, a glass tube for making connexion with a water pump for reducing the pressure over the ammonia, another tube closed by rubber tubing and a pinchcock for the admission of fresh ammonia, and a glass tube drawn to a capillary at its lower end, which reached to the bottom of the vacuum vessel, the top

being also closed by rubber tubing and a pinchcock. The purpose of this tube will be explained presently.

Between the water pump and the vessel containing the ammonia was interposed a piece of rubber pressure tubing, which could be more or less closed by means of a screw clip. To obtain any desired temperature below the boiling point of the ammonia, the pump was set in action while a stream of air was admitted through the capillary. The ammonia boiled under the reduced pressure, and its temperature fell. The air stream served to prevent superheating and subsequent bumping, and also to stir the liquid and obtain a uniform temperature throughout the bath. When the temperature was near the desired point, the pressure tubing was partly closed by means of the screw clip, thus checking the rate of withdrawal of the ammonia vapour, and consequently the rate of evaporation, so lessening the heat absorption and fall of temperature. In a short time a state of equilibrium was reached, and by this means the temperature could be kept constant to $0\cdot1°$ for half an hour. If it varied, a slight turn of the screw clip occasionally sufficed to adjust it again. It was possible to run for half an hour without adding fresh ammonia.

A normal pentane thermometer, reading to $-115°$, was used. It was not wholly immersed, and there was a large correction for the exposed portion of the stem, which correction is probably nearly correct at the lower temperatures, but may have an error of about a degree at the higher. As our object was to work at a constant temperature rather than to know its exact value, slight errors are in our case not important, as our vapour pressure-composition curves are constructed at constant temperature.

The construction of the actual apparatus will be apparent from Fig. 1. A description of the method of working should render the use of the various parts clear.

Fig. 1.

The temperature of the ammonia-bath was reduced to well below the boiling point of the liquid it was desired to use. The liquid previously condensed in another vessel was then distilled into the apparatus through O and the three-way tap B. The first few drops of liquid condensed collected in the bend F, after which all uncondensed gas travelled round the spiral G rather than force its way against the pressure of the liquid in F. By this means, thorough condensation was secured. The capacity of the apparatus was known at various points, so that mixtures of any desired strength could be made up approximately by distilling in the necessary volumes of each liquid. This was more necessary in changing the composition of a previous mixture than in preparing the first one, when the volumes of liquid distilled in could, of course, be measured. About 25 c.c. of liquid were necessary to fill the apparatus to the amount necessary for its correct working.

To ensure thorough mixing of the two liquids, a hydrogen generator was connected to D, and hydrogen passed through E. When the gas reached the point H, it broke into bubbles, which ran around the spiral G, carrying liquid with them into the bulb I, from whence the liquid flowed back through M, while the gas passed out at C. The hydrogen pressure was now applied at C, the taps B, J, and K having been closed. These taps were then carefully opened, when the liquid rose, filling the bulbs E and L, and on reaching the warm tubes boiled and displaced the contained air. The capacities of the various parts were so arranged that when E and L were full of liquid there was still some in the spiral and tube M, whilst when E and L were empty the level of the liquid in I was above the entrance of the spiral.

Having displaced the air as described above, the manometer and its connecting tube were exhausted through the tap N by means of an efficient water pump, B being kept closed. B was then turned to admit vapour into the manometer. By alternately filling and exhausting the manometer several times, the air was all displaced. Suction was now applied at C until the liquid level was nearly at the bottom of the bulb E, and at this stage, after the temperature had been constant for several minutes, a vapour pressure reading was taken. The whole process described above was now repeated until the vapour pressure was constant, when the temperature was varied, and a series of vapour-pressure readings was taken. The volumes of the manometer and its connecting tube were small, and did not require much vapour to fill them, consequently the composition of the liquid would not be much changed by the exhausting process; in any case, as the readings

and subsequent samples were all taken after the exhaustion, any slight change would be of no importance.

It was found that after taking a series of vapour-pressure readings the pressure appeared to increase slightly. This was attributed to decomposition of the halide vapour by the tap grease with consequent production of hydrogen. To reduce any error caused by this, the manometer was occasionally exhausted during a series of readings. The vapour pressures were plotted against the temperatures, and from the curves the vapour pressure at any desired temperature could be calculated. These curves are referred to later in the paper.

Having obtained the vapour-pressure curve, it was necessary to obtain samples of the liquid and gas phases for analysis. For this purpose, it was necessary to isolate and absorb completely a portion of the liquid in order to get its true composition. This was accomplished by means of the bulb L. By means of the hydrogen pressure, the bulb E was filled with liquid, and by then applying pressure alternately at C and K and suitably opening the taps, L was alternately filled with and emptied of liquid to ensure having a true sample. Finally, a small quantity of liquid was left in L, and the hydrogen pressure applied at J, keeping the tap shut. Geissler tubes, as used for carbon dioxide absorption in combustions, were attached at K and C by rubber tubing, the taps being closed. On opening the tap J, the hydrogen pressure forced a few bubbles of gas into L and E, and left the connecting tube full of gas, thus separating the two portions of liquid. The taps K and C were now carefully opened. A stream of gas passed down the tube J, and at O divided into two portions. One stream bubbled through L, evaporating the contained liquid, which was absorbed by the alkali in the Geissler bulb attached to K. P is a fairly fine capillary tube, which served to prevent diffusion backwards of vapour from L. The other gas stream passed into E and down the tube to H, where it broke into bubbles at the constriction. The tube leading from E to L has a capillary constriction, which served to increase the velocity of the gas stream, and thus helped to prevent diffusion of vapour from E to L, which would cause an error in the analysis.

The bubbles of hydrogen, on forming at H, ran around the spiral G, which contained over a metre of glass tubing. These bubbles, as explained previously, caused thorough mixing of the liquid, and ensured it being of uniform composition, and at the same time became saturated with the gas phase in equilibrium with the liquid. Finally, the hydrogen saturated with the vapour passed through the tap C and through the attached Geissler bulb, where absorbable

gases were collected. A little experience showed how much liquid it was necessary to have in L in order to obtain convenient analytical results, and also how long to pass the hydrogen through the spiral to get the gas composition.

When the absorption was complete, each Geissler bulb was removed, and its contents thoroughly mixed by blowing them from one bulb to the other. The solution was then blown into a beaker, and as only ratios were required it was not necessary to remove the whole contents, but it was necessary to have them thoroughly mixed before removal. Aliquot parts of the solution were removed for analysis by means of pipettes, the necessary volumes for convenient titration values being judged from knowledge of the approximate composition of the mixtures and from previous analyses.

Sulphur dioxide and hydrogen sulphide were determined by titration with $N/10$-iodine solution, and the halogen hydrides by Volhard's method, using $N/10$-silver nitrate and potassium thiocyanate. As silver sulphide is not easily dissolved by nitric acid, it was necessary to remove hydrogen sulphide from solutions before estimating the halogen. This was done by oxidation with sodium peroxide and subsequent removal of excess of hydrogen peroxide by boiling. The quantities of gas removed for an analysis were insufficient to change appreciably the composition of the liquid remaining. A series of analyses of gas and liquid was made at different temperatures, thus obtaining a number of values for the composition of the liquid which should agree, and other values for the composition of the gas which should either agree or show regular variation with temperature.

To prepare a fresh mixture, the cap Q was removed, a fine glass tube passed into I, and a portion of the liquid sucked out by means of a water pump. The cap was then replaced, and fresh liquid distilled in.

The apparatus was contained in a vacuum vessel measuring about 4·5 cm. by 20 cm., internal dimensions.

The apparatus we have described could be made on a larger scale if the liquids to be used were more easily prepared and less expensive. It might be useful at the ordinary temperature for liquids which are hygroscopic or decomposed by air. If used on the larger scale, it could be applied to liquids which cannot be directly absorbed or estimated, sufficient liquid being used to allow a quantity sufficient for analysis by physical measurements to be distilled out and condensed without appreciably changing the composition of the residue. With modern means of obtaining low temperatures, even very volatile substances might be thus condensed,

Experimental Results.

The experimental results are given in the following tables.

For several reasons it was possible to obtain data for the construction of complete vapour pressure-composition curves over a limited range of temperature only. The analyses could not be performed when the vapour pressure of the solution was greater than

FIG. 2.
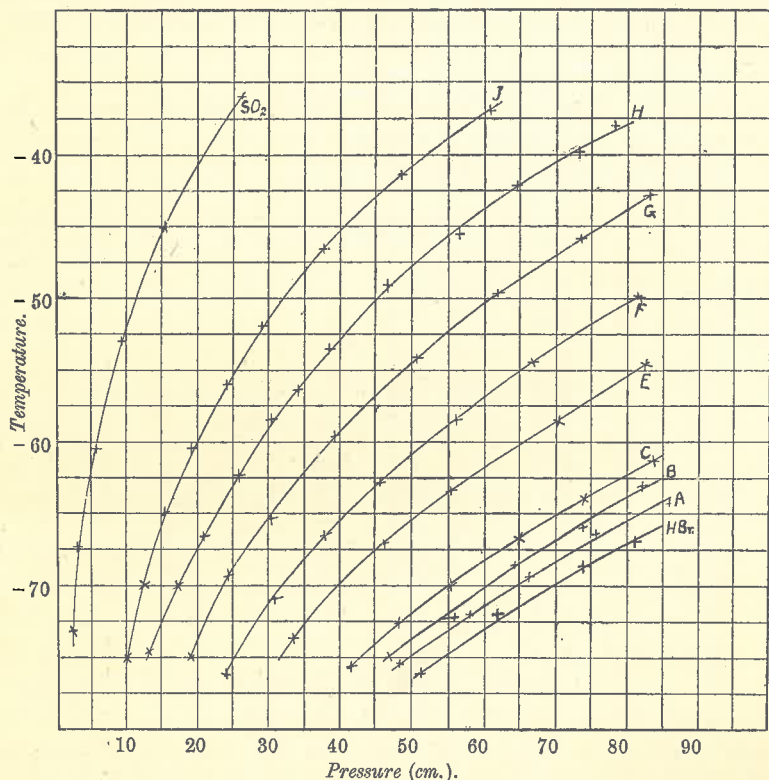
Sulphur dioxide—hydrogen bromide.

atmospheric, whilst, owing to the differences in the boiling points of the two constituent mixtures rich in the less volatile constituent, they could be analysed at a higher temperature than those containing more of the more volatile constituent. A lower limit was fixed by the lowest temperature that could be conveniently obtained with the liquid ammonia, whilst with the hydrogen iodide a limit was fixed by the freezing of solutions rich in that compound.

A vapour pressure-composition curve has been constructed for each pair of liquids at that temperature at which most complete data are available.

Portions of curves for other temperatures can be constructed from the data given.

Sulphur Dioxide and Hydrogen Bromide.

Table I gives the vapour-pressure readings for mixtures of sulphur dioxide and hydrogen bromide, whilst in table II is given, as a typical example, the results of the analyses of mixture F. The vapour pressure-temperature curves are shown in Fig. 2. The letters at the heads of the columns of tables I and II and the curves in Fig. 2 all refer to the same mixtures. Pressures are given in cm. of mercury. All compositions of mixtures are expressed as molecular percentages of halogen hydride.

TABLE I.

Mixture.									
HBr	Temp.	$-76°$	$-72°$	$-68·6°$	$-66·8°$				
	V. P.	51·7	61·7	73·9	80·9				
A.	Temp.	$-75·5°$	$-72°$	$-69·3°$	$-66·4°$	$-64·3$			
	V. P.	48·5	57·9	66·4	75·7	85·8			
B.	Temp.	$-75°$	$-72·3°$	$-68·6°$	$-65·9°$	$-63°$			
	V. P.	46·9	55·8	64·4	73·8	82·1			
C.	Temp.	$-75·7°$	$-72·6°$	$-70°$	$-66·7°$	$-63·9°$	$-61·3°$		
	V. P.	41·6	48·2	55·2	65·0	74·1	83·5		
E.	Temp.	$-73·7°$	$-67·1°$	$-63·5°$	$-58·5°$	$-54·6°$			
	V. P.	33·0	46·2	55·1	70·1	82·5			
F.	Temp.	$-76·0°$	$-71°$	$-66·5°$	$-62·7°$	$-58·5°$	$-54·4°$	$-49·8°$	
	V. P.	24·1	30·7	37·9	45·8	56·0	66·7	81·5	
G.	Temp.	$-75·0°$	$-69·3°$	$-65·3°$	$-59·6°$	$-54·2°$	$-49·6°$	$-46·0°$	$-42·8°$
	V. P.	19·0	24·6	30·4	39·3	50·6	61·8	72·8	82·9
H.	Temp.	$-75·1°$	$-70·0°$	$-66·5°$	$-62·4°$	$-58·5°$	$-56·3°$	$-53·5°$	$-49·4°$
	V. P.	14·0	17·2	21·0	25·8	30·5	34·1	38·6	46·6
	Temp.	$-45·6°$	$-42·1°$	$-39·3°$	$-38·0°$				
	V. P.	56·4	64·5	73·1	78·1				
J.	Temp.	$-75·0°$	$-70·0°$	$-63·0°$	$-60·3°$	$-55·9°$	$-52·0°$	$-46·6°$	$-41·4°$	$-37·0°$
	V. P.	10·0	12·3	15·3	19·2	24·1	29·0	37·7	48·6	60·7
SO_2	Temp.	$-73·0°$	$-67·3°$	$-60·3°$	$-53·0°$	$-45·0°$	$-36·0°$			
	V. P.	2·1	3·0	5·8	9·4	15·2	26·0			

TABLE II.

| Mixture.	Temperature.	Molecular percentage of HBr (liquid).		Molecular percentage of HBr (gas).	
			Value used.		Value at $-66°$.
F.	$-75°$	28·5	29	95·3	
	$-67·5$	30		94·3	94
	$-60·3$	29		93·1	
	-53	28·5		92·2	

The samples of gas and liquid were usually taken first at the lowest temperature, then at the highest, followed by others at

intermediate temperatures. An examination of table II shows that the temperature has a distinct effect on the composition of the gas, increasing temperature causing an increase in the relative quantity of sulphur dioxide in the gas phase.

The vapour pressure-concentration curve has been drawn for a temperature of $-66°$, and is shown in Fig. 3. If necessary, the gas composition at this temperature was calculated from the values at surrounding temperatures.

At lower temperatures the points do not fit so well to the curves, which, however, appear to conform to the same type. The type of

FIG. 3.

Sulphur dioxide—hydrogen bromide.
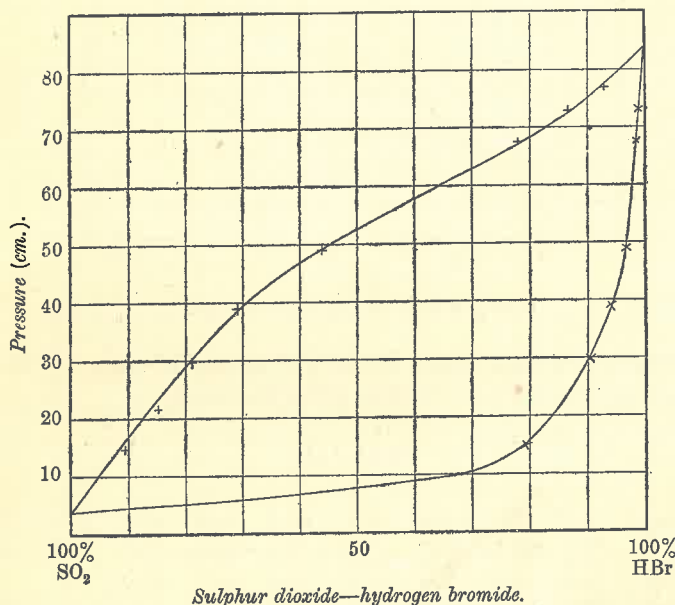
curve is well known, and is of the general shape one might expect from a knowledge of the properties of the constituents and of the mixtures. The partial pressure curves have not been drawn. That for hydrogen bromide will nearly correspond with the total pressure curve, whilst the sulphur dioxide curve will lie almost along the line of zero pressure.
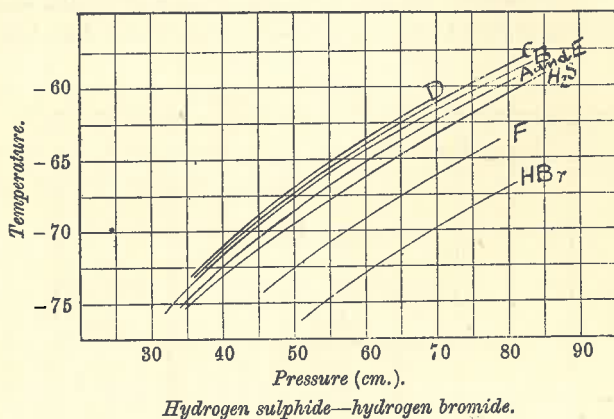
Hydrogen Sulphide and Hydrogen Bromide.

Table III contains the vapour-pressure readings for mixtures of hydrogen sulphide and hydrogen bromide. As before, pressures

are given in cm. of mercury, and compositions of mixtures are expressed as molecular percentages of halogen hydride.

The vapour pressure-temperature curves are shown in Fig. 4. As the curves lie so closely together, the points through which they were drawn are not marked. Reference to the tables will show that the points fit the curves closely. By chance, mixtures *A* and *E* have the same vapour pressure, and are represented by the same curve

FIG. 4.

Pressure (cm.).

Hydrogen sulphide—hydrogen bromide.

AE. The curves show that a mixture of minimum vapour pressure and consequent maximum boiling point is formed.

TABLE III.

Mixture.										
H_2S	Temp.	$-75·1°$	$-73·1°$	$-71·0°$	$-69·0°$	$-66·6°$	$-65·0°$	$-63·0°$	$-61·0°$	$-59·3°$
	V. P.	35·3	39·8	45·6	52·6	58·6	64·5	70·9	77·6	85·3
A.	Temp.	$-75·0°$	$-72·7°$	$-70·0°$	$-67·5°$	$-65·0°$	$-62·2°$	$-59·5°$		
	V. P.	34·9	39·5	46·8	53·2	60·6	70·6	81·5		
B.	Temp.	$-75·4°$	$-71·7°$	$-67·6°$	$-64·4°$	$-60·9°$	$-58·5°$			
	V. P.	32·6	39·6	50·1	59·9	72·7	83·0			
C.	Temp.	$-75·0°$	$-72·0°$	$-68·2°$	$-64·6°$	$-60·1°$	$-58·0°$			
	V. P.	33·8	38·7	47·7	58·4	73·6	82·2			
D.	Temp.	$-72·7°$	$-64·0°$							
	V. P.	36·0	58·4							
E.	Temp.	$-74·2°$	$-69·0°$	$-65·7°$	$-60·9°$					
	V. P.	36·3	49·0	58·9	76·2					
F.	Temp.	$-74·1°$	$-72·0°$	$-69·0°$	$-63·8°$					
	V. P.	46·4	51·2	60·7	78·3					

The gas composition was not so regular as with the sulphur dioxide mixtures, and, as a rule, the mean value has been taken in constructing the vapour pressure-concentration curve, which has been drawn for $-70°$ (Fig. 5). The minimum referred to is well shown.

Ostwald has pointed out that in all cases the partial pressure curves of the components of a binary mixture must be symmetrical, being, in fact, mirror images of each other except as regards vertical measure. The partial pressure curves of hydrogen bromide and hydrogen sulphide, which are shown by dotted lines in Fig. 5, furnish an example of this.

Hydrogen Sulphide and Hydrogen Iodide.

Table IV gives the vapour-pressure readings for the mixtures of hydrogen sulphide and hydrogen iodide. The vapour pressure-composition curves are shown in Fig. 6.

Reference to Fig. 6 will show that the vapour-pressure measure-

FIG. 5.

Hydrogen sulphide—hydrogen bromide.
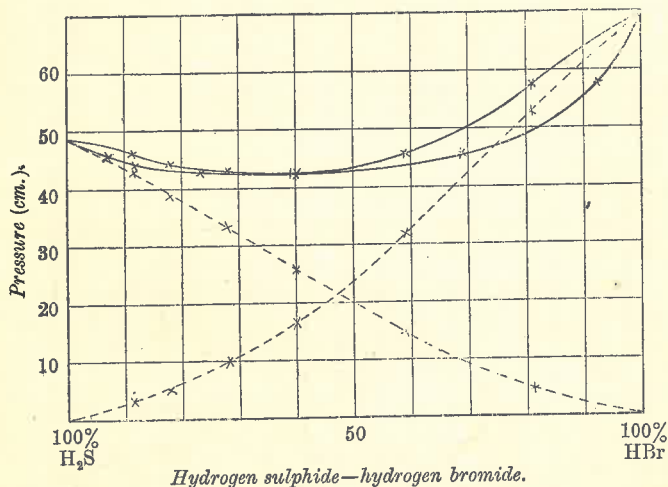
ments for pure hydrogen iodide have not been carried below the freezing point, which is about $-52.5°$ by the thermometer used.

Owing to the higher vapour pressure of the hydrogen sulphide, it was necessary to work at temperatures not much above $-60°$ with mixtures rich in that constituent. To plot the complete vapour pressure-composition curve at $-60°$, we required the vapour pressure, not of solid hydrogen iodide, but of the supercooled liquid. This was obtained by exterpolation, the exterpolated portion of the curve being shown by the broken line.

Two separate series of experiments were performed with these substances, and are given in the tables as series I and series II.

TABLE IV.—*Series I.*

Mixture.

HI.	Temp.	$-39 \cdot 5°$	$-43 \cdot 0°$	$-45 \cdot 8°$	$-49 \cdot 2°$	$-52 \cdot 3°$	
	V. P.	$74 \cdot 3$	$63 \cdot 8$	$53 \cdot 9$	$45 \cdot 0$	$38 \cdot 3$	
$A.$	Temp.	$-62 \cdot 0°$	$-57 \cdot 7°$	$-51 \cdot 3°$	$-47 \cdot 8°$		
	V. P.	$30 \cdot 5$	$37 \cdot 9$	$51 \cdot 6$	$62 \cdot 4$		
$B.$	Temp.	$-68 \cdot 4°$	$-62 \cdot 5°$	$-57 \cdot 6°$	$-52 \cdot 8°$	$-49 \cdot 4°$	
	V. P.	$28 \cdot 5$	$38 \cdot 6$	$50 \cdot 7$	$63 \cdot 7$	$76 \cdot 5$	
$C.$	Temp.	$-73 \cdot 0°$	$-68 \cdot 4°$	$-64 \cdot 0°$	$-59 \cdot 5°$	$-55 \cdot 0°$	$52 \cdot 5°$
	V. P.	$26 \cdot 4$	$34 \cdot 3$	$42 \cdot 3$	$55 \cdot 6$	$70 \cdot 2$	$88 \cdot 5$
$D.$	Temp.	$-73 \cdot 0°$	$-68 \cdot 0°$	$-63 \cdot 5°$	$-58 \cdot 5°$	$-56 \cdot 0°$	
	V. P.	$30 \cdot 2$	$40 \cdot 4$	$51 \cdot 5$	$66 \cdot 6$	$75 \cdot 7$	
$E.$	Temp.	$-71 \cdot 5°$	$-67 \cdot 0°$	$-62 \cdot 5°$	$-58 \cdot 5°$		
	V. P.	$38 \cdot 8$	$49 \cdot 6$	$63 \cdot 1$	$77 \cdot 3$		

TABLE V.—*Series II.*

Mixture.

| $F.$	Temp.	$-61 \cdot 5°$	$-60 \cdot 3°$	$-59 \cdot 0°$
	V. P.	$37 \cdot 6$	$40 \cdot 0$	$42 \cdot 9$
$G.$	Temp.	$-62 \cdot 0°$	$-60 \cdot 2°$	$-58 \cdot 8°$
	V. P.	$48 \cdot 0$	$53 \cdot 4$	$57 \cdot 6$
$H.$	Temp.	$-62 \cdot 0°$	$-60 \cdot 2°$	—
	V. P.	$56 \cdot 6$	$62 \cdot 0$	—

Fig. 6.

Hydrogen sulphide—hydrogen iodide.
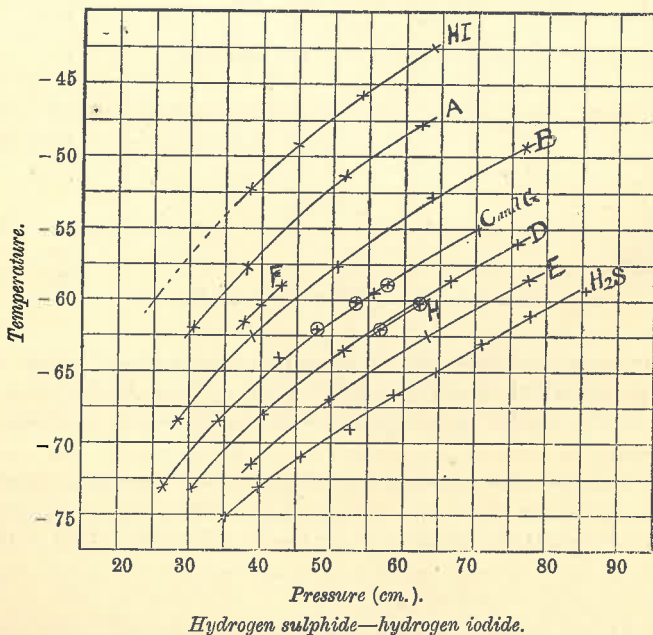
The vapour pressure-composition curve at $-60°$ is shown in Fig. 7. The partial pressure curves are shown by the dotted lines.

A comparison of Figs. 5 and 7 shows a surprising contrast in the nature of the curves obtained when hydrogen bromide and hydrogen iodide respectively are mixed with hydrogen sulphide. In the case of the former substance (Fig. 5), a well-marked minimum of vapour pressure is found. The occurrence of a minimum such as this is characteristic of a few pairs of substances, the majority of which, such as the mixtures of water with the mineral acids, present as their most striking characteristic the formation of highly ionised mixtures. Other systems presenting the same type of vapour pressure-concentration curves are mixtures of a few nitrogen bases

FIG. 7.

Hydrogen sulphide—hydrogen iodide.
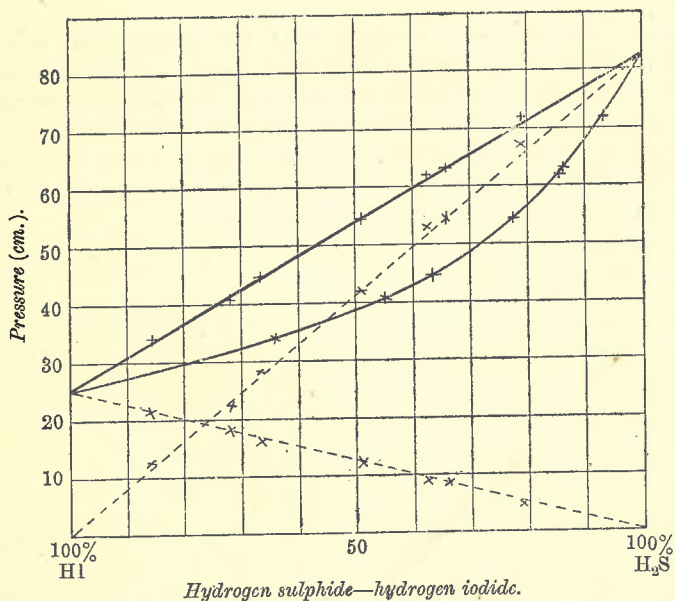
with fatty acids, and in the case of these there is no doubt that combination occurs to a large extent.

Roozeboom has pointed out that in nearly all cases where such minima occur we have independent evidence of (a) ionisation of one component, (b) combination between the components, or (c) association of one or both components.

From this point of view the behaviour of this pair of substances is the more remarkable, since there is no evidence of appreciable ionisation in any of the mixtures, and measurements of the molecular surface energy which were made by Steele, McIntosh, and Archibald yielded no evidence of association either of hydrogen sulphide or

of hydrogen bromide, and did not point to any difference in the molecular complexity of hydrogen bromide and hydrogen iodide. Of the three alternatives suggested by Roozeboom, there remains therefore only the possibility of compound formation between hydrogen bromide and hydrogen sulphide, and of this no evidence is yet forthcoming.

The system hydrogen sulphide and hydrogen iodide is interesting as adding another to the very short list of pairs of liquids which form ideal solutions, solutions for which Raoult's law applies over the whole range of concentration. This is shown in Fig. 7 by the occurrence of straight lines for the vapour pressure-liquid concentration curve, and for the two partial pressure curves.

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