

ELECTROLYSIS IN LIQUEFIED SULPHUR DIOXIDE.

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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.

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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

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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

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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 ₂ O Solution.	Of K in SO ₂ .	Of S in SO ₂ .	K in SO ₂ . Ag in H ₂ O.	S in SO ₂ . Ag in H ₂ O.
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 :—

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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 TRIMETHYL-SULPHONIUM 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-

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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 electrolysis 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.

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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

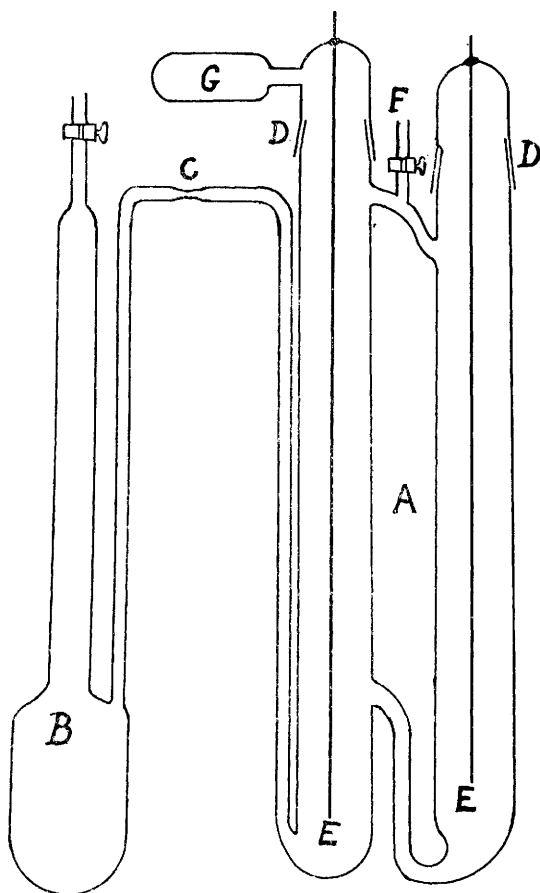


FIG. 1.

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.

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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

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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 $Zn_3(NMe_4)_3(SO_3)_4$ S = 19·3 per cent.

Zn = 29·5 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.

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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 benzophenone 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.

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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 -8° 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. $\text{H}_2\text{O} + \text{HBr} \rightleftharpoons \text{H}_3\text{OBr}$, oxonium bromide.
2. $\text{H}_3\text{OBr} \rightleftharpoons \text{H}_3\text{O}^+ + \text{Br}'$, and during electrolysis.
3. $2\text{H}_3\text{O}^+ + 2\theta \rightarrow \text{H}_2 + 2\text{H}_2\text{O}$ (at cathode).
4. $2\text{Br}' - 2\theta \rightarrow \text{Br}_2$ (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.

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The specific conductivity, K , of pure sulphur dioxide = 1.5×10 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 r Gram. of SO ₂ .	Dilution.	Specific Conductivity.	Molecular Conductivity.
	<i>Ether.</i>				
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	2.95×10^{-3}	3.69
	<i>Dimethylpyrone.</i>				
0.0	0.0011	10.17	$6.1 \times 10^{+3}$	1.5×10^{-4}	9.15×10^{-1}
0.011	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	1.47×10^{-3}	1.67×10
0.011	0.0011	33.8	2.02×10^4	0.908×10^{-3}	1.83×10
	<i>M. dinitrobenzene.</i>				
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	1.50×10^{-4}	1.65×10^{-1}
	<i>Acetone.</i>				
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	1.85×10^{-2}	1.67×10
0.016	0.007	20.34	1.9×10^3	7.46×10^{-3}	1.43×10
	<i>Benzophenone.</i>				
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
	<i>Benzaldehyde.</i>				
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)
	<i>Water.</i>				
.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}	> 3.3

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.

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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 H₂O, 125.
2. HBr in SO₂, '0405.
3. Acetone in SO₂, '0053.
4. HBr Acetone in SO₂, 16'7.
5. HBr Ether in SO₂, 3'7.
6. HBr Dimethylpyrone in SO₂, 17'4.
7. HBr Benzaldehyde, 6'95.
8. HBr Benzophenone, 10'8.
9. HBrH₂O in SO₂, > 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 ₂ O '0083 gr. mols	780	0
HBr '035 gr. mols in 6'5 c.c. of SO ₂ ...		30
Ether '0051 gr. mols	1,250	0
HBr '049 gr. mols in 6'4 c.c. of SO ₂ ...		90
Acetone '007 gr. mols... ..	900	0
HBr '010 gr. mols in 6'23 c.c. of SO ₂ ...		25
Acetone '007 gr. mols	1,900	0
HBr '016 gr. mols in 13'4 c.c. of SO ₂ ...		40

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.

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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.

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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.

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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 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

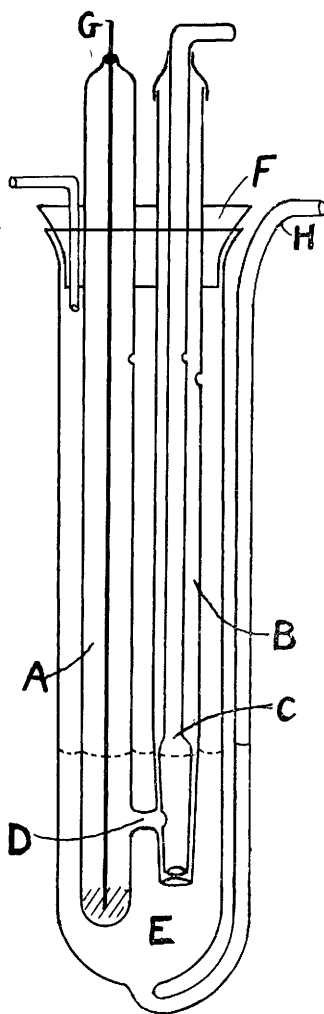


FIG. 2.

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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 SO₂/SO₂/PbCl₂ in SO₂/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/PbCl₂/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/ZnBr₂/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/CdI₂/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

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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.

In conclusion, the authors wish to express their thanks to the Government Grant Committee of the Royal Society for a grant made to one of us by means of which a large portion of the expense of the work has been met. We also wish to express our thanks to Messrs. Felton, Grimwade & Co. for their kindness in presenting us with large quantities of liquefied ammonia.

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