

ON THE ELECTROLYSIS OF SALT SOLUTIONS IN LIQUEFIED SULPHUR DIOXIDE AT LOW TEMPERATURES.

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The investigation of which this is a preliminary notice is a natural continuation of the research started by Dr. M'Intosh and myself in 1903. The investigation has for its object the study of the electrolysis of salts dissolved in certain liquefied gases, and of the products formed during electrolysis. The first system that has been investigated is that of a solution of potassium iodide dissolved in sulphur dioxide, and a large number of experiments extending over several months have been carried out.

My attention having been called to a proposed investigation along similar lines, of which an abstract appears in the *Journal of the Chemical Society* for April, 1907 (Giuseppe Magri, *Ȣ.C.S.*, 92. 11, p. 237), I thought it best to publish the following brief summary of the conclusions that have been so far arrived at :—

(1) When a nearly saturated solution of potassium iodide in sulphur dioxide is electrolysed between electrodes consisting of thin platinum wires, and with a potential difference of between 10 and 20 volts, a current of about 80 to 100 milliamperes is obtained during the first instant. The current immediately begins to fall rapidly to a value considerably less than 1 milli-ampere. With a potential difference of about 40 volts apparent gas evolution occurs (possibly ebullition of sulphur dioxide), and on breaking the circuit a polarisation e.m.f. of over 1 volt is obtained.

(2) With larger platinum electrodes the fall in current is much slower, but after several hours falls to a similar extremely low value. In this case a scarcely detectable polarisation voltage can be observed.

(3) Similar results are obtained when mercury electrodes are used, but the fall in current is not so marked.

(4) With platinum and mercury electrodes the current, which is extremely variable and inconstant, appears to depend on the previous history of the electrodes.

(5) It has been found that a constant and consistent current can be obtained by using a silver, copper, or iron kathode of large area.

(6) The following changes occur at the anode :

When a platinum anode is used iodine is liberated and dissolved in the surrounding solution.

When a zinc anode is used no iodine is liberated, and the solution remains yellow in colour. It is probable that zinc iodide is formed and dissolved in the solution.

When an iron anode is used no iodine is liberated, but the solution surrounding the anode becomes blackish-green in colour.

When a mercury anode is used mercurous iodide is formed and precipitated, forming a layer on the electrode which appears to cut off the current.

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(7) The following changes occur at the kathode :

When currents of 20 milliamperes and over are used with a platinum kathode there is formed a dark-coloured crystalline deposit, which on drying in an atmosphere of dry sulphur dioxide becomes white. Small quantities of sulphur are always found mixed with this deposit.

The deposit on analysis was found to have a composition very closely corresponding with that required for potassium sulphite, in some cases being, however, much richer in sulphur dioxide.

The platinum kathode, if very small currents are used, is still coated with the potassium sulphite compound, but contains little, if any, admixed sulphur, which is, however, in all cases found dissolved in the solution surrounding the kathode.

The extraordinary manner in which the current falls after the first few moments is thus accounted for by the deposition of a thin film of insulating sulphur on the surface of the kathode.

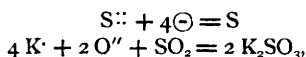
The deposition of sulphur is prevented by using either a silver or a copper kathode. Under these circumstances a black deposit is formed on the kathode. This deposit is probably silver sulphide or copper sulphide, as the case may be, and as both of these are conducting substances the current is not seriously diminished.

No evidence has yet been obtained of the deposition of potassium as metal on the kathode.

(8) By means of a specially constructed piece of apparatus the conductivity of the solution in the neighbourhood of the kathode was determined during the progress of the experiment, and in all cases an increase of resistance was observed.

In the same way as the liberation of hydrogen at the kathode during the electrolysis of a solution of potassium iodide in water is regarded as evidence of the occurrence of hydrogen cations in the aqueous solution, so the liberation of sulphur at the kathode in the foregoing experiments indicates the occurrence of sulphur cations in a solution of potassium iodide in sulphur dioxide, and similarly the formation of what is probably potassium sulphite in the latter system is analogous to the formation of potassium hydroxide in the former.

The following is a possible representation of the changes which take place :—



the sulphur and the potassium sulphite being deposited together at the kathode.

This would explain not only the formation of these two substances but also the observed diminution in conductivity of the solution immediately surrounding the kathode.

(9) After the necessary conditions for obtaining a steady current had been worked out, a special apparatus was designed and constructed for the measurement of ionic velocities of the ions in sulphur dioxide solution, and a few preliminary measurements have been made with this apparatus.

It is intended to extend these measurements and to investigate thoroughly this and other similar systems.

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