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XVIII. *On certain Cases of Electrolytic Decomposition.* By
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THE atomic or molecular conditions which determine metallic or electrolytic conduction are of great interest, but seem as yet too obscure to allow of any definite general conclusions respecting their nature, beyond regarding a free motion of the particles resulting either from fusion or from solution as necessary for electrolytic conduction. Even this is not without noteworthy exceptions; for Faraday has described some binary compound liquids (SnCl_4 , AsCl_3 , &c.†) which neither conduct nor decompose; whilst, on the other hand, some compound solids are known which conduct metallically ($\text{Cu}_2\text{Se}\ddagger$, $\text{Ag}_2\text{Se}\ddagger$, SnS_2 , $\text{CuS}\ddagger$, to which perhaps must be added PbO_2 , MnO_2 , and Ag_2O), and some bodies which are solid and yet conduct electrolytically ($\text{Cu}_2\text{S}\S$, $\text{Ag}_2\text{S}\parallel$). Further, zincic iodide $\parallel$ neither conducts nor is decomposed when rendered fluid by heat; whilst others ($\text{HgI}_2\parallel$, $\text{HgCl}_2\parallel$, $\text{PbFl}_2\P$) have been considered as conducting without decomposition under the same circumstances. The nature of the conduction of the metallic sulphides is very imperfectly known**.

Whilst thinking over these facts about a year and a half ago, it seemed to me very probable that a careful study of these exceptions to the general laws of electrolytic decomposition might result in more definite conjectures respecting the condition of internal or molecular structure required for conduction and decomposition. To make such a study complete requires the determination and comparison of a number of physical constants (*e. g.* colour, conductivity, expansion, specific and latent heat, refractive index, specific inductive capacity, &c.) for substances which are normal and abnormal in their electrolytic behaviour. This cannot be completely

* Read May 23, 1885.

† Faraday, 'Experimental Researches,' vol. i.

‡ Hittorf, *Pogg. Ann.* Bd. lxxxiv. 1851. § Hittorf (*l. c.*). || Faraday.

¶ Faraday. Beetz (*Pogg. Ann.* Bd. xcii. 1854) has since shown that conduction takes place in a normal electrolytic way. Faraday discovered that the solid Plumbic Fluoride began to conduct below a red heat.

** See Faraday, 'Experimental Researches'; and Hittorf (*l. c.*).

done at present for want of data; but before passing to the consideration of those bodies to which my own investigation refers, I wish to briefly refer to a few previous papers relating to substances of remarkable electrolytic behaviour from this point of view.

Hittorf states that sulphide of silver fuses at a clear red heat, but at a temperature of 180° C. it is sufficiently soft to adapt its shape slowly to that of the surface upon which it rests, and at the ordinary temperature it is malleable: a cast stick of it can be slightly bent without fracture, and it can be cut with a knife or turned in a lathe. This substance has a very low resistance, and even at the ordinary temperatures is electrolytically decomposable by a feeble current. Hittorf (*l. c.*) has concluded, from a long and careful series of experiments upon it, that it conducts electrolytically only, and that its apparent metallic conduction results when a fine thread of metallic silver has formed between the terminals of the sulphide of silver bar.

Hittorf (*l. c.*) has discovered that cuprous sulphide also conducts electrolytically "und besitzt entweder gar keine oder ganz geringe metallische Leitung." Unlike sulphide of silver this body has a high resistance, but, like it, the conductivity increases with increased temperature. Cuprous sulphide melts at a white heat, and may be cast in the form of a rod which at the ordinary temperature is very brittle, although at a "higher" temperature it may be bent.

Hittorf (*l. c.*) points out the difficulty of proving *experimentally* that the conduction of Cu_2S and Ag_2S is *entirely* electrolytic, because the formation of copper or silver by the action of the current in the substance of the bars places their ends in true metallic communication with the battery-terminals.

Cuprous selenide and argentic selenide closely resemble their corresponding sulphur compounds to which reference has just been made, and are described as being "soft" and "slightly malleable" respectively (Watts's 'Dictionary of Chemistry'). Selenides ordinarily closely resemble sulphides in their physical and chemical relations, and are consequently regarded as being possessed of similar molecular constitutions. Hittorf, however, says of cuprous and of argentic selenide,

that "beide sind gute metallische Leiter." Their electrical behaviour is therefore of an exactly opposite nature to that of their corresponding sulphur compounds.

Faraday has noticed that conduction commences in heated electrolytes at very different degrees of liquefaction and softening.

Plumbic chloride* conducts very appreciably at a temperature far below that at which it fuses, and at which it is not noticeably soft. Beetz (*l. c.*) has shown that glass begins to conduct between 200° C. and 220° C., and Dr. Lodge reminds me that this has recently been shown to take place at 100° C.

It appears from the behaviour of these bodies that—

(i.) *In some solid electrolytes there is a sufficient mobility of the molecules at the ordinary temperature to enable electrolytic conduction to take place; in others it is conferred by a rise of temperature which is insufficient to render the solid liquid or even soft. A rise of temperature which is insufficient to render a solid liquid, or so soft as to change its shape, is also sufficient for the equalization of strain as is shown in the annealing of glass. Both electrolytic conduction and the annealing of glass take place more readily at a high than at a low temperature.*

(ii.) *Substances of apparently similar constitution may exhibit opposite forms of electrical conduction (Cu_2Se , Ag_2Se , and Ag_2S , Cu_2S).*

The bodies to which my investigation refers are mercuric chloride and mercuric iodide, which Faraday believed to conduct metallically in the fused condition.

Beetz, as I have recently found, states in a paper, "Ueber die Leitungsfähigkeit für Elektrizität welche Isolatoren durch Temperaturerhöhung annehmen" (*l. c.*), that he has obtained evidence of the electrolytic decomposition of fused mercuric iodide; and he attributes its apparent conduction without decomposition to recombination of the products. So far as I am aware, no attempt has been made to examine the nature of the conduction of fused mercuric chloride since Faraday concluded that it probably conducted metallically.

* E. Wiedemann, *Ber. d. Kgl. Sachs. Gesellschaft der Wissenschaften*, 1874. I have unfortunately been unable to refer to this paper; but since the above was written the author has kindly referred me to *Die Elektrizitätslehrer* (G. Wiedemann), Bd. i. S. 558, wherein it is stated that the iodide and bromide of lead behave similarly.

Mercuric Iodide.

Mercuric iodide is dimorphic, and at the ordinary temperature forms a scarlet powder which at 110° C. becomes yellow, and at that temperature acquires a very slight electrical conductivity (Beetz). Mercuric iodide melts at 247° C. and boils at 342° C. It is an interesting substance on account of the ease with which it volatilizes at temperatures much below its melting-point; and it is not unlikely that the ease with which the molecules are thus shown to be leaving the solid substance may be connected with a high diffusive rate when it is fused, and this may partially explain the readiness with which the products of its electrolytic decomposition often mix and recombine, thus simulating conduction without decomposition. The mercuric iodide which I have used in the following experiments was prepared either by the precipitation of recrystallized and sublimed mercuric chloride with pure potassic iodide and sublimation of the product, or by the sublimation of the commercially pure substance.

It may not perhaps be out of place to point out, in the first instance, the effect of heat upon mercuric iodide; as it is sometimes stated in text-books of Chemistry that, when heated, it undergoes partial dissociation with liberation of iodine, where the edge of the liquid is in contact with the hot glass vessel. I have, however, convinced myself that this statement applies only to the commercially pure substance, which on sublimation leaves a little impure oxide of iron, and which, on the edges of the glass vessel in which fusion and sublimation are effected, may decompose, yielding free iodine vapour. Pure mercuric iodide may be fused and sublimed without undergoing any such change; nor have I any reason to believe that, when strongly heated in a sealed glass tube, iodine is ever set free, a slight darkening in the colour of the fused substance being the only apparent alteration which it then undergoes.

Here, too, perhaps it may be convenient to describe the preparation of the graphite electrodes, which for some years past I have found very convenient for the decomposition of such substances as act upon platinum. These electrodes are best made from the "leads" of Rowney's HH cedar pencils, which may be easily removed after a few hours' soaking in

water has softened the glue sufficiently to allow of the pencil being split in half. The "lead" is then removed with a knife, and only requires heating to bright redness in a Bunsen-flame (to get rid of the shellac (?) which it contains) to render it fit for use. A platinum wire twisted or bound round one end makes a good connection for the battery-terminals.

When pure mercuric iodide in a sealed glass tube is kept in a state of fusion over a gas-flame, and electrolyzed by means of two platinum-wire electrodes passing through its ends, evidence of its decomposition may be obtained from the iodine set free about the + pole, although no mercury is discoverable at the negative. The quantity of iodine thus set free is, however, small, and does not usually seem to increase with the length of time that the current is allowed to pass; whilst the decomposition, judging from the liberation of iodine vapour about the positive or upper electrode in the tube, appears to take place at temperatures very little above the solidifying-point of the liquid mercuric iodide.

Electrolysis of this substance kept fused in narrow V- and W-shaped tubes over a gas-flame yields much the same results; but in such tubes the resistance is very high, and it is moreover difficult to ascertain precisely what is taking place within them. I therefore adopted a simple V-shaped glass tube of $\frac{3}{4}$ ths of an inch diameter and bent at an angle of about 30° , into which was placed a sufficient quantity of mercuric iodide for the experiment. The substance was then kept fused over a gas-flame, and the two graphite electrodes introduced, one at each end of the tube. In such a tube the behaviour of the substance is easily observed; and by blowing air dried over chloride of calcium into the end, the issuing vapours are readily tested for iodine with starch-paper. Under these conditions, I found that when the substance was at a temperature near the melting-point iodine could usually be detected with ease, although at a higher temperature none could be shown to exist in the free state. A control experiment with fused chloride of lead, using a current of the same strength and the same distance between the electrodes, gave evidence of chlorine without difficulty.

Hence it appeared possible that this substance conducted (as Ag_2S had been supposed to do) in two ways—(α) electro-

lytically, at a temperature at which it just became liquid; and (β) metallicly, at higher temperatures. But during some observations upon the expansion of fused mercuric iodide in a thermometer-like tube, I noticed that the liquid underwent great contraction during cooling from a temperature a little above the melting-point, accompanied by a distinct loss of fluidity. To the latter change I at once attributed the evidence of electrolytic decomposition, which I had observed at a corresponding temperature, to be probably due, as it would be less favourable to the mixing and recombination of the products of electrolytic decomposition; and I therefore turned my attention to the construction of an apparatus in which they should be so separated as to render this less easy.

The form of apparatus which I finally adopted is shown in section in fig. 1. The tube (*abc*) containing two small porous battery-pots (*gf*), the graphite electrode, and the mercuric iodide to be electrolyzed, is U-shaped, and the two branches are connected by a constricted portion (*c*), which further materially hinders the mixing of the fused products of decomposition in the two branches of the tube. This apparatus passes through a hole in the tin cover (*ji*) which supports it, and dips into the oil in the beaker, which is heated to the desired temperature by means of a gas-flame or sand-bath, at which it is kept constant by placing the bulb of the air-thermometer (*h*) in communication with a gas-regulator. When mercuric iodide

Fig. 1.

is electrolyzed in such an apparatus with a current of about 0.02 ampere, iodine is liberated at temperatures far above the melting-point of the substance. If the current was too strong the circuit was usually broken, apparently in consequence of the heat generated at the + electrode volatilizing, or other-

wise causing the mercuric iodide to disappear from the porous pot. After passing the current for some hours the gas was extinguished, and when the apparatus had become cool the two branches of the U-tube were cut asunder and broken open for examination. In the + branch, both within and without the porous pot, mercuric iodide and black feathery streaks of iodine were found which gave the starch reaction, and the upper part of the glass tube was coated with volatilized iodine.

Iodine dissolves freely in fused mercuric iodide, producing but little change in the colour of the latter ; but just as solidification commences, more or less complete separation seems to take place with the formation of these black patches rich in iodine (and Hg_4I_6 ?) and an evolution of iodine vapour, which in the previous experiments also helped to lead to the conclusion that electrolytic decomposition occurred only near the melting-point of mercuric iodide.

The contents of the negative branch and porous pot were found to be of a slightly altered colour ; but no free mercury was discoverable. Repeated exhaustion of its pulverized contents with absolute alcohol revealed the presence of mercurioso-mercuric iodide (Hg_4I_6 or 2HgI_2 , Hg_2I_2), which might perhaps be inferred to be the first product of the electrolytic decomposition of HgI_2 , since it is formed when metallic mercury and mercuric iodide are titrated together in the proper proportions. Mercurioso-mercuric iodide is ordinarily regarded as a distinct compound, and I suppose rightly so ; for it can exist without decomposition at a temperature at which mercurous iodide undergoes decomposition with liberation of free mercury ; but the stability of this body seems to be greatly increased by the presence of a slight excess of mercuric iodide. Mercurous iodide (Hg_2I_2) dissolves readily in fused mercuric iodide in the proportion to form mercurioso-mercuric iodide. The formation of mercurioso-mercuric iodide by the action of the current upon mercuric iodide may therefore be represented by

or, considering it to take place in one step,

The action being slow I repeated the experiment, replacing the mercuric iodide in the apparatus just described by some mercurous-mercuric iodide precipitated nearly according to the equation

The precipitate was then washed, dried, fused, and finally sublimed from an evaporating dish on a sand-bath into a clock-glass which covered it. The substance contained a little mercuric iodide as impurity.

The products of the electrolytic decomposition of this substance are mercury and iodine, of which the former is deposited in the metallic condition, apparently according to the equation

whilst the iodine is absorbed by the Hg_4I_6 in the positive branch of the tube, forming mercuric iodide; thus,

These results may be summarized as follows:—

The conduction of fused mercuric iodide is electrolytic; but decomposition and recombination may take place so rapidly as to give rise to an apparent metallic conduction; but my investigation gives no grounds for supposing that it does not quantitatively conform to Faraday's Laws.

The causes rendering the proof of its electrolytic decomposition difficult may be summed up as follows:—

(1) *Iodine is soluble in fused mercuric iodide, and so is mercurous iodide, in the latter case with the formation of Hg_4I_6 .*

(2) *Mercuric iodide is volatile, and the presence of its vapour renders the detection of free iodine difficult by the ordinary test, and also promotes mixture in the electrolytic apparatus by distillation.*

(3) *It also seems possible that fused mercuric iodide possesses a high diffusive rate, which would further facilitate the mixture and recombination of the products of its electrolytic decomposition.*

(4) *The electrical resistance of fused HgI_2 is high.*

When pure mercuric iodide is fused over a gas-flame in a straight glass tube, of about 6 centim. in length and 0.5 centim. in breadth, and electrolyzed between platinum wire or graphite electrodes with a current of about 0.20 ampere, the resistance

shows some remarkable changes. Thus:—In an experiment which I copy from my laboratory journal, the resistance of the mercuric iodide in a sealed tube decreased as the temperature rose, until the needle of the tangent-galvanometer which was included in the circuit stood at 20° ; and on allowing the temperature to rise still higher, it fell to 9° . During cooling the inverse change occurred; for on extinguishing the gas and allowing the tube to cool, the needle advanced from 9° to 20° or 21° , and then fell gradually to 0° as conduction ceased. The cause of this change in the resistance is not very clear. I have assured myself that it is not due to any impurity in the mercuric iodide employed, nor is there a sufficient change in polarization of the electrodes at the different temperatures to account for it. With a very feeble current these resistance-changes are not marked, and indeed may escape observation in an experiment such as that which I have described. I believe this effect to be due, first to the formation, and then to the dissociation or other alteration at the higher temperature of the mercurous-mercuric iodide produced; in support of which it may be stated that mercurous iodide undergoes rapid decomposition with separation of mercury at about the same temperature at which this change of resistance takes place. Perhaps not entirely unconnected with increase of resistance is the heat generated by the current, in consequence of the transition-resistance at the common surface of the + electrode and fused mercuric iodide, which may occasion the formation of vapour on the surface of the electrode. I have observed this give rise to a crepitating noise, and to the formation of a wave-motion spreading from the + electrode over the surface of the fused substance, and, under favourable circumstances, becoming so marked as to throw the whole tube in which the decomposition was being effected into violent oscillation.

Mercuric Chloride.

Mercuric chloride far exceeds mercuric iodide in the ease with which it volatilizes at temperatures below its melting-point. It melts at 265° C. and boils at 295° C., and is more difficult to decompose with the current than mercuric iodide. This is to some extent due to its higher electrical resistance, which prevents

the use of any complex apparatus designed to represent the products of decomposition and prevent their recombination. The mercuric chloride which was used was prepared by the sublimation of the repeatedly recrystallized pure commercial salt.

The apparatus with which I have succeeded in effecting the electrolytic decomposition of fused mercuric chloride is shown in section in fig. 2, and consists of a glass tube of about $\frac{5}{8}$ ths of an inch in diameter bent at an angle of 30° . The porous pots (*ab*) and graphite electrodes (*cd*) project at each end, and the requisite temperature was supplied by the hot sand of a sand-bath. With potassic iodide and starch test-paper the evolution of chlorine at the + pole was readily detected, even when a very feeble current was employed. After the current had been passed through the fused mercuric chloride for some time, the apparatus was allowed to cool, and its contents were subsequently

Fig. 2.

pulverized and exhausted with water, which left an insoluble residue of mercurous chloride (Hg_2Cl_2), which was not entirely confined to the inside of the — porous pot.

Mercurous chloride dissolves in fused mercuric chloride, probably giving rise to a mercurioso-mercuric chloride of analogous composition to some of the well-known double chlorides which mercuric chloride forms. The want of time consequent upon the completion of an investigation on the influence of pressure on electrolytic conduction, upon which I have long been engaged, has prevented my examining this point.

The conduction of mercuric chloride is electrolytic, giving rise to chlorine and mercurous chloride; and there seems no reason to doubt that it conforms quantitatively to Faraday's Law; but the volatility of this substance, as also in the case of

mercuric iodide, and of the products of their decomposition, would render its further proof difficult.

The causes rendering its electrolytic decomposition difficult may be summed up as follows :—

(1) *The volatility of mercurous chloride and its solubility in mercuric chloride.*

(2) *The near melting- (265° C.) and boiling- (295° C.) points and great volatility of mercuric chloride facilitate the mixing and recombination of the products of its decomposition, and the vapour renders the detection of chlorine by the ordinary test difficult.*

(3) *As previously stated in reference to mercuric iodide, it is possible that the volatility of these substances is connected with a high diffusive rate, when fused, which would facilitate the recombination of the products of its electrolytic decomposition.*

(4) *The electrical resistance of the fused substance is much higher than that of the mercuric iodide.*

Before concluding this paper, I wish briefly to refer to the properties of fused mercuric iodide and chloride with reference to the porous battery-pots in which the electrodes were placed, and which seems sufficiently important to merit a few words of description. These porous pots were 2 inches long, $\frac{1}{4}$ inch in diameter, and varied from $\frac{1}{16}$ inch to $\frac{1}{8}$ thick in the walls. My attention was first attracted to their behaviour by noticing that when they were partially dipped into fused mercuric iodide, that liquid rapidly made its appearance in the pot; and the subsequent analysis of the substance surrounding the porous pots after an experiment, showed the presence of small quantities of the products of the decomposition effected by the current, such as iodine, mercurous-mercuric iodide, and mercurous chloride. Control experiments with water and with fused plumbic chloride showed that these liquids were unable to penetrate the walls of the porous pots.

The explanation of the facility with which fused mercuric iodide penetrates the walls of a porous pot and rises within it seems to be of a complex nature. The imbibition of this fused substance in the porous walls of the pot is due to capillary action, and does not account for the liquid filling the pot; for

since it is of a capillary nature, this action must cease as soon as the inner surface or wall becomes wetted. In the case of a volatile liquid such as fused mercuric iodide this action may be somewhat prolonged by its volatilization from the inner surface of the pot-wall, and by the direct formation of crystals from the vapour. The subsequent fusion of these crystals will account for the presence of some liquid mercuric iodide within the porous pot, but then this action must cease. Moreover this explanation apparently requires a difference of temperature within and without the porous pot, which, from some special experiments made upon the subject, can scarcely be assumed to exist; and I therefore think that *the explanation of the penetration of the liquid through the walls of the porous pot must be mainly sought in an easy transpiration of the fused mercuric iodide through its pores in consequence of the small initial difference of level ("head") of the liquid.*

I have already stated that analysis showed the presence of some of the products of decomposition formed within the porous pots in the undecomposed substance in which the latter were partially immersed; and this seems attributable to diffusion through the pot-walls. Little seems known respecting the rates of diffusion of fused substances through porous diaphragms; but the particular difficulties in the way of their determination for such volatile substances (which may so readily mix by distillation) seems of itself suggestive of a molecular activity not unconnected with a long free mean molecular path and of rapid diffusion.

XIX. *On the Sensitiveness of Selenium to Light, and the Development of a similar Property in Sulphur.* By SHELFORD BIDWELL, M.A., LL.B.*

THE remarkable property apparently possessed by crystalline selenium of having its electrical resistance varied by the action of light, a property which was first announced by Mr. Willoughby Smith in 1873, has been the subject of many investigations†. Of these the best known, and by far

* Read May 23 and June 13, 1885.

† Willoughby Smith, Journ. Soc. Tel. Eng. ii. p. 31; Earl of Rosse,