XVII. *On the Properties of Electro-deposited Antimony* (concluded). *By* G. Gore, *Esq. Communicated by Professor* Stokes, *Sec. R.S.*

Received May 24,—Read June 19, 1862.

Second variety of active Electro-deposited Antimony.

92. In addition to the variety of electro-deposited antimony obtained from a solution of teroxide of antimony and hydrochloric acid, a second variety may be obtained from a solution of terbromide of antimony in the following manner.

93. Dissolve one part of teroxide of antimony in 10 parts of hydrobromic acid of sp. gr. about 1·3, filter the solution through a funnel loosely plugged with asbestus, and electrolyse it by means of three Smee's elements and an anode of antimony in the usual manner, at a speed of deposition of about 3 to 5 grains per square inch per hour. The exact proportion of the ingredients of the solution is not a matter of great importance.

94. The electrolytic conduction is free, and a coherent metallic deposit is quickly obtained. The deposit, when thin, is occasionally quite bright and black, and very similar in appearance to that obtained in the chloride solution, but generally it is of a much lighter colour and quite dull in aspect; it is at first scaly, exhibiting the unequal cohesive action already described (17.), but in a less degree than the first variety, and emitting but slightly audible crackling sounds during its formation. During the process of deposition solitary bubbles of gas occasionally adhere to the receiving surface, and cause deep conical holes in the deposit, especially if the solution is not sufficiently dilute; in escaping, these bubbles sometimes emit a chirping sound; in some instances the holes were so numerous as to give to the substance the appearance of a metallic sponge.

95. The deposited substance is firm and moderately hard, but rather less so than that formed in the chloride solution; its fractured surface has also a bright metallic lustre similar to that of the first variety. The specific gravity of two specimens was 5·415 and 5·472 at 60° Fahr.

96. By contact with a red-hot wire, it exhibits a similar molecular and thermic change to that manifested by the chloride variety (19.). A piece $\frac{1}{8}$th of an inch thick, at 60° Fahr., touched by a red-hot wire, exhibited strong molecular action at the points touched, but the action did not spread throughout the mass. A second similar piece, heated to about 200° Fahr. in a porcelain capsule upon the surface of boiling water, when touched by the heated wire manifested stronger and more extended change, but did not discharge the whole of its heat except by numerous contacts of the wire. A third piece in a platinum dish upon the surface of a solution of chloride of calcium at 268° Fahr., evolved all its heat instantly with explosive violence and projection of pieces of the metal by a

single contact of the red-hot wire. Pieces $\frac{1}{10}$th of an inch thick in a platinum dish upon a solution of chloride of calcium at 295° Fahr., did not discharge their heat by repeated scratching with a sharp steel pointer, but instantly discharged it by contact of a heated wire, and shattered themselves to pieces.

97. On placing a small fragment upon melted fusible alloy, and gradually heating the latter, the fragment discharged all its heat suddenly and powerfully, and shattered all to pieces, when the alloy obtained a temperature of 318° Fahr. A similar piece upon the surface of mercury discharged itself similarly when the mercury attained a temperature of 322° Fahr. And another piece, $\frac{1}{8}$th of an inch thick, weighing 33 grains, immersed in a solution of chloride of calcium at 272° Fahr., suddenly discharged its heat and shattered to pieces at the end of four minutes, when the solution was at 275° Fahr. A fragment $\frac{1}{10}$th of an inch thick, formed three years and four months previously (viz. in December 1858), was put in a platinum dish upon a solution of chloride of calcium at 268° Fahr., and touched with red-hot wire; it instantly discharged its heat with violence, scattering fragments of the metal in all directions. The temperature of sudden discharge appears from these circumstances to lie between 270° and 300° Fahr.; but depends upon several conditions, especially upon the degree of rapidity with which the heat is carried away in relation to that with which it is generated. The fractured surface of pieces suddenly discharged is brighter than that of the unchanged substance.

98. Thick pieces of the active substance may be easily reduced to powder in a mortar without causing them to discharge their heat. A small quantity of the powder formed into a train upon the surface of glass or metal at 60° Fahr., and touched by a red-hot wire, only exhibited the change near where it was touched; but if the powder was previously placed in a platinum dish upon a solution of chloride of calcium at 265° Fahr., and then touched at one end by the heated wire, it discharged its heat gradually, and the change, attended by evolution of fumes, was slowly propagated to the distant extremity.

99. The active substance was *gradually* discharged of its heat in the following manner:—A piece barely $\frac{1}{8}$th of an inch thick, and weighing 40·05 grains, was suspended during thirty minutes in a solution of chloride of calcium at 252° Fahr.; when taken out, washed with water, dried at 240° Fahr., cooled and weighed, it had lost 2·45 grains =6·117 per cent. It was then reheated in a platinum dish upon a solution of chloride of calcium at 250° Fahr., and touched six or eight times with a red-hot wire; not the slightest sign of molecular change occurred, and its weight remained but slightly altered: on breaking, it was found to have become less brittle and of stronger cohesion; its fractured surface was quite dull and earthy, and exhibited the appearance of a dark inner core surrounded by a layer of a lighter colour, as if an action or change had proceeded from the outer surface towards the centre.

100. 20·3 grains of it, fused in an analysis-tube (82.), gave 17·20 grains in the form of a metallic button,[*] =79·52 per cent. of metal, and 20·48 per cent. of volatile matter, in the original unchanged substance; and there distilled into the bent part of the tube a

quantity of colourless buttery substance, which was slightly semifluid at 60° Fahr., and doubtless consisted of terbromide of antimony and a little aqueous hydrobromic acid, but was not further examined. In another case, two portions of the unchanged substance lost respectively 18·42 and 20·40 per cent. of volatile matter by fusion in the analysis-tube; the two portions were parts of a single piece of the deposited substance, the one losing 18·42 per cent. being from the upper part, and the other from its lower part, as it hung in the electrolyte.

101. Another mode of *gradually* discharging its heat was as follows:—A piece $\frac{1}{8}$th of an inch thick was placed upon the surface of mercury at 260° Fahr. during $1\frac{1}{4}$ hours, at the end of which time it was found, by repeated contacts of a red-hot wire, to have entirely lost its heating power; its cohesion was greatly increased, and its fractured surface was dull and earthy in appearance; its odour and taste were also acid: a portion was reduced to powder; the powder also possessed an acid taste, and strongly reddened damp litmus paper, whilst the powder of the *unchanged* substance did not. Another piece $\frac{1}{10}$th of an inch thick, weighing 23·52 grains, was placed upon platinum foil upon the surface of mercury at 265° Fahr., and kept at that temperature forty-five minutes, then cooled and weighed; it had lost 1·38 grain =5·86 per cent.; it was then reheated on the foil and mercury to 270° Fahr., and touched several times with a red-hot wire, but no signs of the change occurred.

102. The electro-chemical equivalent of this substance was examined in the following manner:—Two similar depositing cells, one filled with the chloride solution (90.) and the other with the bromide liquid (93.), and containing anodes of antimony and previously weighed cathodes of sheet platinum of equal size, were connected in a single line with five SMEE's elements, and deposits simultaneously formed upon them during two days; they were then taken out, wiped dry, allowed to stand twelve hours to further dry the one from the bromide solution on account of its porosity, and then weighed; then replaced in the liquid to receive further deposits during two days, and again dried and weighed. In two determinations of this kind there were obtained respectively 50·07 and 50·11 parts of the bromide deposit for every 42·5 parts of the chloride deposit, or for every single equivalent, or 32·2 parts of zinc consumed; and in two other determinations 51·2 and 51·4 parts of bromide deposit were obtained. Each of these quantities of deposit contains the same amount of metallic antimony, viz. 40 parts, or $\frac{1}{3}$rd of an equivalent. The variation in the numbers obtained was probably caused by the porosity of the deposit formed in the bromide solution.

Third variety of active Electro-deposited Antimony.

103. A third variety of heat-giving electro-deposited antimony remains to be described, and was obtained in the following manner:—Dissolve 1 part by weight of teroxide of antimony in 15 parts of hydriodic acid of sp. gr. 1·25; filter the solution from any oxide that may remain undissolved, and electrolyse it by two or three SMEE's elements very feebly excited and an anode of antimony in the usual manner, and at a speed of deposition not

exceeding 1 grain per square inch per hour. The exact proportion or strength of the ingredients is not important, provided the acid is not too concentrated, sufficient oxide is dissolved in it, and the electric current is very feeble.

104. The deposit is generally at first scaly, especially if the voltaic current is rather strong; but afterwards it is dull in appearance and grey like that formed in the bromide solution, and the tendency to the evolution of gas is much greater than in that liquid. It is also liable to cohesive action and crackling (17. 94.), but in a less degree than the other kinds. Its cohesion is very feeble, and it is much more friable than the bromide variety; its fractured surface is dull and earthy in appearance, and it has a much less metallic character than either of the other kinds, unless it has been deposited with extreme slowness; it is then sometimes bright and black like a blackleaded surface of iron; its cohesion is then also greater, and its fractured surface black and bright. The specific gravity of one specimen which had been formed moderately slowly was 5·27 at 60° Fahr.

105. Repeatedly in depositing this variety in a coherent state at a moderate speed, I observed at the lower part of the deposit on each side of the cathode horizontal lines about $\frac{3}{8}$ths of an inch apart, of a lighter colour than the rest of the deposit. The contrast of colour was caused by a black powdery deposit adhering to the other portions and not upon the lines, and appeared to be more prominent at the lines; but what was the cause of the lines I have not ascertained.

106. On immersing dry pieces in water a hissing sound is produced, evidently by powerful absorptive action, and numerous bubbles of gas are evolved from the whole of its surface during about five or ten seconds, and a few small ones afterwards.

107. A small piece, $\frac{1}{9}$th of an inch thick, placed upon platinum foil upon mercury at 200° Fahr. and touched by a red-hot wire, exhibited no signs of evolving heat; but with the mercury at 338° Fahr., and touched as before, it discharged its heat feebly and slowly, and evolved iodide of antimony. A second similar piece, heated from 300° Fahr. upwards upon platinum foil upon mercury, discharged its heat with evolution of iodide of antimony when the mercury had attained a temperature of 350° Fahr.; but the thermic action was feeble, and occupied about 20 seconds. Its temperature of sudden discharge appears therefore to be about 340° Fahr., and the amount of heat evolved is apparently very much less than with the other varieties. If exposed to strong sunlight during two hours, it acquires a reddish-brown colour externally.

108. The dried substance, fused in an analysis-tube (82.), gave 77·76 per cent. of a metallic button, and a solid, red, easily fusible sublimate, together with a little moisture, manifestly teriodide of antimony, and a little aqueous hydriodic acid.

109. The electro-chemical equivalent of this variety was examined in the same manner as the preceding one (102.). In two determinations, first with slow action (0·5 gr. per square inch per hour), 50·39 parts of deposit were obtained; and second, with very slow action (0·2 gr. per square inch per hour), 48·07 parts were obtained for every single equivalent, or 42·5 parts in the chloride solution. The numbers were lessened in con-

sequence of a small quantity of the deposited substance, which was not firmly deposited, falling off in a state of powder to the bottom of the electrolyte.

Further particulars respecting the first variety.

110. Several experiments (of which the following is an example) were made to determine the influence of speed of deposition upon the state of aggregation, &c. of the deposited metal. Five parts of pure oxychloride of antimony were dissolved in 20 parts of pure hydrochloric acid of sp. gr. 1·15, and the solution (contained in one vessel) electrolysed simultaneously by two separate currents from two single Smee's elements, one of which contained plates 6·3 times the size of the other, each charged with the same exciting liquid, viz. 1 measure of acid to 18 of water: the antimony anode of the large battery possessed six times the amount of surface of that of the other, but the cathodes were of equal size. The speed of deposition by the small battery was 0·75 gr. per square inch per hour, and by the large one 3·22 grs., or 4·26 times the amount. The rapid deposit exhibited much scaly cohesive action (17.), but the slow one did not. The slow deposit consisted nearly wholly of grey crystalline metal, which did not possess the thermic power, whilst the rapid one was nearly wholly black and amorphous, and possessed the usual heating quality. Owing to the decline of the current, the deposit upon both sides of the slow one was at first black and amorphous, and then became grey; and that upon the back of the rapid one consisted of alternate layers, black, grey, and black, produced by variations of the electric current, by gradual decline, and additions of acid.

111. It is particularly worthy of notice, that whether the alteration of electric power was gradual, as by slow exhaustion of the battery liquid, or sudden, as upon the additions of acid, the change of aggregation and of chemical composition of the deposited metal was sudden in both cases, in accordance with that rigid distinction or want of gradation between the two varieties of deposit already noticed (3.). The cohesion between the alternate layers was much more feeble than between the parts of the layers themselves, and the layers could be readily separated by means of a knife; the lines of junction were quite distinct and definite, although the layers were in perfect contact, and no films of depositing liquid appeared to be enclosed between them. These sudden changes of aggregation are particularly interesting.

112. It appears from this and other similar experiments, that with a suitable liquid, &c., when the quantity of the electric current is small in relation to the amount of receiving surface, the deposited metal is grey and crystalline, and possesses no heating power; and that when it is relatively large the metal is dark-coloured and amorphous, and has the peculiar thermic properties; other circumstances, such as high temperature of the solution, or excess of acid (9. 10. 11.), will also produce grey metal.

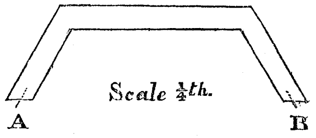
113. In several instances, when the active variety had been *rapidly* deposited, it was less bright and smooth, its colour was lighter, its fractured surface was coarse, and on

discharging its heat by a heated wire, the thermic change was unusually rapid and strong, shattering the metal throughout into scaly particles with almost explosive violence. The shattered mass consisted of parallel scaly layers, possessing an angular position with regard to the receiving surface, their horizontal edges pointing upwards at an angle of about 40° towards the surface of the liquid.

114. Two deposits were also simultaneously formed, both of the black amorphous kind, but at *equal* and nearly uniform rates of deposition, viz. 0·55 gr. per square inch per hour, upon cathodes of equal size and at equal distances from the anodes, by two separate currents, in a similar solution to that of the previous experiment (110.) contained in a single vessel, one current being generated by one SMEE'S element of large surface, and the other by twenty of small surface, the exciting liquid in each battery being the same, and the plates the same distance asunder. Both the deposits appeared alike, except that the one formed by the single element had a few small nodules of grey metal formed upon it during the latter part of the process. The active deposit formed by the twenty elements lost 7·4 per cent. by fusion in the analysis-tube (82.), and 2·7 per cent. by discharging it in the air at 60° Fahr. by a heated wire; and that formed by the single element lost respectively 7·1 and 1·86 per cent. under similar circumstances. These differences of results in the two cases may have been due to other circumstances than the difference of number of elements.

115. It has been already shown (66. 75. 83.) that the discharge of heat may take place gradually, or even in fragmentary portions, by careful management of the temperature in an air-bath, or easily by immersing the substance for a greater or less period of time in boiling water. By suitable treatment, different parts of a given piece of the active substance may also be either wholly or partly discharged of their heat. In one instance about $\frac{3}{4}$ths of an inch of the lower end of an active bar, 2 inches long, $\frac{1}{2}$ an inch wide, and $\frac{3}{16}$ths of an inch thick, was immersed in cold water, the water heated to boiling in 6 minutes, and kept boiling 20 minutes; the lower end was then found to have lost its heating power, whilst the upper end remained unaltered; and in several other similar experiments similar results were obtained. In these and all other cases where the active substance was slowly discharged, the substance became much harder and much more difficult to break.

116. The thermo-electric relation of the changed to the unchanged substance was examined as follows:—Two similar active bars were made of the shape of the annexed figure, containing small silver studs (A and B) in their extremities, enclosed by the antimony during the process of deposition; one bar was discharged of its heat gradually by immersing it in boiling water one hour; it was then placed parallel to the other, but separated by bits of cork and india-rubber; the two studs at one end of the compound bar were connected together by silver wire, and that end immersed in a solution of chloride of calcium at 60° Fahr.; the other studs and ends, being previously connected by silver wires with a galvanometer, were



wrapped in oil-silk and immersed in water at 60° Fahr.; the chloride-of-calcium solution was now heated to 212° Fahr. in 35 minutes; a gradually increasing deflection, amounting at its maximum to 42½ degrees, occurred, the discharged bar being thermo-electro-positive to the active one; the temperatures were maintained during 2 hours and 40 minutes, during which time the deflection decreased to 38½ degrees. A second similar experiment was made with a pair of bars like the last, one of them being wholly active, and the other previously made inactive at one end only, viz. the end most distant from the galvanometer, by gradual discharge in boiling water during 30 minutes. With one end of this compound bar in water at 50° Fahr., and the other in boiling water, a deflection of 28 degrees occurred, the discharged end being thermo-electro-positive to the active end of the adjoining bar. A similar experiment with a single active bar of the above angular shape, with its ends dipping into two vessels of water, one at 57° and the other at 212° Fahr., and connected with the galvanometer by silver wires, gave a deflection of 42½ degrees, which decreased to 40 degrees in 1 hour and 25 minutes.

117. In numerous experiments the suddenly and also the gradually discharged substance was found in every instance to be decidedly electro-positive to undischarged portions of the same pieces in the following liquids—pure sulphuric, hydrochloric, or nitric acids, freely diluted with water; also in aqueous solutions of ammonia, sesquicarbonate of ammonia, hydrate of potash, and carbonate of soda.

118. A bar of the unchanged substance placed axially in a copper wire helix, the ends of which were connected with a galvanometer, on having its heat suddenly discharged by contact of a heated wire with one of its extremities excited no appreciable electric current in the wire.

Comparison of the three varieties.

119. They each require a solution containing an excess of free acid in addition to the amount necessary to dissolve the teroxide, the proportion of free acid necessary being greatest with the chloride and least with the iodide.

120. The rate of deposition admissible to obtain a firm deposit, and also the range of speed of deposition, is greatest in the chloride and least in the iodide solution; being about 0·5 to 10·0 grains per square inch per hour in the chloride, 3 to 5 grains in the bromide, and 0·5 grain or less in the iodide. The tendency to the evolution of hydrogen gas at the cathode is least in the chloride and greatest in the iodide: this tendency frequently causes the iodide deposit to be completely disintegrated.

121. Each of the deposits exhibits the phenomenon of unequal cohesion and cracking (17.), but that formed in the chloride solution exhibits it the most strongly. The metal obtained from the iodide solution is the most friable, and that from the chloride the least so. The chloride compound is the most metallic in appearance, and the iodide one the least. The specific gravities of the three varieties are also in series; that of the chloride deposit is 5·8, the bromide one 5·44, and the iodide one 5·25.

122. They each possess the power of evolving heat, and this quality appears at

different temperatures in the three substances, being at about 200° Fahr. in the chloride deposit, about 280° in the bromide, and about 340° in the iodide. The manifestations of heat evolved also vary, being considerable in the chloride deposit (73.), apparently less in the bromide one, and but very small in the iodide compound. They each become much less metallic in appearance by a gradual discharge of their heat, and the gradual discharge is also attended by an increase of cohesive force, most in the chloride and least (if any) in the iodide deposit. The iodide compound is also the most affected by solar light.

123. The chloride deposit contains about 6·3 per cent. of saline matter, the bromide about 20, and the iodide about 22·2. The pseudo-electro-chemical equivalent (if I may apply this term to such cases) varies in each variety, and is dependent upon the amount of saline matter which unites with the true equivalent of metallic antimony deposited; it is about 42·5 with the chloride deposit, 50 with the bromide, and 51 with the iodide.

Conclusion.

124. A probably correct explanation of the formation and properties of these several metallic deposits is as follows:—The electric current in passing decomposes the salt of antimony, setting free 1 equivalent of chlorine, bromine, or iodine, and $\frac{1}{3}$rd of an equivalent of antimony for every single equivalent of zinc consumed (48. 102. 109.). The antimony in the act of depositing, being in what is termed the "nascent" state, unites chemically, in a comparatively feeble or unstable manner, with the elements of the electrolyte, combining with them in an indefinite and somewhat variable proportion. The $\frac{1}{3}$rd equivalent, or 40 parts of antimony, carry down from $2\frac{1}{2}$ to 3 parts from the chloride solution, about 10 parts from the bromide liquid, and about 11 parts from the iodide solution, and thus occasion about 42·75 parts of deposit in the first liquid, about 50 parts in the second, and 50·5 parts in the third solution, for each equivalent of zinc consumed.

125. Another explanation, which has nearly an equal weight of evidence in its favour, is that the antimony is deposited in the "*amorphous*" state, and the chloride or other salt is enclosed mechanically in it during the process of deposition, and that the change consists in the assumption by the metal of the crystalline state, whereby it is converted into an inconceivable number of crystals of insensible size, and the imprisoned salt is set free.

126. Antimony is not the only metal that manifests this property of uniting during electrolysis with portions of the electrolyte; several other metals also show it: it is well known that silver deposited by electrolysis from a solution of the double cyanide of silver and potassium containing a little bisulphide of carbon, is harder and very much brighter than that deposited from the same solution without that ingredient; this bright deposit is not wholly metallic silver, but contains a small proportion (about 1 per cent.) of some other ingredients of the electrolyte.

I have not examined the laws or conditions that regulate the proportions of the substances that unite by this species of combination.

127. The substance formed in either of these solutions of antimony may be viewed as a feeble chemical compound of metallic antimony with a salt of antimony: that it is not a purely mechanical mixture is rendered very probable by the fact of its powder not reddening moistened litmus paper, especially in the case of that obtained from the bromide solution, which contains as much as 20 per cent. of saline and acid matter, whereas immediately after the gradual change has occurred it has the power of reddening litmus strongly (101.), and the salt of antimony contained in it may be much more readily extracted by dilute hydrochloric acid (83.); these facts also indicate that the change is, at least in part, a case of chemical decomposition, the substances remaining together after the decomposition in a state of mechanical mixture.

128. The compound deposited is evidently not a *direct* result of electrolysis, otherwise it would be deposited in the proportion of its electro-chemical equivalent; nor is it a *definite* chemical compound, because there is no equivalent or atomic proportion between the quantity of metallic antimony and that of the salt with which it is combined, and because the proportions of these two ingredients are in each case somewhat variable.

129. The decomposition of these deposits, like that of peroxide of hydrogen, is attended by evolution of much heat; it cannot, however, like the decomposition of that substance, be viewed as a result of a tendency of the separated ingredients to assume the gaseous or even the liquid state, because the compound set free is in each case in a nearly solid condition, but must be referred to some other and at present unknown cause.

130. The union of the nascent antimony with the salt of antimony is evidently dependent upon the rate of deposition; for when the speed of deposition in the chloride solution fell below about 0·75 or 0·5 grain per square inch per hour, the antimony lost its power of combining with the antimonial salt, and was deposited alone in the grey or crystalline state (110.). It is also dependent upon the temperature of the liquid (11.), and upon the proportions of the ingredients of the solution (9.).

131. Numerous and varied electrolytic experiments were made with solutions of arsenic, and small portions of scaly deposit were obtained from the aqueous fluoride, which exhibited in a comparatively feeble and indistinct degree (like the third variety of active antimony) a similar thermic property to that manifested by electro-deposited antimony.