XLIII.—*On the Properties of Electro-deposited Antimony.*

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WHILST engaged in depositing antimony by the electro-process, in October, 1854, I observed a singular development of heat by the deposited metal when scratched or rubbed, and published a brief account of it in the *Philosophical Magazine*, for January, 1855. I afterwards investigated the phenomenon more fully; and the following account, condensed from the *Transactions of the Royal Society*, contains all the leading facts relating to it.

When a current of electricity from two or three small elements of Grove's or Smee's battery is passed, by means of an anode of antimony and a cathode of copper, silver, or platinum, through a solution of terchloride of antimony, there is generally deposited upon the cathode a bright black amorphous metallic coating, which, if scratched by a needle or touched by a heated wire, instantly rises in temperature several hundred of Fahrenheit's degrees, sometimes with explosive violence, and evolves a small quantity of acid fumes.

If, instead of the terchloride solution, a solution of either terbromide or teriodide of antimony is employed, the deposited coating possesses somewhat similar properties, but in a much less conspicuous degree, especially the deposit from the teriodide. And if a solution of fluoride of antimony is employed, the deposited metal is of a grey colour, perfectly crystalline, and entirely destitute of the peculiar heating property. Under some circumstances, this crystalline variety of deposit may also be obtained by electrolysis from a weak solution of terchloride of antimony, especially if the battery power is very feeble, or the liquid is employed in a dilute or heated state.

The best solution for forming the strongly thermic variety of deposit is composed of one avoirdupois ounce of teroxide of antimony, or oxychloride of antimony, dissolved in five or six ounces of hydrochloric acid of sp. gr. 1.12; or it may be made by saturating two measures of hydrochloric acid with oxide or oxychloride of antimony, and then adding one measure more of the acid.

In common with electro-deposits generally, the inner and outer surfaces of both the black and grey deposits are in unequal states of cohesive tension, frequently in so great a degree as to rend the deposit extensively, and raise it from the cathode in the form of a curved sheet, with its concave side towards the anode. This state of tension is most manifest with rapidly formed thin deposits, especially upon extended flat surfaces.

It is worthy of notice that if the speed of deposition was *gradually* diminished to about 0.5 grain per square inch of cathode per hour, when it attained a certain degree of slowness (about 0.7 grain per square inch per hour), the character of the metal depositing *suddenly* changed from the amorphous black to the crystalline grey variety, without exhibiting the slightest gradation between; and the two layers of active and inactive metal might be readily separated by means of a knife. With deposits *very rapidly* formed, the fractured surface was coarse and less black, and the thermic change was found to be very strong, shattering the metal with almost explosive violence.

Faint crackling sounds frequently issued from the depositing metal, evidently caused in most instances by the cohesive action just mentioned; but in other cases they were due to the sudden expulsion of bubbles of gas from holes in the deposited metal, especially with the bromide variety, or by depositing upon an iron cathode in the terchloride solution. The deposit obtained in the bromide solution was frequently perforated with holes all over its surface, and had the appearance of a metallic sponge, caused by the numerous bubbles of gas.

The thermic property of the deposit from the terchloride gradually disappears; the substance in a state of powder loses its power in six months; fragments, $\frac{1}{16}$ th of an inch thick, lose their power in the course of twelve months; whilst others, $\frac{1}{4}$ th of an inch thick, still possess a portion of their heating power at the end of three or four years.

Each of the varieties of active antimony is fragile and easily broken; that from the iodide solution is extremely so. Thin pieces, $\frac{1}{16}$ th of an inch thick, of the chloride variety may be broken in the air at 60° Fahr. without discharging their heat, if broken with care; thicker pieces should be broken under the surface of cold water, by gentle blows with wood or other substance not very hard. Very thin pieces may with care be reduced to fine powder in a mortar, under a mixture of ice and water; and the powder so

produced, after drying in a slightly warm place, possesses all the heating property of the original solid mass.

Heating the chloride variety to 212° Fahr. for one hour in boiling water, or keeping it at somewhat lower temperature (185° or 190° Fahr.) for a longer period in an air-bath, causes it *gradually* to evolve its heat and lose its peculiar heating power.

A cylindrical bar of the chloride variety, about $\frac{1}{2}$ an inch in diameter, formed upon a rod of grain tin $\frac{1}{8}$ th of an inch thick, when changed by the momentary contact of a heated wire, evolved sufficient heat to melt the tin completely, and the tin ran out through a crack in the antimony, and remained liquid a short time.

By applying momentary heat to the ends of deposits formed upon heliacal copper wires, the action was gradually transmitted to the opposite ends at a speed varying from twelve to thirty feet per minute, the rapidity of progress depending chiefly on the absence of cooling influences, cracks in the metal, and grey crystalline deposit. The progress of the change was rendered visible by the evolution of a small cloud of vapour at its advancing point, and by a peculiar snake-like movement in the coils at that part, apparently produced by the cohesive change in the deposit. With massive deposits the speed of transmission would doubtless be much greater.

The specific gravity of the active chloride variety varied from 5.739 to 5.944; but after having been discharged suddenly of its heat, its specific gravity varied from 5.748 to 6.029. The specific gravity of the inactive or crystalline variety varied from 6.369 to 6.673.

Their electro-chemical equivalents, determined by electrolysing their solutions simultaneously with a solution of sulphate of copper, and weighing the deposits, were 42.30 to 43.81 parts of the active variety, and 40.41 to 40.79 parts of the crystalline kind, for every 31.7 parts of copper deposited in the copper solution.

The peculiar change in the active chloride variety is attended by alterations in the colour, cohesion, and fractured surfaces of the substance; from a bright steel colour and glassy fracture, it passes to a dull grey colour and granular fracture, and its cohesive power greatly increases. These changes occur whether the heat has been evolved suddenly, or very gradually by long lapse of time. Similar effects are observed, but in different degrees, with the bromide and iodide deposits. Straight bars of the active chloride variety suddenly discharged, become curved by the heat, the outer side or

that last deposited invariably becoming concave; this is similar to the effect of heat upon electro-deposited metals generally.

The heat evolved by the peculiar change in the chloride variety is not due to cohesive action; for it has been found that the amounts of heat evolved by similar weights of the substance in a single solid mass, in small pieces, and in fine powder, in a calorimeter, were not sensibly different. Nor is the heat due to alteration of the specific heat of the substance during the change. The specific heats and gravities of several bars of the active substance were determined; the bars were then suspended in an air-bath at about 185° Fahr., or in boiling water, until their heat had all been *gradually* evolved, which occupies about half-an-hour in the water; their specific heats and gravities were then redetermined and found to be scarcely at all altered. With similar bars and pieces *suddenly* discharged, the specific heat decreased from 0.0631 to 0.0543, and the specific gravity increased; the reason being, that by the *sudden* discharge they had been heated to a much higher degree, and the greater degree of heat had expelled a much larger proportion of the inclosed chloride of antimony, which the *amorphous* chloride variety always contains.

The temperature to which the active chloride variety must be raised either locally or throughout its mass, to produce the *sudden* discharge, varies according to several circumstances, but is generally about 200° or 210° Fahr., in an air-bath. The discharge is not limited to one particular temperature, but commences between 170° and 190° , and gradually increases in rapidity by rise of temperature to some point about 200° or 210° Fahr., when it attains its maximum, and discharges all its remaining heat suddenly. When the amount of cooling influences is great in relation to the amount of heat to be discharged, and the heat is conveyed away as fast as it is set free, as by immersion of the substance in boiling water, and the substance therefore never attains so high a temperature as when heated to 200° or 210° Fahr. in the air, the discharge of heat and the change of state of the substance is *gradual*, and may be made even fragmentary by repeated brief immersions in the boiling water. A rod of the substance may be gradually discharged of its heat at one end, without discharging the opposite end, by immersing that end for one hour in nearly boiling water.

The total amount of heat evolved by the sudden discharge of the chloride variety was considerable, and was sufficient in most instances to raise the temperature of an equal weight of ordinary

antimony of specific heat 0.0508 about 650 or 700 Fahr. degrees, and in one instance 705.89 Fahr. degrees, above the atmospheric temperature (60° Fahr.) at which it was discharged.

When the active chloride variety is *suddenly* discharged of its heat, there is invariably evolved from it a small quantity (generally about 3.5 per cent.) of vapour, consisting almost entirely of terchloride of antimony. This evolution of vapour is not a *cause* but an *effect* of the heat; it does not occur when the temperature of the substance during discharge is not sufficiently high to volatilize the inclosed chloride, as when the substance is *gradually* discharged of its heat.

It is important to observe that the amount of heat evolved by this sudden change of antimony is different at different temperatures, and is greater at high temperatures than at low ones. A bar cooled to 34.0° Fahr. and discharged, evolved sufficient heat to raise the temperature of its own weight of ordinary antimony (specific heat = 0.0508) 638 Fahr. degrees; whilst a similar one, heated to 157° Fahr. and discharged, evolved sufficient heat to raise its own weight of ordinary antimony 732.8 degrees.

The grey or crystalline variety of deposited antimony is generally very free from impurities, and from the constituents of the depositing liquid; whilst the amorphous or active kind contains small portions of all the constituents of the electrolyte, and invariably contains about 6 or 6½ per cent. of terchloride of antimony.

The following are the results of two analyses of specimens obtained from a pure solution of the chloride :—

No. 1.			No. 2.		
Sb ..	..	93.36	Sb ..	..	93.51
SbCl ₃ ..	..	5.98	SbCl ₃ ..	..	6.03
HCl ..	..	0.46	HCl ..	..	0.21
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99.80			99.75		

If a quantity of the active variety in a state of fine powder is kept in a closed bottle for twelve months and then examined, it is found to emit a slightly acid odour, and to have lost all its heating power; similar results occur if a flask containing some active powder is immersed in boiling water for an hour.

Equal quantities of active powder and powder gradually discharged of its heating power, were digested at 60° Fahr. with

dilute hydrochloric and tartaric acid for two days; the discharged powder was then found to have yielded to the dilute acid, by solution, about twice the quantity of its chloride of antimony that the other had yielded; showing that, with the loss of heating power, there occurs a diminished degree of union between the deposited metal and its associated chloride of antimony.

It would appear that the heating power is closely dependent upon the presence of the associated chloride: for in every instance where the chloride was extracted, by digesting the powder at 60° Fahr. for weeks or months in various solvents, the heating power disappeared.

There are no circumstances at present known under which the substance retains its heating power unimpaired by lapse of time.

The foregoing remarks apply chiefly or nearly wholly to the variety of active deposit obtained in a solution of terchloride of antimony, because that variety is the most readily obtained, the most powerful in its action, and the most definite in its results.

The second variety of active antimony may be obtained as follows: Dissolve one part of teroxide of antimony in 10 parts of hydrobromic acid of specific gravity about 1.3; filter the solution, and electrolyse it by means of three Smee's elements and an anode of antimony, at a speed of deposition of about 3 to 5 grains per square inch of receiving surface per hour.

This variety is of a lighter colour than that from the chloride, and is generally quite dull in aspect. It exhibits less of the cohesive cracking action than the first kind, and is less hard. Its specific gravity at 60° Fahr. varies from 5.415 to 5.472.

By momentary contact of a red-hot wire, it exhibited a similar molecular and thermic change, but the action did not spread throughout the mass unless it was previously raised to a temperature of about 250° Fahr.; if then touched with the wire, it evolved all its heat instantly with explosive violence and projection of pieces of the substance. Scratching the heated substance by a steel pointer did not cause it to discharge its heat. Pieces heated upon mercury or melted fusible alloy, discharged themselves suddenly and powerfully when the bath attained a temperature of about 320° Fahr.

Thick pieces may be easily reduced to powder in a mortar without causing a discharge of heat. A train of the powder heated upon a platinum dish in a bath of chloride of calcium at 265° Fahr., and touched at one end by a red-hot wire, discharged its

heat gradually, and the change, attended by evolution of fumes, was slowly propagated to the distant extremity.

This variety was *gradually* discharged of its heat by placing it upon the surface of mercury at 260° Fahr. for one hour; or by suspending it during 30 minutes in a solution of chloride of calcium at 252° Fahr. During this latter period it lost 6.117 per cent. in weight.

By fusion in a bent tube of refractory glass, it was found to consist of 79.52 per cent. of metal and 20.48 per cent. of volatile matter, a colourless buttery substance, slightly semifluid at 60° Fahr., which doubtless consisted of terbromide of antimony and a little aqueous hydrobromic acid. Other specimens treated thus gave respectively 18.42 and 20.40 per cent. of volatile matter; the two specimens being parts of a single deposit, the first being from the upper and the second from the lower part of the deposit as it was suspended in the electrolyte.

The electro-chemical equivalent of this variety was determined by depositing it simultaneously by the same current with the chloride variety; and ascertaining the relative weights of the two deposits. In two experiments of this kind there were obtained respectively 50.09 and 50.11 parts of this variety for every 42.5 parts of the active chloride variety, 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 contained the same amount of *metallic* antimony, viz., 40 parts, or $\frac{1}{3}$ rd of an equivalent; the remainder being the associated salt of antimony. The variation in the numbers of the bromide deposit probably arose from absorption of moisture caused by its porosity.

After gradual discharge, the cohesion of this variety, like that of the previous kind, was found to be greatly increased, its fractured surface became less metallic, and was dull and earthy in appearance; reduced to powder, it strongly reddened damp litmus paper, whilst the powder of the unchanged substance did not; the odour and taste of the changed substance were also acid. These results indicate that the change and evolution of heat is attended by a diminished degree of attraction between the metal and its associated saline or acid matter, similar to the change in the chloride variety.

The third variety of heat-giving electro-deposited antimony was obtained as follows: Dissolve one part by weight of teroxide of antimony in fifteen parts of hydriodic acid of specific gravity 1.25,

and electrolyse it at a speed not exceeding one grain per square inch of cathode per hour.

The deposit is scaly-grey, dull in appearance, very friable, and much less metallic in character than either of the other kinds, unless it has been deposited with extreme slowness. The specific gravity of a slowly-formed specimen was 5.27. On immersing dry pieces in water, a hissing sound, as of strong absorption, occurred, and numerous bubbles of gas issued from all parts of its surface during a few seconds. The tendency to evolution of hydrogen gas in the solution is so great as frequently to disintegrate the deposit completely.

Pieces 1.9th of an inch thick required to be heated upon mercury to 338° Fahr. before the contact of a red-hot wire would cause a discharge of heat; it then discharged but feebly, with evolution of red vapours of iodide of antimony. A similar piece heated upon mercury discharged itself feebly when the mercury attained a temperature of 350° Fahr.; the action was slow, and occupied about twenty seconds. By exposure to strong sunlight, during two hours, this variety acquires externally a reddish-brown colour.

By fusing the unchanged substance in a glass-tube, it yielded 77.76 per cent. of metal, and a solid, red, easily fusible sublimate, together with a little moisture, evidently teriodide of antimony, and a little aqueous hydriodic acid.

Its electro-chemical equivalent was determined in the same way as the previous kind. With slow action (0.5 grains per square inch of cathode per hour) 50.39 parts of deposit were obtained; and with very slow action (0.2 grain per square inch per hour) 48.07 parts were obtained for every 42.5 parts of deposit in the chloride solution.

The following are some recapitulations, with comparisons of the three active varieties. The solution for obtaining each requires an excess of free acid, greatest with the chloride, and least with the iodide. The rate of deposition admissible to obtain firm deposits, is greatest with the chloride, and least with the iodide. The phenomenon of unequal cohesion and cracking is exhibited most in the chloride variety, and least in the iodide. The chloride deposit is the most metallic in appearance, and has the strongest cohesion; the iodide is the least metallic, and has the weakest cohesion. The specific gravities of the deposits are also in series; that from the chloride is 5.8, from the bromide 5.44, and from the

iodide 5.25. The temperatures of sudden discharge are, for the chloride variety, about 200° Fahr. ; the bromide, about 280° Fahr. ; and the iodide, about 340° Fahr. The manifestation of heat is great in the chloride deposit, less in the bromide, and least in the iodide. They each become less metallic in appearance by the thermic discharge, and acquire increased cohesion. The chloride variety contains about 6.3 per cent. of saline matter, the bromide about 20, and the iodide about 22.2. The pseudo-electro-chemical equivalents of the deposits, which depend upon the amount of saline matter united to an equivalent of metallic antimony in them, is about 42.5 for the chloride variety, 50 for the bromide, and 51 for the iodide.

In conclusion I beg to submit the following remarks respecting the formation and properties of these substances :

The electric current in passing decomposes the salt of antimony, setting free 1 eq. of chlorine, bromine, or iodine, and $\frac{1}{3}$ rd of an eq. of antimony for every single equivalent of zinc consumed. 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 ingredients of the electrolyte, combining with them in a somewhat variable proportion. The $\frac{1}{3}$ rd eq., or 40 parts of antimony, carry down about $2\frac{1}{2}$ or 3 parts from the chloride solution, about 10 parts from the bromide liquid, and about 10.5 parts from the iodide solution, and thus occasion about 42.75 parts of deposit in the first liquid, 50 parts in the second, about 50.5 parts in the third solution, for each equivalent of zinc consumed. I have ventured to call those numbers the pseudo-electro-chemical equivalents of the deposits to distinguish them from the true equivalent of antimony which they disguise.

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 inclosed 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.

Antimony is not the only metal that manifests this property of uniting during electrolysis with ingredients of the electrolyte ; silver deposited from a cyanide solution containing a small quantity of bisulphide of carbon, retains a small proportion of some of the

ingredients of the electrolyte, and possesses very different properties from silver deposited from other cyanide solutions. It would be desirable to examine further the conditions which regulate this species of combination, and that influence the proportions of the substances which unite by it. In the case of antimony, the combination is evidently dependent upon the rate of deposition; for when the speed in the chloride solution fell below about 0.75 or 0.5 grain per square inch of cathode per hour, the antimony lost its power of combining with the antimonial salt, and was deposited alone in the grey or crystalline state. It is also dependent upon the temperature of the liquid, and upon the proportions of the ingredients of the solution. In an experiment already mentioned, the proportion of antimony that united with the bromide of antimony, varied with the depth of immersion of the cathode in the depositing liquid.

Either of the active varieties 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 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, and the salt of antimony contained in it may then be much more readily extracted by dilute hydrochloric or tartaric acid. 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.

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 appear to be in each case somewhat variable.

Numerous electrolytic experiments were made with solutions of arsenic, and small portions of scaly deposit from the aqueous fluoride appeared to exhibit in a feeble degree (like the third variety of active antimony) a thermic property similar to that of electro-deposited antimony.