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On the Reciprocal Precipitations of the Metals.

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IN a paper read at the Cheltenham meeting of the British Association, I observed that "when metallic cadmium is introduced into an acidulated or non-acidulated solution of chloride of copper, with, or more slowly without, ebullition, the whole of the copper is deposited in a red pulverulent state; but that when a piece of clean copper foil is immersed in a boiling, moderately concentrated, and slightly acidulated solution of chloride of cadmium, after some little time, a very brilliant coating of cadmium, of a white or yellowish-white colour, is precipitated upon the copper." This last decomposition being in very curious antagonism to Bergmann's view of single elective affinity, I was induced to make some further experiments upon the reciprocal precipitations of the metals. The results I have obtained form the subject of my present communication to this society.

Silver and Mercury.—The introduction of metallic mercury into a solution of nitrate of silver is followed by a beautiful growth of crystalline silver, constituting the well-known *Arbor Lunæ;* but when a piece of clean silver foil is immersed in a solution of mercurous nitrate, the foil becomes eventually covered with a semiliquid layer of amalgam, is rendered very brittle throughout, and, when heated in a tube, affords an abundant mercurial sublimate. The same result was obtained with pure metallic silver, reduced from the chloride by carbonate of soda. Acidification and continued ebullition of the solution, facilitate, but are not by any means essential to, the deposition of the mercury. Thus it appears that, under circumstances of the greatest similarity, mercury will precipitate silver, and silver will precipitate mercury, from their respective nitric solutions. Moreover, silver, when boiled in an acidified solution of corrosive sublimate, becomes covered with a layer of calomel and metallic mercury, but the result is not so striking as that with the mercurous salt.

Silver and Copper.—When metallic copper is introduced into a solution of nitrate or sulphate of silver, or into a liquid turbid from the suspension of chloride of silver, a precipitate of silver takes place almost immediately. The deposit is generally pulverulent, but may be obtained from the sulphate and chloride as a brilliant metallic coating, provided the dilution be very considerable. Ebullition facilitates the deposition of silver from dilute solutions, but interferes with the appearance of the coating. When on the contrary a piece of silver foil, or of pure silver reduced from the chloride, is boiled in an acidulated and strong solution of sulphate of copper, after some time, the silver acquires a faint coating of metallic copper. When viewed in certain positions, the red colour of the copper is very apparent. When, however, the cupric coating is so thin as to be imperceptible to the eye, the presence of the metal may be evidenced by moistening the foil with ammonia, whereby the deep blue-coloured solution of cupramide is gradually developed; or better still, by heating the foil, when the redness of copper or its suboxide is frequently brought out with such intensity as entirely to conceal the colour of the silver. With a solution of nitrate of copper, the silver becomes discoloured, but there is no decided metallic precipitate. With solution of chloride of copper the results are most decided. The silver foil, or reduced silver, becomes almost immediately covered, even in the cold, with an opaque layer of a pale dull copper colour. By continued ebullition the colour of the coating becomes much deeper and less red. The deposit is capable of receiving a polish. It does not dissolve in cold hydrochloric acid, dilute or concentrated, but simply becomes more bright and red coloured. By boiling the coated foil, however, for some time, in strong hydrochloric acid, the copper disappears with the evolution of gas, and the silver remains coated with chloride of silver, which a slight rubbing readily removes. On gently heating the coated foil, a fine bronze colour is developed. That the coating is really metallic copper, and not the suboxide, to the colour of which it sometimes most approximates, is, I consider, unquestionable. Its insolubility in cold hydrochloric acid, and its solubility in the boiling acid with the evolution of gas, leave no doubt upon the subject. I have satisfied myself by a great number of experiments, that pure metallic copper is soluble to a very manifest extent in boiling hydrochloric acid. There is, indeed, no difficulty in collecting considerable quantities of hydrogen generated by the reaction of hydrochloric acid and copper. I have employed wire, foil, gauze, electrotype copper, and copper reduced from the chloride by zinc, always with the same result. Moreover, pieces of electrotype copper and thin foil, after a very protracted ebullition, disappear completely in the acid, and that without any absorption of oxygen from the air. Throughout the experiment, hydrogen continues to be liberated, the dissolved copper exists in the state of subchloride, and the liquid consequently remains colourless.

Antimony and Copper.—The precipitation of antimony upon copper was, I believe, originally pointed out by Reinsch as giving rise to a possible fallacy in the use of his process for the detection of arsenic, and the re-action is now well known to chemists; but I find that, when pure metallic antimony is boiled with an acidulated solution of chloride of copper, the antimony receives a thin, but obvious coating of copper. The deposition of copper upon antimony takes place also in the cold, though much less quickly. In this case, the presence of the copper may be readily evinced by means of ammonia.

Bismuth and Copper.—The reciprocal precipitations of these two metals resemble very closely those of antimony and copper. The precipitate of copper upon pure bismuth, however, is not so manifest to the eye as is the cupric deposit upon antimony, owing probably to the greater want of contrast in the colours of the metals.

Copper and Tin.—When an acidulated solution of chloride of copper is boiled with metallic tin, the whole of the copper is deposited in a red or black pulverulent state. I find, on the other hand, that when clean copper is boiled in a moderately strong and rather acid solution of stannous chloride, the tin is deposited upon the copper in the form of a brilliant metallic coating of a somewhat darker colour than either the arsenical or antimonial coatings. In operating with dilute tin solutions, from which under any circumstances it is difficult to obtain a deposit, I have not found a large excess of acid advisable. Reinsch alludes to a tarnish being produced upon copper when boiled in tin solutions.

Copper and Lead.—The introduction of a piece of clean lead into a solution of chloride of copper is followed by a precipitation of metallic copper in a red or black pulverulent state. But I find, contrary to the usual statements on the subject, that copper immersed in a boiling, saturated, and strongly acidified solution of chloride of lead, acquires, after some few minutes ebullition, a beautiful metallic coating of a somewhat bluish colour. When the liquid is but slightly acidified, the deposit is very faint, and amounts only to a tarnish.

Copper and Cadmium.—These results have been already alluded to. For the precipitation of cadmium upon copper, especially when the solution is somewhat weak, the acidification must be very slight, or be dispensed with altogether. When the precipitation takes place slowly, the gradual concealment of the colour of the copper by the deposit of cadmium gives rise to some very beautiful chromatic appearances. An equivalent of cadmium will completely abstract the copper from a solution of the neutral chloride, containing very much more than an equivalent of copper. In one experiment, only 72·75 per cent. of an equivalent of cadmium precipitated an equivalent of copper. Of course a portion only of the precipitated copper was in the metallic state. I have not succeeded in obtaining a *decided* deposit of cadmium upon pulverulent copper precipitated by cadmium or zinc. Moreover, it is difficult to obtain a coating upon electrotype copper until the metal has been fused and hammered. When a plate of cadmium and a plate of copper are immersed in dilute acid, the electric current proceeds, as is well known, from the copper to the cadmium, and when the two metals are immersed in a boiling solution of chloride of cadmium, the current maintains the same direction. During the passage of the current, it seems that the cadmium is deposited electrolytically, and that no solution of the copper takes place.

Tin and Lead.—When clean lead is introduced into an acidified and moderately strong solution of stannous chloride, with or without ebullition, a deposition of metallic tin in the form of a powder, or of minute crystals, is produced. The decomposition is, however, very incomplete. On the other hand, when a piece of tin foil, or pure tin, is introduced into an acidified, boiling solution of chloride of lead, a deposit of lead speedily takes place. So uniform is the coating, and so well marked its colour, that the tin actually appears to have been converted into lead foil. Fischer alludes to the precipitation of lead from the acetate by means of tin, but his reaction is much less marked than that with the chloride.

Tin and Cadmium.—The introduction of cadmium into an acidified solution of stannous chloride is followed by the formation of the well-known tin tree or *Arbor Jovis.* But when a piece of tin foil, or pure tin, is immersed in a solution of chloride of cadmium, the latter metal is deposited upon the tin as a film having a somewhat iridescent appearance. By boiling a piece of tin in a strong solution of chloride of cadmium, a very abundant deposit of cadmium may be obtained.

Tin and Iron.—A piece of clean iron or steel, immersed in a boiling and tolerably concentrated solution of stannous chloride, acquires after some little time a pulverulent coating of tin; but when a piece of tin foil, or pure tin, is boiled in an acidulated solution of ferrous chloride, the tin receives a black-coloured coating, and becomes extremely brittle throughout. After being well washed with water, and boiled with hydrochloric acid, it yields a solution in which the presence of iron is abundantly manifest. The brittle residue, moreover, exerts a slight effect upon a delicate magnet. The reciprocal actions of tin with nickel and cobalt respectively, resemble perfectly the above-mentioned reactions with iron.

Lead and Cadmium.—Lead is readily precipitated by cadmium. From a solution of acetate of lead the *Arbor Saturnii* is produced with nearly as much facility by cadmium as by zinc. But when clean lead, pure or commercial, is boiled in a moderately concentrated solution of cadmic chloride, it speedily receives a brilliant, uniform, yellowish-white coating of metallic cadmium.

Cadmium and Iron.—A piece of clean iron or steel, when boiled in a solution of cadmic chloride, acquires a complete coating of metallic cadmium, having exactly the same appearance as when precipitated upon copper or lead. On the other hand, cadmium foil boiled in a solution of ferrous chloride receives a black coloured coating. This coated foil acts slightly on the magnet, and when washed with water and boiled with hydrochloric acid, yields a solution in which the presence of iron is at once evidenced by the usual reagents. Nickel and cobalt respectively reciprocate with cadmium in a manner precisely similar to that of iron. I find also that iron is precipitated to a very great extent by zinc; but I have not been able to reverse the experiment and precipitate zinc upon iron. In estimating iron by means of a standard solution of permanganate of potash, zinc is occasionally added to the iron solution, for the purpose of reducing the ferric to the ferrous salt. Unless care be taken to boil the liquid for some time with hydrochloric acid after the disappearance of the zinc, a very serious error may be introduced into the process by the abstraction of iron from the liquid.

From the above described experiments it appears that the reciprocal precipitation of the metals is a phenomenon of considerable generality; how, then, are the apparently antagonistic results to be explained? There can, I conceive, be no doubt whatever that, under certain specified conditions, the tendencies to the formation of some one particular compound are greater than the tendencies to the formation of some other analogous compound. Thus at a red heat, the tendencies to the formation of protoxide of lead are greater than the tendencies to the formation of the analogous protoxide of silver. Disregarding its etymology, we make use of the word affinity to express the tendencies which lead and oxygen have to unite with each other.* Admitting then to the full, that there are stronger tendencies or affinities leading to the production of one compound AB, than of another AC, we have to inquire how it is that AC is sometimes produced to the prejudice of AB.

From a variation in the conditions of the experiment.—It seems that the affinities leading to the production of any compound are not absolute, but variable, according to circumstances. Thus, at a red heat the tendencies to the production of oxide of iron or oxide of lead are greater than at ordinary temperatures. Now it is not improbable that the affinity of A for B shall in one set of conditions be greater than, and in another set of conditions be less than, that of A for C. But irrespective of any absolute variation in the powers of the different affinities, an alteration in the condition of the experiment brings other forces into play. Thus the well-known results of passing hydrogen over red-hot oxide of iron, and steam over red-hot metallic iron, have received an explanation from Mr. Graham to the effect—that in the

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* In such a simple case as the above, the expressions affinity and chemical attraction are perfectly admissible. But when applied to more complex instances of combination, the phraseology becomes objectionable as necessarily representing to our minds some one or other speculative view concerning the constitution of the body under consideration. Thus in sulphate of barium, Ba^2SO^4, are we to speak of the affinity of baryta, Ba^2O, for sulphuric anhydride SO^3; or that of barium, Ba^2, for oxysulphide, SO^4; or that of peroxide of barium, Ba^2O^2, for sulphurous anhydride, SO^2; &c., &c. It is in this point of view that I take exception to the word affinity, which, however, it is scarcely possible to avoid employing.

former case, the diffusive tendency of steam into an atmosphere of hydrogen determines the reduction, and in the other, the diffusive tendency of hydrogen into an atmosphere of steam determines the oxidation of the iron. In a similar manner, when copper is boiled in a strong solution of chloride of cadmium, the diffusive or solvent force of chloride of copper may determine its formation. Water saturated with chloride of cadmium would be greedy of chloride of copper, and would yield the former metal in willing exchange for the latter. The solvent power of the cadmic solution for the cupric salt would exert a disposing affinity.

From the effect of mass.—The amount of evidence in favour of the general proposition by Berthollet, that "la quantité peut suppléer à la force de l'affinité pour produire un même degré de saturation," is now so great, as to render it almost indisputable. It is highly probable indeed that, were it not for interfering circumstances, if we had the electro-negative body A, and the metals B and C in excess, A would divide itself in the ratio of $\frac{x\,b}{x\,b + y\,c}$ to $\frac{y\,c}{x\,b + y\,c}$, where the tendency to form AB $= b$, the tendency to form AC $= c$, the amount of B $= x$, and the amount of C $= y$. It is obvious, however, that in many cases, superficies rather than mass will most influence the result. Mass may possibly exert a considerable effect in the cases where the precipitation of a metal from its acid solution is accompanied by a liberation of hydrogen. It is not improbable that the nascent hydrogen may preferably reduce the metal which was originally dissolved, in consequence of the greater quantity of the original, than of the subsequently formed salt. I find also that when a piece of clean iron is boiled in a solution of cadmic chloride containing a little cupric chloride as an impurity, copper and cadmium are simultaneously precipitated upon the iron which thus becomes coated with a species of brass. The precipitation of cadmium, however, despite its superior affinity, takes place to a very much greater extent than does the precipitation of copper, in consequence, I believe, of its superior mass. With a strong solution of cadmium the whole of the copper is not precipitated by iron, even after a somewhat protracted ebullition. Copper may, however, be readily removed from a dilute solution of cadmium, by agitating it with clean iron in the cold.

As a result of double decomposition from homogeneous affinity.—The propriety of representing chlorine, hydrogen, and the metals, as binary molecules Cl Cl, H H, M M, respectively, as advocated by Brodie, Laurent, Gerhardt, and others, appears to receive confirmation from the phenomena of the mutual precipitation of the metals. By considering the precipitation of one metal upon another as an instance, not of single, but of double decomposition, I was enabled to explain several of the results I have already described. But, curiously enough, I find, not only that my explanation has been in its general nature anticipated by Berthollet, but that our modern notion of the homogeneous affinity of Cu for Cu, Hg for Hg, &c., is described by the same author in unmistakeable language. In accordance with these views, the precipitation of cadmium upon copper may be represented by the equation Cu Cu + Cd Cl = Cu Cd + Cu Cl, and the decomposition be determined by the circumstance that, in the conditions of the experiment, the sum of the affinities of Cu for Cd, and of Cu for Cl exceeds that of the affinities of Cu for Cu and Cd for Cl. Is there, however, any proof that a cadmide of copper is really formed? We know that an alloy differs greatly from a mixture of two metals, in the phenomena of its solution in acids. Thus an alloy of silver and platinum dissolves in nitric acid; but with the two metals in contact or mixture, there is an electric current generated; the silver is dissolved, and the platinum is left. An alloy of zinc and copper dissolves in hydrochloric acid; but with the two metals in contact or mixture, there is an electric current generated; the zinc is dissolved, and the copper remains. The solubility of pure copper in hydrochloric acid, to which I have before adverted, is not opposed to this result. Iron by itself is readily soluble in hydrochloric acid, but is not so in the presence of zinc. Now I find that a piece of copper coated with cadmium, and a coil of copper and cadmium foils rolled up together, behave very differently when treated with hydrochloric acid. Hydrochloric acid of the ordinary strength was diluted with a third of its volume of water and two equal portions boiled. Into one of the boiling liquids was immersed the compound coil, and into the other the coated foil. In both cases there was a considerable evolution of hydrogen, greater, however, with the coil than with the foil. The liquid in which the coil was immersed remained perfectly colourless, and even after a lapse of several hours had not dissolved a trace of copper. The liquid in which the coated foil was immersed became immediately green, and long before the cadmium had disappeared, contained copper in very considerable quantities, thus proving that the metallic deposit partook of the characters of an alloy. In this case the solution probably took place according to the equation

$$\begin{aligned} &\mathrm{Cu\,Cd + H\;\;Cl + H\;\;Cl =} \\ &\mathrm{H\;\;H\;\; + Cu\,Cl + Cd\,Cl.} \end{aligned}$$

It might possibly have been

$$\begin{aligned} &\mathrm{Cu^2\,Cd + H\;\;Cl + H\;\;Cl =} \\ &\mathrm{H\;\;H\;\; + Cu^2\,Cl + Cd\,Cl;} \end{aligned}$$

but I am inclined to think from the instantaneous development of the green colour, in circumstances where an absorption of oxygen would have been difficult, that the former equation is correct. If the precipitation of one metal upon another be really due in great measure, as I believe it to be, to the affinity of the one metal for the other, the general result that I have arrived at, namely, that if the metal A can precipitate the metal B, the metal B will also precipitate the metal A, is sufficiently accounted for. This reciprocity, of course, will not be manifested when the tendency to form the salt of the one metal is very much greater than the tendency to form the salt of the other metal.

Note on the purity of the metals employed in the above-described experiments.

The pure silver was reduced from chloride of silver by fusion with carbonate of soda. The pure copper was precipitated electrolytically, upon a copper surface, by the current of a Daniell's cell. To obtain pure bismuth, nitrate of bismuth, after several crystallizations, was ignited, and the heated oxide reduced in a bulb-tube by a current of hydrogen gas. The hydrogen, prepared from the reaction of zinc and sulphuric acid, was passed successively through a solution of nitrate of silver, through a solution of hydrate of potash, and through oil of vitriol. 33·230 grains of oxide of bismuth, lost 3·445 grains. This result corresponds very closely with that obtained by Gmelin:—

		Calculated.	Lagerhjelm.	Gmelin.	Odling.
Bi . .	213	89·87	89·863	89·67	89·64
O . .	24	10·13	10·137	10·33	10·36

The pure lead was obtained from re-crystallized nitrate of lead. The salt was ignited and fused before the blowpipe with carbonate of soda. The pure tin was obtained electrolytically by immersing a bar of tin into two strata of liquid, the lower being a solution of crystallized stannous chloride, the upper being acidulated water. The pure antimony was obtained by incinerating re-crystallized tartar-emetic with carbonate of soda. The cadmium foil came into my hands as such. In its solution I was unable to detect the presence of zinc, or, with the exception of a very minute trace of iron, any other metal. The iron was employed only in the forms of commercial rolled iron and hard steel.