CXV.—*Solution and Diffusion of certain Metals and Alloys in Mercury.* (Second Paper.)

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IN a previous communication (Trans., 1896, **69**, 243), I gave the results of an examination of the solution and diffusion of bismuth, copper, lead, silver, tin, and zinc in mercury. The present paper contains the results of a similar investigation with aluminium, antimony, cadmium, magnesium, thallium, and a few alloys.

The method of investigation was the same as before; that is, to fill an upright vessel of uniform cross section with pure mercury, place on the free surface of the mercury a solid piece of the metal to be examined (freshly amalgamated at the surface of contact), and, after allowing the whole to remain a certain length of time in a place free from disturbances, and of fairly constant temperature, to take, through properly constructed side tubes at definite depths below the surface, samples of the mercury, and examine them for the foreign metals carried down by diffusion.

For a detailed description of the two classes of mercury tanks (glass and wooden) used, and of the method of drawing off the samples for analysis, reference is made to the previous paper. The cross sections of the mercury columns of the wooden tanks, A and B of the table, were each squares of 25 mm. on the side, whilst those of the glass tanks, C and D of the table, were circles 25 mm. in diameter. In all the experiments, the distance from the surface of the mercury to the first side tube was 25 mm.; this was also the distance from the first tube to the second, from the second to the third, from the third to the fourth, and from the fourth to the bottom of the tank.

Some difficulty was found in experimenting with aluminium, owing to the rapid oxidation of its amalgamated surface, which soon separated it from the mercury. However, after several fruitless trials of different kinds, it was found that one way to prevent this trouble was to cover the aluminium immediately after putting it on the mercury with soft petroleum vaseline that had been freed from water by boiling. At the end of six days, a large portion at least of the amalgamated surface was still in contact with the mercury, but, as shown in the table of results, the solution and diffusion was so slight that it was impossible to detect the aluminium 25 mm. from the surface.

In the case of antimony, the amount that went into solution, although it was distinctly present, was so exceedingly small, that it seemed best to report it as a mere trace.

It will be seen from the table that cadmium dissolves in mercury to a considerable extent, and diffuses through it quite readily. It seems from the results that no cadmium amalgam heavier than mercury (though cadmium is said to form such an amalgam) is obtained under these conditions, or, if obtained, that it is quickly changed to one lighter than mercury. The process of analysis was to volatilise most of the mercury, and to dissolve the remainder, rich in cadmium, in nitric acid, evaporate slowly to dryness in a platinum dish, then gently, and at last strongly, heat, thus getting rid of the oxide of mercury and leaving the oxide of cadmium, from which the percentage of cadmium in the original weighed sample of amalgam could be calculated.

The peculiar behaviour of magnesium amalgam led at first to a few disappointments, although the method finally adopted left but little to be desired. The amalgamation was obtained by placing the magnesium in contact with a small globule of mercury, and heating them until the latter began to volatilise quite freely. In this way a small amalgamated spot was obtained, which, by the gradual addition of more mercury, could readily be extended to any size desired, even at a temperature much lower than that at which the amalgamation began, although not (in open air) below that of boiling water. The amalgamated surface remained bright, and readily took up additional mercury so long as the temperature was kept up to or above 100° , but on cooling below this point it rapidly tarnished, and then refused further union with mercury. It was found that if a piece of amalgamated magnesium be left in the open air, it will slowly increase in bulk to several times its original size, meanwhile assuming a shape suggestive of some vegetable growth, the colour being anything, from a medium grey, to a dull or lustreless black approaching closely that of lamp-black. It is well known that magnesium amalgam acts violently on water, forming hydrogen and magnesium hydroxide, and it was found that the same action takes place in the air, unless absolutely dry, in which case there is no action. It is the hydrogen thus formed that causes the mass to swell up and assume a plant-like form. The dark colour is due to excessively finely divided mercury.

From the above, it is evident that success in the diffusion experiment depended on keeping all traces of moisture away from the amalgamated magnesium. It may be worth while to state that it was found that the amalgamated surface would remain bright indefinitely under melted paraffin, and that additional mercury would sink through the paraffin and adhere to this surface at once. However, the temperature at which solid paraffin melts excluded its use in the diffusion experiment. The substance used was semi-fluid vaseline

that had been well freed from moisture by boiling. Before the freshly amalgamated magnesium had cooled to 100° , it was placed in a bath of melted vaseline, and, when it had cooled to about the temperature of the room, it was transferred to the diffusion tank, where its union with the mercury was easily obtained; it was then covered with additional vaseline and left the desired length of time. It was also found necessary to boil the wooden rods (see description of apparatus in previous paper) used to close the side tube, in vaseline, because, when this was not done, the small amount of moisture in them acted on the amalgam and prevented it from running out when they were withdrawn.

Of course, the amalgam tarnished instantly when it was drawn out into the side tubes, but it was all washed out and digested for some time in warm dilute hydrochloric acid; in this way, all the magnesium was dissolved, and the pure mercury was then collected, dried, and weighed. The magnesium was determined in the usual way as pyrophosphate, and, from the data thus obtained, the percentage of magnesium in the original amalgam was calculated.

No trouble whatever was found in amalgamating thallium, but the tabulated results for it are probably too low: first, because it had all completely dissolved in the mercury before the samples were withdrawn, which was not the case with any other metal examined; and, secondly, because the method of separation from the mercury gave results which were probably somewhat low. The method was as follows: After most of the mercury had been separated by distillation, the remaining amalgam was dissolved in nitric acid and the mercury precipitated by sulphuretted hydrogen, and from the filtrate the thallium was separated as thallous iodide by the method given by Crookes. Sulphuretted hydrogen does not precipitate thallium when alone in a nitric acid solution, although a small amount of it may come down with the sulphide of mercury. At any rate, two test analyses were made in this way, and each gave results somewhat more than 3 per cent. too low. Want of time prevented a further examination of the above method of separating thallium and mercury, as well as a search for any other.

Several alloys were examined, and of these the alloy of approximately equal parts of lead and tin dissolves more readily, and the constituent metals diffuse more rapidly, than does either of them separately. The same seems true of the alloy of equal parts of cadmium and lead, but it is probably not true of the alloy of equal parts of cadmium and zinc, although this, too, dissolves and diffuses quite freely.

In the case of the above amalgams, the mercury was removed by distillation as far as was possible without loss of the dissolved metals

occurring. The residual lead and tin amalgam was then treated with nitric acid, which dissolved the lead and mercury, but left the tin in a form from which it was obtained as the oxide. To the filtrate containing the mercury and lead, sulphuric acid was added, and the lead estimated as sulphate in the usual way. The separation of the lead and cadmium from the remaining mercury and from each other was effected by dissolving them in nitric acid, evaporating to dryness, driving off the mercury by heat, and leaving the lead and cadmium as oxides; these were again dissolved in nitric acid, the lead precipitated as sulphate, and from the filtrate the cadmium was thrown down as sulphide. The amalgam of zinc and cadmium was dissolved in nitric acid, evaporated to dryness, and the mercury volatilised; the residual oxides of zinc and cadmium were then dissolved in nitric acid, from which the cadmium was obtained as sulphide; and on evaporating the filtrate to dryness and heating, the zinc was obtained as oxide.

One experiment was made with speculum metal, but it was not entirely satisfactory, owing to the fact that, after standing between seven and eight days, the tank began to leak, and continued to do so until about half the mercury had run out. However, careful examination failed to show a trace of copper or tin either in the portion which had run out or in that which still remained in the tank. Solution and diffusion in this case was certainly very slight, although the amalgamation was excellent.

As shown by the table, the alloy consisting of 90 per cent. of copper and 10 per cent. of tin gave a diffusion of copper only. The amount of copper found was just the same as if pure copper, instead of the alloy, had been used.

The behaviour of brass in this respect was also tried, and found to be very interesting. The sample used was made for the occasion from nearly equal parts, by weight, of electrolytically prepared copper and chemically pure zinc. The brass was cast and then cut open, so that the surface to be amalgamated should come from the interior. Although it amalgamated with the greatest ease, not a trace of either zinc or copper could be found at the end of fifteen days in any part of the mercury which was 3 mm., or more, from the brass. Of course there may be an exceedingly slow solution and diffusion of the brass, or of its constituents, and an experiment is now in progress to test this point.

The behaviour of brass suggested trying the diffusion of copper through a uniform zinc amalgam, the ratio of the mercury to the zinc being, approximately, 1000 to 1; the diffusion of copper through this amalgam, however, was sensibly the same as through pure mercury.

It will be noticed that, of the alloys used, those which dissolve and diffuse readily in mercury, namely, the alloys of lead and tin, of lead and cadmium, of cadmium and zinc, are all believed to be mere mixtures, whilst speculum metal and brass, which certainly do not dissolve and diffuse in mercury with anything like the ease with which the individual constituents do, are probably true chemical compounds. Possibly, the alloy of copper and tin that gave a diffusion of copper only consisted of a compound of copper and tin with an admixture of copper.

It would seem, from the behaviour of the alloys examined, that solution and diffusion in mercury may serve in many cases to distinguish between mere mixtures and true compounds, and, in the latter case, to determine when an excess of one of the constituents is present.

The results for magnesium, cadmium, and thallium are represented graphically by two sets of curves (p. 1684). Those to the left of the median line have for abscissæ the depths, in millimetres, below the surface of the points from which the samples were taken, and for ordinates the percentages of the metals found. The time, in days, of diffusion is marked on each of these curves. The other curves, those to the right, have for abscissæ the time, in days, of the diffusion, and for ordinates the percentages of the metals found; the depths, in millimetres, are marked on these curves. In the cases of magnesium and thallium, the curves to the right are drawn in part from analogy to the corresponding curves for other metals, and are necessarily imperfect, since only two points on them are known.

The extent to which a metal dissolves in mercury, that is, the percentage of it in the saturated solution, at the temperatures at which I worked; and the amount of it that will dissolve in a given time, when undisturbed, in a mercury column of infinite extent (a function of the coefficient of diffusion), seem to be in some measure functions of its position among the elements. Whether the relations in these respects among the elements be accidental, despite their regularity, or essential I do not pretend to judge, but simply call attention to the fact, hoping that they may suggest further work, since every relation between the elements, when once established, must give a clearer conception of them, and, perhaps ultimately of the nature of matter itself.

The metals used were selected chiefly with a view to the ease with which they amalgamate, but it will be noticed that, like mercury itself, they all belong to the uneven series of the Mendeléeff table. If we consider those metals that belong to the same group, it will be seen that the solution and diffusion increase with increase of atomic weight. Thus in Group I the solution and diffusion of copper are

less than those of silver, which in turn, from the results of Dudley, (*Proceedings of American Association for the Advancement of Science*, 1889), are less than those of gold (a saturated solution of gold in mercury contains about 0.06 per cent. gold). In Group II, the order of

increase in the magnitude of these results is given by the following order of the elements, namely: magnesium, zinc, cadmium, and mercury (considering mercury to dissolve in mercury) Group III gives the order aluminium, indium (examined as to solution only),

thallium. Group IV gives the order tin and lead. Group V gives the order arsenic (examined as to solution only), antimony, and bismuth.

Again, if we consider the different series, we find the greatest values belonging to the metals of the mercury group, and the further away, in respect to valency, a metal is from this group the less its solution and diffusion in mercury. Thus the values for magnesium are greater than those for aluminium. The values for copper are less than those for zinc which in turn are greater than those for arsenic. So too the values for silver are less than those for cadmium, from which the order of decrease is indium (probably), tin, and antimony. Indium amalgamates with the greatest ease, and certainly dissolves to a greater extent than tin, possibly to even a greater extent than cadmium, but I cannot speak definitely on this point as I had not enough indium at command to test this point fully. Finally, the values for gold are less than those of mercury, from which there is a decrease in the order of thallium, lead, and bismuth. These results are shown in the table of elements examined (p. 1691), the arrows pointing in the direction of increase in solubility and diffusion, with the possible exception of indium as explained above.

Attention should be called to the fact that Dr. Guthrie (*Phil. Mag.*, 1883, **16**, 321), obtained values for the solution and diffusion of sodium and potassium greater than my values for either copper or silver. This seems to be at variance with the law of increase of solution and diffusion with increase of atomic weight of elements of the same group—or rather of the same half of a Mendeléeff group. Possibly the law does not hold for sodium when compared with copper, silver, and gold, but it should be remembered that Dr. Guthrie worked with a sodium amalgam, whilst my work was done with solid pieces of the metals, and consequently a comparison can scarcely be made.

It may be worth while to state that those metals whose particles move through mercury with the greatest velocities, all belong to the first group. In my previous communication I called attention to the relatively great velocity of copper, and especially of silver; a small amount at least of sodium and potassium also moves through mercury with great velocity, as shown by some of Dr. Guthrie's (*ibid.*) experiments. At present I do not know with what velocity gold diffuses through mercury, though from the above facts it might be expected to diffuse very rapidly.

I trust that I shall be able, at an early date, to take this whole matter up in much greater detail, since all my results so far must be regarded as preliminary, although I hope they may serve to point

TABLE OF RESULTS.

Substance dissolved.	Time of diffusion.	Average temperature, in degrees C.	Depth of sample in millimetres.	Percentage of metal.	Tank	Remarks.
Aluminium.....	6 days	26.3°	25	nothing	D	
"	"	"	50	"	"	
"	"	"	75	"	"	
"	"	"	100	"	"	
Antimony.....	15 days	24.6°	10	trace	"	
"	"	"	25	"	"	Sample from (estimated) depth of 10 mm.
"	"	"	50	"	"	taken out by pipette.
"	"	"	75	"	"	
"	"	"	100	"	"	
Cadmium	1 day	29.7°	25	0.761	C	
"	"	"	50	0.020	"	
"	"	"	75	0.001	"	
"	"	"	100	nothing	"	
"	5 days	29.4°	25	2.952	"	
"	"	"	50	1.067	"	
"	"	"	75	0.262	"	
"	"	"	100	0.048	"	
"	10 days	27.4°	25	3.510	"	
"	"	"	50	1.835	"	
"	"	"	75	0.812	"	
"	"	"	100	0.312	"	
"	5 days	27.8°	25	0.132	D	
Magnesium.....	"	"	50	0.036	"	
"	"	"	75	0.006	"	
"	"	"	100	nothing	"	
"	10 days	30.7°	25	0.238	"	
"	"	"	50	0.130	"	
"	"	"	75	0.071	"	
"	"	"	100	0.028	"	

TABLE OF RESULTS—*continued*.

Substance dissolved.	Time of diffusion.	Average temperature in degrees C.	Depth of sample in millimetres.	Percentage of metal.	Tank.	Remarks.
Thallium.....	1 day	31·5°	25	1·442	C	Thallium completely dissolved. Percentage of thallium probably too low.
"	"	"	50	trace	"	"
"	"	"	75	nothing	"	"
"	"	"	100	"	"	"
"	3 days	24·8°	25	3·674	"	Thallium completely dissolved. Percentage of thallium probably too low.
"	"	"	50	0·633	"	"
"	"	"	75	0·046	"	"
"	"	"	100	nothing	"	"
Alloy (Pb and Sn).						
Pb.....	5 days	31·2°	25	0·859	B	Percentage of tin in alloy 52, of lead 48.
"	"	"	50	0·193	"	"
"	"	"	75	0·024	"	"
"	"	"	100	trace	"	"
Alloy (Pb and Sn).						
Sn.....	"	"	25	0·564	"	Tin and lead both determined from same sample of amalgam.
"	"	"	50	0·158	"	"
"	"	"	75	0·033	"	"
"	"	"	100	trace	"	"
Alloy (Pb and Sn).						
Pb.....	10 days	26·5°	25	0·954	"	Percentage of tin in alloy 52, of lead 48.
"	"	"	50	0·392	"	"
"	"	"	75	0·113	"	"
"	"	"	100	0·015	"	"

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TABLE OF RESULTS—continued.

Substance dissolved.	Time of diffusion.	Average temperature in degrees C.	Depth of sample in millimetres.	Percentage of metal.	Tank.	Remarks.
Alloy (Pb and Sn).						
Sn	10 days	26.5°	25	0.642	B	Tin and lead both determined from same sample of amalgam.
"	"	"	50	0.272	"	
"	"	"	75	0.102	"	
"	"	"	100	0.017	"	
Alloy (Pb and Cd).						
Pb	3 days	26.3°	25	0.530	C	Percentage of lead in alloy 50, of cadmium 50.
"	"	"	50	0.046	"	
"	"	"	75	nothing	"	
"	"	"	100	"	"	
Alloy (Pb and Cd).						
Cd	"	"	25	1.929	"	Cadmium and lead both determined from same sample of amalgam.
"	"	"	50	0.385	"	
"	"	"	75	0.048	"	
"	"	"	100	0.002	"	
Alloy (Cd and Zn).						
Cd	"	"	25	1.357	B	Percentage of cadmium in alloy 54, of zinc 46.
"	"	"	50	0.286	"	
"	"	"	75	0.022	"	
"	"	"	100	nothing	"	
Alloy (Cd and Zn).						
Zn	"	"	25	0.658	"	Zinc and cadmium both determined from same sample of amalgam.
"	"	"	50	0.147	"	
"	"	"	75	0.023	"	
"	"	"	100	nothing	"	

TABLE OF RESULTS—continued.

Substance dissolved.	Time of diffusion.	Average temperature in degrees C.	Depth of sample in millimetres.	Percentage of metal.	Tank.	Remarks.
Alloy (Cu and Sn).						
Cu.....	10 days	26·2°	25	0·003	C	Percentage of copper in alloy 90, of tin 10.
".....	"	"	50	0·003	"	"
".....	"	"	75	0·003	"	"
".....	"	"	100	0·003	"	"
Alloy (Cu and Sn).						
Sn.....	"	"	25	nothing	"	Copper and tin both determined from same sample of amalgam.
".....	"	"	50	"	"	"
".....	"	"	75	"	"	"
".....	"	"	100	"	"	"
Alloy (Cu and Sn).						
Speculum metal.....	7—8 days	24·5°	—	nothing	B	Not satisfactory owing to accident, but no evidence of diffusion of either tin or copper.
Alloy (Cu and Zn).						
Cu.....	10 days	30·0°	25	nothing	A	Percentage of copper in alloy 53, of zinc 47.
".....	"	"	50	"	"	"
".....	"	"	75	"	"	"
".....	"	"	100	"	"	"
Alloy (Cu and Zn).						
Zn.....	10 days	30·0°	25	nothing	A	Copper and zinc both determined from same sample of amalgam.
".....	"	"	50	"	"	"
".....	"	"	75	"	"	"
".....	"	"	100	"	"	"

TABLE OF RESULTS—*continued*.

Substance dissolved.	Time of diffusion.	Average temperature in degrees C.	Depth of sample in millimetres.	Percentage of metal.	Tank.	Remarks.
Alloy (Cu and Zn).	15 days	24.6°	3	"	"	Percentage of copper in alloy 53, of zinc 47. Samples from (estimated) depths of 3 and 10 mm. taken out by pipette.
"	"	"	10	"	"	
"	"	"	25	"	"	
"	"	"	50	"	"	
"	"	"	75	"	"	
"	"	"	100	"	"	
Alloy (Cu and Zn).	"	"	3	"	"	Copper and zinc both determined from same sample of amalgam.
Zn	"	"	10	"	"	
"	"	"	25	"	"	
"	"	"	50	"	"	
"	"	"	75	"	"	
"	"	"	100	"	"	
Copper.	"	"	"	"	"	Percentage of mercury in amalgam used 99.9, of zinc 0.1 approximately.
Cu in zinc amalgam.	4 days	24.5°	25	trace	C	
"	"	"	50	"	"	
"	"	"	75	"	"	
"	"	"	100	"	"	

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out lines of further investigation and even to indicate more or less clearly in some cases the results that may be anticipated.

TABLE of *Elements examined, showing Relative Extent of their Solution and Diffusion in Mercury.*

Series.	Group I.	Group II.	Group III.	Group IV.	Group V.
3		Mg ↓	←Al ↓		
5	Cu→ ↓	Zn ↓			←As ↓
7	Ag→ ↓	Cd ↓	←In ↓	←Sn ↓	←Sb ↓
11	Au→	Hg	←Tl	←Pb	←Bi

This investigation was originally suggested to me by Dr. J. W. Mallet, of the University of Virginia, and the results of the present communication were obtained there under his supervision during the summer of 1896. In closing I wish to thank him for his constant interest in this work and for his kind and valuable assistance.