XI.—*The Freezing Point of Triple Alloys.*

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Gold and Cadmium.

IN the Chemical Society's Journal (Trans., 1891, **59**, 936), we described the peculiar fluctuations in the freezing point of mixtures of gold and cadmium dissolved in tin, and we showed that many of the

effects could be explained by the assumption that the two metals combine to form a compound of the formula AuCd .

This substance we afterwards obtained in a pure state (Trans., 1892, 61, 914), and we have since found that the behaviour of these two metals to each other is substantially the same, whether they are dissolved in tin, bismuth, thallium, or lead.

From the curves and tables now given, it will be seen that if we make a solution of either gold or cadmium in any of the above-mentioned solvents, and then add doses of the complementary metal, cadmium or gold respectively, the same phenomena repeat themselves. That is to say, the addition of the third metal sometimes causes a small further fall in the freezing point, but, as more of this metal is added, the freezing point begins to rise, and reaches a maximum when an equal number of atomic weights of gold and cadmium have been added.

This maximum freezing point is the same whether gold or cadmium is added first, and is independent of the concentration,* so long as we observe the condition of maintaining an equal number of atoms of gold and cadmium in the mixture.

After the maximum freezing point has been reached, a further addition of either metal causes a fall, but, as we see in the curve with thallium as solvent, the maximum freezing point can be recovered by adding a sufficient amount of the complementary metal.

Whatever be the explanation of these phenomena, we here see that the reaction between the two metals is remarkably independent of the nature of the solvent. As the new solvents give results so similar to those recorded in our previous paper, where tin was the solvent, we feel no doubt that the cause is the same, namely, the formation and partial precipitation of the compound AuCd , and that this substance exists in solution in equilibrium with free gold and cadmium, *whatever be the solvent*.

It is seldom possible to study the formation of the same compound in so many solvents, and the uniformity of the results appears strongly to bear out the view that solution in itself is a physical, rather than a chemical, action.

Silver and Cadmium.

The behaviour of silver and cadmium, when dissolved together, is recorded in the Tables V—VIII (pp. 71—73) and Figs. 5—8† (p. 68). It will be seen that these two metals produce in the freezing point of the solvent changes very similar to those caused by gold and cadmium. In each case, the addition of the third metal causes a rise, which reaches a maximum value and then declines as more of this metal is added.

* The maximum is not reached in very dilute solutions.

† See "Explanation of the Charts," p. 74.

Although we have not much experimental proof, yet we have no doubt that, as with gold-cadmium, this maximum freezing point will turn out to be constant for each solvent, independent of the absolute amounts of silver and cadmium present, but reached when the ratio of these two attains a certain value. In tin or lead, this maximum is reached when the ratio of the two metals is exactly $2\text{Ag}:\text{Cd}$. In thallium, the ratio is nearly the same, and we think that experimental errors would account for the discrepancy. In bismuth, the ratio at the highest point is not far from $4\text{Ag}:\text{Cd}$. The experimental error is probably small in the bismuth series, but, without further trial, we do not feel certain that this ratio would be maintained at other concentrations.

TABLE I.—*Cadmium and Gold in 400 grams of Lead.*

Total weight of gold present.	Total weight of cadmium present.	Atoms of gold per 100 of lead.	Atoms of cadmium per 100 of lead.	Freezing point of solution.
0	0	0	0	327.60°
"	0.188	"	0.087	327.24
"	0.407	"	0.188	326.85
"	0.942	"	0.435	325.80
"	1.950	"	0.900	323.86
"	4.264	"	1.967	319.62
"	6.624	"	3.057	315.48
"	10.634	"	4.906	308.76
0.985	"	0.258	"	310.04*
2.083	"	0.546	"	312.00
3.037	"	0.797	"	313.44
5.089	"	1.335	"	314.60
5.717	"	1.500	"	315.10
7.021	"	1.842	"	316.05
9.353	"	2.453	"	317.25
14.041	"	3.683	"	318.35
18.704	"	4.906	"	318.55
21.631	"	5.674	"	316.91
25.914	"	6.797	"	312.40

* As soon as the first portions of gold were added, a grating of the stirrer was noticed, and other proofs of a precipitate which rapidly increased. Much precipitate was found in the crucible at the termination of the experiment.

If we compare together the curves for gold-cadmium, and silver-cadmium, in bismuth, and then compare them with all the others, we shall see that these two stand somewhat apart. We do not yet know whether this is due to the specific action of bismuth as a solvent, or to a cause of experimental error, which we have, hitherto, failed to detect.

Curve 5 of cadmium added to a saturated solution of silver in tin is singularly like the saturated gold-cadmium curves of our previous paper: the initial fall caused by the cadmium, followed by what may

be a short flat, is to be seen, also, in the gold-cadmium curves. We have traced experimentally a 3-atom silver and cadmium curve in tin, where, just as in the 3-atom gold-cadmium curves, there is no maximum freezing point. This curve is not given in the present paper.

TABLE II.—*Gold and Cadmium in 400 grams of Lead.*

Total weight of gold present.	Total weight of cadmium present.	Atoms of gold per 100 of lead.	Atoms of cadmium per 100 of lead.	Freezing point of solution.
0	0	0	0	327·64°
0·322	„	0·085	„	327·10
0·632	„	0·166	„	326·54
1·742	„	0·457	„	324·70
5·417	„	1·421	„	318·45
9·451	„	2·479	„	311·61
12·553	„	3·292	„	306·44
15·251	„	4·000	„	301·84
„	0·159	„	0·073	301·77
„	0·441	„	0·204	301·57
„	0·730	„	0·337	302·53
„	1·083	„	0·500	303·69
„	1·756	„	0·810	305·51
„	3·345	„	1·543	309·62
„	5·418	„	2·500	314·13
„	6·630	„	3·059	316·40
„	7·675	„	3·541	317·72
„	8·666	„	4·000	318·54
„	9·784	„	4·514	318·78
„	11·241	„	5·186	318·47
„	13·364	„	6·165	317·08
„	16·408	„	7·570	315·46
„	18·801	„	8·675	314·90
„	21·463	„	9·903	314·20

A mass of crystalline precipitate was found at the termination of the experiment.

In Series 6 and 8, silver was again added from the point X, and produced, as we expected a rise.

All these curves contain details that we cannot interpret, but we are disposed to explain the general character of 5, 6, and 7 by assuming that a sparingly soluble compound, Ag_2Cd ,* is formed, which can only exist in the presence of free silver and cadmium. Much of what was said in our paper on triple alloys of gold, cadmium, and tin (*loc. cit.*) would then be applicable. The only point we will here consider is the position of the summit C.

Because the summit C is reached at a concentration of $2\text{Ag}:\text{Cd}$, we are hardly entitled to conclude at once that the compound Ag_2Cd

* Our attempts to isolate this compound in the same way as AuCd have so far failed.

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has been formed. But we can arrive at this conclusion more legitimately in the following manner.

TABLE III.—*Gold and Cadmium in Bismuth.*

Total weight of bismuth present.	Total weight of gold present.	Total weight of cadmium present.	Atoms of gold per 100 of bismuth.	Atoms of cadmium per 100 of bismuth.	Freezing point of solution.
350	0	0	0	0	267·54°
365	2·252	"	0·651	"	266·24
380	4·826	"	1·340	"	264·92
395	9·621	"	2·569	"	262·52
410	14·823	"	3·813	"	260·03
425	20·152	"	5·001	"	257·88
"	"	0·115	"	0·05	258·20
"	"	0·227	"	0·10	258·39
"	"	0·467	"	0·204	258·96
"	"	0·936	"	0·408	260·00
"	"	1·884	"	0·822	261·67
"	"	2·917	"	1·273	263·11
"	"	3·903	"	1·704	263·90
"	"	4·913	"	2·145	263·99
"	"	5·207	"	2·274	263·98
"	"	5·720	"	2·498	263·99*
"	"	6·630	"	2·895	264·16
"	"	7·186	"	3·137	264·36
"	"	7·677	"	3·352	264·81
"	"	8·079	"	3·528	265·01
"	"	8·396	"	3·666	265·15
"	"	8·768	"	3·828	265·39
"	"	360	"	4·087	265·81
"	"	979	"	4·357	266·15
"	"	577	"	4·617	266·30
"	"	11·238	"	4·906	{ 266·35
"	"	11·801	"	5·152	{ 266·49†
"	"	12·332	"	5·385	266·29
"	"	13·199	"	5·763	266·00
"	"	14·204	"	6·201	265·64
"	"	15·207	"	6·201	265·10
"	"	16·376	"	6·640	264·30
"	"	17·628	"	7·150	263·43
"	"	19·044	"	7·696	262·46
"	"	20·639	"	8·314	261·41
"	"	22·274	"	9·011	260·35
"	"	23·594	"	9·724	259·00
"	"	25·622	"	10·30	258·05
"	"	27·760	"	11·19	256·66‡
"	"	29·590	"	12·12	255·20
"	"	33·954	"	12·92	254·17
"	"		"	14·825	252·60

* A precipitate here formed.

† Took out thermometer and thoroughly mixed precipitate and liquid.

‡ The precipitate is certainly disappearing.

TABLE IV.—*Cadmium and Gold in 60·34 grams of Thallium.*

Geissler Thermometer.

Total weight of gold present.	Total weight of cadmium present.	Atoms of gold per 100 of thallium.	Atoms of cadmium per 100 of thallium.	Freezing point of solution.
0	0	0	0	301·67°
"	0·104	"	0·312	300·18
"	0·201	"	0·604	298·90
"	0·517	"	1·557	294·86
"	0·998	"	3·006	288·10
"	1·328	"	4·000	284·52*
"	"	"	"	285·42*
0·078	"	0·134	"	284·97
0·408	"	0·700	"	287·28
0·728	"	1·250	"	289·11
1·051	"	1·804	"	291·07
1·409	"	2·419	"	293·16
1·854	"	3·183	"	294·68
2·234	"	3·835	"	294·77
2·514	"	4·316	"	294·29
3·013	"	5·172	"	291·17
3·627	"	6·226	"	285·69
"	1·999	"	6·003	294·40
"	2·046	"	6·166	294·53
"	2·129	"	6·416	294·86
"	2·229	"	6·714	294·66
"	2·511	"	7·568	293·37

* Between these readings, there was an interval of two days, and the block was strongly heated during a part of the time. The discrepancy is probably due to two causes, a rise in the zero of the thermometer and, perhaps, some oxidation of the cadmium.

Suppose that the compound Ag_mCd_n is being formed, but that it can only exist in the presence of free silver and cadmium. Then, if we have present in solution x atoms of free silver, y atoms of free cadmium, and z molecules of the compound Ag_mCd_n , the theories of chemical equilibrium accepted at present indicate that x , y , and z should satisfy the equation $x^m y^n = \kappa z$, where κ is a constant so long as the temperature does not vary much.

Let us consider only that part of the curve where the liquid is saturated with the compound; then, for this part of the curve, z is constant. By adding silver or cadmium, we can vary x and y , but only subject to the condition that $x^m y^n$ is constant.

Now, a maximum freezing point that is a summit C on the curve corresponds to a minimum number of molecules in solution. That is to say, at C we must have $x + y + z$ a minimum, or as z is con-

stant, we must have $x + y$ a minimum subject to the condition $x^m y^n$ constant.

This leads at once to the result that at the summit C the relation between x and y is

$$my = nx.$$

Now, if a and c are the numbers of atoms of silver and cadmium that have been added to the mixture, and P the number of molecules of silver-cadmium that has been formed, then

$$a = mP + x,$$

$$c = nP + y,$$

and multiplying by n and m and subtracting, we see that

$$na = mc$$

or,

$$a : c = m : n.$$

TABLE V.—*Silver and Cadmium in 300 grams of Tin.*

Total weight of silver present.	Total weight of cadmium present.	Atoms of silver per 100 of tin.	Atoms of cadmium per 100 of tin.	Freezing point of solution.
0	0	0	0	231.49°
5.478	"	2	"	225.95
10.956	"	4	"	221.12
13.695	"	5	"	221.04
"	0.285	"	0.1	220.89
"	0.854	"	0.3	220.60
"	1.424	"	0.5	220.33
"	1.993	"	0.7	219.57
"	2.562	"	0.9	219.56
"	3.132	"	1.1	219.64
"	3.701	"	1.3	219.73
"	4.270	"	1.5	219.80
"	4.840	"	1.7	219.84
"	5.470	"	2.1	219.93
"	7.118	"	2.5	219.98
"	8.256	"	2.9	219.97
"	9.395	"	3.3	219.93
"	10.534	"	3.7	219.86
"	11.673	"	4.1	219.77
"	13.950	"	4.9	219.51
"	16.223	"	5.7	219.16
"	19.075	"	6.7	218.68
"	21.922	"	7.7	218.25
"	24.769	"	8.7	218.00
"	25.908	"	9.1	218.22
"	26.477	"	9.3	218.12
"	27.901	"	9.8	217.89
"	29.324	"	10.3	217.62
"	30.748	"	10.8	217.35
"	33.595	"	11.8	216.67
"	36.442	"	12.8	216.02

Therefore the summit will always be reached when the quantities of the two metals added are in the ratio given by the formula of the compound formed. In the case of silver and cadmium, we find that in the solvents tin, thallium, and lead the body formed is Ag_2Cd , whilst in bismuth there is, perhaps, the body Ag_4Cd . In the main, we see that the reaction between silver and cadmium is, like that of gold and cadmium, independent of the nature of the solvent.

TABLE VI.—*Silver in 61·18 grams of Thallium, and then Cadmium added.**

Total weight of silver present.	Total weight of cadmium present.	Atoms of silver per 100 of thallium.	Atoms of cadmium per 100 of thallium.	Freezing point of solution.
0	0	0	0	301·93°
1·326	"	4·1	"	288·10†
"	0·140	"	0·417	290·19
"	0·272	"	0·810	292·04
"	0·424	"	1·263	293·10
"	0·515	"	1·534	293·24
"	0·569	"	1·695	293·27
"	0·602	"	1·793	293·28
"	0·662	"	1·971	293·18
"	0·702	"	2·09	293·08
"	0·969	"	2·886	291·86
1·493	"	4·615	"	292·29
1·598	"	4·940	"	292·48
1·681	"	5·196	"	292·81
1·739	"	5·375	"	292·76
1·821	"	5·628	"	292·86
1·889	"	5·838	"	292·97
1·967	"	6·080	"	292·99
2·060	"	6·367	"	293·04
2·165	"	6·692	"	293·06
4·165	"	12·875	"	293·09

* This series, like all the thallium experiments, was carried out on too small a scale for accurate results.

† More than saturated.

TABLE VII.—*Silver and Cadmium in 400 grams of Lead.*

Total weight of silver present.	Total weight of cadmium present.	Atoms of silver per 100 of lead.	Atoms of cadmium per 100 of lead.	Freezing point of solution.
0	0	0	0	327·60°
0·167	"	0·08	"	327·18
0·687	"	0·329	"	325·62
1·891	"	0·906	"	322·18
3·907	"	1·872	"	316·70
7·149	"	3·425	"	308·64

TABLE VII.—*continued.*

Total weight of silver present.	Total weight of cadmium present.	Atoms of silver per 100 of lead.	Atoms of cadmium per 100 of lead.	Freezing point of solution.
10·440	0	5·002	0	303·06°
12·528	"	6·002	"	303·15
"	0·862	"	0·378	306·62
"	1·404	"	0·648	308·67
"	1·934	"	0·892	310·32
"	2·486	"	1·147	311·66
"	3·502	"	1·616	313·55
"	4·576	"	2·112	314·99
"	6·275	"	2·895	315·75
"	6·771	"	3·125	315·79
"	7·554	"	3·486	315·70
"	8·492	"	3·918	315·39
"	9·470	"	4·370	314·98
"	11·603	"	5·354	313·48
"	14·668	"	6·767	311·99
"	18·634	"	8·598	311·13
"	20·772	"	9·586	311·33
"	24·977	"	11·525	310·30

TABLE VIII.—*Silver and Cadmium in Bismuth.*

Thermometer, Hicks' 12 A.

Total weight of bismuth present.	Total weight of silver present.	Total weight of cadmium present.	Atoms of silver per 100 of bismuth.	Atoms of cadmium per 100 of bismuth.	Freezing point of solution.
350	0	0	0	0	267·87°
370	3·838	"	2	"	263·84
390	7·676	"	3·795	"	260·86
410	10·635	"	5	"	259·53
"	"	0·553	"	0·25	260·74
"	"	1·105	"	0·5	261·42
"	"	1·658	"	0·75	261·85
"	"	2·210	"	1·00	262·16
"	"	2·763	"	1·25	262·33
"	"	3·315	"	1·50	262·42
"	"	3·867	"	1·75	262·44
"	"	4·420	"	2·00	262·41
"	"	4·973	"	2·25	262·34
"	"	5·525	"	2·5	262·20
"	"	6·078	"	2·75	262·04
"	"	7·183	"	3·25	261·61
"	"	8·289	"	3·75	261·19
"	"	9·392	"	4·25	260·67
"	"	10·497	"	4·75	260·05
"	"	11·603	"	5·25	259·43
"	"	13·812	"	6·25	258·63
"	"	16·023	"	7·25	256·55
"	"	20·443	"	9·25	253·50
"	"	24·863	"	11·25	250·60
"	14·881	"	"	"	252·53

EXPLANATION OF THE CHARTS.

The curves give the freezing points of solutions of gold with cadmium, and of silver with cadmium in different solvents.

Each black dot records the concentration and freezing point of a particular mixture. In every case, 100 atomic weights of solvent are assumed to be present. The horizontal distance of a point measured from the left records the total number of atomic weights of foreign metals, other than the solvent present, each square corresponding to one atomic weight.

The vertical distance of a point from the level of the first point on the curve records the fall or rise in the freezing point, each square being one 1° centigrade.

Along the thin line, cadmium is being added; along the thick line, gold or silver.

In Curve 4, we start with a mixture of 4 atoms of cadmium and 100 atoms of thallium; in other cases the curve begins with the pure solvent.

The point A marks where we begin to add the third metal. C is the summit of the curve. The point X marks where we begin again to add the second metal.

The tables are numbered to correspond with the curves. In the tables all weights are in grams, and temperatures in degrees centigrade.

Aluminium and Gold dissolved in Tin.

In striking contrast to the foregoing curves, which owe their character to the partial dissociation of the compound formed, we now give curves showing the freezing points of alloys made by dissolving aluminium in tin and then adding gold. Fig. 9 commences by the addition of aluminium to tin. We see that the aluminium produces an atomic fall of 1.4° , which is half the normal fall produced by other metals in this solvent. This, as we suggested in our previous paper (Trans., 1890, 57, 392), may be explained by assuming that the metal is present in diatomic molecules as Al_2 .

The addition of aluminium was ended at A, almost exactly at the point of saturation of the tin. Gold was then added, as recorded by the thick line. It at once produced a rise, the maximum freezing point C, which was identical with that of *pure tin*, being reached with 2 atoms of aluminium and 0.9 atom of gold, or, in other words with a concentration of $\text{Al}_2\text{Au}_{0.9}$. A further addition of gold produced a fall, which, reckoned from the highest point, is exactly that of gold in pure tin.

In Fig. 10, a total quantity of 4 atoms of aluminium was added up to the point A, saturation occurring at 2 atoms. The first portions of gold produced no effect on the freezing point of the mixture until 0.95 atom had been added, to the point B, but on adding more there was a rapid rise; the highest point, again identical with the freezing point of pure tin, being reached with 1.9 atoms of gold. When we add more gold from this point C, we seem to be starting afresh with a solution of pure tin, and we get the atomic fall 2.86° , which is identical with our old numbers.

The obvious explanation of these results is, that the gold and

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aluminium form a stable insoluble compound of the formula AuAl_2 , the gold completely removing the aluminium from solution. There is no curved part to the locus of the freezing points, inasmuch as free gold and aluminium cannot exist together in solution.

That rather less gold is needed to reach C in both figures, or B in Fig. 10, than the amount corresponding to the compound AuAl_2 , may fairly be put down to the fact that all the loss by oxidation in making the alloys, and probably all the original impurity, falls on the aluminium.

The fact that in Fig. 10 the gold from A to B produced no effect agrees very well with our view that the aluminium flat up to A is due to saturation of the tin with aluminium. If this be so, then, although the first quantities of gold up to B precipitate aluminium, yet some of the excess will come into solution and the freezing point will not alter. But by the time 1 atom of gold has been added, the excess of aluminium will have been used up to form the body Al_2Au , and further addition of gold must decrease the aluminium in solution, and so produce a rise in the freezing point.

The precipitate AuAl_2 is, no doubt, the purple alloy discovered and examined by Professor Roberts-Austen. He finds for his alloy the formula $\text{Al}_2\text{Au}_{0.98}$. Our values deduced from the freezing point curves are:—

At C, Fig. 9	$\text{Al}_2\text{Au}_{0.9}$
" " 10	$\text{Al}_2\text{Au}_{0.95}$
At B, " 10	$\text{Al}_2\text{Au}_{0.95}$

TABLE IX.—*Aluminium and Gold in Tin.*

Thermometer, Hicks' No. 12.

Total weight of tin present.	Total weight of aluminium present	Total weight of gold present.	Atoms of aluminium per 100 of tin.	Atoms of gold per 100 of tin.	Freezing point of solution.
300	0	0	0	0	231.55°
310	0.355	"	0.5	"	230.90
320	1.101	"	1.5	"	229.42
350	1.605	"	0.2	"	228.67
"	"	0.584	"	0.1	228.97
"	"	1.169	"	0.2	229.29
"	"	2.338	"	0.4	229.90
"	"	3.506	"	0.6	230.55
"	"	4.675	"	0.8	231.20
"	"	5.260	"	0.9	231.55
"	"	5.844	"	1.0	231.34
"	"	7.013	"	1.2	230.76
"	"	9.351	"	1.6	229.61

Tables IX and X give the experimental numbers from which the aluminium curves were drawn.

TABLE X.—*Aluminium and Gold in Tin.*

Thermometer, Hicks' No. 11.

Total weight of tin present.	Total weight of aluminium present.	Total weight of gold present.	Atoms of aluminium per 100 of tin.	Atoms of gold per 100 of tin.	Freezing point of solution.
250	0	0	0	0	231·65°
275	1·261	„	2·0	„	228·72
280	1·605	„	2·5	„	228·69
300	2·752	„	4·0	„	228·70
„	„	2·506	„	0·5	228·73
„	„	3·750	„	0·75	228·71
„	„	4·260	„	0·85	228·73
„	„	4·761	„	0·95	228·74
„	„	5·263	„	1·05	229·07
„	„	7·769	„	1·55	230·57
„	„	9·022	„	1·8	231·35
„	„	9·523	„	1·9	231·59
„	„	10·024	„	2·0	231·29
„	„	12·530	„	2·5	229·86

*Sidney College,
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