LXXXII.—*On the Freezing Points of Triple Alloys of Gold, Cadmium, and Tin.*

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IN previous communications to the Society (Proc., No. 65, p. 41; Trans., 1889, **55**, 667; 1890, **57**, 376) we described experiments on the freezing points of alloys of two metals. In the course of subsequent work, of which a brief abstract has been published (Proc., No. 88, p. 158), we found that when several metals are in solution together their effects

in lowering the freezing point of the solvent metal were independent of each other's presence, so long as the solution remained dilute. The present communication contains the results of experiments on more concentrated solutions, containing gold and cadmium, dissolved in tin. In these cases, as will be seen, the phenomena are of an entirely different character, and there is no simple relation between the quantity of foreign metal present and the fall of the freezing point.

The experiments were made as described in the paper on tin solutions (*Trans.*, 1890, **57**, 376), in the axis of thick iron cylinders, except that to ensure a greater accuracy the thermometers were graduated* every 10 mm. against a platinum thermometer, as described by Griffiths (*B.A. Reports*, 1890), and the results, mapped on a large scale, were used for determining temperatures.

In order, as far as possible, to protect the long stem of the thermometer from currents of heated air, the top of the iron block was covered with a plate of asbestos, 14 inches square. The same precaution had been previously taken when determining the fixed points on the thermometer. When working with concentrated solutions, we found it necessary to drop in small nuclei of previously solidified alloy, in order to prevent too great surfusion; without this precaution we were unable to obtain concordant results.

The course of an experiment was as follows:—300 grams of pure tin was placed in the block, and the freezing point taken several times with great care; weighed quantities of one of the foreign metals were then added in successive doses, until the requisite quantity was present, the freezing point being determined after each addition, vigorous automatic stirring being maintained. To this solution, the second foreign metal was added in the same way. Since both gold and cadmium dissolve in tin with great ease, it was found sufficient to drop the weighed quantities of gold and cadmium directly into the block. The results were mapped on a large scale, by marking off the number of atoms of foreign metal present per 100 atoms of tin, horizontally, from left to right, and the temperatures of the freezing point vertically downwards. The curves thus obtained, showing the connection between the composition of the alloy and the freezing temperature, are reproduced on a small scale with the present paper. In the tables which accompany this paper, the actual experimental results are given.

The curves obtained in this way present certain similarities which allow of their being classified into three types:—Type I, when the

* We were greatly assisted in the work of graduating the thermometer by Mr. G. M. Clark, of Sidney College, and also by Mr. E. H. Griffiths, and we wish here to record our best thanks to them.

first metal (Au or Cd) is not present to the extent of more than 3 atoms per 100 atoms of tin.*

Type II, when the first metal is present to the extent of more than 3 atoms, but does not saturate the liquid.

Type III, when more of the first metal has been added to the tin than is required to produce the *eutectic* or saturated alloy.

Curves of Type I may be diagrammatically represented thus—

TYPE I.

Vertical distances are falls in temperature; horizontal distances, atoms of Au or Cd.

AB = fall caused by gold.
BCD = „ „ cadmium.

Curves of this type have only been produced by adding gold first, and then cadmium. It will be seen that each addition of cadmium produces a further effect, but the magnitude of this effect varies very much from place to place, being a minimum, or, perhaps, *nil*, at the points of inflexion. (See Plate 1, p. 966, and Tables I and II.)

The 3-atom gold curve, Table III, and Plate 1, shows the transition from a curve of Type I to one of Type II.

* In future, we propose to speak simply of the *number of atoms* of foreign metal present. By this we mean the number of foreign atoms per 100 atoms of tin.

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TABLE I.—300 grams of Tin taken as Solvent.

Grams of Au added in succession.	Grams of Cd added in succession.	Total weight of Au or Cd added.	Freezing point of solution.	Atoms of Au or Cd per 100 atoms of tin.	Falls in °C. D.	Remarks.
— 10·026	— —	— 10·026	(tin 231·42) 225·73	— 2·0	— 5·69	*
Now added Cadmium.						
—	1·374	1·374	224·68	0·483	6·74	No infusible residue.
—	1·539	2·913	223·66	1·024	7·76	
—	3·790	6·703	220·94	2·355	10·48	

TABLE II.—300 grams of Tin taken as Solvent.

Grams of Au added in succession.	Grams of Cd added in succession.	Total weight of Au or Cd added.	Freezing point of solution.	Atoms of Au or Cd per 100 atoms of tin.	Falls in ° C. D.	Remarks.
— 1·650	— —	— 1·650	(tin 231·42) 230·55	— 0·3292	— 0·87	
Now added Cadmium.						
—	0·308	0·308	230·27	0·1082	1·15	Nuclei of alloy used in all these experiments.
—	0·277	0·585	230·05	0·2055	1·37	
—	0·308	0·893	229·78	0·3137	1·64	
—	0·2782	1·171	229·55	0·4114	1·87	
—	0·3980	1·569	229·23	0·5512	2·19	
—	0·3890	1·958	228·91	0·6878	2·51	
—	0·902	2·86	228·17	1·0045	3·25	
—	1·238	4·098	227·11	1·439	4·31	
Now added Gold.						
4·737	—	6·387	224·72	0·9451	6·70	
3·639	—	10·026	222·77	2·00	8·65	

* As a general rule, each series of experiments was carried out with the thermometer known to us as Hicks' No. 10. When the temperature fell below the range of this thermometer, we used Hicks' No. 9.

TABLE II—*continued*.

Grams of Au added in succession.	Grams of Cd added in succession.	Total weight of Au or Cd added.	Freezing point of solution.	Atoms of Au or Cd per 100 atoms of tin.	Falls in ° C. D.	Remarks.
Now added Cadmium.						
—	3·880	7·978	220·11	2·802	11·31	
—	1·535	9·513	219·01	3·341	12·41	
—	1·449	10·962	218·1	3·85	13·32	
—	1·424	12·386	217·33	4·35	14·09	
—	1·102	13·488	216·76	4·73	14·66	
—	1·375	14·863	216·04	5·220	15·38	
—	1·796	16·659	215·21	5·851	16·21	
—	3·449	20·108	214·41	7·062	17·01	
—	1·816	21·924	213·87	7·70	17·55	
—	1·109	23·033	213·41	8·09	18·01	
—	2·135	25·168	212·45	8·839	18·97	Changed to Hicks' No. 9.
—	2·414	27·582	211·48	9·687	19·94	
—	2·831	30·413	210·73	10·681	20·69	
—	2·843	33·256	210·42	11·679	21·00	
—	2·712	35·968	210·24	12·631	21·18	
—	3·062	39·03	209·72	13·706	21·70	
—	3·168	42·198	208·91	14·82	22·51	
—	4·143	46·341	207·76	16·27	23·66	
—	7·915	54·256	205·2	19·05	26·22	

Curves of the second type, when the first metal is present in quantity insufficient to saturate the liquid, are represented by the broken line OABCDE, where the line OA corresponds to the fall caused

TYPE II.

by the first metal, say gold, and the remainder to the effect of adding cadmium. The point B is certainly an angle, and a precipitate is

formed after this point is reached. C is a rounded summit. D appears to be an angle, or a very sharp curve, whilst at E the change of curvature is gradual.

Here it will be seen (Plate 2, p. 966) that the summit C, and in those cases in which gold is the first metal added, the flat DE, always occur at the same temperature, whatever the amount of gold or cadmium initially added. *The summit C invariably reached when the number of gold atoms is equal to the number of cadmium atoms*, in other words, the minimum fall in the freezing point of tin is produced with this ratio of gold to cadmium. Thus, for example, the summit C has been reached with 4 atoms of gold and 4 atoms of cadmium, 5 atoms of gold and 5 atoms of cadmium, 9 atoms of gold and 9 atoms of cadmium per 100 atoms of tin, and all these alloys are *isotectic*.*

TABLE III.—300 grams of Tin taken as Solvent.

Grams of Au added in succession.	Grams of Cd added in succession.	Total weight of Au or Cd added.	Freezing point of solution.	Atoms of Au or Cd per 100 atoms of tin.	Falls in ° C. D.	Remarks.
—	—	—	(tin 231·44)	—	—	
15·07	—	15·07	222·77	3·007	8·69	
Now added Cadmium.						
—	1·011	1·011	222·14	0·355	9·30	Same reading with nuclei of either Sn or alloy.
—	1·144	2·155	221·38	0·757	10·06	
—	1·703	3·858	220·28	1·355	11·16	
—	1·463	5·321	219·37	1·869	12·07	
—	1·512	6·833	218·3	2·400	13·14	
—	1·669	8·502	217·26	2·986	14·18	
—	1·561	10·063	216·93	3·534	14·51	
—	1·499	11·562	217·2	4·061	14·24	
—	1·209	12·772	217·06	4·485	14·38	
—	1·658	14·430	216·86	5·068	14·58	
—	2·528	16·958	216·37	5·956	15·07	
—	3·025	19·983	215·55	7·018	15·89	
—	3·269	23·25	214·38	8·166	17·06	
—	2·845	26·097	213·35	9·165	18·09	
—	3·720	29·817	211·77	10·47	19·67	Changed thermometer.
—	3·990	33·807	210·69	11·872	20·75	
—	3·183	36·99	210·65	12·99	20·79	
—	3·366	40·35	210·51	14·172	20·93	
—	4·161	44·517	210·46	15·633	20·98	
—	6·242	50·76	209·08	17·825	22·36	
—	8·845	59·604	206·32	20·931	25·12	

* Isotectic substances are those which melt at the same temperature.

TABLE IV.—300 *grams of Tin taken as Solvent.*

Grams of Au added in succession.	Grams of Cd added in succession.	Total weight of Au or Cd added.	Freezing point of solution.	Atoms of Au or Cd per 100 atoms of tin.	Falls in ° C. D.	Remarks.
—	—	—	(tin) (231·42)	—	—	—
2·087	—	2·087	230·22	0·4164	1·20	—
11·99	—	14·077	223·41	2·809	8·01	—
5·848	—	19·925	219·95	3·976	11·47	—

Now added Cadmium.

—	0·951	0·951	219·37	0·334	12·05	—
—	1·015	1·966	218·66	0·691	12·76	—
—	1·157	3·123	218·0	1·097	13·42	—
—	1·062	4·185	217·28	1·47	14·14	—
—	1·022	5·206	216·76	1·83	14·66	—
—	1·265	6·473	217·01	2·274	14·41	—
—	1·004	7·477	217·17	2·625	14·25	—
—	1·362	8·839	217·32	3·104	14·10	—
—	1·720	10·559	217·41	3·709	14·01	—
—	0·912	11·471	217·54	4·032	13·88	—
—	1·242	12·713	217·37	4·469	14·05	—
—	1·477	14·19	217·1	4·988	14·32	—
—	1·438	15·628	216·93	5·493	14·49	—
—	1·404	17·032	216·67	5·986	14·75	—
—	1·416	18·448	216·34	6·483	15·08	—
—	1·37	19·818	215·95	6·963	15·47	—
—	3·220	23·038	214·87	8·095	16·55	—
—	3·038	26·076	213·78	9·162	17·64	—
—	3·168	29·244	212·5	10·275	18·92	—
—	3·715	32·96	210·9	11·58	20·52	—
—	3·175	36·134	210·66	12·695	20·76	—
—	3·027	39·161	210·56	13·76	20·86	—
—	3·595	42·756	210·19	15·02	21·23	—
—	1·757	44·513	210·72	15·638	20·70	—
—	10·476	54·989	209·73	19·318	21·69	—
—	5·112	60·101	208·43	21·114	22·99	—
—	5·30	65·401	206·78	22·976	24·64	—
—	5·15	70·551	204·95	24·785	26·47	—
—	5·315	75·866	203·08	26·652	28·34	—
—	7·130	82·996	200·48	29·153	30·94	—

Curves of the third type are obtained when more gold has been added than the amount required to saturate the tin. Here the slope OA and the flat AP are due to the gold. PQ shows the effect of the first quantities of cadmium, the fall from P to Q being independent of the amount of gold present; this is true for all the curves of Type III. Directly the point Q is reached a precipitate begins to separate out in the block and remains to the end of the experiment. The part QR is of different lengths in different curves; it is probable,

however, that the horizontal distance PR equals AP, in other words, that the cadmium begins to produce a rise when as many atoms of it

TYPE III.

are present as there are atoms of gold in excess of the saturation amount.

From R onwards the curve closely resembles Type II, the summit C of least effect, and the flat DE occurring at identical temperatures in the two classes of curves; moreover, C is reached when the number of atoms of cadmium is equal to the number of atoms of gold.

TABLE V.—300 grams of Tin taken as Solvent.

Grams of Au added in succession.	Grams of Cd added in succession.	Total weight of Au or Cd added.	Freezing point of solution.	Atoms of Au or Cd per 100 atoms of tin.	Falls in ° C. D.	Remarks.
—	—	—	(tin 231·55)	—	—	—
25·06	—	25·06	217·12	5·0	14·43	—
Now added Cadmium.						
—	1·045	1·045	216·5	0·367	15·05	—
—	1·14	2·185	215·88	0·767	15·67	—
—	1·30	3·485	215·16	1·224	16·39	—
—	1·025	4·51	214·64	1·58	16·91	—
—	0·5585	5·068	215·24	1·78	16·31	—
—	0·7445	5·813	215·7	2·041	15·85	—
—	1·46	7·273	216·39	2·554	15·16	—
—	1·315	8·588	216·84	3·015	14·71	—
—	1·174	9·762	217·15	3·428	14·40	—
—	1·364	11·126	217·42	3·907	14·13	—
—	0·936	12·062	217·58	4·235	13·97	—
—	0·897	12·959	217·64	4·55	13·91	—
—	0·753	13·712	217·69	4·82	13·86	—
—	0·720	14·432	217·69	5·07	13·86	—

TABLE VI.—300 grams of *Tin* taken as a *Solvent*.

Grams of Au added in succession.	Grams of Cd added in succession.	Total weight of Au or Cd added.	Freezing point of solution.	Atoms of Au or Cd per 100 atoms of tin.	Falls in ° C. D.	Remarks.
—	—	—	(tin 231·41)	—	—	
1·249	—	1·249	230·66	0·249	0·75	
1·610	—	2·858	229·78	0·57	1·63	
4·6125	—	7·471	227·14	1·491	4·27	
10·3785	—	17·850	221·1	3·561	10·31	
8·0565	—	25·907	216·37	5·17	15·04	
5·314	—	31·22	213·51	6·23	17·9	Changed thermometer to Hicks' No. 9.
1·925	—	33·15	213·36	6·614	18·05	
Now added Cadmium.						
—	1·0465	1·0465	213·15	0·3675	18·26	
—	3·122	4·1685	212·64	1·464	18·77	
—	2·713	6·881	212·64	2·417	18·77	Hicks' thermo. No. 10.
—	3·101	9·982	215·71	3·506	15·7	
—	3·063	13·045	216·81	4·581	14·6	
—	3·1475	16·193	217·48	5·686	13·93	
—	2·63	18·823	217·65	6·61	13·76	
—	2·921	21·744	217·28	7·636	14·13	
—	2·58	24·324	216·93	8·542	14·48	Raised to high temp. for 1 hour.
—	2·576	26·90	216·29	9·447	15·12	
—	3·09	29·99	215·3	10·532	16·11	
—	3·89	33·88	213·84	11·898	17·57	
—	3·58	37·47	212·33	13·155	19·08	
—	11·772	49·232	210·60	17·29	20·81	Changed to Hicks' No. 9.
—	3·826	53·058	210·6	18·633	20·81	
—	4·643	57·70	210·59	20·26	20·82	
—	10·065	67·766	210·03	23·799	21·38	

TABLE VII.—300 grams of *Tin* taken as *Solvent*.

Grams of Au added in succession.	Grams of Cd added in succession.	Total weight of Au or Cd added.	Freezing point of solution.	Atoms of Au or Cd per 100 atoms of tin.	Falls in ° C. D.	Remarks.
—	—	—	(tin 231·51)	—	—	
30·57	—	30·57	213·75	6·099	17·76	
1·031	—	31·601	213·55	6·305	17·96	
4·661	—	36·262	213·49	7·235	18·02	
3·834	—	40·096	213·46	8·00	18·05	
5·012	—	45·108	213·45	9·00	18·06	Hicks' No. 9.

TABLE VII—*continued*.

Grams of Au added in succession.	Grams of Cd added in succession.	Total weight of Au or Cd added.	Freezing point of solution.	Atoms of Au or Cd per 100 atoms of tin.	Falls in ° C. D.	Remarks.
Now added Cadminm.						
—	1·077	1·077	213·0	0·378	18·51	
—	1·298	2·375	212·68	0·834	18·83	
—	1·231	3·606	212·46	1·266	19·05	
—	1·446	5·05	212·44	1·775	19·07	
—	1·177	6·229	212·45	2·188	19·06	
—	1·466	7·695	212·55	2·703	18·96	
—	1·367	9·062	212·55	3·183	18·96	
—	1·412	10·474	212·72	3·679	18·79	
—	1·65	12·124	213·33	4·258	18·18	Changed to Hicks' No. 10.
—	1·998	14·122	214·54	4·960	16·97	
—	1·818	15·940	215·5	5·599	16·01	
—	1·525	17·465	216·19	6·134	15·32	
—	1·585	19·050	216·83	6·691	14·68	
—	1·945	20·995	217·36	7·374	14·15	
—	1·374	22·369	217·59	7·856	13·92	A large quantity of precipitate at bottom of block.
—	1·648	24·02	217·7	8·436	13·81	
—	1·520	25·537	217·68	8·97	13·83	
—	1·506	27·043	217·52	9·498	13·99	
—	2·208	29·251	217·17	10·274	14·34	
—	3·806	33·06	216·3	11·611	15·21	
—	3·285	36·34	215·2	12·765	16·31	
—	4·853	41·195	213·33	14·47	18·18	
—	3·947	45·14	211·4	15·851	20·11	Thermo.
—	1·424	46·566	210·75	16·354	20·76	Hicks' No. 9.
—	1·352	47·92	210·6	16·829	20·91	
—	1·579	49·497	210·66	17·384	20·85	
—	1·714	51·211	210·63	17·986	20·88	
—	1·762	52·973	210·6	18·61	20·91	
—	2·01	54·983	210·6	19·311	20·91	
—	2·095	57·08	210·6	20·05	20·91	
—	1·650	58·73	210·6	20·63	20·91	
—	1·062	59·79	210·6	21·0	20·91	
—	1·71	61·50	210·51	21·6	21·00	
—	1·761	63·26	210·66	22·22	20·85	
—	2·744	66·0	210·55	23·18	20·96	
—	2·959	68·96	210·46	24·22	21·05	
—	2·666	71·63	210·44	25·156	21·07	
—	1·850	73·48	210·43	25·81	21·08	
—	2·286	75·764	210·03	26·61	21·48	

TABLE VIII.—300 grams of *Tin* taken as *Solvent*.

Grams of Au added in succession.	Grams of Cd added in succession.	Total weight of Au or Cd added.	Freezing point of solution.	Atoms of Au or Cd per 100 atoms of tin.	Falls in ° C. D.	Remarks.
—	—	—	(tin 231·57)	—	—	
25·06	—	25·06	217·23	5·0	14·34	
5·012	—	30·072	214·29	6·0	17·28	
0·802	—	30·874	213·77	6·16	17·80	
0·511	—	31·385	213·6	6·262	17·97	
2·232	—	33·617	213·57	6·707	18·00	
5·048	—	38·665	213·53	7·714	18·04	
8·932	—	47·597	213·53	9·497	18·04	
7·535	—	55·132	213·52	11·00	18·05	
Now added Cadmium.						
—	0·3585	0·3585	213·47	0·1259	18·10	
—	0·664	1·0225	213·43	0·359	18·14	
—	0·530	1·5525	213·32	0·5454	18·25	
—	0·752	2·3045	213·12	0·8095	18·45	
—	0·498	2·8025	213·01	0·9844	18·56	
—	0·575	3·3775	212·9	1·1864	18·67	
—	0·480	3·858	212·86	1·355	18·71	
—	0·770	4·628	212·81	1·625	18·76	
—	1·006	5·634	212·78	1·978	18·79	
—	1·465	7·099	212·8	2·493	18·77	
—	6·638	13·737	212·86	4·8246	18·71	
—	6·558	20·295	215·66	7·128	15·91	
—	2·683	22·979	216·88	8·0713	14·69	
—	2·028	25·006	217·49	8·7835	14·08	

TABLE IX.—300 grams of *Tin* taken as *Solvent*.

Grams of Au added in succession.	Grams of Cd added in succession.	Total weight of Au or Cd added.	Freezing point of solution.	Atoms of Au or Cd per 100 atoms of tin.	Falls in ° C. D.	Remarks.
—	—	—	(tin 231·51)	—	—	
—	2·694	2·694	229·2	0·946	2·31	
—	3·048	5·742	226·71	2·017	4·80	
—	2·454	8·196	224·75	2·878	6·76	
—	3·194	11·390	222·45	4·0	9·06	

TABLE IX—*continued.*

Grams of Au added in succession.	Grams of Cd added in succession.	Total weight of Au or Cd added.	Freezing point of solution.	Atoms of Au or Cd per 100 atoms of tin.	Falls in ° C D.	Remarks.
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Now added Gold.

1·1295	—	1·1295	221·95	0·2253	9·56	
0·99	—	2·1195	221·53	0·4228	9·98	
1·059	—	3·1785	221·05	0·634	10·46	
1·011	—	4·1895	220·59	0·8358	10·92	
1·122	—	5·3115	220·12	1·0596	11·39	
1·018	—	6·329	219·62	1·263	11·89	
1·047	—	7·376	219·17	1·472	12·34	
1·008	—	8·384	218·71	1·673	12·8	
1·01	—	9·394	218·26	1·874	13·25	
1·01	—	10·403	217·77	2·075	13·74	
1·005	—	11·481	217·36	2·276	14·15	
1·082	—	12·491	216·88	2·492	14·63	
1·003	—	13·493	217·11	2·692	14·4	
1·001	—	14·495	217·27	2·892	14·24	
1·002	—	15·496	217·38	3·09	14·13	
1·013	—	16·509	217·49	3·294	14·02	
1·001	—	17·511	217·55	3·493	13·96	
1·085	—	18·595	217·59	3·71	13·92	
1·008	—	19·603	217·69	3·911	13·82	
1·044	—	20·647	217·69	4·12	13·82	
2·0	—	22·647	217·65	4·518	13·86	
3·015	—	25·662	217·38	5·120	14·13	
4·045	—	29·707	216·97	5·927	14·57	
2·763	—	32·471	216·62	6·478	14·89	
2·035	—	34·506	216·16	6·884	15·35	
2·299	—	36·805	215·54	7·343	15·97	
2·51	—	39·32	214·79	7·843	16·72	
2·55	—	41·86	213·99	8·352	17·52	
2·662	—	44·53	212·77*	8·383	18·74	
2·591	—	47·117	212·77	9·4	18·74	
2·795	—	49·91	212·77	9·96	18·74	
2·706	—	52·62	212·77	10·498	18·74	
2·601	—	55·22	212·77*	11·02	18·74	
2·555	—	57·774	212·77	11·526	18·74	
2·096	—	59·87	212·77	11·944	18·74	
2·6	—	62·47	212·77	—	18·74	
2·586	—	65·056	212·77*	—	18·74	
2·428	—	67·484	212·77	—	18·74	
2·596	—	70·078	212·77	13·98	18·74	

Now added Cadmium.

—	14·859	26·25	214·16	9·217	17·35	
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* Fluctuations did not exceed 0·03°.

TABLE X.—300 grams of Tin taken as Solvent.

Grams of Au added in succession.	Grams of Cd added in succession.	Total weight of Au or Cd added.	Freezing point of solution.	Atoms of Au or Cd per 100 atoms of tin.	Falls in ° C. D.	Remarks.
—	—	—	(tin 231·58)	—	—	
—	3·726	3·726	228·37	1·309	3·21	
—	3·932	7·658	225·23	2·69	6·35	
—	3·668	11·326	222·53	3·975	9·05	
—	8·609	19·935	217·79*	7·0	13·79	

Now added Gold.

1·2685	—	1·2685	217·32*	0·2531	14·26
1·0895	—	2·358	216·7*	0·47	14·88
1·5655	—	3·9235	216·07	0·783	15·51
1·333	—	5·3065	215·55	1·059	16·03
1·0645	—	6·371	215·18	1·271	16·40
2·251	—	8·622	214·38	1·72	17·20
1·112	—	9·734	214·59	1·942	16·99
1·486	—	11·22	214·92	2·239	16·66
1·126	—	12·346	215·13	2·461	16·45
1·215	—	13·561	215·43	2·703	16·15
6·483	—	20·05	216·44	4·0	15·14

In order to gain some insight into the changes that have gone on in the blocks, analyses were made of the liquid portion and the precipitate at various points on the curves of Types II and III.

The collection of pure samples of the liquid and precipitate presents considerable difficulty, for the composition of the liquid is affected by the change of solubility of the precipitate with the temperature, whilst the composition of the precipitate is affected by the mother liquor adhering to it. After several trials, the following plan for collecting the liquid and precipitate was found to yield fair results:—At the termination of an experiment the temperature of the block or crucible was kept as nearly as possible stationary, a few degrees above the freezing point of the alloy, rapid stirring being maintained for a quarter of an hour. The thermometer was then withdrawn, the stirrer stopped, and the precipitate allowed to subside for two or three minutes. Some of the supernatant liquid was then sucked up by means of a very fine pointed pipette, which had been previously heated to prevent the alloy solidifying. Owing to the fine point of the pipette and the time allowed for the precipitate to subside, the mechanical introduction of

* Some experimental error which apparently corrects itself later on.

the precipitate, along with the fluid part, was to a large extent avoided. After the alloy had solidified, the pipette was broken, and the cylinder of metal was cleaned from adhering paraffin,* remelted at as low a temperature as possible, and afterwards granulated by throwing into water.

To obtain the precipitate, the residue in the block, after withdrawing part of the fluid, was poured into an iron-wire gauze bag, placed in a bath of molten paraffin, at a temperature above the melting point of the fluid part of the alloy; by repeatedly raising the bag out, and tapping it against the iron block, the precipitate could be obtained fairly free from mother liquor. The precipitate crystallised in well-marked hexagonal plates. The analysis of the fluid part, or mother liquor, and the precipitate, was made as follows:—

A weighed quantity of the alloy, from 2 to 3 grams, was placed in a beaker, and treated with pure, concentrated hydrochloric acid, and digested for several hours on a sand-bath, the liquid being decanted off, and fresh portions of hydrochloric acid added from time to time. The gold left behind after the solution of the cadmium and tin, was collected, washed, and weighed.

The separation of the cadmium and tin contained in the wash waters was effected by a modification of Löwenthal's method. The mixture of stannous and cadmium chlorides was oxidised with bromine, and the liquid neutralised with ammonia until a precipitate just formed. The solution was then diluted, warmed upon a sand-bath, and a concentrated solution of a mixture of sodium sulphate and ammonium nitrate† added; the whole was then left for some hours on the sand-bath, and, after cooling, the precipitate of hydrated tin dioxide was collected and washed on a filter pump. In a few cases this precipitate was repeatedly ignited and weighed in order to estimate the tin directly; but usually the tin was determined by difference.

After the separation of the tin, the cadmium in the filtrate was precipitated as sulphide by sulphuretted hydrogen. The cadmium sulphide was filtered and washed to free it from ammonium and sodium salts, and then dissolved off the filter by hot dilute hydrochloric acid. After filtering, the pure solution of cadmium chloride was precipitated at the boiling point with sodium carbonate. The precipitated cadmium carbonate was collected on a filter, washed, dried, and transferred, as far as possible, to a porcelain crucible; the filter paper, with adhering traces of cadmium oxide, was burnt after

* The whole of our freezing-point experiments were conducted under a layer of molten paraffin.

† We found the mixture of Na_2SO_4 and NH_4NO_3 act much more rapidly than NH_4NO_3 alone, as recommended by Löwenthal.

previous moistening with ammonium nitrate. The cadmium carbonate was ignited over the blowpipe and weighed as cadmium oxide. The results are almost certainly too low,* owing to a slight reduction of the oxide and volatilisation of the cadmium. The purity of the ignited cadmium oxide was ascertained by dissolving it in warm dilute nitric acid, any residue left being collected and weighed as tin dioxide.† The cadmium results have in several instances been confirmed by simply treating weighed quantities of the alloy with nitric acid, evaporating to dryness, and igniting the residue. The cadmium oxide was dissolved out with dilute nitric acid, precipitated as carbonate, and weighed as oxide; the results of this control gave in all cases 0.2–0.3 per cent. more cadmium than the previous method.

For the convenience of description and classification, the results in Table XI (pp. 951, 952) are not given in chronological order.

On examining the numbers in the tables, it will be seen that, although the gold and cadmium have been dissolved in tin in very various proportions, the ratio of gold atoms to cadmium atoms are as 1 : 1 in the precipitate, or, as analysis shows (with the exception of the results of Table VI), more nearly $\text{Au}_{1.18}\text{Cd}$. With regard to the large quantity of tin present in the precipitates, part, no doubt, is due to adhering mother liquor;‡ but we have strong reason for believing that another part enters as an essential constituent of the compound. We have made several attempts to clear up this point by endeavouring to reduce, as far as possible, the adhering tin. For this purpose, experiments were made on the precipitate collected after the results given in Table IX. Analysis of this precipitate have as mean results Au 31.96 per cent., Cd 14.62 per cent.

A solid steel piston, about half an inch in diameter, was turned to fit a hole in a steel block or cylinder about 3 inches deep. The bottom of this cylinder was perforated by a number of fine holes over which was placed a disc of fine iron-wire gauze. This cylinder was placed in the axis of one of our large blocks and heated to the necessary temperature. From 2 to 3 grams of the precipitate were then placed in the cylinder and kept at a temperature nearly 100° above the melting point of the liquid part of the alloy; the piston was then hammered in with a mallet, when a considerable portion of

* Fresenius (English translation, 1876), 7th ed., p. 266, says that the "results of estimating cadmium as oxide are generally a little too low."

† The frequent presence of a little SnO_2 in this precipitate confirms the work of previous observers, that all attempts to precipitate Sn as hydrated oxide in presence of hydrochloric acid are only partially successful.

‡ This tin would doubtless be accompanied by corresponding quantities of gold and cadmium.

TABLE XI.—*Analyses.*

Original composition of mixture in block.				Composition of fluid part.			Composition of the insoluble precipitate.			
Reference to tables.	Au.	Cd.	Sn.	Au p.c.	Cd p.c.	Sn p.c.	Au p.c.	Cd p.c.	Sn p.c.	Atoms Au : atoms Cd in precipitate.
II.	2 atoms 8.3 p.c.	19.05 atoms 16.9 p.c.	100 atoms 74.8 p.c.	— 2.15	— —	— —	— 13.7	— —	— —	
III.	3 atoms —	20.9 atoms —	100 atoms —	— 1.96	— —	— —	— 13.5	— —	— —	
IV.	3.976 atoms 4.78 p.c.	29.15 atoms 20.63 p.c.	100 atoms 74.6 p.c.	— 1.4 1.5	— — —	— — —	28.5 18.8 28.5	— — —	— — —	
V.	5 atoms 7.38 p.c.	5.03 atoms 4.25 p.c.	100 atoms 88.37 p.c.	4.98 4.92 5.1 5.13	2.51 — — 2.4	— — — —	23.99 22.89 22.01 —	11.82 — 11.4 —	— — 65.8 —	Au ₁₁ is Cd. Au _{11.09} Cd.
VI.	6.61 atoms 8.27 p.c.	23.8 atoms 16.9 p.c.	100 atoms 74.8 p.c.	3.66 3.52 —	— — —	— — —	18.4 28.02 20.31	— — —	— — —	

TABLE XI—continued.

Original composition of mixture in block.				Composition of fluid part.			Composition of the insoluble precipitate.			
Reference to tables.	Au.	Cd.	Sn.	Au p.c.	Cd p.c.	Sn p.c.	Au p.c.	Cd p.c.	Sn p.c.	Atoms Au: atoms Cd in precipitate.
VII.....	11 atoms	8.78 atoms	100 atoms	5.81	—	—	29.16*	13.83	56.67	Au _{1.2} Cd.
	14.5 p.c.	6.38 p.c.	78.9 p.c.	5.93	—	—	30.57	14.73	—	Au _{1.15} Cd.
	—	—	—	5.73	1.83	—	30.45	—	—	—
	—	—	—	5.74	—	—	—	—	—	—
	—	—	—	5.8	2.29	—	—	—	—	—
VIII.....	—	—	—	5.72	2.12	—	—	—	—	—
	9 atoms	26.6 atoms	100 atoms	3.51	—	—	23.54	29.27	—	AuCd _{2.18} †
	10.72 p.c.	18 p.c.	71.28 p.c.	3.38	9.86	86.3	—	—	—	AuCd _{2.3} .
IX.....	—	—	—	—	—	—	34.04†	43.97	—	—
	—	—	—	8.68	—	—	31.6	15.0	—	Au _{1.19} Cd.
	—	—	—	8.7	1.7	—	31.7	14.1	53.6	Au _{1.28} Cd.
	13.98 atoms	9.217 atoms	100 atoms	8.71	1.56	—	32.6	14.76	52.6	Au _{1.25} Cd.
	17.68 p.c.	6.62 p.c.	7.57 p.c.	8.75	1.38	89.07	—	—	—	—
X.....	—	—	—	8.57	1.52	88.8	39.02†	18.81	—	Au _{1.18} Cd.
	—	—	—	8.81	1.3	—	40.67†	20.18	—	Au _{1.14} Cd.
	—	—	—	—	—	—	—	—	—	—
	4 atoms	7 atoms	100 atoms	3.46	4.48	91.61	24.96*	14.6	59.2	Au _{0.975} Cd.
	5.86 p.c.	5.89 p.c.	38.24 p.c.	3.58	4.96	90.02	13.74	8.74	77.01	Au _{0.884} Cd.
	—	—	—	—	—	—	17.5	11.58	—	Au _{0.889} Cd.

* Sample of precipitate collected off thermometer stem.

† This point is on the flat D.E.

‡ Hammered disc of precipitate.

the fluid part was expelled, the residue being left as a thin wad or disc which could easily be driven out of the cylinder.

Two experiments were made on the precipitate obtained in Table IX.

Disc I, hammered at 280°, weighed 3·3815 grams.

Analysis gave—

39·02	per cent.	Au,
18·81	„	Cd,
42·17	„	Sn (by difference).

This gives the formula $\text{Au}_{1.13}\text{CdSn}_{2.13}$.

Disc II, hammered above 300°, weighed 1·3425 grams.

Analysis gave—

40·67	per cent.	Au,
20·19	„	Cd,
39·14	„	Sn (by difference).

This gives the formula $\text{Au}_{1.14}\text{CdSn}_{1.84}$.

Before hammering, the precipitate gave as the mean of three concordant experiments, Au 31·94, Cd 14·62, Sn 53·44. Theory requires for the body Sn_2AuCd .

Au.....	36·2	per cent.
Cd.....	20·5	„
Sn.....	43·3	„

It will be seen that whilst the percentage of tin was reduced in the one case by 11·3, and in the other by 14·3, the ratio of the Au to the Cd remained almost the same as before the experiment. The foregoing precipitate was produced during an experiment which was concluded just before the angle D of the final flat was reached (see Plate 3).

From the above experiments we conclude that the gold and cadmium unite atom for atom, for the following reasons:—

- (a.) 12 analyses of five different precipitates give the mean ratio $\text{Au}_{1.1}\text{Cd}$.
- (b.) This ratio remains the same, although the proportions in which the gold and cadmium were dissolved in the tin varied from 5·86 atoms Au for 5·89 atoms Cd to 14·5 atoms of Au for 6·2 atoms of Cd.
- (c.) The ratio Au : Cd cannot be disturbed by liquation.
- (d.) The minimum lowering of the freezing point of the tin is produced when the gold and cadmium are present atom for atom.
- (e.) From solutions containing low percentages of gold and cadmium, we obtain precipitates rich in these metals.

Special interest attaches to the 3rd flat DE in the curves on Plate 3 (p. 966) of Table VII.

Here in one case the gold and cadmium had been dissolved in the ratio 9Au : 26·6Cd.

Analysis of the precipitate gave 23·54 per cent. Au,
29·27 „ Cd,

corresponding to the formula $\text{AuCd}_{2.19}$.

On liquating and hammering a portion, as previously described, the following results were obtained:—

Disc hammered at 310° weighed 2·503 grams.

Analysis gave—

34·04 per cent. Au,
43·97 „ Cd,
21·99 „ Sn (by difference),

corresponding to the formula $\text{AuCd}_{2.3}\text{Sn}_{1.1}$.

Hence we conclude that two compounds are formed. Up to the angle D (Curves Types II and III, Plates 2 and 3) the compound formed is AuCdSn_2 ; on the further addition of cadmium, one of the atoms of tin is displaced, and the compound AuCd_2Sn is formed.

The discussion of the results of analysis of the fluid part of the alloy is given at the end of the paper, but it will be sufficient to point out here that if the tin is rich in gold it is poor in cadmium, and *vice versa*.

Interpretation of above Results.

In attempting to interpret these curves in a more precise manner, we must start from the principle that, when any single metal is in solution in tin, the fall in the freezing point is a measure of the number of molecular weights of this metal present. Our previous experiments have made it probable that the molecule of a metal when dissolved in tin consists of 1 atom. If, therefore, gold and cadmium, when dissolved together in tin, produce a total fall which is less than the sum of the falls that each alone would produce, the difference is probably produced by the action of the gold and the cadmium on each other.

A certain influence, which we may call mechanical or thermodynamical, is exerted by each dissolved metal on the osmotic pressure of any other dissolved metal, and therefore on the fall in the freezing point of the solvent caused by the latter. Moreover, gold probably increases the apparent effect of another dissolved metal by combining with some of the tin, and so practically decreasing the amount of the solvent, and making the solution of the other metal more con-

centrated. But these are minor causes, and would not produce the phenomena recorded in the curves.

The main cause is probably the combination of the gold and cadmium atoms to form molecules. It is clear that this would cause a rapid decrease in the total fall even if everything remained in solution; but our filtration experiments above the freezing point of tin, when large quantities of precipitate were formed, seem to prove that the new body is very sparingly soluble in tin. Hence, when gold and cadmium are brought together in solution in tin, a considerable quantity of these metals is removed from solution, and the total fall becomes much less than the sum of the separate falls.

The analyses of the crystalline precipitate, and to some extent a study of the part from A to R in curves of Type III (p. 943), point to the conclusion that 1 atom of gold combines with 1 atom of cadmium, so that as far as these metals are concerned, the molecule of the compound formed has the formula Au_nCd_n . It will be seen, when we consider the equations of equilibrium, that the occurrence of the summits C, corresponding to a minimum fall, at the moment when an equal number of atoms of gold and cadmium have been added, strongly supports the formula Au_nCd_n .

It is very probable that the tin also reacts chemically with the other two metals, and may be an important constituent of the molecule of the compound; but the tin, from its large amount compared with the amounts of the gold and cadmium, must have a practically constant active mass, and hence it does not seem indispensable to take it into consideration in discussing the equilibrium.

We shall, therefore, in what follows assume that a portion of the gold and cadmium combine to form molecules of the type Au_nCd_n , while the remainder of the two metals is present in the form of monatomic molecules.

Let a and c be the total numbers of gold and cadmium atoms for every 100 atoms of tin *present in the vessel*, x and y the number of monatomic molecules of these metals present, and z the number of molecules of the body Au_nCd_n that has been formed. Then it is obvious that

$$a = x + nz; \quad c = y + nz.$$

Let us consider the progress of the changes during the experiments recorded by a curve of the Type II. As we start from the state A of a pure solution of gold in tin, and advance towards B by adding cadmium, we have at each step a state of equilibrium between x atoms of gold, y atoms of cadmium, and z molecules of Au_nCd_n .

It seems probable that up to the point B the compound all remains in solution, but that B corresponds to the saturation of the tin by

the compound. Indeed, soon after B is past, we can detect a precipitate at the bottom of the block.

As the fluctuations of temperature along any one of the curves only amount to about 20°, a small fraction of the absolute temperature of 500°, we propose in the equation of equilibrium to ignore these changes and regard the equilibrium as isothermal.

The principle of Guldberg and Waage then leads to the equation

$$\frac{xy}{\sqrt[n]{z}} = \kappa \dots \dots \dots (1),$$

where κ is a constant which ought to be the same for all points between A and B on all the curves.

From B onwards it seems that all the additional compound AuCd that is formed is precipitated. Hence, if z_B is the amount in existence at the point B, the active mass of the compound remains constant, and equal to z_B from this point onwards.

The equation of equilibrium then becomes

$$\frac{xy}{\sqrt[n]{z_B}} = \kappa \dots \dots \dots (2),$$

or, more simply, $xy = \text{const.}$

The flat DE probably corresponds to a state in which the concentration of the cadmium in the liquid is so great that it begins to react with the precipitate, and to form a substance richer in cadmium. Under these circumstances we should expect the cadmium now added to be wholly appropriated, and not to remain in solution. Thus the fall in the freezing point would remain the same until all the insoluble body was transformed. We know that *pure* cadmium in *pure* tin does not give a constant freezing point until 47 atoms of cadmium are present for every 100 atoms of tin, so that the flat DE is caused in some way by the presence of the gold. Analysis of the precipitate beyond E shows it to be richer in cadmium than the formula AuCd requires. See Table XI, Sect. VIII (p. 952).

The second flat, QR, in the curves of Type III also receives a general explanation, for, the equation of equilibrium being still $xy = \kappa z^{\frac{1}{n}}$, we have here x and z constant, for the liquid is saturated with gold and with the compound. It follows that y must also remain constant, even though cadmium be added, that is to say, all the cadmium added is here appropriated by the excess of gold to form more precipitate. Thus the composition of the liquid part remains the same, and therefore the freezing point is constant.

We have not examined the part near R minutely enough to be certain that there is an angle at R like that at B, but it is certain

that there is a very abrupt change of curvature here. After R, the explanation of Type III does not differ from that given for Type II, as from that point the liquid is no longer saturated with gold.

The slope from P to Q in the Type III curves corresponds to the part AB in the Type II curves, and is in a general sense intelligible, but the drop from P to Q is not nearly so great as the calculations from the rest of the curves seem to require: in fact, we have here a point where our hypotheses are seen to be imperfect.

Exactly similar phenomena repeat themselves in the curves of Type II, when cadmium is the first metal added to the tin, and gold the second. But in this case the final flat DE occurs at the temperature of the flat QR, and corresponds to the same state.

In order to subject the above considerations to a numerical test, we have carefully re-examined the behaviour of pure gold and pure cadmium, when each of these metals is dissolved by itself in pure tin.

We find that when gold is dissolved in tin its atomic fall is quite constant, and equal to 2.88° up to the concentration of 6.16 atoms of gold per 100 atoms of tin. This is the composition of the eutectic alloy, and further addition of gold causes no further fall.* We have carried the addition of gold as far as 11 atoms without producing any change in the freezing point of the eutectic alloy. Thus a atoms of gold dissolved in 100 atoms of tin causes a fall of $2.88a$, so long as a is less than 6.16. In the case of cadmium, the atomic fall is less, even in very dilute solutions, and it decreases somewhat rapidly as the solution becomes stronger in cadmium.

If we denote by $f(y)$ the total fall in the freezing point of the tin caused by dissolving y atoms of cadmium in 100 atoms of tin, then up to $y = 4$ the experiments are well represented by the equation

$$f(y) = 2.51y - 0.06y^2 \dots \dots \dots (3).$$

At the point $y = 4$ there appears to be a slight change, as can be seen by plotting the falls, and the experimental numbers agree better with the equation

$$f(y) = 9.08 + 1.668(y - 4) - 0.01063(y - 4)^2 \dots \dots (4).$$

The following Table XII of experimental numbers will serve to verify these equations:—

The following falls produced by gold in tin show that the effect of gold in lowering the freezing point in tin is strictly proportional to the amount of gold added.

* We believe that not more than 6.16 atoms of gold can dissolve in 100 atoms of tin at the temperature of solidification, in other words, the eutectic alloy is a saturated solution of gold in tin.

TABLE XII.

Atoms of Au per 100 atoms of Sn.	Total fall in degrees centigrade caused by the Au.	Atomic falls.
0·249	0·755	3·02
0·4164	1·20	2·88
0·57	1·63	2·85
1·491	4·27	2·86
2·809	8·01	2·85
3·561	10·31	2·89
3·976	11·47	2·88
5·00	14·43	2·88
5·17	15·04	2·91

TABLE XIII.—*Table of the Fall in Freezing Point caused by adding Pure Cadmium to Pure Tin.*

Atoms of Cd per 100 atoms of Sn.	Total fall in degrees centigrade caused by the Cd.	Atomic falls.
0·0607	0·152	2·5
0·153	0·382	2·5
0·946	2·31	2·44
0·998	2·42	2·44
1·811	4·29	2·37
2·017	4·80	2·38
2·878	6·76	2·348
4·000	9·10	2·28
4·000	9·06	2·265
4·021	9·05	2·25
4·767	10·32	2·165
5·165	10·98	2·116
5·693	11·85	2·085
6·143	12·57	2·046
6·397	12·97	2·028
8·193	15·89	1·94
9·423	17·85	1·894
10·152	18·91	1·862
13·100	23·44	1·789

The change of character in $f(y)$ after $y = 4$ is not due to a change of thermometers or to different samples of cadmium being used.

In the calculations which follow, we have, where it was possible, extracted $f(y)$ from a large-scale curve in preference to using equations (3) and (4).

We can now test the truth of the equations of equilibrium (1) and

(2). First assume $n = 1$, or that the molecule of the compound in solution is AuCd .

Consider the part between A and B. If we suppose that the free gold and free cadmium each exert the same effect as if the other metal were not there, and that the compound causes the normal molecular fall M, then D being the total fall observed and $F(x)$ the fall caused by x atoms of free gold, we must have

$$F(x) + f(y) + Mz = D \dots\dots\dots (5).$$

Using the fact that $x = a - z$, $y = c - z$, we may write the above as

$$F(a - z) + f(c - z) + Mz = D.$$

Now $F(a - z)$ is very nearly $2.88(a - z)$, but as $F(a)$ can often be obtained by direct observation in the experiment itself, we will replace $F(a - z)$ by $F(a) - 2.88z$.

If we also expand $f(c - z)$, we get the following quadratic for z :—

$$\frac{1}{2}f''(c)z^2 - [f'(c) + 2.88 - M]z = D - F(a) - f(c) \dots\dots (6).$$

In this equation, $f'(c)$ and $f''(c)$ are the first and second differential coefficients of $f(c)$ and can be got at once from equation (3) or (4).

We must also assume some value for M. In a previous paper, the value of M deduced by the theory of osmotic pressure from Person's value of the latent heat of tin and other constants came out 3° . But our numerous experiments on tin as a solvent lead to the conclusion that this number is a little too great; we have therefore in what follows taken $M = 2.88$.

Equation (6) is thus by means of equation (3) reduced to the form

$$z^2 + (41.83 - 2c)z = \frac{f(c) + F(a) - D}{0.06} \dots\dots (7).$$

If c were much greater than 4, we ought to use the other form derived from equation (4), namely:

$$z^2 + (164.92 - 2c)z = \frac{f(c) + F(a) - D}{0.01063} \dots\dots (8).$$

In these equations, the three quantities in the numerator of the fraction on the right are experimental numbers. In a series of experiments in which gold was the first metal added, $F(a)$ is the total fall caused by the gold, $f(c)$ is taken from a curve plotted from the table of cadmium falls, and D is the total observed fall caused by the mixture of cadmium and gold. There is but little error if we neglect z^2 in these equations, and Table XIV (p. 961) can be quickly verified by thus treating (7) as a simple equation.

The following table, XIV (next page), gives the values of z , x , and $\kappa = xy/z$ for points between A and B on the different curves. It was drawn up by solving equation (7) as a quadratic.

It is evident from this table that for very different concentrations, from 0.5 to 5 atoms of gold and 0.5 to 4 atoms of cadmium, the value of κ does not vary much from the mean value of 8.8, while z increases to a somewhat uncertain maximum at the point B.

It must be remembered in judging of the constancy of κ that the value of z is very nearly proportional to the experimental number $F(a) + f(c) - D$, and that this, which depends on three experiments made at different times, is a small difference of temperature ranging from 0.3° to 1.6° . Thus small errors of observation cause a large percentage error in z and a larger one in κ , which is $\frac{(a-z)(c-z)}{z}$.

In fact the constant κ is very sensitive to experimental errors and such errors would account for larger fluctuations of κ than are seen in the table.

There are, however, other causes of variation at work, for with much gold κ has high values and with much cadmium low values. At the point $a = 1$, $c = 7$ of a series of experiments in which 7 atoms of cadmium were added and then gold, the value of κ calculated as in the table is $\kappa = 4.3$, and other points in this 7-atom cadmium curve give values of κ which are much too low. Here the large amount of cadmium has altered the conditions so that the free gold in the liquid does not produce quite its usual fall.

The theory of osmotic pressure, in fact, warns us that this must occur, for the presence of the cadmium lowers the osmotic pressure exerted by the gold in two ways, by lowering the freezing temperature, and, also, probably by increasing the volume of the alloy.

The gold, for an unknown reason, perhaps because it appropriates tin and so decreases the amount of the solvent, has an opposite effect. It maintains its own effect undiminished right up to saturation and it probably increases the effect of any other metal which is in the same solution but not combined with it.

It might be possible to apply corrections for these disturbing causes, but for the present we propose to consider only those moderately dilute solutions where they do not have much effect.

The Part BCD of the Curves.—After the angle B we must suppose that the tin has become saturated with the compound, the amount z_B , which was formed at B, alone remaining in solution, however much may be formed.

The resulting equation of equilibrium $xy/z_B = \kappa$, or $xy = \text{const.}$, explains a very marked feature in the curves, namely, that a maximum freezing point, that is, a *minimum fall*, occurs when the number

TABLE XIV.—Table for the part AB of the Curves giving z , x , y , and $\kappa = \frac{xy}{z}$, calculated from the Equation

$$z^2 + (41.83 - 2c)z = \frac{F(a) + f(c) - D}{0.06}.$$

Table.	a .	c .	D .	$F(a)$.	$f(c)$.	z .	x .	y .	κ .	—	κ .
I and II	2.0	0.5	6.7	5.68	1.25	0.093	1.907	0.407	8.3		4.93
"	2.0	1.0	7.73	"	2.43	0.16	1.84	0.84	9.9		7.7
"	2.0	2.0	9.76	"	4.77	0.30	1.7	1.7	9.6		10.8
"	2.0	3.0	11.77	"	7.01	0.42	1.58	2.58	9.7		13.47
"	2.0	4.0	13.55	"	9.08	0.58	1.42	3.42	8.3		13.60
III	3.01	0.5	9.60	8.67	1.25	0.131	2.88	0.369	8.1		6.06
"	3.01	0.99	10.51	"	2.41	0.237	2.77	0.753	8.8		8.86
"	3.01	1.99	12.34	"	4.75	0.452	2.56	1.538	8.7		—
"	3.01	2.99	14.18	"	6.99	0.662	2.35	2.37	8.3		15.4
IV	4.0	0.5	12.27	11.86	1.25	0.138	3.86	0.362	10.1		6.27
"	4.0	1.0	13.14	"	2.43	0.27	3.73	0.73	10.1		10.9
"	4.0	1.5	13.98	"	3.60	0.416	3.58	1.084	9.3	Angle B	—
"	4.0	1.85	14.53	"	4.42	0.538	3.46	1.312	8.4		13.7
V	5.0	0.5	15.27	14.43	1.25	0.167	4.83	0.333	9.7		8.57
"	5.0	1.0	16.06	"	2.43	0.331	4.67	0.669	9.4		11.8
"	5.0	1.59	16.91	"	3.81	0.564	4.44	1.03	8.1	Angle B	13.7
IX	0.5	4.0	10.17	—	9.06	0.161	0.339	3.84	8.1		7.3
"	1.0	4.0	11.28	—	"	0.321	0.679	3.679	7.8		10.0
"	2.0	4.0	13.5	—	"	0.637	1.363	3.363	7.2		13.5
"	2.49	4.0	14.63	—	"	0.765	1.725	3.235	7.3	Angle B	15.0

33

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2

of atoms of gold and of cadmium in the block is equal. It does not matter whether we start a series with 4, 5, 6.6, or 9 atoms of gold, or with 4 atoms of cadmium, we always reach the summit C at a constant temperature when the number of atoms of the second metal added equals that of the first. The explanation on the hypothesis of the formation of the body Au_nCd_n is obvious. A minimum fall means a minimum number of molecules in solution. So that at C, $x + y$ must be minimum with the condition $xy = \text{const.}$

It is well known that under this condition the minimum is reached when $x = y$, and as $a - x = c - x$ it follows that $c = a$.¹

This agreement of experiment with the theory seems a strong confirmation of the latter.

We can apply a numerical test to the equation $xy/z_B = \kappa$, as before.

The equation to obtain z is now

$$F(a - z) + f(c - z) + 2.88z_B = D \dots\dots\dots (9).$$

This can be reduced to a quadratic, as before.

If $c - z$ is less than 4, we use equation (3), and so obtain

$$z^2 + (89.83 - 2c)z = \frac{F(a) + f(c) + 2.88z_B - D}{0.06} \dots (10).$$

z_B is somewhat uncertain, but from Table XIV it seems to be not far from the value 0.6. We shall use this value.

Where the gold is added first, and the tin is not saturated, we have used the value of $F(a)$, obtained from the particular experiment under discussion, but when gold is the second metal, or, as in the 6.6- or 9-atom gold curves, we have been obliged to use $F(a) = 2.88a$. If c was less than 4, $f(c)$ was taken from a large-scale curve, but in the case where c was greater than 4, whilst $c - z$ was less than 4, $f(c)$ was taken from equation (3). In the numerous cases where $c - z$ turned out to be greater than 4, we used equation (4) to reduce equation (9), thus getting, instead of (10), the equation

$$z^2 + (435.84 - 2c)z = \frac{F(a) + f(c) + 2.88z_B - D}{0.01063} \dots\dots (11).$$

In the following table, XV, the first column indicates which of equations (10) or (11) has been used.

The table shows that, with one or two exceptions, where the concentrations are extreme, κ does not differ much from a mean value of 9.

The value of x and y at the summit C is very constant: $x = y = 2.31$.

TABLE XV.—Table for the part BCD of the Curves giving z , x , y , and $\kappa = \frac{xy}{0.6}$, calculated by means of Equations (10) and (11).

Table	a .	c .	D.	F(a).	$f(c)$.	z .	x .	y .	κ .	
I and II	2.0	5.0	15.05	5.68	10.74	0.68	1.32	4.32	9.3	(11).
"	2.0	7.0	16.97	"	13.99	0.985	1.01	6.01	10.2	(11).
" III	3.0	4.0	14.24	8.67	9.08	1.05	1.95	2.95	9.6	(10).
"	3.0	6.0	15.07	"	12.35	1.69	1.31	4.31	9.4	(11).
IV	4.0	3.0	14.10	11.47	7.01	1.20	2.80	1.80	8.4	(10).
"	4.0	4.0	13.88	"	9.08	1.68	2.32	2.32	9.0	(10) Summit C.
"	4.0	7.0	15.47	"	13.99	2.60	1.4	4.4	10.3	(11).
"	4.0	10.0	18.49	"	18.68	3.01	0.99	6.99	11.5	(11).
V	4.0	11.75	20.58	"	—	3.24	0.76	8.51	10.8	(11) Angle D.
"	5.0	3.0	14.71	14.43	7.01	1.65	3.35	1.35	7.5	(10).
"	5.0	5.0	13.84	"	11.01	2.69	2.31	2.31	8.9	(10) Summit C.
VI	6.6	2.43	18.62	19.01	5.76	1.52	5.08	0.91	7.7	(10).
"	6.6	6.6	13.77	"	13.95	4.30	2.3	2.3	8.81	(10) Summit C.
"	6.6	10.0	15.62	"	18.67	5.32	1.28	4.68	10.0	(11).
"	6.6	14.53	20.81	"	25.65	5.83	0.77	8.7	11.2	(11) Angle D.
VII	9.0	6.0	15.46	25.92	12.9	5.05	3.95	0.95	6.3	(10).
"	9.0	9.0	13.81	"	17.73	6.7	2.30	2.30	8.82	(10) Summit C.
"	9.0	13.0	16.56	"	23.29	7.74	1.26	5.26	8.9	(11).
"	9.0	16.45	20.61	"	30.96	8.68	0.32	7.77	4.1	(11)* Angle D.
IX	3.0	4.0	14.17	8.64	9.06	1.06	1.94	2.94	9.5	(10).
"	4.0	4.0	13.82	11.52	"	1.69	2.31	2.31	8.9	(10).
"	6.0	4.0	14.61	17.28	"	2.65	3.35	1.35	7.5	(10).
"	8.88	4.0	18.74	25.57	"	3.44	5.44	0.56	5.1	(10)*

* In these cases where the greater part of one of the metals has been removed from the solution, a small percentage error in z causes a large error in κ .

Hence we see why the 2-atom gold curve cannot have a summit, for $x = 2.3$ implies $a = 2.9$. The 3-atom gold curve is just on the border-line between Type I and Type II.

κ Deduced from Analyses.

Table XI (pp. 951, 952) contains the analyses of the liquid alloy at four points on the part BCD of the curves; and these analyses can be used to calculate x , y , z , and κ , instead of employing the freezing point determinations. In Table XVI, Columns 1 and 2 contain the original composition of the mixture in the block, expressed as usual in terms of a and c . Column 3 contains the mean of two or more analyses, in each case, of the liquid alloy. Column 4 contains the number of atomic weights of gold and cadmium per 100 atomic weights of tin, calculated from Column 3. Column 5 contains the values of x and y , obtained by subtracting 0.6 from each of the numbers in Column 4. In column 6 is given κ or $xy/0.6$. As by the theory $z = a - x = c - y$, we have tabulated under z the values of these two quantities as deduced from the analyses: they ought of course to be equal.

TABLE XVI.—*Table of κ deduced from Analysis.*

1	2	3			4	
a .	c .	Sn.	Au.	Cd.	Au.	Cd.
4.0	7.0	91.76	3.52	4.72	2.3	5.42
5.0	5.05	92.52	5.03	2.45	3.25	2.79
13.98	9.22	89.8	8.7	1.49	5.8	1.75
11.0	8.78	92.2	5.78	2.08	3.75	2.38

5		6	z .	
x .	y .	κ .	$a - x$.	$c - y$.
1.7	4.82	13.6	2.3	2.18
2.65	2.19	9.7	2.35	2.86
5.2	1.15	10.0	8.8	8.0
3.15	1.78	9.4	7.85	7.0

It can be seen from the table that the results of the analyses are quite consistent with the equation of equilibrium, although they

afford results inferior in accuracy to the freezing point determinations.

The preceding results appear to us to prove that the gold and cadmium combine in the ratio $\text{Au} : \text{Cd}$; but the proof that the molecule of the compound, when in solution, is AuCd , and not Au_2Cd_2 , or Au_3Cd_3 , &c., is much weaker. The results of the analyses, and the common temperature at the summit C, of course, throw no light on this point.

We might hope to solve it if the body were more soluble, by calculating tables of κ for other values of n , and the examination of the part AB, by means of the formula Au_2Cd_2 , does throw the only light we have on the matter. If we assume Au_2Cd_2 , the equation of equilibrium for the part AB is $xy/\sqrt{z} = \kappa$, a constant, and the equation to get z is

$$z^2 + (32.917 - c)z = \frac{F(a) + f(c) - D}{0.24}.$$

The resulting values of κ are tabulated in the extreme right-hand column of Table XIV (p. 961). It will be seen that the numbers in the column are not at all constant, but vary from 5 to 15. If we keep the gold constant, κ increases *pari passu* with the amount of cadmium added.

Thus the formula Au_2Cd_2 does not, for the part AB, agree with the experimental facts. The formula Au_3Cd_3 also fails to give a constant κ .

When we consider the part BCD, we find κ equally constant, whether we use the formula AuCd or Au_2Cd_2 ; and this clearly should be the case, for in this part of the curves the bulk of the compound is out of solution, and so its molecular weight becomes of less importance. The equation of equilibrium, $xy = \text{constant}$, is of the same form, whatever value of n we take.

Thus, the only part of the curve that can help us to decide the molecular weight of the compound is the part AB, and the values of κ deduced from this, point pretty clearly to the molecular formula AuCd .

Description of the Plates.

The plates (see next page) represent the fall below the freezing point of pure tin of an alloy of gold and cadmium.

The number of atomic weights of foreign metals present per 100 atomic weights of tin is indicated by the numbers counted from left to right. The observed fall in the freezing point in degrees centigrade is indicated by the numbers counted vertically downwards from 0.

Down to the point A, only one metal (gold in every case but one) was added to the tin. The part beyond A corresponds to the addition of the second metal.

In Plate 1 we have curves of Type I, which may be called the 2- and the 3-atom gold curves. In Plate 2 we have Type II, the 4- and 5-atom gold curves, and the 4-atom cadmium curve. This latter is shifted five spaces to the right, to avoid confusion. Plate 3 contains the saturated gold curves, in which 6.6, 9, and 11 atoms of gold, respectively, were first added. In the upper part of Plate 3 is seen the part PQ of the 11-atom gold curve which is due to the first additions of cadmium. This portion was examined with especial care.

The curves here given are merely intended to serve as diagrams, but in order to calculate the tables of z and κ the original numbers have been charted on the scale of two degrees or two atoms to a decimetre. Even on this large scale most of the experimental points lie on the curve.

A 7-atom cadmium curve has been worked through, and has the same character as the 4-atom curve, but it is not given in the plates.

In conclusion, we must express our best thanks to Miss Field, of Newnham College, for her able assistance in making a large number of freezing point determinations and analyses.

We are also much indebted to Dr. G. H. Milnes for making several control analyses.

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