

XXVII.—*The Molecular Weights of Metals when in Solution.*

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IN a communication made to the Chemical Society, and published in the Proceedings, 1889, p. 41, we described some preliminary experiments made by us to ascertain the application of the method developed by Raoult to the case of metals in solution in each other. Since then we have continued our work in this direction, and published the results, obtained by dissolving metals in sodium (*Chem. Soc. Trans.*, 1889, **55**, 666).

We now wish to bring forward the conclusion we have arrived at by using tin as the solvent. In carrying out this work we have had three chief points in view: α .—To ascertain how far the general conclusions arrived at by Raoult held for the solution of one metal in another. β .—To ascertain the atomicity (number of atoms) of the elementary molecules in solution. And γ .—To compare metallic solution with the solution of salts. We therefore propose to consider the work in three sections:—

A. Method of experimenting, with tables of results obtained.

B. Discussion of these results as bearing on the general theory of solution.

C. Methods of measuring accurately the temperatures we have employed.

Section A.

The experiments were made in the heavy iron blocks, as described in our paper on the lowering of the freezing points of sodium (*loc. cit.*), using paraffin on the top of the tin, in order to prevent oxidation. The molten tin was kept continually stirred by means of a water motor, and the rate of cooling of the blocks was regulated by surrounding them with asbestos cloth. The thermometers will be fully described in Section C; suffice it to say for the present that they were carefully calibrated, and would read accurately differences of temperature of 0.01°C . We may also state that, owing to the method by which the fixed points of our thermometers were determined, the temperatures given are nearly those of an air thermometer.

From an inspection of the tables, it will be seen that we have at present carried only a few of the metals to saturation; in some cases such as cadmium and lead, not given in the tables, we have found the limit of solubility, but cannot at present give the corresponding

temperature until we have calibrated and determined the fixed points of our thermometers for measuring the lower temperatures.

To make it clear how the atomic falls are arrived at from our experimental values, we give a simple example. Thus in Experiment 3, Table I, silver in tin, we had a total weight of 4.3085 grams of silver dissolved in 400 grams of tin, that is, $\frac{4.3085}{108}$ atomic weights of silver.

Hence in 100 atoms of tin we had

$$\frac{4.3085 \times 118 \times 100}{108 \times 400} = 1.177 \text{ atoms of silver.}$$

Now the observed freezing point of the tin was 231.68° , and of the alloy of tin and silver containing 1.177 atoms per 100 atoms of tin, 228.29° ; the fall, therefore, was 3.39° . Hence the atomic fall, or fall for 1 atom per 100 of tin was $\frac{3.39}{1.177} = 2.875$.

TABLE I.—*Silver in Tin.*

Expt. No.	Weight of tin in block.	Weight of silver added in succession.	Total weight of silver present.	Freezing point of solution.	Atoms of silver per 100 of tin.	Atomic fall.
1	400	0.3645	0.3645	231.68°	0.099	2.96
2		1.556	1.9205	231.385	0.524	2.93
3		2.388	4.3085	230.15	1.177	2.875
4		3.9012	8.2097	228.295	2.242	2.775
5		5.355	13.565	225.46	3.705	2.855
6		6.874	20.439	221.1	5.582	
7	450			221.1	4.962	
8	500		"	221.1	4.466	
9	550		"	221.1	4.06	
10	600		"	221.86	3.722	2.638
11	650		"	222.575	3.435	2.65

Second Series (obtained with a different thermometer from above).

1	300	2.9215	2.9215	231.74	1.064	2.927
2	"	5.317	8.239	228.626	3.00	2.728
3*	"	3.300	11.539	223.555	4.204	
4	"	1.05	12.589	221.12	4.585	
5	350		"	221.32	3.93	2.651
6	400		"	222.507	3.44	2.685
7	450		"	223.482	3.063	2.696

* Very steady temperature.

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Silver prepared by Stas' method in finely-powdered, spongy condition was dropped in and dissolved easily.

TABLE II.—*Nickel in Tin.*

Expt. No.	Weight of tin in block.	Weights of nickel added in succession.	Total weight of nickel in block.	Freezing point of solution.	Atoms of nickel per 100 of tin.	Atomic fall.
	300			231·595°		
1	330	0·161	0·161	231·3	0·098	3·01
2	360	0·1855	0·3465	231·035	0·1933	2·897
3	390	0·169	0·5155	230·81	0·2655	2·957
4	420	0·1905	0·706	230·82	0·3378	
5	472·8			230·825	0·3001	
6	525·2			230·88	0·270	2·648
7	575·2			230·925	0·2466	2·717

The sample of nickel used was thin sheet, part of a crucible cover. Each quantity of nickel was kept for some time at a dull-red heat in a vacuum with weighed quantities of tin; it dissolved slowly.

TABLE III.—*Gold in Tin.*

Expt. No.	Weight of tin in block.	Weight of gold added in succession.	Total weight of gold present.	Freezing point of solution.	Atoms of gold per 100 of tin.	Atomic fall.
	200			231·8°		
1		0·2211	0·2211	231·62	0·0663	2·72
2		0·543	0·7641	231·14	0·2292	2·88
3		0·509	1·2731	230·675	0·3818	2·94
4		0·513	1·7861	230·23	0·5356	2·95
5		0·520	2·3061	229·74	0·6915	2·98
6		0·5235	2·8296	229·29	0·8686	2·89
7		1·011	3·8406	228·4	1·152	2·93
8		1·2992	5·1398	227·3	1·542	2·918
9		1·2695	6·3093	226·18	1·892	2·97
10		1·9205	8·2298	224·45	2·465	2·98
11		2·197	10·4268	222·425	3·127	2·997
12		2·2075	12·7343	220·425	3·818	2·913
13		1·5865	14·3208	219·39	4·294	2·89

The gold used was pure, obtained from Johnson and Matthey's; it dissolves at once on adding it to the tin. Unfortunately, the thermometer with which these experiments were made was broken before it was calibrated, but by a comparison of the results with other experiments we have been able to effect a partial calibration.

TABLE IV.—*Copper in Tin.*

Expt. No.	Weight of tin in block.	Weights of copper added in succession.	Total weight of copper in block.	Freezing point of solution.	Atoms of copper per 100 of tin.	Atomic fall.
1	400			231·611°		
2	420	0·3118	0·3118	231·215	0·1388	2·85
3	440	1·2345	1·5463	229·692	0·657	2·921
4	460	3·646	5·2923	226·758	2·151	2·25
5	510		„	226·758	1·94	
6	560		„	226·758	1·767	2·746
	610		„	227·07	1·623	2·798

The copper was electrolytic sheet, it was dissolved like the aluminium, nickel, &c., in a vacuum. The saturated or eutectic alloy contains 1·74 atoms of copper per 100 of tin.

TABLE V.—*Thallium in Tin.*

Expt. No.	Weight of tin in block.	Weights of thallium added in succession.	Total weight of thallium in block.	Freezing point of solution.	Atoms of thallium per 100 of tin.	Atomic fall.
1	400			231·543°		
2	„	0·77	0·77	231·2	0·112	3·09
3	„	0·7264	1·497	230·92	0·217	2·897
4	„	1·7537	3·25	230·235	0·4707	2·778
5	„	2·057	5·307	229·384	0·751	2·877
6	„	3·366	8·673	228·048	1·256	2·78
7	„	4·083	12·756	226·473	1·847	2·78
8	„	4·751	17·51	224·619	2·514	2·754
9	„	5·801	23·31	222·591	3·376	2·652
10	„	4·731	28·04	220·825	4·113	2·668
11	„	7·712	35·75	218·243	5·178	2·569
12	„	8·723	44·47	215·555	6·44	2·483
13	„	10·53	55·01	212·502	7·97	2·39
14	„	9·987	64·99	210·202	9·41	2·268
15	„	9·046	74·04	207·828	10·72	2·212
16	„	9·631	83·67	205·415	12·12	2·155
	„	13·168	96·84	14·03	202·3	2·084

The alloy when poured out weighed 495·9 grams; hence the loss was 0·94 gram or 0·2 per cent.

TABLE VI.—*Sodium in Tin.*

Expt. No.	Weight of tin in block.	Weight of sodium added in succession.	Total weight of sodium present.	Freezing point of solution.	Atoms of sodium per 100 of tin.	Atomic fall.
1	400	1·027	1·027	231·695°	1·317	2·82
2	"	1·4285	2·456	227·974	3·15	2·855
3*	"	1·233	3·689	222·708	4·73	2·469
4†	"	1·475	5·164	220·016		

In these experiments the sodium was added directly to the tin, which was kept at the high temperature of 260° C., and vigorously stirred while the sodium was added. This was necessary, as otherwise a hard, infusible body was formed.

TABLE VII.—*Palladium in Tin.*

Expt. No.	Weight of tin in block.	Weight of palladium added in succession.	Total weight of palladium present.	Freezing point of solution.	Atoms of palladium per 100 of tin.	Atomic fall.
1	400			231·54°		
2	450	0·125	0·125	231·47	0·0308	2·28
3	470	0·5501	0·6751	231·072	0·159	2·943
4	490	0·5725	1·2476	230·9	0·282	2·27
5	590		"	230·9	0·234	
6	690		"	230·995	0·2003	2·722
	740		"	231·02	0·1863	2·792

In Experiment 1 the palladium was a black powder which dissolved only slowly in tin at a red heat. In the other experiments palladium foil was used; when heated in a vacuum with fused tin, it became incandescent at the moment of solution.

Platinum was also tried in tin; whilst it dissolves freely at high temperatures with vivid incandescence, it appears to separate out completely before the freezing point of tin is reached.

* Stirrer grated.

† Stirrer stuck 4° C. above last reading.

TABLE VIII.—*Magnesium in Tin.*

Expt. No.	Weight of tin in block.	Weight of magnesium added in succession.	Total weight of magnesium present.	Freezing point of solution.	Atoms of magnesium per 100 of tin.	Atomic fall.
	350			231·545°		
1	380	0·7500	0·7500	228·855	0·973	2·76
2	410	1·216	1·966	224·83	2·364	2·84
3	440	1·008	2·974	222·45	3·332	2·728
4	460	0·541	3·515	220·92	3·766	2·82
5	480	2·1355	5·650	214·97	5·803	2·856
6	500	2·1395	7·750	209·8	7·64	2·846

The magnesium alloys were made by fusing magnesium in a vacuum with small quantities of tin.

The alloys were very crystalline and attacked glass considerably.

Potassium in Tin.

Potassium in tin was tried, but the experiment failed. A hard, infusible compound was formed.

Potassium-tin alloys were afterwards made in a vacuum, but when exposed to the air at ordinary temperatures, they ignited and smouldered.

TABLE IX.—*Lead in Tin.*

Series I.

Expt. No.	Weight of tin in block.	Weights of lead added in succession.	Total weight of lead present.	Freezing point of solution.	Atoms of lead per 100 of tin.	Atomic fall.
	300			231·595°		
1	„	0·3004	0·3004	231·445	0·0573	2·62
2	„	0·4034	0·7038	231·23	0·1341	2·722
3	„	0·6945	1·3983	230·878	0·2665	2·69
4	„	0·8646	2·2629	230·39	0·4312	2·794

Series II.

	300			231·64°		
1	„	2·828	2·828	230·135	0·5389	2·792
2	„	2·6503	5·4783	228·835	1·044	2·687
3	„	2·2055	7·6838	227·74	1·4643	2·663

TABLE IX—*continued*.

Series III.

Expt. No.	Weight of tin in block.	Weights of lead added in succession.	Total weight of lead present.	Freezing point of solution.	Atoms of lead per 100 of tin.	Atomic fall.
1	300	10·269	10·269	231·62°	1·957	2·56
2	"	5·353	15·627	224·75	2·978	2·307
3	"	10·485	26·112	219·58	4·976	2·42
4	"	10·935	37·047	215·31	7·06	2·31
5	"	12·3675	49·415	210·893	9·417	2·202

This experiment was continued to saturation, which occurred at 35 atoms of lead per 100 of tin.

Lead foil dissolves freely on direct addition to the fused tin.

TABLE X.—*Zinc in Tin*.

Expt. No.	Weight of tin in block.	Weight of zinc added in succession.	Total weight of zinc present.	Freezing point of solution.	Atoms of zinc per 100 of tin.	Atomic fall.
1	400	0·326	0·326	231·735°	0·148	2·54
2	"	0·3603	0·6863	231·36	0·311	2·562
3	"	0·4433	1·1296	230·92	0·5118	2·667
4	"	0·9469	2·0765	230·37	0·9409	2·65
5	"	2·8265	4·943	229·242	2·222	2·631
6	"	3·429	8·332	225·89	3·775	2·589
7	"	5·915	14·247	221·96	6·456	2·489
8	"	9·533	23·78	215·665	10·775	2·065
9*	"	11·967	35·747	206·89	16·197	2·065
10	"	3·7096	39·457	198·28		
11	450		"	198·28		
12	500		"	200·44	14·303	2·188

Zinc dissolves like sugar in water on direct addition to the tin.

In Experiments 9 and 10 the stirrer grated considerably, long before the temperature fell to the freezing point; but as at the freezing point there was surfusion, it appears clear that zinc alone had crystallised out; otherwise there would have been no surfusion at the freezing point.

* On ceasing to stir, the temperature rose slightly, and then was very steady.

TABLE XI.—*Cadmium in Tin.*

Expt. No.	Weight of tin in block.	Weights of cadmium added in succession.	Total weight of cadmium present.	Freezing point of solution.	Atoms of cadmium per 100 of tin.	Atomic fall.
	400			231·617°		
1	420	0·242	0·242	231·465	0·0607	2·504
2	440	0·3982	0·6402	231·235	0·1533	2·492
3	450	2·0565	2·6967	230·094	0·6314	2·412
4	460	5·209	7·906	227·295	1·811	2·386
5	470	10·034	17·904	222·465	4·0139	2·28
6	480	10·047	27·9867	218·84	6·143	2·08
7	490	10·1	38·0867	215·48	8·193	1·97
8	500	10·265	48·352	212·375	10·193	1·899

The cadmium alloys were obtained by heating weighed quantities of cadmium and tin in vacuous hard-glass tubes. The tin was saturated with cadmium, when about 47 atoms of cadmium were present per 100 atoms of tin.

TABLE XII.—*Mercury in Tin.*

Expt. No.	Weight of tin in block.	Weights of mercury added in succession.	Total weight of mercury present.	Freezing point of solution.	Atoms of mercury per 100 of tin.	Atomic fall.
	400			231·63°		
1	"	0·6175	0·6175	231·40	0·0911	2·525
2	"	0·608	1·226	231·2	0·1809	2·377
3	"	0·8945	2·120	230·893	0·3127	2·366
4	"	1·8725	3·9924	230·223	0·5889	2·377
5	"	3·3156	7·308	229·05	1·078	2·393
6	"	4·3905	11·6985	227·53	1·7256	2·376
7	"	7·0925	18·791	225·05	2·772	2·374
8	"	7·5555	26·3465	223·07	3·886	2·206
9	"	15·2845	41·631	219·395	6·141	1·993
10	"	20·813	62·44	214·62	9·21	1·846
11	"	6·9755	69·42	213·06	10·24	1·814

The addition of mercury was continued, and the fall in freezing point noted until 183 atoms of mercury were present per 100 atoms of tin; after this the surfusion ceased to be perceptible, and the experiment, therefore, was discontinued.

TABLE XIII.—*Bismuth in Tin.*

Expt. No.	Weight of tin in block.	Weight of bismuth added.	Total weight of bismuth present.	Freezing point of solution.	Atoms of bismuth per 100 of tin.	Atomic fall.
	400			231·73°		
1	"	0·1166	0·1166	231·69	0·0164	2·44
2	"	0·1939	0·3105	231·62	0·0436	2·525
3	"	0·1987	0·5092	231·55	0·0715	2·518
4	"	0·3425	0·8517	231·42	0·1196	2·592
5	"	0·6692	1·5209	231·2	0·2137	2·48
6	"	1·7922	3·313	230·65	0·4653	2·32
7	"	1·7083	5·021	230·1		
8	"	2·176	7·197	229·4	1·011	2·306
9	"	2·652	9·849	228·49	1·383	2·356
10	"	5·683	15·532	226·82	2·18	2·252
11	"	2·224	17·756	226·19	2·495	2·22
12	"	2·545	20·301	225·475		
13	"	3·458	23·759	224·43	3·34	2·136
14	"	4·865	28·624	223·03	4·02	2·17
15	"					

The bismuth dissolved easily on direct addition to the tin. The same thermometer was used as in the gold series.

TABLE XIV.—*Calcium in Tin.*

Expt. No.	Weight of tin in block.	Weight of calcium added in succession.	Total weight of calcium present.	Freezing point of solution.	Atoms of calcium per 100 of tin.	Atomic fall.
1	200			231·5°		
2	230	0·0888	0·0888	231·2	0·114	2·63
	260	0·068	0·1568	231·1	0·178	2·24

The calcium was from Harrington's, of Cork, in round lumps, very hard, and had to be cut with a cold chisel. The alloys of calcium and tin were made by heating in a hard-glass tube in a current of hydrogen. At the moment the calcium dissolves, there is vivid incandescence and a slight reduction of the glass at the point of contact. In a previous experiment the calcium was thrown directly into the block, but did not all dissolve. 0·0991 gram of calcium or 0·139 atom gave an atomic fall of 2·1 with the same minimum temperature of 231·1° as in the above experiments; hence we conclude that the solution was saturated.

TABLE XV.—*Indium in Tin.*

Expt. No.	Weight of tin in block.	Weights of indium added in succession.	Total weight of indium in block.	Freezing point of solution.	Atoms of indium per 100 of tin.	Atomic fall.
	200			231·585		
1	„	0·2246	0·2246	231·322	0·1173	2·24
2	„	0·202	0·4266	231·18	0·2227	1·82
3	„	0·5715	0·9981	230·64	0·5208	1·813
4	„	0·4235	1·4216	230·22	0·7423	1·839
5	300		1·4216	230·65	0·495	1·889

Indium dissolves readily on direct addition to molten tin.

TABLE XVI.—*Aluminium in Tin.*

Series I.

Expt. No.	Weight of tin in block.	Weights of aluminium added in succession.	Total weight of aluminium present.	Freezing point of solution.	Atoms of aluminium per 100 of tin.	Atomic fall.
	400			231·642°		
1	420	0·4805	0·4805	231·017	0·5	1·25
2	440	1·193	1·6735	229·33	1·662	1·303
3	460	0·9575	2·631	228·723	2·5	1·167
4	480	0·5	3·131	228·726	2·851	
5	530*		„	228·726	2·581	
6	580		„	228·71	2·171	
7	630		„	228·9	2·01	1·363

Series II.

	350			231·507		
	435	1·696	1·696	229·264	1·704	1·317
	445†	1·3565	3·0525	228·639	3·00	0·956
	455	0·349	3·4015	228·63	3·27	
	475‡		„	228·63		
	575		„	228·63		
	625		„	228·63		
	675		„	228·63		
	695		„	228·779	2·14	1·275
	715		„	228·852	2·08	1·275

* Temperature very steady.

† Very stationary.

‡ Raised to 278° C. before finding freezing point

Series I.—Experiments 1 and 2 were made with thin aluminium foil; Experiments 3 and 4 were made with a new sample of aluminium from Johnson and Matthey's; purest by the sodium method.

Series II.—Johnson and Matthey's pure sheet aluminium was used. A different sample from Series I.

The aluminium was got into solution by fusing with weighed quantities of tin in hard-glass tubes in a vacuum; under these conditions, it dissolves freely at a low red heat. The rich alloys of aluminium with tin, obtained in the tubes, were brittle and friable. At the end of Series I, the paraffin above the alloy in the block appeared as a thick, white, gelatinous substance.

Other experiments, using aluminium from quite different sources, have confirmed these results.

From the foregoing experiments we conclude that, as in the case of gold and other metals dissolved in sodium (*q.v.*), the addition of a metal to tin causes a depression in the freezing point at first proportional to the weight of metal added, but that as the solution grows stronger and the volume increases, this proportion does not appear to hold (see Section II). A depression is maintained with each successive addition up to the very point when no further effect whatever is produced (see curves for zinc, Table XVIII, and for silver, copper, aluminium, nickel, and palladium, Table XVII).

The following table gives the minimum freezing point which can be obtained by dissolving in tin each of the metals mentioned:—

TABLE XIX.—*Eutectic Alloys of Tin.**

Metal alloyed with tin.	Atoms per 100 of tin.	Percentages of added metal per 100 of alloy.	Freezing point.
Aluminium.....	2.11	0.48	228.73°
Copper	1.73	0.915	226.76
Nickel.....	0.26	0.13	231.82
Palladium.....	0.20	0.18	230.90
Zinc	15.73	7.98	198.28
Silver	4.0	3.53	221.1
Cadmium	45 (about)		
Lead.....	35 (about)		182° (about)

The behaviour of antimony when alloyed with tin is very remarkable, for of the seventeen metals we have examined it is the only one

* An eutectic alloy (as used by Guthrie) is that particular mixture of two metals which solidifies at the lowest temperature, namely, it is the temperature at which the solvent becomes saturated with the added metal.

which behaves abnormally, namely, by its addition to tin it produces a rise in the freezing point instead of a depression (see Table XX).

TABLE XX.—*Antimony in Tin. Antimony causes a Rise.*

Expt. No.	Weight of tin in block.	Weight of antimony added in succession.	Total weight of antimony present.	Freezing point of solution.	Atoms of antimony per 100 of tin.	Atomic rise. _j
	400					
1		0·1437	0·1437	231·54°		
2		0·1640	0·3077	231·675	0·056	2·4
3*		2·101	2·409	231·75	0·0756	2·64
4		2·1694	4·578	233·05	0·592	2·55
5		2·944	7·522	234·23	1·126	2·39
6		3·1275	10·649	235·8	1·849	2·3
				237·32	2·618	2·21

In Experiment 6, the stirrer worked with much grittiness towards the end.

There was very little surfusion with antimony.

Section B.

Discussion of the Experimental Results.

Our experiments lead to the following conclusions as to what takes place when an alloy is near its solidifying point. For example, taking the case of copper dissolved in tin as typical, we will consider what happens when it contains less than 0·915 per cent. of copper. As the solution cools below the freezing point of tin, pure tin crystallises out, the remaining liquid becoming more and more concentrated.† As the result, this liquid will have a lower freezing point (for freezing point is approximately proportional to the concentration). As the still liquid portion cools, pure tin continues to crystallise out at continually lower temperatures until the concentration of 0·915 per cent. is reached. At this moment copper begins to separate *pari passu* with the tin, and the concentration of the liquid does not alter, but the whole solidifies gradually at the constant temperature of 226·76°. When we start with an alloy of a concentration of 0·915 per cent. of copper in tin, it solidifies to a mass in which the copper is uniformly distributed throughout the tin;‡ a substance which is mechanically

* Very constant temperature.

† It thus behaves exactly like a dilute solution of common salt in water when cooled below zero.

‡ In the case of gold dissolved in sodium we find on treating the alloy with alcohol, that the gold is left in the form of a spongy mass of needle-shaped crystals.

homogeneous. It is difficult to see how a solution either stronger or weaker than this can solidify slowly and remain homogeneous. The behaviour of an alloy on cooling was well shown in the case of zinc; when supersaturated (above 7.98 per cent. zinc), and at a temperature above the freezing point of tin the whole alloy was liquid, but as it cooled a considerable quantity of solid matter separated out, and the stirrer scraped against the sides of the crucible as the solution solidified; at a temperature of 198.28° well-marked surfusion took place. This solid matter which separated out cannot, therefore, have been tin, or otherwise it would have acted as a nucleus and prevented all surfusion taking place. It must, therefore, be either zinc or a compound of zinc and tin; we have experiments in view by which we hope to clear up this point. The above experiments with zinc, as also many other metals, show that the solubility of metals in tin increases with the temperature as for most other cases of solution. The behaviour of a solvent in crystallising out before the substance dissolved (in dilute solutions) is taken advantage of in concentrating brine in cold climates and in the separation of lead from silver (Pattinson's method). The experiments of Roberts Austen on the regulus of Venus and other alloys also illustrate the same point. It also accounts for the capability of being moulded possessed by the solder used in "wiping" plumbers' joints.

The difficulty of obtaining a plate of pure gold for a "trial plate" in the Mint is possibly due to the allied metals partially separating from the solvent as it cools.

Comparison of our Results with the Empirical Laws of Coppet and Raoult.

These laws are:—

(1.) That for moderate concentrations the fall in the freezing point is proportional to the weight of the dissolved substance present in a constant weight of solvent.

(2.) That when the falls produced in the same solvent by different dissolved substances are compared, it is found that a molecular weight of a dissolved substance produces the same fall whatever the substance is.

(3.) That if we take a constant number of molecular weights of the solvent, then the fall is independent of the nature of the solvent.

The first of these laws is well borne out by our results, as a study of any one of the tables or diagrams will show.

The second law cannot be tested without some assumption, for we had no means of deciding how many atoms of a metal form its mole-

cule when in solution in tin. But from the fact that atomic weights of different metals produce the same fall, we might conclude that if Raoult's second law be true, then the molecules of these metals are all of the same type, say X_n , where n is the constant number of atoms in the molecule. By making the bold assumption that the molecule of zinc or of mercury is monatomic in solution in tin, as it is when in the gaseous state, one might infer that n was unity for the other metals.

Raoult's third law we found to be probably incorrect; for one atomic weight of gold when in solution in 100 atomic weights of a solvent causes a fall of about 4° when the solvent is sodium, and about 3° when the solvent is tin, and about 1.8° when the solvent is potassium. Van't Hoff has already shown that this law is false in fact and in theory (*Phil. Mag.*, 1888, **26**, 81).

Thanks to Professor Ramsay's translation of Van't Hoff's paper quoted above, we became aware, soon after we had commenced our experiments, of the theoretical explanation of the lowering of the freezing point. Van't Hoff, from the theory of osmotic pressure and the second law of thermodynamics, obtains the formula $\delta\theta = 0.02 \frac{\theta^2}{\lambda}$ for the lowering $\delta\theta$ of the freezing point when 1 mol.

weight in grams of a substance is dissolved in 100 grams of a solvent. In this formula, θ is the freezing temperature of the solvent reckoned from the absolute zero of the air thermometer, and λ is the latent heat of fusion of the solvent.

The application of this formula shows that 1 mol. of any metal dissolved in 100 atomic weights of tin ought to cause a depression of 3° Centigrade in the freezing point. As this is so near the fall produced by an atomic weight of most of the metals we have examined, it seems at least very probable that the molecules of the metals are monatomic when in solution in tin (see Table of Atomic Falls, p. 392).

Professor J. J. Thomson ("Application of Dynamics to Chemistry and Physics," p. 263) has obtained by entirely different reasoning, based on Lagrange's equation of motion, but with the same assumptions as to osmotic pressure, the really identical formula $\delta\theta = \frac{\omega\theta}{\rho\lambda}$, where ρ is density of the solvent, $\delta\theta$, θ , λ have the same values as before, and ω is the osmotic pressure, that is the pressure, that the molecules of the dissolved substance are exerting inside the solution. Van't Hoff assumes and has done much to prove that this pressure obeys Boyle's, Gay Lussac's, and Avogadro's laws, and so can be easily calculated.

It is not necessary to give here a rigid proof of the above formula,

This number is so nearly equal to the fall produced by 1 *atomic* weight of most of the metals examined as to make it very probable that their molecules, when in dilute solution in tin, are monatomic.

Professor Ramsay (Trans., 1889, 55, 521), by his experiments on the vapour pressure of solutions of metals in mercury, and G. Tammann,* by experiments similar to ours but using mercury as the solvent, have arrived at the same result.

The atomic falls obtained for aluminium are so nearly half the average atomic falls that it seems probable that the molecule of aluminium when in solution in tin consists of 2 atoms.

To show this, we have in the diagram plotted the falls of aluminium on double the scale of the other metals.

We think that this method might be applied as a control for atomic weights, similar to that afforded by Dulong and Petit's law of specific heats.

The freezing points are so definite that they might, with advantage, be used for giving fixed points on thermometers.

Van't Hoff's formula cannot be applied to more concentrated solutions, but perhaps J. J. Thomson's might be so applied.

To do so, we must bear in mind that w varies as $\theta - \varepsilon\theta$ and not as θ , and also that the volume of the solution is getting larger than the volume of the original solvent. To find the total volume, we must find by experiment the density of the liquid alloy. We hope to determine these densities and so trace the changes in the atomic falls and in the osmotic pressure in concentrated solutions.

In order to obtain from the observations the most probable value of the atomic fall in dilute solutions, it seems best to add together all the total falls below the freezing point of tin, to add together all the fractions of an atom of the dissolved metal used, and to divide the first sum by the second.

Thus in the case of thallium in tin, the experiments in which the concentration was less than 1 atom of thallium in 100 atoms of tin were:—

Atoms, f. p.	Falls below f. p. of tin.
0.1115	0.345° C.
0.2168	0.628
0.4707	1.308
0.7510	2.159
Totals. 1.55	4.44

Then $\frac{4.44}{1.55} = 2.86^\circ \text{C.}$ is the mean.

* "Zur Konstitution der Legierungen," *Zeitschrift für physikalische Chemie*, III Band, 5 Heft.

392 MOLECULAR WEIGHTS OF METALS WHEN IN SOLUTION.

We *add* the falls because each is liable to the same absolute error in the temperature.

The following table has been calculated as above from the experimental results under 1 atom :—

Atomic Falls for a Concentration of under one Atom.

I.	{	Nickel	2.94	3 experiments.
		Silver	2.93	2 „
		Gold	2.93	6 „
		Copper	2.91	2 „
		Thallium	2.86	4 „
		Sodium	2.84	2 expts. concn. 1—3 atoms.
		Palladium	2.78	4 experiments.
		Magnesium	2.76	1 „
		Lead	2.76	8 „
II.	{	Zinc	2.64	4 „
		Cadmium	2.43	3 experiments.
		Mercury	2.39	4 „
		Bismuth	2.40	6 „
		Calcium	2.40	2 „
III.	{	Indium	1.86	5 experiments.
		Aluminium	1.25	1 „

With the exception of calcium, where the error may be large, there can hardly be an experimental error of 5 per cent. in these, and we should think that in most cases it is much less.

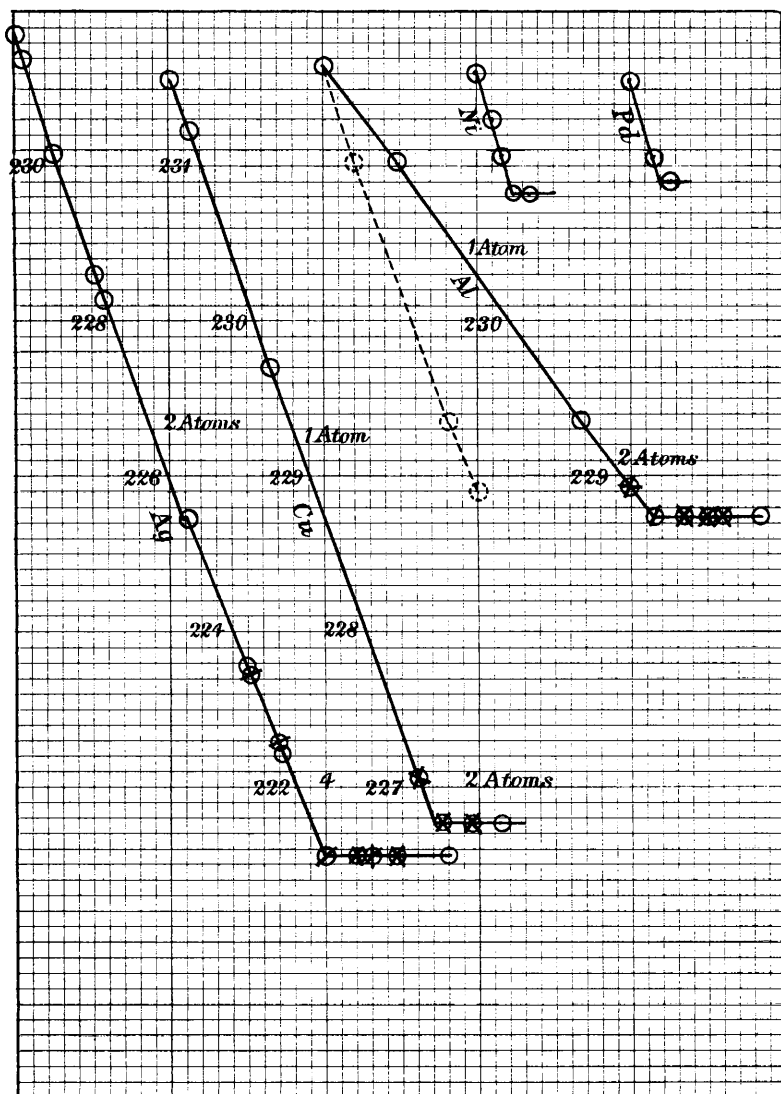
In a few cases, by taking a stronger solution than 1 atom per 100, it would be possible to bring the numbers more together, for example, the atomic fall for magnesium increases to 2.86°, if not more. Similarly, aluminium increases to 1.4°. Antimony causes a rise of about 2.5° per atom, but this may be due to other causes and have no connection with the other numbers; at all events, we do not see how, on theoretical grounds, this rise can be explained.

It seems clear that the nature of the metal in solution has some effect on the fall, although the atomic falls for Group I are so near the theoretical molecular fall of 3° as to make it seem very likely that their molecules are monatomic in solutions in tin.

It is curious that cadmium, mercury, and to some extent zinc, whose molecules in the gaseous state are believed to be monatomic, should give falls abnormally low, as if there were some condensation in these cases.

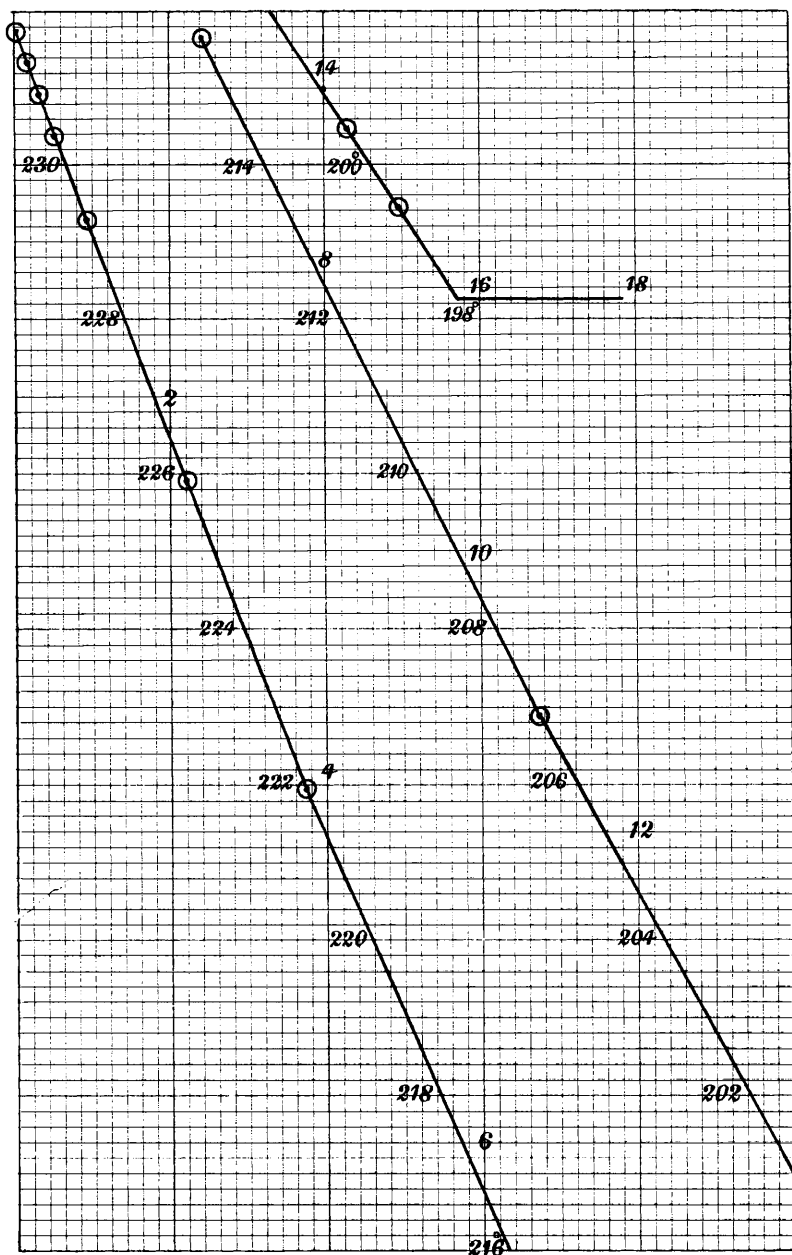
The case of indium suggests partial condensation, and that of aluminium strongly suggests diatomic molecules.

PLATE 1.
METALS SPARINGLY SOLUBLE IN TIN.



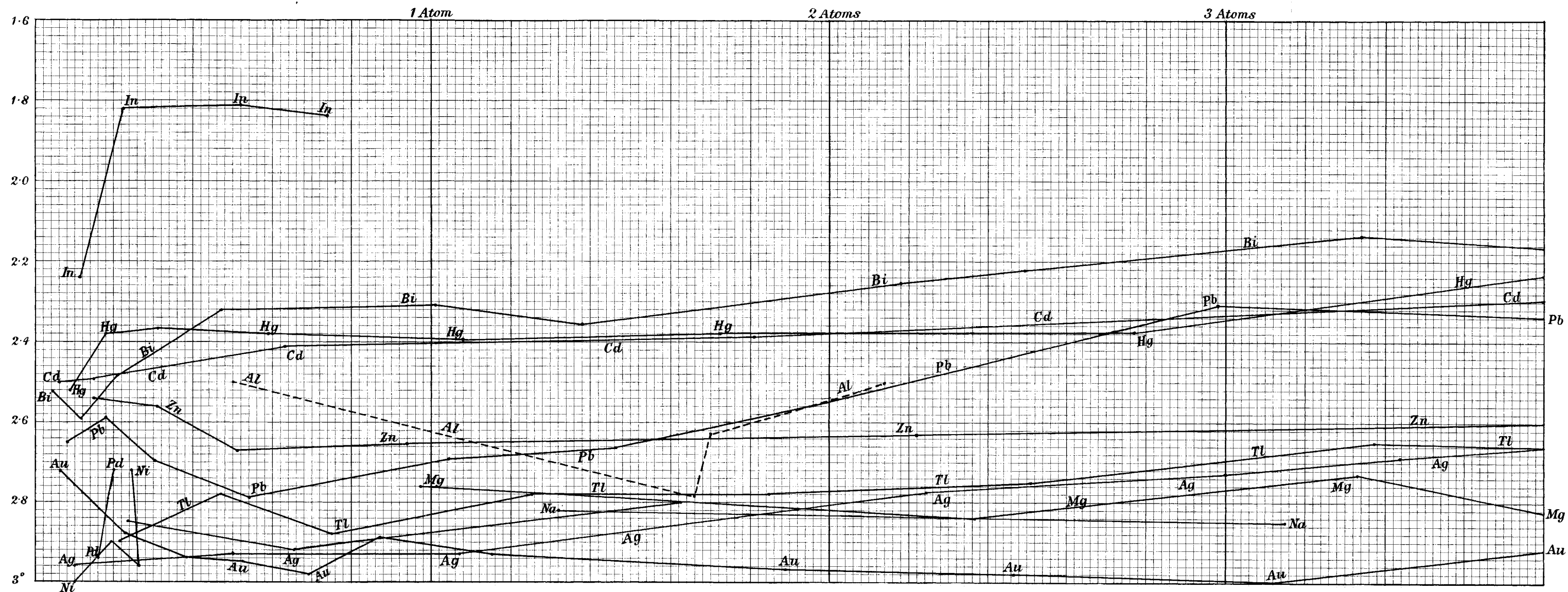
THE DIAGRAM SHOWS THE TEMPERATURE AT WHICH SOLUTIONS OF DIFFERENT CONCENTRATIONS BEGIN TO FREEZE. NUMBERS ON THE LEFT ARE CENTIGRADE TEMPS. THE DOTTED LINE FOR ALUMINIUM CORRESPONDS TO A MOLECULAR WEIGHT OF 54. POINTS MARKED WITH A CROSS WERE OBTAINED BY ADDING TIN TO THE SATURATED ALLOYS.

PLATE 2.
ZINC IN TIN.



NUMBERS ON THE LEFT HAND SIDE OF THE CURVE ARE CENTIGRADE TEMPERATURES.

NUMBERS ON THE RIGHT ARE THE NUMBER OF ATOMS ZN. PRESENT PER 100 ATOMS OF SN.



IN THIS DIAGRAM THE NUMBER OF ATOMS PRESENT IS MEASURED HORIZONTALLY FROM THE LEFT.
 THE ATOMIC FALLS ARE MEASURED VERTICALLY DOWNWARDS FROM A POINT 7 INCHES ABOVE THE TOP LINE.
 THE DOTTED LINE MARKED *Al* GIVES TWICE THE OBSERVED FALLS CAUSED BY THE PRESENCE OF THIS METAL.

The cases of gold, magnesium, and aluminium, in which the atomic fall seems really to rise or remain constant with increasingly concentrated solutions, probably point to the appropriation of some of the tin by the dissolved metal, as in the formation of hydrated salts, but until we have determined the densities of the liquid alloys, it is not possible to calculate the theoretical value of the osmotic pressure with sufficient accuracy to discuss this.

(To be continued.)

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