Complete Freezing-Point Curves of Binary Alloys Containing Silver or Copper Together with Another Metal

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II. *Complete Freezing-Point Curves of Binary Alloys containing Silver or Copper together with another Metal.*

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SECTION I.

THIS paper contains some results of a study of the freezing points of binary alloys, the freezing points being traced for all proportions of the two metals, so that the results when plotted give a complete freezing-point curve.

The freezing point, properly speaking, is the temperature at which a liquid and some solid that can be formed from it are in equilibrium. In practice, at all events when working with alloys, it is necessary to take as the freezing point the temperature at which solid matter begins to separate from a liquid that is being slowly cooled. The first indication of this formation of solid is generally afforded by a thermometer immersed in the liquid, the heat given out when solid matter separates arresting the fall in temperature and causing the thermometer to register a constant temperature for a shorter or longer time. It is evident that, except when we are dealing with a pure substance, the freezing point obtained in this way must be below the true freezing point. This cause of error can be diminished by using a sensitive thermometer, by using a large mass of substance, and by causing the rate of fall to be very slow.* Surfusion also, where it occurs, must be prevented by the usual method of dropping in nuclei. When the freezing point changes a good deal for a small change in the concentration, this method is liable to give values of the freezing point considerably below the true value.

The general theory of the equilibrium between a liquid mixture of two bodies and the various solids that can be formed from such a mixture, has been developed by LE CHATELIER, VAN'T HOFF, BAKHUIS ROOZEBOOM, KÜSTER, and other writers, and it will be convenient to give here a brief outline of that part of their conclusions which we shall afterwards need.

The solid which separates when a homogeneous liquid mixture of two bodies is cooled may consist of either of the two substances, or it may be a compound formed

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* See note, Section IV.

from them; it may also in certain cases be a solid solution, or it may be an isomorphous mixture of the two bodies, or of a compound with one of them.

To take the simplest case first. Let us suppose that the pure substance A separates in the solid form when we cool the homogeneous liquid AB.* If θ is the equilibrium temperature (the freezing point) reckoned from the thermo-dynamic zero, x the molecular concentration of A in the liquid AB, that is, the fraction of a molecular weight of A contained in every molecular weight in AB, λ the latent heat of solution of a molecular weight of A in AB at the equilibrium temperature, then it is known that these quantities are connected by the equation

$$2 \cdot \frac{dx}{x} = \frac{\lambda}{\theta^2}\, d\theta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

When x is near unity, that is, when but little of B is present, we may fairly take λ to be the latent heat of fusion of A, and θ and $d\theta$ being known by experiment, we may use equation (1) either to deduce x and therefore the molecular condition of B from the known value of λ, or following the reverse order we may obtain λ on some assumption as to the molecular state of B. This course has been largely followed in the study of solutions in water and in organic solvents, but the method has not, so far as we know, been applied to the study of metals of high melting point except by ourselves.

A great and valuable extension of equation (1) is due, we believe, to LE CHATELIER. He assumes, as a first approximation, that λ is independent of x and of θ, and he is thus able to integrate the equation, obtaining

$$2 \log_e x = \lambda \left(\frac{1}{\theta_0} - \frac{1}{\theta} \right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2),$$

where θ_0 is the freezing point of pure A, corresponding to the concentration $x = 1$.

If now we plot as abscissæ the values of x from 1 to 0, and as ordinates the corresponding values of θ calculated from equation (2), we get the ideal freezing-point curve of A. The corresponding curve for B can be plotted in the same way, but from right to left.

The highest point of each curve gives the melting point of the pure substance; and the intersection of the two curves (see fig. 1) gives, as OSTWALD has pointed out, an approximation to the melting point and composition of the eutectic alloy. The freezing-point curves found by experiment will resemble fig. 1, but on account of many causes, which may be summed up as changes in the value of λ, cannot be expected to be identical with it. In fig. 4, we give ideal curves for silver and copper, using in equation (2) the values of λ found by us. If we use PERSON'S value of the

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* By the symbol AB we mean, not a compound of A and B, but any mixture of the two bodies.

latent heat of silver, the two curves will be found to intersect at a composition very near that of the eutectic alloy. The intersection of the experimental curves in the eutectic point terminates the part of each curve which is generally realizable, although by utilizing phenomena of selective surfusion, both Le Chatelier* and Dahms† consider that they have, in one or two cases, traced the lower branches for a short distance.

In a certain sense the phenomenon of the eutectic state gives rise to a horizontal branch of the freezing-point curve, passing through the eutectic point E, fig. 1; for if we take a mixture represented by the point X and allow it to cool, the changes in its state will be represented by points on the vertical XYZ. There will be a freezing point at Y followed by a slow fall in temperature until the temperature Z is reached, when the part *still liquid* will have the composition of the eutectic state E, and will solidify without further fall in temperature, thus giving a second very well marked freezing point. This phenomenon of double freezing points has long been known, and is well shown in the silver-copper curve given in this paper.

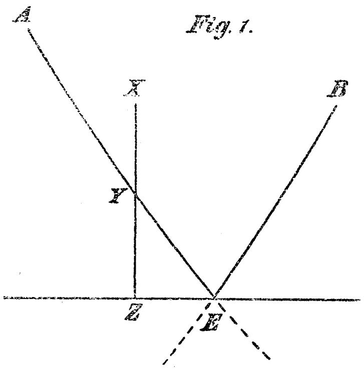
Fig. 1.

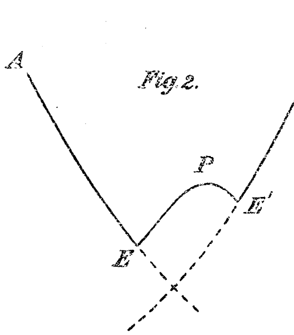
Fig. 2.

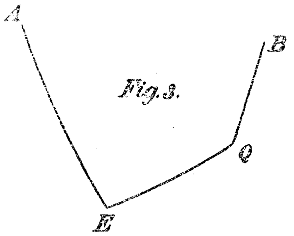
Fig. 3.

Let us now suppose that a compound C of A and B exists, whose composition and melting point in the pure state are given by the point P. Then, if P lies above the curve of fig. 1, and C is not completely dissociated by melting, we shall get a freezing-point curve such as fig. 2, with two eutectic points E and E′. This sort of curve is well illustrated by the copper-aluminium curve given by Le Chatelier (‘Revue Générale des Sciences,’ 30 June, 1895), and in the work of Roozeboom on the equilibrium between water, hydrochloric acid, and ferric chloride (‘Zeitsch. Phys. Chem.,’ vol. 15, p. 588). If more than one compound is possible, the main curves of fig. 1 may be interrupted by more than one such middle curve.

If the compound C is not at all dissociated by melting, then P may be an angle and will divide the figure into the two complete systems AC and CB, each corresponding to the case of fig. 1, and obeying the equations discussed above; but the

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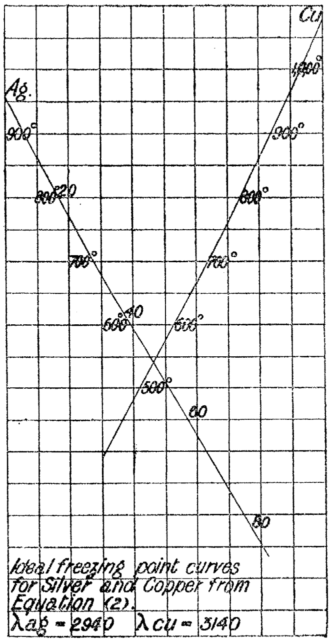
* ‘Comptes Rendus,’ April 9, 1894.

† ‘Ann. Phys. Chem.,’ 1895, vol. 54, 386.

more C is dissociated the more rounded will be the point P, and the less conspicuous the "middle" curve, of which it is the summit. Attention has been drawn to this by LORENTZ and STORTENBECKER ('Zeitsch. Phys. Chem.,' vol. 10, p. 194). If C is wholly dissociated by fusion, we should not expect its existence to be indicated by the freezing-point curve; and as LE CHATELIER has pointed out, if its melting point* lies below the curve of fig. 1, the existence of the compound may equally fail to appear in the freezing-point curve. We believe that such cases of partial dissociation on fusion are probable in the case of alloys (see 'Jour. Chem. Soc.,' 1891, p. 936, and 1894, p. 65).

Fig. 4.



In fig. 3 we have a case of probably frequent occurrence, where P, the melting point of C, lies below the curve B, but a portion of the system CA is possible, as shown by the curve QE. Both LE CHATELIER and ROOZEBOOM give examples of this, and some of the curves occurring in this paper probably contain examples of the same phenomenon.

Thus an intermediate maximum indicates a compound and gives its composition, while an angle such as Q may *indicate* a compound, but does not necessarily give its composition.

If, instead of one of the pure bodies A or B, or a compound, the substance formed is a "solid solution," in VAN'T HOFF's sense of the word, we should expect the line of freezing points starting from the point A to rise, or at all events the fall in the

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* In such a case the compound decomposes into a solid and a liquid part; as when the deca-hydrate of sodium sulphate "melts" in the presence of a saturated solution of the salt.

freezing point caused by the presence of B to be less than the normal. It is not quite certain that the experiments described in the present paper contain any examples supporting VAN'T HOFF's theory of solid solutions.

On the other hand, the fact proved experimentally by KÜSTER and by LE CHATELIER, that when the solid separating is an isomorphous mixture of A and B, all the freezing points lie on a straight line joining A to B, is probably illustrated by part of the copper-tin curve.

When the liquid AB separates into two conjugate liquids before the formation of solid, this process, which, since it generally occurs with falling temperature, may be expected to be exothermic, might evolve enough heat to affect the thermometer and give a false freezing point. The freezing point curve of a pair of conjugate liquids in contact with each other is perfectly illustrated by our copper-lead curve.

SECTION II.

The Experimental Method.

The experimental details of our work, including the method of employing and standardising the pyrometers, has been fully described in a paper already published by us;[*] we shall, therefore, treat these matters with great brevity.

The composition of each alloy was determined synthetically: a weighed amount of one metal being melted, and successive weighed quantities of the second metal added to it. Each freezing point was in general determined twice, the alloy being completely re-melted before the second reading. When the two differed, the second was generally a little higher than the first, and was accepted as the most trustworthy.

The alloys were fused in cylindrical salamander (plumbago) crucibles, 42 millims. wide and 105 millims. high; these were in most cases surrounded by an outer crucible, to secure a slow rate of cooling. The crucibles were heated in a small Fletcher blast furnace, so arranged that the products of combustion escaped at the side. The oblique hole, usually seen in the cover of these furnaces, was replaced by an axial circular hole that exactly fitted the crucible. The mouth of the crucible passed through this hole, and the joint was made approximately gas-tight by a packing of asbestos paper. The surface of the alloy was in this way protected against the furnace gases. As there was thus no draught across the mouth of the crucible, we were able to keep a small flame of coal-gas, or hydrogen, constantly burning over the surface of the metal. This was introduced into the crucible through a pipe-stem, and effectually prevented the oxidation of the metals or the absorption of oxygen by the silver. The hydrogen was made by the action of sulphuric acid on zinc free from arsenic, but we did not find that the substitution of coal-gas altered the freezing point. For all temperatures above the melting point of silver, the coal-gas, burning

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[*] 'Chem Soc. Jour.,' 1895, p. 160.

in the crucible with an insufficient supply of air, deposited so much carbon that the crucible soon became full; we were therefore obliged to employ hydrogen in such cases.

Before and during the reading of the freezing point the metal was stirred by means of a plunging stirrer. This stirrer consisted of a carbon rod screwed into a semi-annular foot cut from a plate of gas-carbon so as nearly to fit the crucible. Without efficient stirring it is impossible to obtain sharp and consistent readings of the freezing point when the solutions are at all concentrated. The stirring was in some cases effected automatically by means of a small water motor, but more often hand stirring was adopted. Hand stirring, though not so vigorous as an automatic stir, has the advantage that the person stirring can note the formation of precipitate and observe its character.

The pyrometers employed were of the CALLENDAR-GRIFFITHS type, in which the temperature is determined by the change in the electrical resistance of a platinum wire. Their constants were re-determined from time to time during the progress of the experiments, using as fixed points, ice, steam, and the vapour of boiling sulphur (444·53°). These three points are sufficient for reducing, by CALLENDAR'S rule, the observed resistance to the temperature on the Centigrade-air scale. The justification for this rule is to be found in CALLENDAR'S[*] comparison with the air thermometer up to 600° C., and in the identity of the freezing point of copper, as determined by us and by HOLBORN and WIEN,[†] the latter observers virtually using the air thermometer. This point has also been discussed by GRIFFITHS.[‡] The exact accuracy of this reduction to the Centigrade-air scale is not, however, of moment for the purpose of the present paper; it is sufficient that these pyrometers give consistent temperatures on a scale that nowhere differs much from the true scale. The additional experience gained in making the experiments described in the present paper has confirmed us in the opinion that such is the case.

SECTION III.

The Tables of Experimental Results.

Each table gives the freezing points for a pair of metals. The weight of pure metal that we start with is given at the head of the table or section.

Column (1) gives the total weight of the second metal present at the moment of taking the freezing point.

Column (2) gives the percentage of the second metal present in the alloy. The percentage of the first metal present can be obtained by subtracting the numbers of column (2) from 100.

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[*] CALLENDAR, 'Phil. Trans.,' A., 1887, p. 161; A., 1891, p. 119.

[†] HOLBORN and WIEN, 'Ann. Phys. Chem.,' 1892, **47**, 107.

[‡] GRIFFITHS, 'Nature,' November 14, 1895, and February 27, 1896.

Column (3), the *Atomic Percentage* of the second metal, gives the number of atoms of the second metal in every 100 atoms of the alloy. It would be more satisfactory if we could calculate the number of molecules of the second metal in every 100 molecules of the alloy, but unfortunately we can only make uncertain guesses as to the molecular weights. As before, by subtracting the number in column (3) from 100 we get the atomic percentage of the first metal. Columns (2) and (3) are not calculated beyond the second decimal place, as this gives a degree of accuracy equal to that of the freezing points in column (4).

Column (4) gives the freezing point. This temperature was read to one-hundredth of a degree, but in the tables we, as a rule, only give the tenths of a degree.

Column (5), the *Atomic Fall*, is obtained by dividing the total depression of the freezing point, taken from column (4), by the atomic percentage taken from column (3). This column shows how far the law of proportionality between the concentration and the total depression of the freezing point holds good. For concentrated solutions the atomic fall has no simple meaning, and in such cases it is not given in the tables. In applying equation (1) to the case of dilute solutions, for which alone the conception of the atomic fall is useful, we must regard dx as identical with $1 - x$. This is the atomic percentage divided by 100, so that the atomic fall is $\frac{1}{100} \cdot d\theta/dx$, a quantity which equation (1) tells us is equal to $\cdot 02\theta^2/x\lambda$. If we use the more accurate equation (2), then the atomic fall is $\dfrac{\theta \, . \, \theta_0}{\lambda\,(1 - x)} \cdot 02 \log_e x$. The two expressions become identical when x is unity.

Numbers in column (4), which are enclosed in brackets, are *second* freezing points, corresponding to a eutectic state.

Each series in a table corresponds to an entirely new alloy, and the horizontal spaces dividing a series into sections indicate that a portion of the alloy has been extracted from the crucible and the experiments continued with the residue.* It will be seen that the freezing point was always taken *after* as well as *before* such an extraction.

The notes and remarks at the end of each table are substantially copied from the laboratory note-book.

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* Table IIA contains examples of this.

TABLE IA.—Freezing Points of Alloys formed by adding Copper to Silver.

Series 1.—348·9 *grams Silver.*

(1.) Total weight of copper present.	(2.) Percentage weight of copper.	(3.) Atomic percentage of copper.	(4.) Freezing point on the Centigrade scale.	(5.) Atomic fall.
0	0	0	960·0	
1·074	·31	·52	957·2	5·4
2·101	·60	1·02	954·3	5·6
4·195	1·19	2·01	948·7	5·6
8·11	2·27	3·81	938·6	5·61
13·59	3·75	6·23	925·3	5·57
24·03	6·44	10·50	902·4	5·49
44·87	11·39	17·99	864·9	5·28
Series 2.—200 *grams Silver.*				
0	0	0	959·3	
7·305	3·52	5·86	926·1	5·66
22·35	10·05	16·00	865.3	5·88
32·86	14·11	21·88	847·3	5·12
43·57	17·88	27·08	825·3	4·95
55·67	21·77	32·18	805·0	4·80
61·74	23·59	34·48	797·0	4·71
"	"	"	(778·0)	
67·95	25·36	36·67	788·9	4·65
"	"	"	(778·6)	
74·05	27·02	38·70	781·7	4·59
"	"	"	(778·6)	
78·16	28·10	40·00	778·65	
82·16	29·12	41·18	779·1	
90·34	31·12	43·50	790·3	
"	"	"	(778·6)	
103·02	34·00	46·75	805·3	
"	"	"	(778·2)	
118·38	37·19	50·22	818·80	

Series 1.—Before adding the last quantity of copper the galvanometer was balanced, and it was observed that at the moment after the addition of the copper there was no sudden change of temperature. The total weight of the metals used in this series was 393·8 grams, but the ingot of alloy was found to weigh 379 grams. Although some of the alloy adhered to the crucible and to the pyrometer stem, and hence was not weighed, yet these numbers point to a probable loss of metal during the course of the experiments. The metal was molten for periods amounting to about five hours in all.

Series 2.—The first two freezing points of the alloy in this series prove, when plotted, to be inconsistent with the results of the other series and with the later points of this series. A probable explanation is that the silver was not fully molten at the moment of adding the first and second quantities of copper, and so the solution, whose freezing point was taken, was at the time richer in copper than the figures indicate.

At 16 atoms, precipitate begins to form at the freezing point and can be watched forming freely as the mass slowly falls in temperature.

At 34·48 atoms, a second lower freezing point, much more constant in temperature than the upper point, was noted. This is reached when the still liquid portion attains the composition of the eutectic alloy—40 atoms of copper. This freezing point, and all other similar eutectic points, *have the temperature placed in brackets*, to distinguish it from the upper first freezing point at which solid *begins* to separate. This eutectic point is probably the same whatever the proportions of copper and silver. When an alloy by partial solidification reaches this temperature, the thermometer no longer falls slowly as solidification progresses, but registers a quite constant temperature. until the whole mass is solid.

The total weight of the metals used in this series was 318·4 grams, but the ingot of alloy was found to weigh 315 grams, and a little was left on the stirrer.

At 32·18 atoms there was a trace of surfusion.

TABLE IA.—Freezing Points of Alloys made by adding Copper to Silver.

Series 3.—182·57 *grams Silver.*

(1.) Total weight of copper present.	(2.) Percentage of copper.	(3.) Atomic percentage of copper.	(4.) Freezing point on the Centigrade scale.	(5.) Atomic fall.
8·739	4·57	7·55	917·0	5·70*
17·447	8·72	14·01	883·7	5·44
18·65	9·27	14·83	880·0	5·39†
19·99	9·87	15·73	875·4	5·38
21·41	10·50	16·67	870·7	5·36
23·03	11·20	17·70	866·0	5·31
24·74	11·93	18·77	861·1	5·27
26·54	12·69	19·86	856·3	5·22
28·24	13·40	20·87	851·8	5·18
30·25	14·22	22·03	846·7	5·14
33·25	15·41	23·70	839·5	5·08
39·66	17·85	27·03	825·5	4·98‡

* As usual, at this stage, there was an abundant precipitate at and after the moment of reading, and a few degrees below the recorded freezing point stirring became impossible.

† Here the period of stationary temperature was very short.

‡ In most of the above experiments there was an abundant precipitate at the moment of reading the temperature, but the freezing point, though quite marked, was not constant for long.

These experiments, when plotted, show that there is no inflexion in the curve on the silver side.

The ingot of alloy weighed 220·5 grams, while the metals used weighed 222·2 grams.

At the first three readings of this series surfusion was noticed.

TABLE IB.—Freezing Points of Alloys made by adding Silver to Copper.

Series 1.—200 *grams Copper.*

(1.) Total weight of silver present.	(2.) Percentage of silver.	(3.) Atomic percentage of silver.	(4.) Freezing point on the Centigrade scale.	(5.) Atomic fall.
0	0	0	1081·5	..
1·023	·51	·30	1079·1	8·0*
4·374	2·14	1·27	1071·1	8·2
9·532	4·55	2·72	1059·1	8·24
14·84	6·91	4·17	1048·1	8·01
29·85	12·99	8·05	1019·6	7·69
"	"	"	1020·8	7·54†
45·06	18·39	11·67	996·5	7·28
60·07	23·10	14·98	976·0	7·04
80·34	28·66	19·07	953·5	6·71
100·54	33·45	22·77	934·4	6·46
120·68	37·64	26·15	917·4	6·28‡

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* When the silver was dropped into the molten copper it appeared to boil.

† Up to this point coal-gas had been used to protect the surface of the copper from oxidation, but so much finely divided gas carbon had formed in the crucible that pure dry hydrogen was henceforward used. The gas carbon does not form over molten silver at its melting point. This reading was taken two days after the preceding.

‡ The weight of the metals used was 320·7 grams, but the ingot, after dipping while hot in dilute sulphuric acid, weighed 310·4 grams. The surface of the ingot was mottled with white spots on a ground of copper colour.

TABLE IB.—Freezing Points of Alloys made by adding Silver to Copper.

Series 2.—124·73 *grams Copper.*

(1.) Total weight of silver present.	(2.) Percentage of silver.	(3.) Atomic percentage of silver.	(4.) Freezing point on the Centigrade scale.	(5.) Atomic fall.
75·27	37·64	26·15	916·5	6·31*
90·43	42·03	29·84	900·2	6·08
110·58	47·00	34·22	881·6	5·84
130·60	51·16	38·06	866·5	5·65
150·70	54·72	41·48	852·9	
175·86	58·51	45·27	837·2	
"	"	"	(778·4)	†
200·94	61·71	48·59	823·7	
"	"	"	(778·6)	‡

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* Series 2 begins where Series 1 ends. The difference of ·9° C. between the last reading of Series 1 and the first reading of Series 2 is perhaps a measure of the changes in composition that the mixture of Series 1 has undergone by volatilization and oxidation. If so, these two causes of error, when taken together, are not very important. A shift in the constants of the pyrometer during Series 1 might well amount to as much as 1° C.

† Partial stirring was possible until the temperature fell to the eutectic point

‡ The ingot of alloy weighed 319 grams instead of the 325·6 grams of metal used, but several fragments of alloy adhering to the apparatus were not weighed, so that the loss from all causes was small during the experiments.

TABLE Ic.—Freezing Points of the Eutectic Alloy of Silver and Copper.

200 *grams Silver*.

(1.) Total weight of copper present.	(2.) Percentage of copper.	(3.) Atomic percentage of copper.	(4.) Freezing point on the Centigrade scale.
72	26·47	38·03	783·44
"	"	"	(777·15)
74·05	27·02	38·70	780·4
76·04	27·55	39·33	(777·25)
"	"	"	779·11
77·80	28·01	39·87	777·59
79·11	28·34	40·27	777·76
82·13	29·11	41·18	780·45
"	"	"	781·49
"	"	"	778·55
87·15	30·35	42·63	787·09
"	"	"	778·45

The ingot of alloy weighed 286·5 grams, while the total weight of the metals used was 287·15.

At temperatures but little above the eutectic, the stationary temperature at the F.P.* lasted but a short time, so that there was some danger of reading these freezing points too low; to meet this, nuclei of alloy were extracted from the crucible and dropped in just before the temperature fell to the freezing point. This method removes the risk of surfusion and slightly raises the observed F.P.

There was an interval of a night between the earlier readings of this series and the last four, but the constants of the pyrometer were not re-determined. A change in the constants may be the cause of the fact that the first F.P. on the second day was a degree higher than the F.P. of the same alloy on the previous day. We have, therefore, in drawing the curve of this series subtracted one degree from all the second day's readings.

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* F.P. is "freezing point."

TABLE IIA.—Freezing Points of Alloys made by adding Lead to Silver.

200 *grams Silver.*

(1.) Total weight of lead present.	(2.) Percentage of lead.	(3.) Atomic percentage of lead.	(4.) Freezing point on the Centigrade scale.	(5.) Atomic fall.
0	0	0	959·12	
2·004	0·99	·52	954·34	9·2
4·004	1·96	1·03	949·0	9·8
6·005	2·92	1·54	944·0	9·8
10·005	4·76	2·54	934·4	9·72
14·335	6·69	3·61	924·3	9·67
„	„	„	924·5	*
20·335	9·23	5·04	910·4	9·67
30·335	13·17	7·33	886·6	9·89
45·335	18·48	10·57	853·4	10·00
60·34	23·18	13·60	820·0	10·23
80·34	28·66	17·32	782·7	10·19
105·34	34·50	21·56	741·6	
130·34	39·46	25·37	710·0	
160·33	44·50	29·49	684·1	
200·34	50·04	34·32	659·5	

134·84 *grams Silver.*

(1.) Total weight of lead present.	(2.) Percentage of lead.	(3.) Atomic percentage of lead.	(4.) Freezing point on the Centigrade scale.	(5.) Atomic fall.
135·07	50·04	34·32	659·2	†
175·07	56·49	40·38	635·4	
215·07	61·47	45·42	619·3	
„	„	„	(308·5)	
255·07	65·42	49·66	606·2	
295·07	68·63	53·30	596·1	

77·7 *grams Silver.*

(1.) Total weight of lead present.	(2.) Percentage of lead.	(3.) Atomic percentage of lead.	(4.) Freezing point on the Centigrade scale.	(5.) Atomic fall.
170·00	68·63	53·30	596·3	‡
210·00	73·00	58·51	580·8	
255·00	76·64	63·12	563·0	
315·00	80·22	67·90	548·3	

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* The second freezing point was taken on the resumption of the experiment after a night's interval.

† Residue of the above alloy after the removal of 130·4 grams; the freezing point was taken after a night's interval.

‡ Residue after the removal of 182·2 grams.

For the first 5 atomic per cents. of lead there was an abundant precipitate at the moment of reading. After this concentration the precipitate at the moment of reading gradually became less and less, and before 45 atomic per cents. it ceased to be possible to detect precipitate at the moment of reading or for some time afterwards. At this concentration plenty of precipitate could be felt on the bottom of the crucible when the alloy had cooled 50 or 100 degrees below the F.P.

At 45 atomic per cents. of lead the alloy was allowed to cool to the eutectic point, but stirring had become impossible long before the temperature had fallen to this point.

Beyond 50 atomic per cents. of lead the F.P. is only indicated by a slight decrease in the rate of cooling.

At 34·32 atomic per cents. and at 53·3 atomic per cents. the crucible had become too full and a portion of the alloy was removed. It will be noticed that the F.P. before and after this removal of a part of the alloy is substantially the same.

At the end of the experiments the solidified ingot of alloy was found to weigh 389·8 grams, while from the weights of the two metals used it should have weighed 392·7 grams; part of this loss is due to metal adhering to the pyrometer and the crucible.

Oxidation did not occur either during the experiments or during the cooling.

TABLE IIB.—Freezing Points of Alloys made by adding Silver to Lead.

250 *grams of Lead.*

(1.) Total weight of silver present.	(2.) Percentage of silver.	(3.) Atomic percentage of silver.	(4.) Freezing point on the Centigrade scale.
0	0	0	327·60
5·216	2·04	3·85	306·17
"	"	"	(303·72)
10·431	4·01	7·41	(303·5)
"	"	"	(303·2)
15·647	5·89	10·71	(303·2)
20·862	7·70	13·80	(303·4)
26·078	9·45	16·67	460·6
31·293	11·13	19·36	481·6
39·116	13·53	23·08	505·5
46·94	15·81	26·47	523·6
54·76	17 97	29·58	536·9

The second reading at 7·41 atoms was taken on the day after the first. Until 16·67 atomic per cents. of silver no higher point than the eutectic could be found although the alloys were heated above 500° C., and the cooling carefully watched until the eutectic point was reached. This must be due to the fact that very little solid separates out at the F.P. With more than this proportion of silver the F.C. could be detected, but the indication was slight until 23 atomic per cents. of silver.

The eutectic point deduced from the above is 303·3°; in our previous work ('Chem. Soc. Jour.,' 1892), using mercury thermometers, we made it 303°, the fixed points on the mercury thermometers having been previously determined by comparison with a platinum thermometer.

TABLE IIIA.—Freezing Points of Alloys made by adding Tin to Silver

200 *grams Silver.*

(1.) Total weight of tin present.	(2.) Percentage of tin.	(3.) Atomic percentage of tin.	(4.) Freezing point on the Centigrade scale.	(5.) Atomic fall.
0	0	0	959·2	
1·013	·504	·461	956·1	6·72
2·891	1·425	1·304	950·0	7·06
6·926	3·347	3·067	936·3	7·47
11·172	5·290	4·856	921·8	7·70
19·39	8·839	8·139	891·0	8·38
33·51	14·350	13·28	830·2	9·69
48·63	19·57	18·18	755·9	11·18
63·87	24·20	22·59	691·7	11·84
201 *grams Silver.*				
78·89	28·19	26·40	648·2	11·78
98·92	32·98	31·02	603·1	11·47
119·65	37·32	35·23	567·4	11·12
137·82 *grams Silver.*				
82·04	37·32	35·23	567·6	*
97·43	41·42	39·24	538·7	
117·51	46·02	43·79	510·2	
137·69	49·98	47·72	489·2	
157·96	53·41	51·16	474·0	
179·44	56·56	54·34	464·1	
,,	,,	,,	(220·2)	
91·94 *grams Silver.*				
119·73	56·57	54·34	463·0	†
135·53	59·59	57·38	453·3	
161·11	63·67	61·55	437·9	
188·25	67·19	65·17	424·8	
68·35 *grams Silver.*				
139·97	67·19	65·17	425·0	‡
160·34	70·11	68·19	413·0	
190·42	73·59	71·80	399·2	
230·89	77·16	75·51	381·4	
,,	,,	,,	(221·4)	

* Residue of the preceding alloy after the removal of 100·8 grams.
† ,, ,, ,, ,, ,, 105·6 ,,
‡ ,, ,, ,, ,, ,, 71·9 ,,

For the first five atomic per cents. at least, the moment of freezing is detected by the person stirring a second or two before the observer at the galvanometer, as the walls of the crucible become abundantly coated with a smooth solid.

At 22 atomic per cents. nuclei of silver were added just before the reading, but no effect was noticed, and the nuclei of silver did not melt easily.

At 35·23 atomic per cents., and at a temperature considerably above the F.P., some of the alloy was extracted.

At the higher freezing point at 54·34 atomic per cents., and for 50° or more below the F.P., no solid could be detected, but the reading was well-marked. The lower F.P. was obtained by allowing the alloy to cool to the eutectic state.

A portion of the alloy was now removed; the F.P. afterwards was a degree lower.

At 65·17 atomic per cents. a portion of the alloy was removed, the F.P. before and after this process being the same.

At and after 54 atomic per cents., little or no solid matter can be detected at the point recorded as the F.P., but the cooling at this point suddenly becomes much slower.

At 75·5 atomic per cents. no solid matter could be detected until close to the eutectic point. Soon after this point was reached the alloy set to a solid mass at the eutectic temperature.

TABLE IIIB.—Freezing Points of Alloys made by adding Silver to Tin.

180 *grams Tin.*

(1.) Total weight of silver present.	(2.) Percentage of silver.	(3.) Atomic percentage of silver.	(4.) Freezing point on the Centigrade scale.	(5.) Atomic fall.
0	0	0	232·07	
3·289	1·80	1·96	226·54	2·82
6·579	3·53	3·85	221·67	
8·224	4·37	4·76	(221·59)	
”	”	”	232·5	
11·513	6·01	6·54	259·5	
18·092	9·13	9·91	296·9	
24·67	12·05	13·04	322·6	
36·18	16·74	18·04	355·2	
49·34	21·52	23·08	380·8	

It is clear that the eutectic state is reached with somewhat less than 3·85 atomic per cents. of silver.

The readings, higher than the eutectic, until 10 atomic per cents. of silver, are very fugitive, the F.P. being indicated by a slight change in the rate of cooling. One would expect these readings to be subject to a large experimental error, but the curve shows that they are consistent with each other.

It will be noticed that where the two series meet the latter lies some five degrees higher. The discrepancy may be due to some small extent to a change in the constants of the pyrometer, to a greater extent to an error in the determination of the last F.P. of the first series, but we think it is also due in part to a loss of silver by volatilization and splashing during the course of the first series.

TABLE IVA.—Freezing Points of Alloys made by adding Lead to Copper.

Series 1.—200 *grams Copper.*

(1.) Total weight of lead present.	(2.) Percentage of lead.	(3.) Atomic percentage of lead.	(4.) Freezing point on the Centigrade scale.	(5.) Atomic fall.
0	0	0	1080·8	
1·00	·50	·15	1079·3	10·0
2·122	1·05	·32	1077·1	11·6
5·124	2·50	·78	1071·6	11·8
10·124	4·82	1·55	1062·8	11·6
15·124	7·03	2·26	1055·1	11·37
25·12	11·16	3·70	1039·2	11·25
40·12	16·71	5·78	1018·3	10·81
60·12	23·11	8·42	995·0	10·19
80·12	28·60	10·92	977·6	9·45
105·12	34·45	13·86	963·6	8·46
135·12	40·32	17·13	954·4	
155·12	43·68	19·18	953·3	
175·12	46·68	21·13	953·1	
195·12	49·38	22·99	953·1	
215·12	51·82	24·76	953·2	
Series 2.—96 *grams Copper.*				
104	52·01	24·90	951·1	
164	63·08	34·33	952·3	
254	72·58	44·73	952·0	
394	80·41	55·67	951·2	
424	81·54	57·47	950·8	

TABLE IVB.—Freezing Points of Alloys made by adding Copper to Lead.

Series 1.—250 *grams Lead.*

(1.) Total weight of copper present.	(2.) Percentage of copper.	(3.) Atomic percentage of copper.	(4.) Freezing point on the Centigrade scale.
0	0	0	327·6
1·765	·70	2·26	327·2
4·965	1·95	6·10	327·6
24·29	8·86	24·10	917·0
26·44	9·57	25·70	924·0
29·44	10·54	27·80	932·2
34·46	12·12	31·06	941·1
37·58	13·07	32·94	945·1
41·81	14·33	35·35	948·8
46·83	15·78	37·97	952·6
51·98	17·21	40·47	953·3
"	"	"	326·9
57·21	18·63	42·80	953·7
67·39	21·23	46·85	954·5

Series 2.—400 *grams Lead.*

0	0	0	327·3
2·45	·61	1·97	326·0
21·96	5·20	15·24	858·1
30·04	6·99	19·70	890·8

The following numbers refer to the atomic percentage of lead in table IV.

At ·15 the stirrer set fast soon after the reading of the F.P.

At ·32 there was much precipitate at or just after the reading, but stirring was possible.

At 2·26 a very liquid substance was left on the surface after the bulk had precipitated, or been beaten down by the stirrer to the bottom of crucible.

At 8·4, after the F.P., a solid forms on the top, but it can be beaten down to the bottom of the crucible, until most of the alloy is solid, with some quite liquid at the top.

At 17·13 no precipitate was felt for some time after the F.P.

From 19·18 to quite 50 the temperature at the F.P. is, for some minutes, very constant, like that of a eutectic mixture. There is no perceptible precipitate at the F.P. or for some time after, and then it is noticed adhering as a layer to the walls of the crucible.

From 50 to 60 the temperature, though quite constant at the F.P., did not remain constant for so long a time as before.

From 60 to 85, the last point that could be observed, the halt in the fall of temperature at the F.P. became rapidly less marked, that at 80 and 85 being very transient.

Repeated efforts were made to determine the F.P. of mixtures containing more than 85 atomic percentages of lead, but the only stop in the cooling takes place at 327°·5, the F.P. of pure lead, or more strictly the F.P. of a eutectic mixture of copper and lead. It will be seen that, at 60 atomic percentages of lead, the eutectic point was 327°. In this series of experiments we did not attempt to make a minute study of the eutectic alloy of copper and lead; but on a previous occasion, using a sensitive mercury thermometer ('Chem. Soc. Journ.,' 1892, p. 906), we found that copper lowered the F.P. of lead by 1°·17 C., and that the eutectic alloy contained rather less than ·2 atomic percentage of copper.

The difficulty of tracing the upper branch of the curve between 85 and 100 atomic percentages of lead is not due to the insolubility of copper in lead, for, at a red heat, copper dissolves freely; but rather to the fact that, between these limits, the solubility changes but little with change of temperature, so that at any given temperature the amount of solid that separates is small. It is evident that the curve must become almost vertical for dilute solutions.

At the end of each series, after removing the pyrometer and stirrer, the furnace was closed as completely as possible, and the alloy allowed to cool slowly in a current of reducing gas. When cold, the alloys were weighed. They were in the form of cylinders, 3 centims. wide and from 4 to 7 centims. long. Each ingot was completely covered with a thin layer of soft metal, which appeared to be almost pure lead, but, on cutting a plane face from end to end along the cylinder, the character of the alloy could be studied.

At 24·76 atomic percentages of lead the alloy was found to weigh 413 grains, instead of 415, which is the sum of the weights of the metals used. During the earlier experiments with this alloy, a few particles had been splashed out of the crucible. The alloy appeared quite free from oxide.

The structure revealed by the face cut on the cylinder was as follows:—two or three millims. at the top were lead-coloured, with a few spots of copper that were invisible to the naked eye, but could be seen by the aid of a lens. Below this, for 4·5 centims., the metal was copper-coloured, but the lens, or indeed a careful inspection with the naked eye, showed a great number of irregular roundish spots of lead-coloured metal embedded in the mother substance. The bottom centimetre consisted of grey metal which, to the naked eye, presented a well-marked tinge of red from the large number of spots of copper scattered through it. The lines separating the middle copper layer from the upper and lower layers were perfectly sharp to the naked eye; the upper boundary line was convex, the lower boundary quite straight.

At 54·47 atomic per cents. of lead the ingot weighed 519 grams, while the sum of the weights of the metals used was 520 grams.

The face cut on this ingot showed that the upper layer of lead-coloured metal was so thin as to be barely visible. The copper coloured layer had more grey in it, and was only 5 millims. deep. Its line of separation from the lower lead-coloured layer was somewhat irregular. This grey layer formed the bulk of the alloy, being 6 centims. long.

As before, it had a reddish tinge from the spots of copper scattered through it. These were uniformly distributed, except near the top, where complete separation had not occurred. The copper tinge was less pronounced than at 24·76.

At 53·15 atomic per cents. of lead the ingot weighed 312·5, while the total weights of the two metals come to 317·4.

As might be expected, this strongly resembled the preceding alloy, except that it was less homogeneous, cavities being visible, especially in the lead part, containing octahedral crystals of copper.

At 80·3 atomic per cents. of lead the alloy weighed 427 grams instead of 430. This alloy was homogeneous to the eye, being lead-coloured throughout. In some lights the upper 2 centimetres had the faintest reddish tinge, but this detail was uncertain. Only a very few minute specks of copper could be detected even by careful examination with a lens. There were no cavities in the alloy.

It will be noted, by comparison with fig. 9, that while the first three ingots which show separation into two layers correspond in composition to points on the flat part of the curve, the fourth ingot, which is homogeneous, corresponds to a point on the descending portion of the curve.

TABLE V.—Freezing Points of Alloys made by adding Bismuth to Copper.

250 *grams Copper.*

(1.) Total weight of bismuth present.	(2.) Percentage of bismuth.	(3.) Atomic percentage of bismuth.	(4.) Freezing point on the Centigrade scale.	(5.) Atomic fall.
0	0	0	1077·2	
2·354	·933	·286	1074·0	11·2
7·161	2·79	·87	1067·2	11·5
12·626	4·81	1·51	1059·9	11·46
18·656	6·94	2·22	1052·9	10·94
28·793	10·33	3·39	1041·3	10·59
40·295	13 88	4·68	1029·7	10·15
55·762	18·24	6·36	1014·9	9·79
76·55	23·44	8·52	999·1	9·17

TABLE VI.—Freezing Points of Alloys made by adding Gold to Copper.

250 *grams Copper.*

(1.) Total weight of gold present.	(2.) Percentage of gold.	(3.) Atomic percentage of gold.	(4.) Freezing point on the Centigrade scale.	(5.) Atomic fall.
0	0	0	1079·70	
1·120	0·45	·144	1079·56	1·00
4·336	1·71	·554	1076·95	4·96
10·524	4·04	1·333	1072·08	5·72
16·936	6·30	2·129	1067·88	5·55
26·787	9·68	3·325	1060·61	5·74

TABLE VIIA.—Freezing Points of Alloys made by adding Tin to Copper.

Series 1.—200 *grams Electrolytic Copper.*

(1.) Total weight of tin present.	(2.) Percentage of tin.	(3.) Atomic percentage of tin.	(4.) Freezing point on the Centigrade scale.	(5.) Atomic fall.
0	0	0	1082·1	10·4
1·855	·92	·50	1076·9	11·3
5·549	2·70	1·47	1065·5	11·98
12·062	5·69	3·13	1044·6	13·44
24·152	10·78	6·08	1000·4	
45·192	18·43	10·80	909·6	
71·16	26·24	16·02	788·8	
86·20	30·12	18·77	757·7	
96·40	32·53	20·53	742·0	
„	„	„	742·0*	
101·49	33·66	21·39	738·8	
112·04	35·91	23·10	734·3	
119·96	37·50	24·32	730·8	
123·61	38·20	24·88	729·0	
126·66	38.77	25·35	727·4	
131·67	39·70	26·09	724·5	
137·73	40·79	26·96	720·7	
120·28 *grams Copper.*				
82·84	40·79	26·97	220·6†	
88·05	42·27	28·18	714·9	
98·55	45·03	30·51	702·8	
118·57	49·65	34·57	680·0	
143·88	54·47	39·07	655·1	
173·91	59·12	43·67	633·1	
204·51	62·97	47·68	615·7	
74·56 *grams Copper.*				
126·73	62·97	47·68	616·0‡	
157·00	67·81	53·03	593·8	
187·47	71·55	57·41	576·1	
249·05	76·97	64·17	546·7	

The first three freezing points of this series were well marked, and accompanied by a considerable formation of precipitate.

At 16 atoms of tin the freezing point was a very steady temperature, and there was much precipitate at the moment of reading.

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* Determined the day after the previous reading.

† Residue of the preceding alloy after the removal of 134·6 grams.

‡ „ „ „ „ „ 123·5 „

The freezing points from 20·53 to 24·32 inclusive were noted as being so steady as to resemble eutectic points. This is the region from $SnCu_4$ to $SnCu_3$.

At 24·32 atoms no precipitate was noticed at the moment of reading the freezing point, but before the metal had cooled two degrees below the recorded temperature stirring had become impossible; in fact, this alloy may be said to solidify at a constant temperature.

At 25·35 atoms, that is, with more tin than corresponds to $SnCu_3$, we begin again to notice an abundant precipitate at the moment of reading the freezing point.

After the first reading at 26·96 atoms of tin a portion of the alloy was removed from the crucible. This alloy was white, hard, and brittle, with a conchoidal fracture.

At 30·51 atoms the freezing point was not so well marked as hitherto. There was much precipitate soon after the reading.

At 34·57 atoms of tin surfusion was noticed at the freezing point.

From here onwards, as we add more tin, the pause in the cooling, which marks the freezing point, becomes less and less marked, but up to 64·2 atoms of tin there is no difficulty in determining the freezing point. There is now no precipitate observed at the moment of reading the freezing point, or for some time afterwards.

TABLE VIIA.—Freezing Points of Alloy made by adding Tin to Copper.

Series 2.—200 *grams Electrolytic Copper.*

(1.) Total weight of tin present.	(2.) Percentage of tin.	(3.) Atomic percentage of tin.	(4.) Freezing point on the Centigrade scale.	(5.) Atomic fall.
0	0	0	1081·0	
6·046	2·93	1·954	1062·3	11·73
37·07	15·64	9·04	944·8	15·07
67·08	25·12	15·24	797·9	A
”	”	”	793·1	B
83·16	29·37	18·23	762·8	

The points A and B are two well-marked freezing points of the same alloy, the lower temperature B corresponding to some eutectic state (see Curves).

For the purpose of drawing the curve, in order to bring this series into agreement with Series 1, one degree was added to the first reading given above, and proportional amounts to the lower readings.

TABLE VIIA.—Freezing Points of Alloys made by adding Tin to Copper.

Series 3.—147·6 *grams Copper*.

(1.) Total weight of tin present.	(2.) Percentage of tin.	(3.) Atomic percentage of tin.	(4.) Freezing point on the Centigrade scale.
52·40	26·20	15·99	789·2*
56·42	27·66	17·01	777·9*
61·42	29·39	18·24	763·9
66·43	31·04	19·45	750·1
68·27	31·63	19·87	745·4 A
,,	,,	,,	742·7 B
68·77	31·79	19·99	744·6
69·27	31·94	20·11	743·8
70·29	32·26	20·34	742·5
78·63	34·76	22·22	736·1
86·96	37·08	24·00	731·1
91·47	38·26	24·94	728·1
95·97	39·40	25·85	724·9
100·48	40·51	26·74	721·1

Up to 20 atomic per cents. of tin there was abundant precipitate just at or after the reading of the freezing point.

After 20 atomic per cents. of tin the readings became very steady.

The freezing points A and B are for the same alloy. They indicate different phenomena.

TABLE VIIA.—Freezing Points of Alloys made by adding Tin to Copper.

Series 4.—200 *grams Copper*.

(1.) Total weight of tin present.	(2.) Percentage of tin.	(3.) Atomic percentage of tin.	(4.) Freezing point on the Centigrade scale.
0	0	0	1083·9
41·46	17·17	10	928·9
54·05	21·28	12·65	867·5
58·80	22·72	13·61	845·0
62·81	23·90	14·41	825·5
65·81	24·76	15·00	809·4 A
,,	,,	,,	794·3 B
68·81	25·60	15·57	795·0
71·89	26·44	16·15	788·4
82·07	29·10	18·03	767·5
87·30	30·39	18·96	756·7 C
,,	,,	,,	745·8 D

* Surfusion was noticed.

From 10 to 13·61 atoms of tin, inclusive, it was noticed that a soft precipitate began to form on the walls of the crucible at the moment of reading the freezing point and rapidly increased.

At 12·65 atoms the freezing point was indicated, not by a period of stationary temperature, but by a sudden marked decrease in the rate of cooling.

At 14·41 atoms, in spite of copious precipitate, stirring was quite easy for several degrees below the freezing point. This point was distinctly indicated.

At 15 atoms, readings A and B, different freezing points for the same alloy, correspond to different phenomena. At A there was little precipitate; B was a much steadier temperature, with abundant precipitate of a finely gritty character. At this moment the alloy felt to the stirrer like a mixture of sand and water.

The reading at 15·57 atoms, or just below it, resembled B.

From 16·15 atoms onwards the freezing points are very steady temperatures, quite different in character from the preceding, except B.

C and D correspond to different phenomena, D being so constant as to resemble a eutectic point. At D the alloy sets to a solid mass without a further fall in temperature.

TABLE VIIB.—Freezing Points of Alloys made by adding Copper to Tin.

200 *grams Tin.*

(1.) Total weight of copper present.	(2.) Percentage of copper.	(3.) Atomic percentage of copper.	(4.) Freezing point on the Centigrade scale.	(5.) Atomic fall.
0	0	0	232·32	
1·006	·50	·93	229·69	2·93
1·854	·92	1·70	(227·78)	
5·029	2·45	4·48	(227·77)	
”	”	”	262·60	
10·50	4·99	8·92	364·4	
21·32	9·63	16·39	433·1	
36·82	15·55	25·57	496·3	
46·85	18·98	30·42	521·2	

The freezing point of the pure tin was marked by surfusion.

The atomic fall for copper in tin, 2 93°, is identical with that obtained by us in 1889 with a mercury thermometer (‘Chem. Soc. Jour.,’ 1890, p. 392).

The readings at 1·7 and 4·48 atoms of copper give the freezing point of the eutectic alloy of tin and copper.

The freezing points on the rising branch of the curve up to 16·39 atoms, and to a lesser degree up to 30·42 atoms, are very difficult to observe and are liable to a large experimental error. No solid matter can be detected for some time after the freezing point.

TABLE VIIc.—Freezing Points of Copper-Tin Alloys.

Double Points.

(1.) Total weight of metals present.	(2.) Percentage of tin.	(3.) Atomic percentage of tin.	(4.) Freezing point on the Centigrade scale.
Cu 200, Sn 87·3	30·39	18·96	757·00 A
,,	,,	,,	746·5 B
Cu 202·58, Sn 87·3	30·12	18·77	746·05 B
Cu 212·72, Sn 87·3	29·10	18·04	768·0 A
,,	,,	,,	745·8 B
Cu 300·72, Sn 87·3	22·50	13·47	848·4 C
,,	,,	,,	795·3 D

At the points marked A there was much fine sandy precipitate soon after reading, which rapidly increased until the mass was nearly solid, but not set, as the stirrer could still be moved a little. At the points marked B the stirrer set fast, before the reading the mass was really solid. The reading C was fugitive whilst the reading at D was very steady.

In charting, these temperatures were all reduced by the subtraction of 1·5° to obtain agreement with Series 1. A comparison with Series 4 will show the justice of this correction.

Series VIIc. was carried out six months after the others, and with a different pyrometer.

Table VIIIa.—Freezing Points of Alloys made by adding Antimony to Silver.

200 *grams Silver.*

(1.) Total weight of antimony present.	(2.) Percentage of antimony.	(3.) Atomic percentage of antimony.	(4.) Freezing point on the Centigrade scale.	(5.) Atomic fall.
0	0	0	958·8	
1·089	·542	·486	954·6	8·64
2·758	1·361	1·222	947·8	9·00
5·987	2·907	2·615	934·3	9·37
12·16	5·732	5·173	906·9	10·03
22·39	10·068	9·124	853·6	11·53
41·40	17·15	15·66	734·3	14·33
63·52	24·10	22·17	608·3	15·81
73·92	26·99	24·91	561·5	15·95
84·59	29·72	27·50	545·2	
89·75	30·98	28·71	539·1	
95·23	32·26	29·93	532·5	
106·97	34·85	32·43	520·7	
118·49	37·21	34·70	510·7	
126·39 *grams Silver.*				
74·88	37·21	34·70	511·5[*]	
86·00	40·49	37·90	499·1	
97·18	43·47	40·83	488·9	
117·72	48·23	45·53	493·4	
”	”	”	(485·0)	
”	”	”	(485·4)[†]	
128·31	50·38	47·67	496·8	
158·80	55·69	52·99	509·6	

Up to 40·83 atomic per cents. of antimony the pure metal from tartar emetic was used, beyond this concentration the commercial antimony was used.

Up to 2·6 atomic per cents. the temperature at the F.P. was very steady.

Up to 10 per cents. abundant precipitate was noticed at the moment of freezing. At 15·66 there was but little precipitate noticed at the freezing point, but the person stirring could detect a change at the moment when the pyrometer indicated the freezing point. At 22·17 no precipitate was noticed at the freezing point. At 24·91 a little precipitate was noticed.

At 27·5 there was a copious precipitate at the freezing point. The temperature at the freezing point remained constant for some time, and 20° lower the alloy seemed to set to a solid mass.

From 27·5 onwards the temperatures at the F.P. are very constant to the end of the series at 53 atoms of antimony, the eutectic F.P., 485° C., having its usual character of complete constancy.

[*] Residue of the preceding alloy after removal of 117·2 grams.

[†] Freezing point, taken on the resumption of the experiments next day.

At the end of the experiments the alloy was weighed and found to be 270 grams, while from the statement of the weights of antimony and silver used, the weight should have been 285 grams. Some of this loss is due to metal adhering to the pyrometer, stirrer, and crucible, but the missing 15 grams cannot all be accounted for thus; there has certainly been a loss of alloy by volatilization or splashing. This fact renders the atomic percentages of the latter part of the series somewhat uncertain.

TABLE VIIIB.—Freezing Points of Alloys made by adding Silver to Antimony.

200 *grams Antimony from* (*Tartar Emetic*).

(1.) Total weight of silver present.	(2.) Percentage of silver.	(3.) Atomic Percentage of silver.	(4.) Freezing point on the Centigrade scale.	(5.) Atomic fall.
0	0	0	629·49	
1·05	·52	·58	627·52	3·4
2·735	1·35	1·50	624·44	3·37
6·658	3·22	3·58	617·1	3·45
12·894	6·05	6·70	607·0	3·35
33·178	14·23	15·61	581·7	3·06
64·195	24·30	26·35	555·8	2·79
69·210	25·71	27·84	552·6	
79·223	28·37	30·63	546·5	
94·708	32·14	34·54	538·6	
114·95	36·50	39·04	529·4	
135·27	40·35	42·99	521·9	
”	”	”	(484·9)	
160·32	44·49	47·18	512·3	
180·39	47·42	50·13	504·9	
”	”	”	(485·7)	
152·99 *grams Antimony.*				
138·00	47·42	50·13	505·6*	
158·03	50·82	53·51	497·4	
178·12	53·80	56·48	485·9	
”	”	”	487·9	
188·23	55·17	57·83	486·2	
213·47	58·26	60·87	495·2	
”	”	”	(485·6)†	

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* Residue of the above alloy, after the removal of 89·4 grams.

† The ingot when taken out of the crucible was bright; it weighed 360·8 grams. The calculated weight was 366·46 grams. As the loss was probably for the most part antimony, we see that there was during the experiment a loss of 2 per cent. of this metal. Splashing, spitting, and oxidation will account for this.

TABLE VIIIc.—Freezing Points of the Eutectic Mixture of Antimony and Silver

146 *grams Silver.*

(1.) Total weight of antimony present.	(2.) Percentage of antimony.	(3.) Atomic percentage of antimony.	(4.) Freezing point on the Centigrade scale.
104	41·61	39·00	(484·90)
"	"	"	493·48
104·51	41·73	39·11	(484·59)
"	"	"	493·05
106·08	42·08	39·46	(484·59)
"	"	"	491·76
108·09	42·54	39·92	490·27
"	"	"	(485·09)
111·25	43·23	40·61	488·12
"	"	"	(485·68)*
114·27	43·91	41·25	(485·68)*
"	"	"	485 98
114·97	44·06	41·41	(485·68)
"	"	"	485·99
115·98	44·27	41·62	485·71
"	"	"	485·76
119·13	44·93	42·27	485·66
124·62	46·05	43·37	489·58
133·42	47·74	45·05	493·61*
	"	"	(485·45)†

TABLE IX.—Freezing Points of Alloys made by adding Bismuth to Silver.

283 *grams Silver.*

(1.) Total weight of bismuth present.	(2.) Percentage of bismuth.	(3.) Atomic percentage of bismuth.	(4.) Freezing point on the Centigrade scale.	(5.) Atomic fall.
0	0	0	958·0	
2·149	·75	·39	953·8	10·8
6·151	2·13	1·12	945·8	10·9
12·731	4·30	2·28	933·9	10·57
22·797	7·45	4·01	914·5	10·84
43·963	13·45	7·46	880·0	10·45
77·51	21·50	12·45	808·7	12·00
127·58	31·06	18·96	715·7	12·77

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* Surfusion was noticed at these points.

† In this series no loss by spitting or splashing was noticed, and on account of this comparatively low temperature, little or no white smoke of oxide of antimony was observed. The alloy at the end of the experiment was found to weigh 278·45 grams, while the total weight of metal used was 279·4 grams.

At the conclusion of the experiments the alloy was weighed and found to be 404·5 grams instead of 410·6 grams, the weight of the metals used.

The weight of the silver used was not known to nearer than one gram, and this silver was slightly contaminated with nickel, and perhaps with iron.

Up to 4·01 atoms of bismuth the freezing point was marked by plenty of precipitate. At 12·45 and 18·96 little or no precipitate was noticed at the moment of reading the freezing point, and this point was very fugitive. Some time after the freezing point, a large quantity of a fine sandy precipitate formed, and stirring was possible in this for a considerable time, the rate of cooling being very uniform.

TABLE X.—Freezing Points of Alloys made by adding Thallium to Silver.

200 *grams Silver*.

(1.) Total weight of thallium present.	(2.) Percentage of thallium.	(3.) Atomic percentage of thallium.	(4.) Freezing point on the Centigrade scale.	(5.) Atomic fall.
0	0	0	962·38	
2·639	1·30	·69	956·83	8·01
6·709	3·26	1·74	946·4	9·16
,,	,,	,,	947·1	8·77*
14·127	6·60	3·60	930·5	8·86
21·786	9·82	5·45	913·5	8·97†

SECTION IV.

Discussion of the Experimental Curves.

The curves (figs. 6–20), which embody the results of our experiments, are plotted with the temperature of the freezing point of the alloys measured vertically upwards, and the atomic percentage measured horizontally. We can hence at once get the value of the concentration x for use with equations (1) and (2). The numbers just below the line of the curve give the temperature, those just above give the atomic percentage of one metal. The individual experiments are given by the black points which lie along the course of the curve.

Dilute Solutions.

When a solution is very dilute, the observed depression of the freezing point is necessarily small, and consequently the atomic fall is liable to a large experimental

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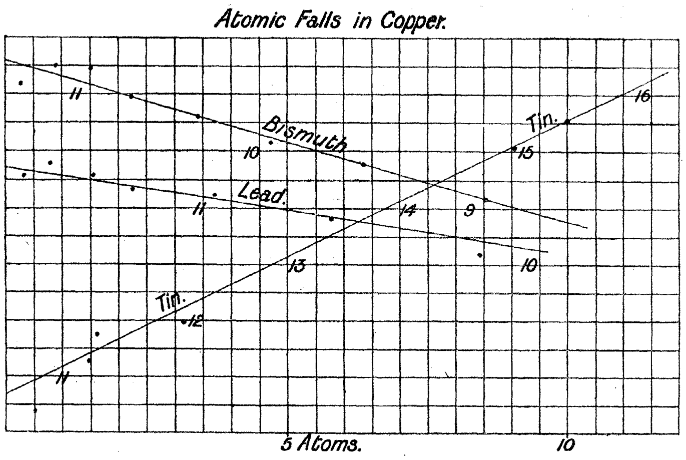
[*] Next day's reading.

[†] At the end of the experiments the alloy was found to weigh 221·2 grams; the total weight of the two metals used was 221·8 grams.

error;* on the other hand, as the solution becomes more concentrated, the atomic fall changes from a number of causes that are but imperfectly understood. It is therefore somewhat difficult to decide how to take the average of a number of atomic falls. Moreover, for the strict application of equation (1) to the purpose of obtaining λ, we need the atomic fall at infinite dilution. We have attempted to get this for copper in fig. 5, by plotting the atomic percentage of dissolved metal horizontally from left to right, and the atomic fall from column (4) of the tables vertically. A line drawn through the points thus obtained and produced to cut the zero ordinate should then give the atomic fall at infinite dilution. Unfortunately, there is a good deal of uncertainty about the exact direction of the lines corresponding to each metal.

Fig. 5.



Each line corresponds to the fall in the freezing point of copper caused by the metal whose name is written above the line. The concentration is written in atoms from left to right. The atomic fall is reckoned for each metal from a different zero, but the numbers below the lines give the atomic falls in degrees Centigrade.

It will be seen that bismuth gives 11·6, lead 11·7, and tin 10·7 for this limiting value of the atomic fall. As bismuth and lead do not appear to combine with the copper, and tin evidently does so, it will be wisest to take the higher value 11·7°. Using this value in equation (1) we find that λ, the latent heat of an atomic weight of copper, is 3138 calories, the melting point being taken as 1082° C. Hence the latent heat of fusion of one gram of copper is 49·6 calories.

If instead of attempting to get the atomic falls at infinite dilution, we mean the atomic falls for concentration greater than ·5 atom and less than 2 atoms, we get,

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[*] We have not hitherto seen a way of applying to our results a correction similar to that suggested by NERNST and ABEGG, but a modification of our method of experiment has been suggested to us that will probably enable us to do so.

as an average from the lead and bismuth, an atomic fall of 11·6° at a concentration of 1·2 atoms. A mean of the two numbers for tin which come within these limits gives 11·5° at 1·5 atoms. These numbers used with equation (2) give a value of λ very slightly greater than the above. Hence we may say that the results of our experiments on the solution of lead, bismuth, and tin in copper lead to the value 50 calories for the latent heat of fusion of copper. We should expect this to be more probably too high than too low.

The atomic fall due to gold dissolved in copper is 5·7° for a mean concentration of 2·26 atoms, using the last three values of the gold-copper table. This corresponds to a value for infinite dilution of 5·8°, which is very nearly half the above value given by lead, bismuth, and tin. Silver in copper produces a fall of about 8·2°, that is, rather more than two-thirds of the normal fall, 11·7.

The half value given by gold may mean that when in dilute solution in copper the gold molecule consists of two atoms, but it will be well to wait for further data before speculating as to the cause of these abnormally small depressions of the freezing point.

The data for the atomic fall, when silver is the solvent, are more numerous, but not on that account easier to interpret. As before, the values given by lead and bismuth are the largest; the most probable value being near 10·3°. This value leads to a latent heat of 27 calories for silver, a value considerably greater than PERSON's value of 21. Here, also, as in the case of the copper, we must hope that further data will help us to decide whether these atomic falls really contain the key to the molecular condition of the metals in solution.

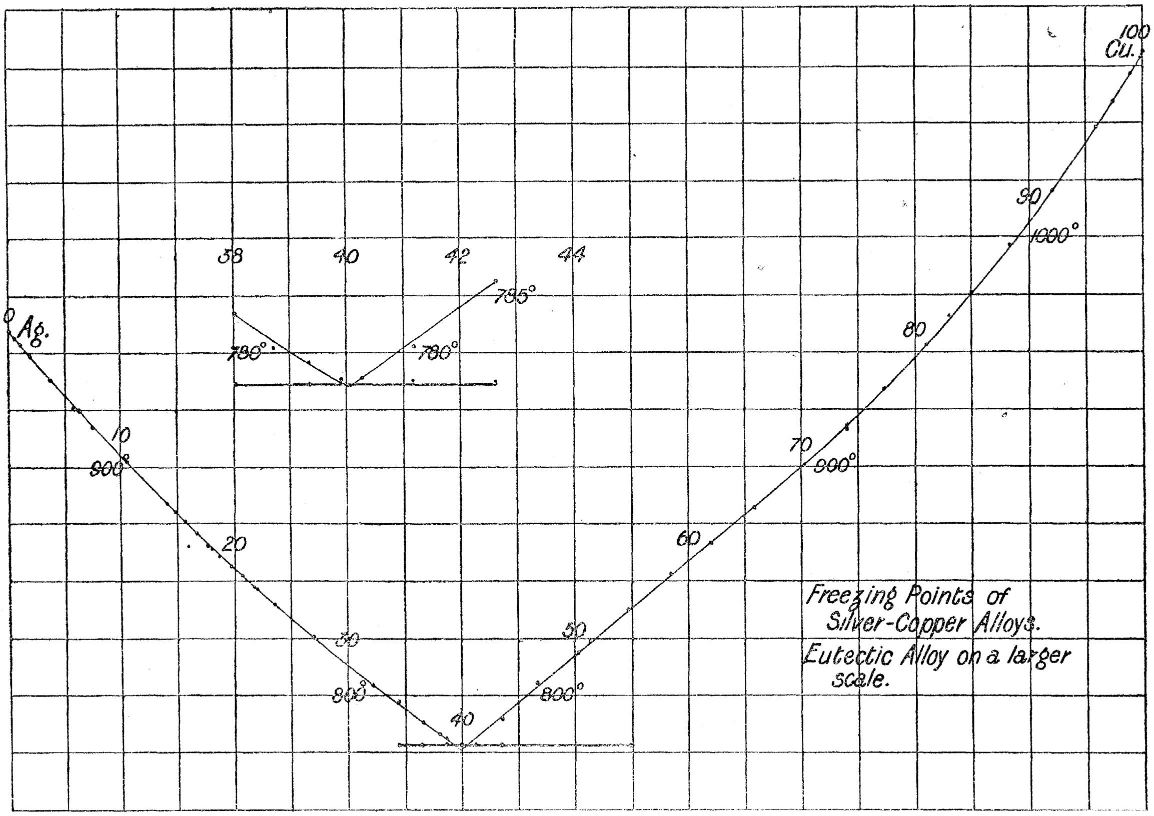
The Silver-Copper Curve. (Fig. 6.)

This, looked at as a whole, in the light of the theory of Section 1, does not at first offer a singularity or an indication of the existence of a compound; but, examined more closely, there are two points worth mention.

The first is that the depressions of the freezing point, even for very dilute solutions, are abnormally small, and the atomic falls decrease slowly in value with increasing concentration. The small depression makes it probable that the molecule of either metal, when in dilute solution in the other, is complex, consisting of more than one atom. The decrease in the atomic falls is by no means rapid, as may be seen from the slight curvature, but so far as it exists, it is an argument against the existence in the liquid alloy of molecules of a compound.

The other feature lies in the exact coincidence of the eutectic alloy, LEVOL's alloy, with the formula Ag_3Cu_2. This struck us in our first series of experiments, but, as during a long series there is always some loss of metal, we thought it well to carry out new experiments, starting with an alloy of a composition nearly corresponding to that of the eutectic point. Table IC. gives this series, and the results are plotted in fig. 6 above the complete curve, and on a larger scale. It is evident that this series confirms the earlier experiments, and puts the eutectic alloy exactly at Ag_3Cu_2.

Fig. 6.



The numbers below the curve give the Centigrade temperature, those above the curve give the atomic percentage of copper.

The theory of the subject, and many experiments of our own and of others, point to the conclusion that the eutectic alloy is not generally a compound, and hence should not have a formula. Some other evidence is, therefore, needed before we can accept Ag_3Cu_2 as a chemical compound.

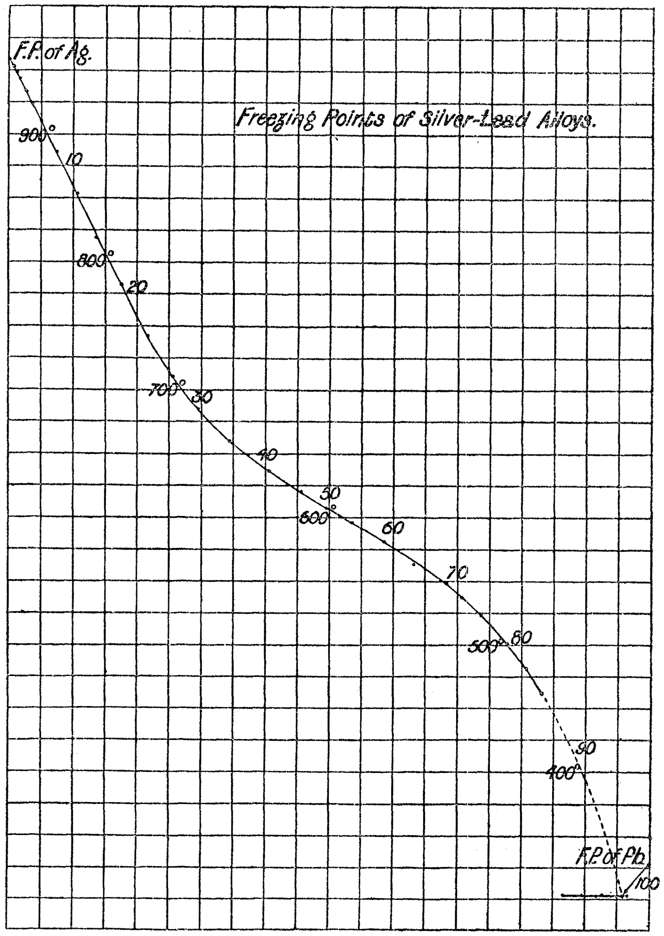
The Silver-Lead and Silver-Tin Curves. (Figs. 7 and 8.)

These two curves resemble each other strongly. Lead and tin being non-volatile and easily fusible metals, the curve consists mainly of the silver branch, although the extreme right shows the depression produced in the freezing point of lead or of tin by the addition of silver, and also the eutectic phenomenon.

The silver-lead curve is almost a straight line until 20 atoms of lead, but soon after this there begins a gradual, though marked, change in the curvature, with a point of inflexion at 50 atoms. In the tin curve the upper part is not straight, and the atomic falls increase with increasing concentration of tin in a way that suggests appropriation of the silver by the tin to form molecules of a compound. Near 50 atoms there is a point of inflexion, as in the lead curve.

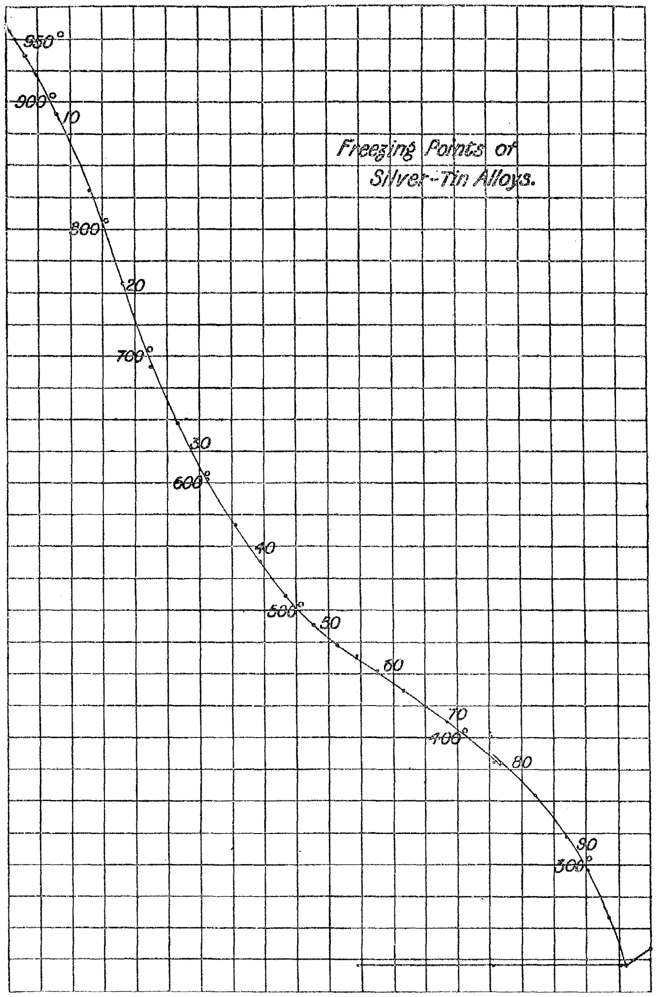
In neither curve is there an angle, until we come to the eutectic point, and from the absence of a well-marked intermediate summit it would appear that, if compounds of these metals with silver exist, they must be largely dissociated under the conditions of the experiment. The shape of the curves is, however, not inconsistent with the reality of such compounds. For example, Ag_4Pb and Ag_4Sn might well have a virtual summit below our curve at 20 atoms. But this view, though plausible, does not appear to us the most probable explanation of the curves; we are disposed to attribute the marked change in the slope, which occurs near 30 atoms in the lead curve and later in the tin curve, to the aggregation of the atoms of these metals to larger molecules, or at all events to compare the state here to the flat part of the copper-

Fig. 7.



In degrees Centigrade and atomic percentages.

Fig. 8.



In degrees Centigrade and atomic percentages.

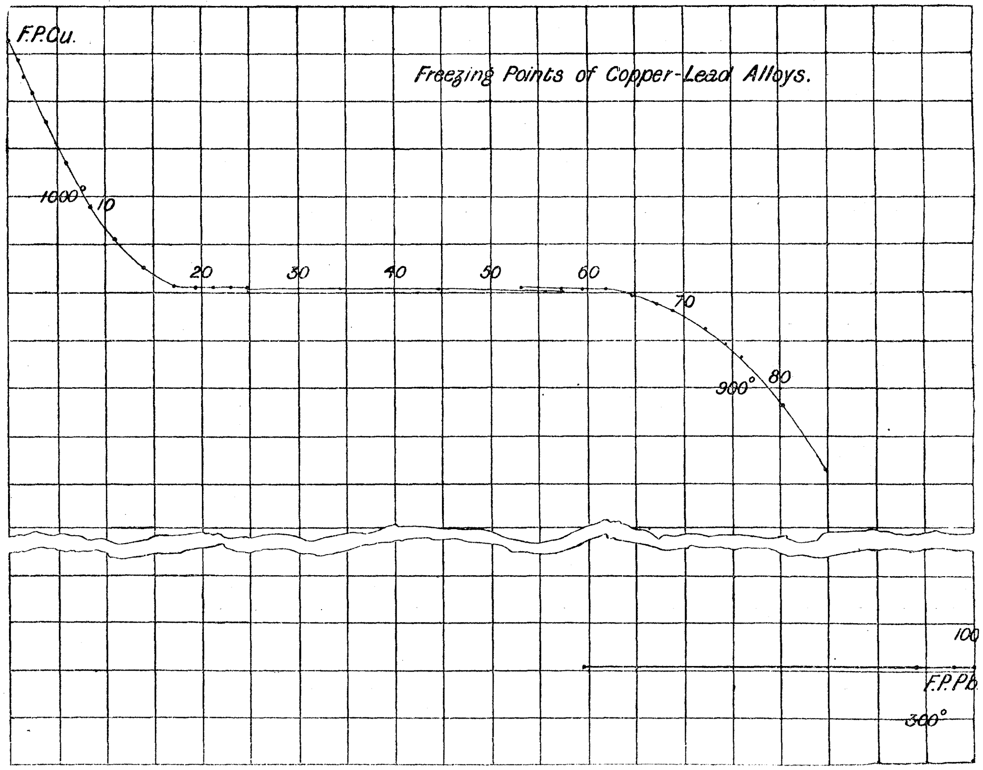
lead curve. Silver-lead and silver-tin do not probably, in our experiments, separate into conjugate liquids, but if they could be examined at a somewhat lower temperature, they perhaps would do so. These curves may be compared with the vapour-pressure curve of a mixture of water and propyl alcohol, a system which stands at the dividing line between wholly and partially miscible liquids. The portion of the silver-lead curve given as a dotted line is hypothetical, as no freezing point could be detected in this region.

The Lead-Copper Curve. (Fig. 9.)

For the first seven atoms at least of lead this curve agrees well with the ideal curve of equation (2), but as more lead is added the curve rapidly approaches the horizontal, until at 17 atoms of lead the addition of this metal ceases to affect the freezing point. From this point until 65 atoms of lead the curve is a horizontal straight line, the freezing point being constant at 954°. On this flat the freezing point of each alloy is marked by a prolonged period of constant temperature, but the character of each freezing point differs from that of a eutectic mixture, inasmuch as after a prolonged halt the temperature begins to fall again while some of the alloy is still liquid. With more than 65 atoms of lead the curve gradually droops and finally becomes nearly vertical.

The character of the solid alloys, as described in the notes to Table IV., throws a clear light on the meaning of this curve. The sloping parts of the curve correspond to the separation of solid matter from a homogeneous liquid, but for all alloys corresponding in composition to points on the flat, the liquid has separated into two conjugate liquids at some temperature above the freezing point. The composition of each of these two liquids will depend on the temperature, but provided there be more than 17, and less than 65 atomic per cents. of lead in the whole alloy, the quantity of lead present will not affect the composition of either conjugate, but only the amount of each conjugate present. Consequently all alloys between these limits are *qualitatively identical*, and therefore must freeze at the same temperature. The prolonged period of constant temperature noticed during the freezing of each alloy whose composition lies between these limits is easily explained. Let us suppose the

Fig. 9.



Degrees Centigrade and atomic per cents. of lead.

freezing point just reached, and that solid is beginning to form, as it must, from *both conjugates at once.** The separation of this solid will cause one conjugate liquid to grow at the expense of the other, but the composition of each will remain the same until one conjugate has ceased to exist. Then, and then only, will the temperature begin to fall. Hence for alloys containing a good deal less than 65 atoms of lead, a large amount of solid matter will form at the freezing point, at a very constant temperature. But, as we found to be the case, the period of constant temperature observed at the freezing point of each alloy becomes shorter as the amount of lead approaches to 65 atoms.

The gradual change of curvature at both ends of the horizontal line may be due to imperfect equilibrium caused by inefficient stirring, too rapid cooling, and other causes. Or it may conceivably be due to the gradual aggregation of the lead atoms into larger masses preparatory to the separation of the alloy into conjugate liquids.

The latter part of the curve from 65 to almost 100 atoms of lead may be called the curve of solubility of copper in lead, and it ought therefore to give us by LE CHATELIER's equation (2) the latent heat of solution of copper in lead. Unfortunately this part of our curve is very steep, and therefore very difficult to determine by our method.

As we have already mentioned, very small amounts of copper produce the RAOULT effect in lead, lowering the freezing point of this metal by the normal amount corresponding to a monatomic molecule of copper (*loc. cit.*). On the flat at the lower part of the figure a eutectic point at 60 atoms will be seen.

The fact that alloys of lead and copper liquate has long been known, and the general character of the freezing-point curve of such a system could have been predicted from the work of ALEXEJEFF and KONOVALOFF, but, so far as we are aware, this is the first case that has been traced experimentally.

The bismuth-copper curve has not been carried beyond 9 atoms of bismuth, but, from an inspection of the solid alloy, we think that it will turn out to be like the lead-copper curve.

The Copper-Tin Curve. (Fig. 10.)

The lower line gives the whole curve; the upper line gives, on a large scale, the more remarkable portion, from 14 to 27 atomic per cents. of tin.

The problem of the copper-tin alloys, one of the most interesting in metallurgy, still remains obscure, in spite of the amount of work that has been done on these alloys by RICHE, BEHRENS, ROBERTS-AUSTEN, and many other writers. We fear that the results here given, though they complicate this problem, do not solve it.†

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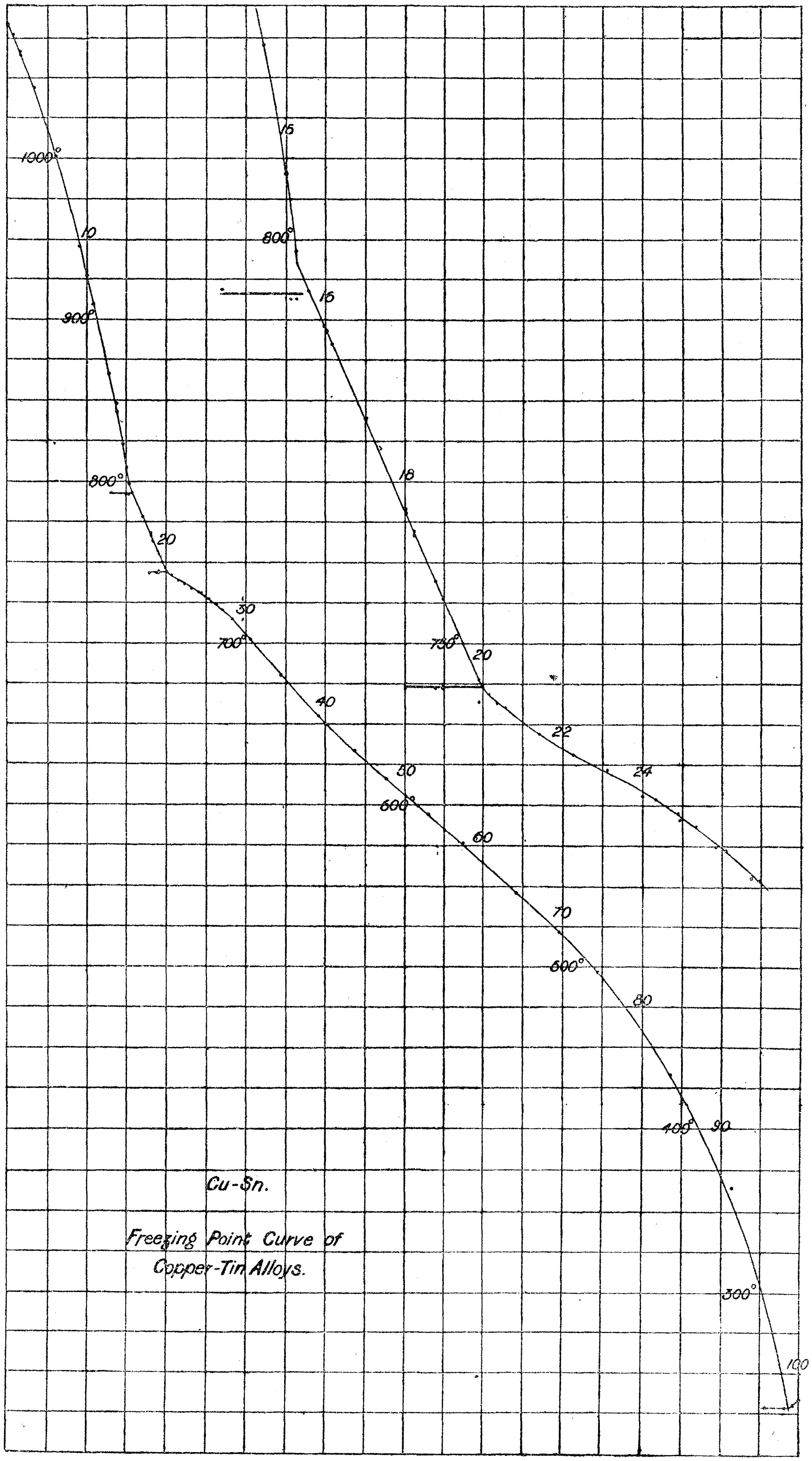
* Pointed out by OSTWALD.

† After a good deal of our work had been carried out, we found in an article on alloys by M. H. LE CHATELIER, which he was kind enough to send to us (*loc. cit.*, p. 27), a complete freezing-point curve for copper-tin. This curve agrees with ours in having an angle at $SnCu_4$, but it is on too small a scale for a comparison of other details.

Fig. 10.



The numbers below the curve give the Centigrade temperature; the numbers above the curve give the atomic percentage of tin in the alloy.

The first point that strikes one in the copper-tin curve is the rapid way in which the steepness increases with increasing percentage of tin. If we bear in mind the fact that, on account of the thermometer lag, so important where the curve is steep, the true equilibrium curve from 5 to 15 atoms of tin may lie perceptibly above our freezing-point curve, while, from the character of the freezing point at 15·5 atoms, the two curves must agree at this point, we can conclude that at 15 the true curve may be almost a vertical line. A not improbable explanation of this feature of the curve is to suppose that the tin is largely combining with the copper to form molecules, such as $SnCu_3$ or $SnCu_4$. As can be proved by the use of this assumption in equation (2), the view that the body in solution is $SnCu_3$ agrees very well with the shape of the curve up to 15 atoms of tin. But we do not attach much importance to this numerical agreement, as the assumption of the existence of molecules of $SnCu_4$, accompanied by some dissociation, would give an equally good agreement.

At 15·5 atoms of tin our curve changes its direction, and becomes a straight line; the freezing point of each alloy is now marked by a steady temperature, lasting for some time. In the figure this point appears to be a triple point, as from 13·5 atoms to 15·5 we observed two freezing points, one a slightly-marked one on the steep part of the curve, the other a very steady temperature identical with the single freezing point at 15·5. We think that the horizontal line of freezing points thus obtained represents the moment for each alloy when, through separation of solid matter at and below the upper freezing point, the still liquid portion attains the composition of 15·5 atoms.

The soft precipitate which forms at, or soon after, the freezing point on the upper branch as far as 15·2 is very unlike the abundant finely-gritty precipitate of these lower freezing points, and of the alloy as far as 18 atoms or beyond.

From 15·5 to 20 atoms the freezing point is plainly marked by a constant temperature lasting for some time; and all the points lie on a line in which we cannot see any curvature. This line ends exactly at 20 atoms, and it will be seen that we have studied this region very minutely.

Below the lower half of this line we find a horizontal line of second freezing points, causing the appearance of a triple point at, or near, 20 atoms. Each of these lower freezing points occurs after a good deal of solid matter has already formed. The alloy sets to a solid mass at the lower point, and this freezing point is marked by a period of absolutely constant temperature. We have no doubt that these lower points indicate the moment when the still liquid alloy has reached the composition of 20 atoms of tin.

From 20 to 25 atoms the curve is very nearly, but not quite, straight, and the fall in temperature caused by the increase of tin from 20 to 25 atoms is comparatively slight, being less than 20°. The freezing point of each alloy is marked by a prolonged period of constant temperature. The freezing points are like those of the eutectic state, and each alloy may be said to solidify at a constant temperature, as if the matter separating out had the same composition as the residual liquid. Little or no precipitate was noticed at the moment indicated by the thermometer as the commencement of freezing. Soon after 25 atoms we begin to have precipitate at the moment of freezing, and the freezing point gradually loses its resemblance to a eutectic point.

A comparison with KÜSTER's work on isomorphous mixtures strongly suggests that between 15·5 and 20 we are in the presence of one, and between 20 and 25 in presence of another, such isomorphous mixture.

At 50 atoms of tin there is a point of inflexion, and, therefore, between 60 and 70, there must be what by a stretch of language might be called a summit.

Before attempting to interpret these phenomena it will be well to consider briefly the conclusions of other workers in the same field.

RICHE ('Ann. de Ch. et Phy.,' 1873, xxx.), found that alloys of copper and tin undergo liquation, except $SnCu_4$ (20 atoms) and $SnCu_3$ (25 atoms); but he does not appear to have examined alloys between these two values.

BEHRENS, whose work, "Das Mikroscopische Gefüge der Metalle und Legierungen," is a mine of valuable information, but a mine wherein one needs to dig diligently, notes a sharp change in the colour, the microscopic structure, and the chemical behaviour of bronzes at 25 per cent., by weight, of tin. This is the same as 15·3 atomic per cents., a point where our curve shows its first angle. His microscopic study of alloys with only a few per cents. of tin shows the crystals of copper embedded in a network of white or yellowish mother substance; but at our first angle, at 15·3 atoms, all distinction in colour between crystals and mother liquor has disappeared. He says that the colour of this alloy is whitish-grey. It has a conchoidal fracture, and examined microscopically is seen to consist of bundles of parallel rods, scattered in all directions. He thinks that we have here to do with a compound $SnCu_6$. At 20 atoms of tin, our second angle, BEHRENS considers that there is another chemical compound. $SnCu_4$. He says, "that with this alloy we reach a maximum of hardness, brittleness, and resistance to chemical solvents." Also, "that if great care is taken to get an alloy of exactly this composition, we have a grey-white metal with a half-glassy, glimmering, minutely conchoidal fracture. There is no sign of crystallization; and polishing and annealing show nothing. The slower the cooling the more brittle the mass." He finds that at 25 atoms of tin the alloy is more easily attacked by reagents than at 20 atoms, and hence, and for other reasons, he refuses to accept the view that $SnCu_3$ is a compound. He is disposed to regard it as a mixture of two alloys, which may, or may not, have separated in the liquid state. He finds that this alloy crumbles under the hammer, or even under a coarse file, into polyhedra with smooth faces.

In contrast to BEHRENS, other writers have accumulated a mass of facts pointing, at least, to the unique character of the alloy with 25 atoms of tin. LAURIE finds that the electromotive force of couples formed of copper and a copper-tin alloy changes abruptly at this composition. We get here a maximum for electrical conductivity, for density, and for coefficient of dilatation.

Hence various writers have concluded that the compound $SnCu_3$ exists; but there has not been the same unanimity with regard to the existence of $SnCu_4$.

Our results, though they cannot be called final, point we think, to the view that when alloys poor in tin begin to freeze, copper separates from a liquid containing molecules of a compound of tin and copper. That when the alloy $SnCu_6$ is reached, copper ceases to separate as such; and instead, this body, or more probably an isomorphous mixture of $SnCu_6$ and $SnCu_4$, separates. The double freezing points from 18 to 20, however, show that the liquid does not solidify homogeneously, so that the isomorphism cannot be of an absolute character.

At 20 atoms of tin we think that the evidence points to the existence of the body $SnCu_4$. Between 20 and 25 atoms, perhaps the most probable explanation is to suppose that an isomorphous* mixture of $SnCu_4$ and $SnCu_3$ solidifies homogeneously. At 64 atoms of tin the curve is not incompatible with the existence of the compound $SnCu_2$, and with still more tin the molecule of any compound that may exist must ultimately, for very dilute solutions of copper in tin, contain only one atom of copper (J.C.S., *loc. cit.*).

The criticisms of BEHRENS, however, on the alloy $SnCu_3$ suggest another explanation of the phenomena which is not without probability. It may be that with more tin than $SnCu_4$, the liquid alloy breaks up into two conjugate liquids, and that this state exists until more than 25 atoms of tin are present. If this were so, we should have expected, as in the copper-lead curve, that this part would have been horizontal; but, assuming the two conjugates to differ little in density, the slight, but real, slope in this part of the curve might be accounted for by imperfect realization of equilibrium at the freezing point.

The interesting complete *cooling* curves of copper-tin alloys given by Professor ROBERTS-AUSTEN, in his Report on Alloys, will, we think, be found to be consistent with the facts observed by us, although we should not perhaps altogether agree with him in the inferences that can be drawn from these facts.

The Silver-Antimony Curve. (Fig. 11.)

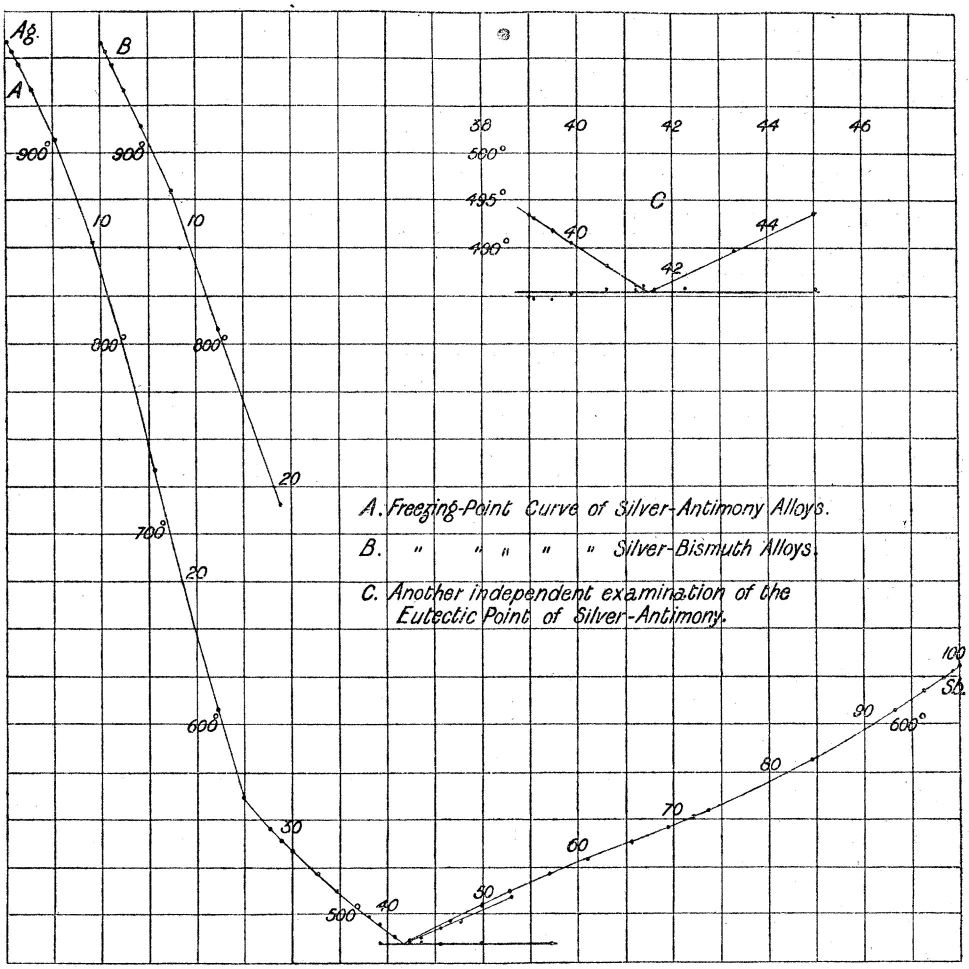
In this curve it will be seen that up to 25 atomic per cents. of antimony the steepness increases with increase in the amount of antimony. As in the case of the similar feature of the tin-copper curve, we can explain this by assuming that the antimony combines with the silver to form a compound molecule.

At 25 atomic per cents. of antimony there is a well-marked angle, and although there is only one point determined between 15 and 25 atomic per cents., yet the direction of the lines leaves little doubt as to the position of this angle. The angle,

* KÜSTER, 'Zeits. Phys. Chem.,' 1890, v., p. 601.

therefore, corresponds to an alloy of the formula Ag_3Sb, a body that is known to exist. An angle such as we have here is not the sort of indication of the existence of a compound that the theory would lead us to expect. Indeed, another examination of this part of the curve with especially pure antimony would be needed before it would be safe to assert that the angle is at exactly Ag_3Sb.

Fig. 11.



The numbers below the curve give the Centigrade temperature.
The numbers above the curve give the atomic percentage of antimony or bismuth.

The first series, Table VIIIA., which ends at 53 atoms of antimony, involved the maintenance of the alloy at a high temperature for a good many hours, and, as the notes show, there was a considerable loss of metal. Consequently we feared that the latter part of the series might not be trustworthy. We therefore carried out a new series, Table VIIIC., beginning near the eutectic point. The result of this is given on a large scale above the main curve, and seems to show that the eutectic alloy has not a formula, although it is not very far from 40 atomic per cents. of antimony, that is, from Ag_3Sb_2. It would require the existence of a good deal of impurity in the antimony to make Ag_3Sb_2 the eutectic point.

The series, Table VIIIB., in which silver was added to antimony, gives us the same eutectic point, namely, 41·5 atomic per cents. of antimony.

The short line, starting from the eutectic point and ending at 53 atoms of antimony, was obtained with commercial antimony, so that the fact that it lies below the rest of the curve needs no comment.

The temperature 629·49° which we obtained as the freezing or melting point of antimony is almost identical with the number 629·54° that we obtained with quite different thermometers a year before ('Chem. Soc. Jour.,' 1895, p. 195). The same sample of antimony was used in both cases, and in our earlier work we noticed that this antimony behaved at its freezing point in the way peculiar to a pure substance. We think it is almost time for the text-books of chemistry to abandon the statement that antimony melts at 440°.

Incomplete Curves.

In fig. 11, the line beginning at B above the silver-antimony curve, gives the result of adding bismuth, up to 19 atomic per cents., to silver. This promises to closely resemble the silver-antimony curve, and we regret that want of time has prevented us from completing it.

In fig. 20 we give the bismuth-copper curve, which, if completed, would almost certainly resemble that of lead-copper.

Fig. 12 is the curve of gold-copper.

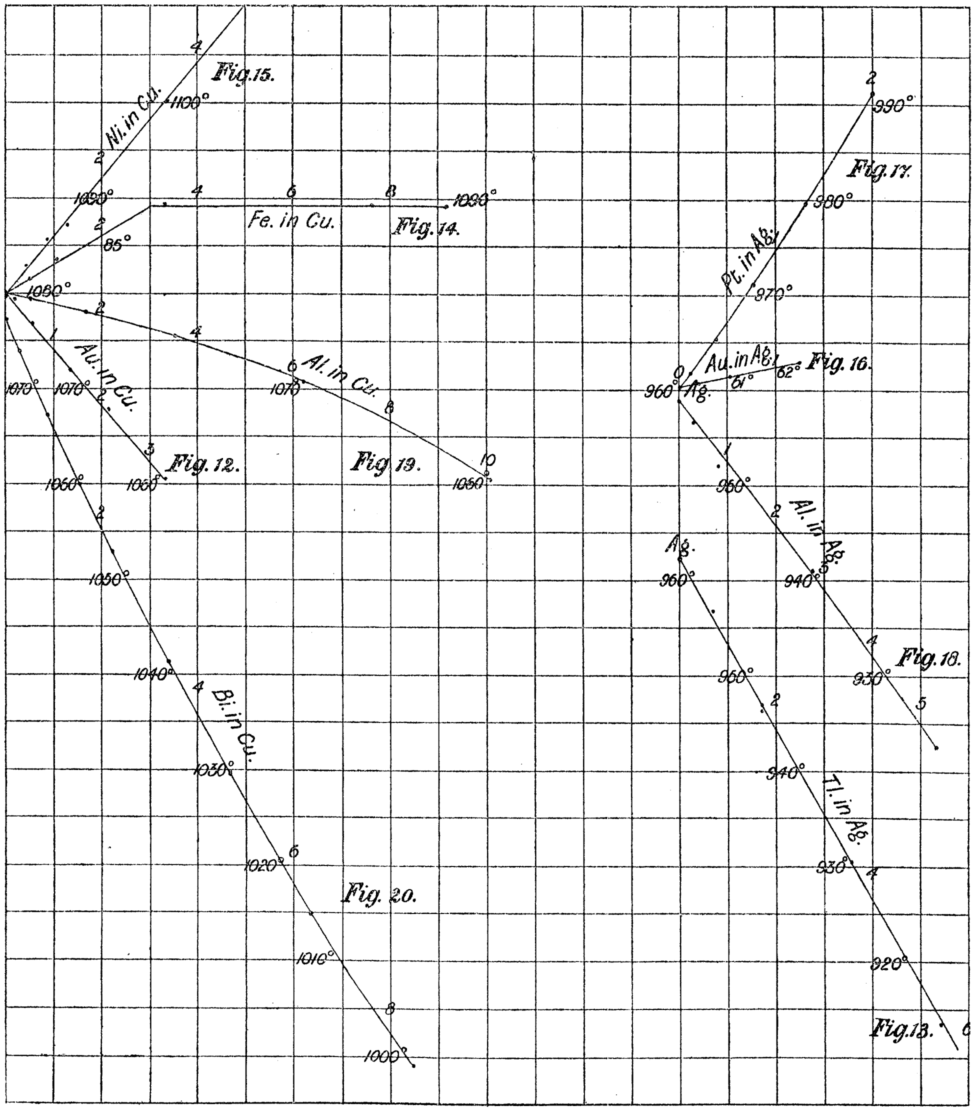
Fig. 13, the curve of thallium added to silver, is, so far as it goes, very straight, like the early part of the lead-silver curve.

The remaining metallic pairs that we have examined require further experiment, we therefore do not give tables for them; but the curves enable the numerical results to be read off with sufficient accuracy.

From figs. 14, 15, 16, 17 it will be seen that the first result of adding iron or nickel to copper, or of adding gold or platinum to silver, is to raise the freezing point. In one case only, that of iron added to copper, did we reach the higher limit of this rise; it will be seen from fig 14 that after 3 atoms of iron a further addition produces no effect on the freezing point, so that a flat occurs in the curve; we have noticed several similar cases, where zinc is the solvent metal. In these cases of rise in the freezing point we hardly think it would be profitable, until the whole curve has been traced, to attempt to distinguish between the phenomena of the separation of isomorphous mixtures, solid solutions or compounds.

In figs. 18 and 19 we give the curves for dilute solutions of aluminium in silver and in copper. We have traced these curves further, finding, as LE CHATELIER had previously found, an intermediate summit at $AlCu_3$, and probably also at $AlAg_3$; but we have been troubled by the oxidation of the aluminium, and hope to get better results. There can be little doubt that the chemical compounds formed by aluminium with other metals are unusually stable.

Figs. 12–20.



Freezing point curves for dilute solutions of metals in silver or copper.
The numbers below the curve give the Centigrade temperature.
The numbers above the curve give the atomic percentage of the dissolved metal.

The experiments described in the present paper were to a large extent carried out with apparatus purchased by funds supplied to us by the Grant Committee of the Royal Society, and we wish here to thank them for the important help that we have received in this way.