XXXIX.—*The Freezing Points of Alloys containing Zinc and another Metal.*

By CHARLES THOMAS HEYCOCK and FRANCIS HENRY NEVILLE.

INTRODUCTION.

THE present paper contains the results of experiments most of which were carried out in 1894 and 1895, but some, including the greater part of the zinc-silver and the zinc-tin series, were performed in 1896. The results are not so complete as we had hoped to make them, but in so large a subject it is hopeless to aim at completeness, and the fact that an increasing number of students is now occupied with the cryo-

scopic study of alloys renders such an aim less necessary, for it may be hoped that one worker's results will complement and correct those of another. M. Henri Gautier[*] has lately published an investigation of the melting points of several alloys, including zinc-silver, that must cover the same ground as our own experiments on that pair of metals, but as we had obtained some remarkable results with dilute solutions of silver in zinc before we were aware that he was occupied with the subject, we have thought it worth while to complete our zinc-silver freezing point curve. In order that our work might have the value attaching to an independent investigation, we have not allowed ourselves the pleasure of studying his paper, although very possibly we might have been saved from some errors by doing so.

The freezing points were determined by means of platinum resistance pyrometers identical with those described in a previous paper (Trans., 1895, **67**, 160). As the methods of using the pyrometers and reducing their reading to the centigrade-air scale are fully described in that paper, we content ourselves in the present case with stating the centigrade temperatures without explanation.

Zinc is, in some respects, a more troublesome metal to use as a solvent than any other, either of higher or lower melting point, that we have as yet employed; for in working near 400°, we have been unable to find any substance which could be used to protect the surface of the molten alloy from oxidation. The paraffins, which we had employed up to the melting point of lead, were too volatile or decomposed at the higher temperature. The plan of introducing a jet of coal-gas into the crucible so that it impinged on the surface of the molten metal was adopted; but although oxygen was thus, to some extent, excluded from the crucible, the reducing action of the unlit coal-gas at so low a temperature as 400° was probably very slight. We do not, however, think that oxidation took place to such an extent as seriously to impair the accuracy of our results.

The alloys were vigorously stirred by a plunging ring stirrer which just fitted the cylindrical crucible. This stirrer was of clay in a few of the earlier experiments, but afterwards we invariably used a stirrer made of gas carbon. In general, this stirrer was worked by a water motor, but in a few cases it was worked by hand.

The experiments at temperatures below 500° were generally carried out in an improvised furnace which allowed of a somewhat more rapid rate of cooling than did Fletcher's furnaces. The base of this furnace was a slab of fire-clay perforated by a circular hole about 2 inches in diameter, and the walls were formed by a cylinder of sheet asbestos. Resting on the top of this cylinder was a circular plate of thick sheet asbestos having a central hole. This formed the top of the furnace, and a

* *Compt. rend.*, 1896; **123**, 172—174.

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cylindrical cast iron crucible with walls half-an-inch thick just fitted the hole in the asbestos top and was thus suspended axially within the furnace. The true crucible of plumbago, which contained the alloy, was a cylinder exactly fitting the inside of the iron crucible. The whole structure rested on an iron tripod so that a Bunsen burner could be placed underneath and raised until the flame more or less entered the hole in the base of the furnace. This arrangement gave us the power of heating rapidly, together with very steady temperatures, and some control over the rate of cooling. We shall call this furnace A, to distinguish it from the Fletcher's furnace and from other arrangements sometimes employed.

At the commencement of a series of experiments, a known weight of one metal was melted in the crucible and its freezing point determined. Successive known weights of the second metal were then added, the freezing point being determined after each addition. Except in the case of the silver-zinc alloys, where we were forced to resort to chemical analysis, the composition of the alloy was deduced from the weights of metal used. This plan, at the comparatively low temperatures needed for zinc, and provided that care is taken to minimise oxidation, is probably as trustworthy as an analysis, at all events when the series of experiments is not too prolonged.

The results are given in tabular form and also expressed as curves. Each pair of metals has a separate table allotted to it, and at the head of the table we state the nature of the alloy and the weight used of what we may term the solvent metal.

The first column gives the percentage by weight of the second metal present.

The second column gives the atomic percentage of the second metal, or, in other words, the empirical formula of the alloy—thus a silver-zinc alloy having 20 atomic per cents. of zinc would have the formula $Ag_{80}Zn_{20}$. This column is calculated from column 1, and from the atomic weights of the metals.

The third column gives the temperature at which the alloy *begins* to solidify—the freezing point or f. p., as we shall, for shortness, term it. It is often easy to *read* this temperature to $0.01°$, although the *true* temperature is no doubt rarely obtained so nearly as this. We think, however, that in certain cases our results would lose in accuracy by rejecting the second decimal place, we have therefore usually retained it.

The fourth column, the atomic fall, is obtained by dividing the total depression of the freezing point by the atomic percentage of the second metal. It is clear that if, as should be the case for dilute solutions, the depressions are proportional to the concentrations, then the atomic fall ought at least, for the same pair of metals, to be a constant. This column is only given for dilute solutions. It is useful, because it

shows at once whether the experiments are consistent with one another. It must be remembered, however, that, for very dilute solutions, the atomic fall necessarily appears to be irregular, as, from the method of calculating it, the experimental error is in such cases greatly magnified.

In the freezing point curves (pp. 404 and 422), the temperature is measured vertically upwards and is indicated by numbers placed at the side of the page or in some cases by numbers placed immediately below the line of the curve. The composition is indicated in atomic percentages, the numbers being placed either along the top or bottom of the page, or in some cases by numbers immediately above the line of the curve. The plan of placing the numbers close to the curve is convenient when it is necessary to make the curve of each pair of metals an independent figure having its own zero, as in Figures 4 and 15. The individual experiments are indicated in the figures by black dots lying on or near the line of the curve.

It will be seen from the tables that we in several cases give more than one series of experiments for the same metallic pair in which the starting point is the same pure metal. But the freezing points of the pure metal in two such series, obtained at different times and probably with different thermometers, are certain to differ a little. We therefore, before charting these series, add to or subtract from every term of one of them the small constant quantity which is needed to make the f. p. of the pure metal the same in both; for example, in all the complete f. p. curves the f. p. of zinc is taken as 419.*

The paper is divided into two almost independent sections. The first deals with those metals which, when added to zinc, begin by lowering its freezing point, the second deals with those metals which raise the freezing point of the zinc.

A reader can most readily obtain an idea of our results by turning at once to the second part of each section in which the individual curves and their meaning are discussed.

SECTION I.

Metals which Lower the Freezing Point of Zinc.

Amongst the metals whose alloys we have examined, we find that the freezing point of zinc is lowered by tin, bismuth, thallium, cadmium, lead, antimony, magnesium or aluminium.

Our experiments with these metals are embodied in Tables I to VIII, and in Figures 1 to 12 (p. 404).

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* In all the experiments ranging over three years in time, and made with many different pyrometers, the extreme divergence from the mean freezing point of zinc was ± 0·7°.

TABLE I A.

CADMIUM ADDED TO ZINC.

Series 1.

200 *grams of Zinc.*

Unlit coal gas on surface of metal.   Hand-stirring.

Percentage of cadmium by weight.	Atomic percentage of cadmium.	Freezing point centigrade.	Atomic fall.
0	0	418·50	
0·259	0·152	417·86	4·21
0·990	0·581	415·82	4·61
2·479	1·464	411·69	4·65
5·167	3·084	404·28	4·61
14·11	8·760	381·80	4·30
16·38	10·275	374·98	*
19·74	12·57	371·26	
22·83	14·74	365·07	
28·42	18·83	355·05	
35·36	24·22	344·30	

Series 2.

129·3 *grams of Zinc.*

35·36	24·22	344·20	
40·89	28·78	336·46	
45·48	32·78	330·70	
49·42	36·17	325·83	
52·91	39·64	321·99	
56·11	42·76	317·77	
60·27	46·98	312·44	
63·75	50·66	308·08	
,,	,,	(264·42)†	

Series 3.

73·76 *grams of Zinc.*

63·12	50·0	307·25	
,,	,,	307·56‡	
64·05	51·0	306·03	
67·25	54·53	301·05§	
70·06	57·76	296·30	
75·09	63·80	285·79	
		286·46	
77·04	66·20	280·92¶	
		281·67	
79·00	68·73	276·10	
,,	,,	(264·62)	

* From this point onwards, the concentration is too great to render the atomic falls of any meaning.

† The freezing point of the eutectic mixture, a very steady temperature.

‡ Read with a layer of ragosine oil on the surface of the alloy.

§ Nuclei of zinc were dropped in, but seemed to have no effect in altering the f. p.

¶ Raised alloy to a red heat after this reading, to make certain that all the zinc was melted.

TABLE I.B.

ZINC ADDED TO CADMIUM.

Series 1.

250 grams of Cadmium.

Percentage of zinc by weight.	Atomic percentage of zinc.	Freezing point centigrade.
0	0	320·55
0·145	0·249	319·88
0·290	0·495	319·33
0·686	1·168	317·32
1·450	2·456	313·77
2·230	3·756	309·51
3·832	6·385	302·74
5·708	9·390	295·03
8·760	14·12	284·41
12·72	19·96	273·10
18·42	27·87	267·04
25·69	37·17	289·54
		(264·56)
32·16 ,,	44·80 ,,	300·21

Series 2.

225 grams of Cadmium.

10·11	16·15	279·40
12·90	20·22	272·92
15·72	24·20	266·62
		(264·43)
16·67 ,,	25·50 ,,	264·76
		(264·54)
17·59 ,,	26·76 ,,	264·54
19·16	28·85	269·06
,,	,,	(264·50)

With the exception of the eutectic points, which could be found by allowing the mixture to cool, and which were quite constant for many minutes, all the freezing points of alloys, rich in both cadmium and zinc, were difficult to observe exactly. They were read with the aid of a metronome to mark the rate of cooling ; there was no period of absolutely constant temperature, but, at the point recorded, the rate of cooling suddenly became three or four times as slow as it had been until then.

TABLE II A.

ALUMINIUM ADDED TO ZINC.

400 *grams of Zinc.*

Coal gas burning over the surface of the metal.

Percentage of aluminium by weight.	Atomic percentage of aluminium.	Freezing point centigrade.	Atomic fall.
0	0	418·6	
0·41	0·99	414·5	4·13
0·82	1·96	410·4	4·11
1·23	2·91	407·7	3·76
2·03	4·76	401·4	
3·20	7·41	392·2	
5·47	12·28	(380·6)*	
7·64	16·67	(380·9)*	
,,	,,	404·9	
9·71	20·64	418·4	
14·53	29·14	447·3	
18·87	36·00	466·1†	
18·86	,,	464·9‡	
25·06	44·71	492·6	
30·37	51·34	508·4†	
36·22	57·87	525·4	

* Very steady eutectic temperatures. The mass was nearly solid before the first of these two points was reached.
† Extracted a portion, weighed it, and continued the experiment with the residue.
‡ The f. p. of residue.

TABLE II B.

ZINC ADDED TO ALUMINIUM.

175 *grams of Aluminium.*

Percentage of zinc by weight.	Atomic percentage of zinc.	Freezing point centigrade.	Atomic fall.
0	0	654·5	
0·90	0·374	652·5	5·35
2·34	0·981	650·4	4·18
3·42	1·44	648·7	4·03
5·83	2·50	644·9	3·84
8·76	3·82	639·5	3·93
11·98	5·33	634·4	3·77
18·23	8·44	623·2	3·71
25·22	12·24	613·0	3·64
31·10	15·73	598·7	3·55
38·39	20·49	584·5	3·41
44·27	24·73	571·1	
49·13	28·54	560·2§	
53·75	32·46	548·5	
56·39	34·84	542·2‖	
		541·4¶	
61·00	39·27	530·8	
65·80	44·31	518·2	

§ After this reading, a weighed amount was extracted, and the experiment continued with the residue. It will be seen that the f. p. was unchanged.
‖ After this reading, we extracted a weighed portion.
¶ The f. p. of the residue.

TABLE III a.

Series 1.

BISMUTH ADDED TO 500 GRAMS OF ZINC.

In a clay crucible placed in the axis of a small iron block.   Stirred by a
clay ring stirrer.   Coal gas burning on the surface of the metal
during cooling.   Platinum pyrometer in porcelain tube.

Percentage of bis-muth by weight.	Atomic percentage of bismuth.	Freezing point centigrade.	Atomic fall.
0	0	418·64	
0·439	0·139	417·94	5·03
0·826	0·262	417·37	4·85
1·217	0·386	416·78	4·82
1·614	0·514	416·31	4·53
1·99	0·635	415·84	4·41
2·44	0·783	415·73	
6·12	2·01	415·66*	
9·48	3·21	415·65*	

Series 2.

Bismuth added to 258 grams of Zinc.

In furnace A.   Coal gas, unlit, over surface of the metal.   Platinum
pyrometer in thin glass tube.   Carbon ring stirrer.

0	0	418·80	
0·200	0·063	418·46	5·4
0·591	0·187	417·71	5·8
2·020	0·645	415·93	Saturated.
2·36	0·756	415·93	,,
9·51	3·20	415·93	,,
17·13	6·11	415·95	,,
26·67	10·28	,,	

Series 3.

Bismuth added to 160·75 grams of Zinc.
Conditions the same as in Series 2.

38·35	16·38	416·20	
44·84	20·38	416·50	
50·92	24·63	416·70	
55·79	28·44	416·80	
59·93	32·02	416·86	
63·20	35·11	416·90	

* In these last two readings a trace of surfusion was noticed.

From 6·11 atomic per cents. of bismuth to the end of Series 3, each freezing point is an extremely steady temperature ; in fact, the temperature was watched for nearly five minutes after reading the freezing point and no fall in temperature noticed.   We did not venture to allow the mass to solidify completely, lest the metal in setting should crush the glass tube of the pyrometer.

A very rapid stir was maintained during Series 3.

At the end of Series 3, the alloy, after being well melted, was allowed to cool slowly, and the ingot of metal was finally extracted from the crucible.   It weighed 431 grams, and there was also a little on the pyrometer stem and the stirrer.   The weight of the metals used was 437 grams.   The alloy consisted of two layers, the lower about twice the amount of the upper.   They were easily separated by a blow from a hammer.

The constants of the pyrometer were found to be the same at the beginning and end of the experiments, hence the slight upward creep of the freezing points along the flat of the curve is probably a real phenomenon, perhaps due to an impurity in the bismuth.

TABLE III B.

ZINC ADDED TO 300 GRAMS OF BISMUTH.

Conditions the same as in Table III A, *Series* 2 *and* 3.

Percentage weight of zinc.	Atomic percentage of zinc.	Freezing point centigrade.	Atomic fall.
0	0	269·37	
1·336	4·12	261·81	1·835
1·954	5·95	258·60	1·810
3·218	9·55	254·51	Saturated.
4·116	12·00	254·37	,,
7·142	19·63	343·0	
8·633	23·08	358·1	
11·63	29·47	387·3	
		388·3	
14·28	34·60	409·4	
15·49	36·78	416·9	
		417·8	
17·85	40·82	417·8	
		417·9	
22·40	47·82	417·2	
26·15	52·93	416·6	

After each addition of zinc, it was necessary to heat the alloy to the melting point of zinc to bring about solution.

In the freezing points, down to 12 atomic per cents. of zinc, surfusion was generally noted, sometimes to the extent of 2°.

The point at 12 atomic per cents. of zinc was a very steady temperature.   Here the rate of cooling was carefully watched from 50° above the recorded temperature, but no higher freezing point could be found.

At 19·63 atomic per cents. of zinc, the freezing point was somewhat fugitive ; this is always the case at the first points on the branch of the curve ascending from the lower eutectic flat towards the melting point of the less fusible metal.

The experiments of Table III B were carried out with a sample of bismuth, believed to be specially pure, which was used by Griffiths in his determination of the freezing point (*Phil. Trans.*, 1891, A, p. 150). He then got 269·22° as the mean of his results. It is interesting to note that our number, obtained without any special attempt to arrive at a standard result, differs from his by only 0·15°. His platinum thermometers were of a different type from ours, and the conditions of the experiment in other respects not the same. We think it very doubtful whether, even at these moderate temperatures, two mercury thermometers would have given so close an agreement.

TABLE IVA.

TIN ADDED TO ZINC.

Series 1.

700 grams of Zinc.

An early series of experiments. The conditions not specially noted.

Percentage weight of tin present.	Atomic percentage of tin.	Freezing point centigrade.	Atomic fall.
0	0	419·57	
0·549	0·305	417·82	5·7
1·088	0·606	416·18	5·6
1·795	1·004	414·14	5·40
3·152	1·772	410·53	5·10
3·450	1·944	409·82	5·02
4·873	2·763	406·40	4·76

Series 2.

150 grams of Zinc.
In furnace A.   Carbon stirrer.

0	0	418·86	
3·23	1·81	409·80	5·00
6·25	3·56	402·61	4·56
11·77	6·88	393·16	
16·67	9·98	387·38	
23·08	14·26	380·56*	
29·57	18·88	374·81	
35·04	23·02	370·07	
41·14	27·94	364·37*	
49·07	34·83	355·62	
55·12	40·53	347·56	

* After these readings, the crucible was too full ; a portion of the alloy was therefore extracted in a molten state, weighed, and the experiment continued with the residue.

TABLE IV A.—*continued.*

Series 3.

200 *grams of Zinc.*

In furnace A. Unlit coal gas. Pyrometer in a glass tube.

Percentage weight of tin present.	Atomic percentage of tin.	Freezing point centigrade.	Atomic fall.
0	0	418·15	
0·356	0·198	417·04	5·60
0·860	0·479	415·52	5·49
1·445	0·806	413·95	5·21
2·120	1·187	412·18	5·03

Series 3 was carried out later than any other work described in the paper, as a check on the large atomic falls of Series 1.

The last reading of Series 3 was repeated several times during an hour, and remained unchanged, hence there does not appear to be any loss of tin by oxidation.

This series is not utilised in drawing the f. p. curves.

TABLE IV B.

ZINC ADDED TO TIN.

150 *grams of Tin.*

Furnace A, &c., as before. Unlit coal gas on surface.

Percentage weight of zinc present.	Atomic percentage of zinc.	Freezing point centigrade.
10·71	17·80	197·79*
11·65	19·23	197·94
,,	,,	228·64†
,,	,,	228·77†
12·58	20·61	197·90
,,	,,	234·82
14·08	22·82	245·61
16·43	26·18	260·80‡
19·68	30·64	281·04
,,	,,	197·77
23·41	35·52	297·87
27·37	40·45	312·40
30·77	44·48	323·72
34·93	49·18	335·47
38·67	53·20	342·70§

* A very steady temperature. No higher point could be detected.

† A slight halt in the cooling here.

‡ From here onwards the freezing points are well marked.

§ At the end of the experiments, the alloy was poured out of the crucible, and examined. A little powder was noticed with the metal. This may have been oxide, but was more probably carbon from the stirrer.

TABLE V.

LEAD ADDED TO 550 GRAMS OF ZINC.

In Salamander crucible in a small Fletcher blast furnace.   A little coal gas burning on the surface during cooling.

Percentage weight of lead.	Atomic percentage of lead.	Freezing point centigrade.	Atomic fall.
0	0	419·22	
0·315	0·10	418·72	5·0
0·628	0·20	418·16	5·3
0·939	0·299	417·74	4·95*
1·25	0·398	417·73	
2·01	0·646	417·73	
4·95	1·62	417·63	
15·15	5·35	417·63	†

* This, and all the following freezing points, are the same, because the zinc is saturated with lead.   These freezing points of the saturated alloy were very constant temperatures, and became more constant with each addition of lead.

† The stationary temperature here lasted 13 minutes without change.

TABLE VI.

ANTIMONY ADDED TO 250 GRAMS OF ZINC.

Coal gas burning over the surface of the metal.

Percentage of anti-mony by weight.	Atomic percentage of antimony.	Freezing point centigrade.	Atomic fall.
0	0	418·78	
0·273	0·149	418·10	4·5
0·669	0·365	417·02	4·8
,,	,,	416·66	5·8
1·46	0·799	414·80	4·98
,,	,,	414·52	5·3‡
,,	,,	414·67	5·1
2·23	1·23	412·84	4·84
3·37	1·86	412·57	
4·47	2·49	412·65	§

‡ The experiments were resumed here after a night's interval.   Before the reading, the alloy was heated to a red heat to ensure the solution of the antimony.

§ A very steady temperature.

TABLE VII.

THALLIUM ADDED TO 250 GRAMS OF ZINC.

Carbon stirrer. Coal gas burning on the surface of metal.

Percentage of thallium by weight.	Atomic percentage of thallium.	Freezing point centigrade.	Atomic fall.
0	0	418·77	
0·392	0·126	418·18	4·7
1·22	0·393	416·79	5·0
2·55	0·831	416·51	Saturated.
3·77	1·241	416·46	,,
5·87	1·962	416·41	,,

TABLE VIII.

MAGNESIUM ADDED TO ZINC.

Series 1.

250 grams of Zinc.

Percentage weight of magnesium.	Atomic percentage of magnesium.	Freezing point centigrade.	Atomic fall.
0	0	419	
0·157	0·42	416·62	5·64
0·320	0·854	414·15	5·67
0·574	1·53	410·04	5·77
0·972	2·57	403·84	5·89

Series 2.

250 grams of Zinc.

0	0	419·05	
0·138	0·37	417·26	4·84
0·364	0·975	413·78	5·41
0·685	1·818	408·92	5·57
1·503	3·936	395·21	6·06

Series 3.

250 grams of Zinc.

Pure hydrogen over surface of alloy.

0	0	419·02	
0·405	1·08	413·39	5·21
1·246	3·18	401·60	5·48
2·361	6·10	382·17	6·04

TABLE VIII.—*continued.*

Series 4.

192 *grams of Zinc.*

In small Fletcher blast furnace.   Current of coal gas burning over surface of metal.

Percentage weight of magnesium.	Atomic percentage of magnesium.	Freezing point centigrade.	Atomic fall.
0	0	419·0	
0·332	0·887	413·93	5·72
0·819	2·17	406·41	5·80
1·486	3·89	395·13	6·14
2·058	5·34	387·44	5·91
3·360	8·55	369·61	5·78
,,	,,	369·74	

The magnesium was in sticks from the Patricroft factory.   It is at once wetted by the zinc, and dissolves easily at temperatures but little above the melting point of zinc, and with no apparent evolution of heat.

Zinc-Cadmium.

Figure 1 (p. 404) gives a complete freezing point curve for all mixtures of these two metals.   It may be regarded as a fairly typical one for metals which do not combine chemically, and which are soluble in each other in all proportions.   It shows that the addition of cadmium to the zinc lowers the f. p. until about 73·5 atomic per cents. of cadmium are present when a minimum f. p. of 264·5° is reached, and that further addition of cadmium raises the f. p. continuously until with 100 atomic per cents. of cadmium the f. p. of that metal is reached.

The determination of the composition of the eutectic alloy, that is the alloy of lowest freezing point, was difficult in this particular case. The freezing points near, but above the eutectic, are always somewhat fugitive temperatures, and in the present case, the chance of oxidation during the prolonged series of experiments makes our knowledge of the composition of the alloy a little uncertain.   It is quite possible that all the causes of error, taken together, may make our estimate wrong by more than one atomic per cent.   In other words, the experiments do not contradict the supposition that the eutectic state occurs at $ZnCd_3$, but this is almost certainly a coincidence, like a similar case we have observed for silver-copper.   There can be no doubt that the eutectic alloy is nothing but that particular mixture of the two metals from which, when liquid, they would both separate in the solid form at

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the same temperature ; there is, therefore, no reason for expecting it
to be a chemical compound. In fact, although from the imperfection
of our experiments we could not trace the curve close to the eutectic
state, and have, therefore, drawn the figure as if the two branches
passed into each other here with a continuous curvature, it is almost
certain that, with perfect experiments, this eutectic point, like others,
would be found to be an angle in which two entirely independent
branches of the curve cut each other. The branch which starts from
the f. p. of pure zinc, may be regarded as the f. p. curve of zinc,
holding cadmium in solution, while the other branch is the f. p. curve
of cadmium, holding zinc in solution. In the upper part of each
branch, there is no doubt that pure zinc or pure cadmium respectively
freeze out at the f. p., and this may, perhaps, be the case throughout
the whole of each branch, but the fact has not been verified by experi-
ment. We have not been able to find freezing points on either branch
below the eutectic point ; the curves, in fact, seem to end at their
intersection, but if it were possible to produce a state of superfusion
in an alloy containing a little more zinc than the eutectic, we might,
by dropping in a nucleus of cadmium, obtain a point on the cadmium
branch below the eutectic. We believe that some experimenters,
using other binary mixtures, have thus traced the two branches a
little way below the eutectic point.[*]

The f. p. of the eutectic alloy is more certainly determinable than
its composition, for it can be found as a second freezing point of alloys
of various compositions. For example, if we take an alloy containing
50 atomic per cents. of zinc, and therefore more zinc than the eutectic,
melt it completely, and allow it to cool, we shall, at 308°, find a f. p.
at which zinc, or, at all events, something containing more zinc than
the liquid, begins to separate as a solid. This process will go on as
the alloy cools, until, by the continual separation of solid matter,
the still liquid portion has reached the composition of the eutectic
alloy. The temperature will now be $264\cdot5°$, and will remain constant
until every particle of the alloy has solidified, for the liquid is now
saturated both with zinc and cadmium, and these metals will freeze
out in the same proportions as those in which they are present in the
liquid. If we start from an alloy on the cadmium side, a similar pro-
cess will take place. Our figure shows the horizontal line of eutectic
freezing points obtained in this manner.

The indications of chemical combination between the zinc and the
cadmium are slight, if, indeed, such indications exist. But at Cd_1Zn_1
there is a perceptible shoulder to the curve, that might be regarded as
a much degraded intermediate summit. This may be interpreted as
indicating the existence of a compound CdZn, which, when melted, is

* Dahms, *Ann. Phys. Chem.*, 1894, **54**, 486.

very largely dissociated into its constituent metals. However, when we come to the consideration of the zinc-tin and zinc-bismuth curves we shall see that another explanation of this feature is possible.

If the compound CdZn exists, then when alloys with more than 50 and less than 74 atomic per cents. of cadmium begin to solidify, we should expect this compound to separate as a solid. If it were possible to collect the first precipitate free from mother liquid, we might settle the question, but the practical impossibility of doing this has caused us to abandon such methods of attacking the problem. A proof, to our minds almost conclusive, against the view that a solid compound of the formula CdZn exists, lies in the fact that the temperature, after freezing had commenced at 50 atomic per cents. of cadmium, was not particularly steady, so that the alloy cannot have solidified homogeneously. In fact, at 50·7 atomic per cents. of cadmium, the eutectic temperature of 264·5° was well marked. This could not have been the case if a compound CdZn had been forming, for, in that case, there would have been little or no liquid left at the eutectic temperature.

Zinc-Aluminium.

Figure 2 (p. 404) gives a complete freezing point curve for these two metals. It is plotted on the same scale as figures 1, 3, 4 and 5, but to economise space the f. p. of zinc and therefore the whole curve is shifted to a lower point on the page. The curve is essentially similar to that of zinc-cadmium. The eutectic alloy has a melting point of 380·5° and contains 11 atomic per cents. of aluminium.

We do not think that the curve shows an indication of chemical combinations in any proportion. The very slight tendency to an inflexion near 40 atomic per cents. of zinc is very probably due to the fact that near here the two series of experiments starting from opposite ends of the curve meet. The losses of metal from oxidation might be expected to produce a fictitious raising of the curve which starts from the zinc end and to lower that starting from the aluminium end, in the exact way shown on the curve.

Alder Wright * says that some alloys of these two metals separate into two liquid layers on standing for some time, but the form of our curve makes us doubt the accuracy of this statement. If it were so, the curve would resemble the zinc-bismuth curve in form.

The zinc-cadmium and zinc-aluminium alloys were amongst the earliest that we examined by means of platinum resistance pyrometers, and the experimental error is perhaps larger than in the case of the other experiments described in the present paper.

* *Proc. Roy. Soc.*, **45.**

Zinc-Bismuth.

The zinc-bismuth curve, Figures 3 and 6 (p. 404), affords a typical example of the process of solidification for an alloy of two metals which are only partially miscible with each other. The curve shows that when bismuth is added to zinc the f. p. of the zinc is at first lowered by an amount which is nearly proportional to the weight of bismuth present, until 0·65 atomic per cents. bismuth have been added. A further addition of bismuth produces absolutely no effect on the f. p. until as much as 63·2 atomic per cents., that is, 84·5 per cent. by weight, have been added. A still further addition of bismuth produces a fall in the f. p. almost as rapid as that caused at first, and at the same time the freezing points, from being extremely steady stationary temperatures lasting for a long time without change, become very fugitive. After 80 atomic per cents. of bismuth, we could no longer detect these freezing points, but the eutectic f. p., again a very steady temperature, began to show itself. We have drawn, as a dotted line, a hypothetical continuation of the f. p. curve to the point where it meets the other branch. We are aided in determining the exact point of intersection by the fact that it must lie on the horizontal line of eutectic freezing points which are so easily determined. The curve shows that the intersection is close to 92 atomic per cents. of bismuth.

Alder Wright * found that when alloys of zinc and bismuth were allowed to remain for a considerable time at a constant temperature of 650°, they separated into two layers containing respectively 2·3 and 85·3 per cent. of bismuth by weight.

We have now to account for the long upper flat on the curve, reaching from 0·65 to 63 atomic per cents. of bismuth. This flat records the fact that between these limits the freezing point is quite independent of the composition of the alloy. But there is another peculiarity of this region. It is that each freezing point is a well-marked steady temperature remaining quite unchanged until a large amount of solid has been formed. In some cases, however, we watched the thermometer until the temperature of the mass began to fall again, and this took place before the alloy set to a solid mass. In this latter feature only does the process of solidification differ from that of a pure metal.

We have already, in a paper about to appear in the *Transactions of the Royal Society,* discussed a similar phenomenon.† We shall, therefore, here treat the point very briefly. The existence of the flat, and also the extremely steady temperature of each freezing point on it, are

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* *Proc. Roy. Soc.,* **50**, 388.

† See also Neville, *Science Progress,* iv., p. 4.

due to the alloy in this region consisting of a pair of conjugate liquids —zinc saturated with bismuth and bismuth saturated with zinc. The composition of these conjugates is given by the atomic percentages at the ends of the flat. Each of these liquids remains unchanged in composition throughout the flat, but as the total percentage of bismuth increases, the alloy richest in bismuth grows at the expense of its conjugate. Moreover, both conjugates have the same freezing point and therefore, as the freezing proceeds, the residual liquid will still consist of the same two alloys. It will consequently not fall in temperature until one conjugate has wholly disappeared. When the conjugate richest in zinc has gone, either through the separation of solid zinc or the addition to the mixture of bismuth, we have a state of affairs represented by the second sloping line. Here, most probably, solid zinc is separating out of a solution of zinc in bismuth, and from the slope of the line it would appear that the latent heat of solution of zinc in such a mixture is almost the same as the latent heat of fusion of pure zinc. One of us has already drawn attention to the fact,* not then verified, that if such a pair of conjugate alloys be raised to a sufficiently high temperature it must become a uniform liquid. In fact, starting from the two ends of our upper flat, a dome-shaped curve could be drawn giving the critical temperature of complete miscibility of every alloy of zinc and bismuth. Whether there would be a well-marked thermal change at the moment when a homogeneous alloy began, through cooling, to separate into conjugates is doubtful : we have not hitherto been able to detect the phenomenon by means of our thermometers. Alder Wright's values for the composition of the two conjugates at 650° give two points on the critical curve, and Spring and Romanoff † have lately found that for zinc-bismuth the summit of the critical curve is near 850°, whilst for the similar case of zinc-lead it is near 950°.

Our curve seems to show that the change from the homogeneous liquid to the pair of conjugates and *vice versa* is a very sharp one at the freezing point ; hence the two sloping parts of the curve meet the flat in angular points. This is not the case for all alloys which separate into conjugates.

It ought to be possible to continue the flat to the left beyond the angle at 0·65 atomic per cents. of bismuth, second or eutectic freezing points being found for alloys with less than this proportion of bismuth corresponding with the moment when the still liquid portion of each alloy has, by the separation of solid zinc, reached the state of being saturated with bismuth. Unfortunately, we omitted to look for such points during our experiments.

* *Science Progress (loc. cit.).*
† *Zeit. anorg. Chem.*, 1896, **13**, 29.

Zinc-Tin.

In Figure 4 (p. 404), we give the f. p. curve of these two metals plotted on the same scale as the zinc-bismuth, and lying nearly between the same limits of temperature. There is here no angle except that which always occurs where the two branches of the curve meet at the lower eutectic point. The changes in curvature are all gradual, as we should expect in the case of two such metals as zinc and tin, whose alloys do not, under any circumstances, separate into conjugate liquids. In fact, the zinc-tin resembles the zinc-cadmium curve, but the first ten atomic per cents. of tin produce a more rapid curvature than is the case with cadmium ; and a shoulder at 50 atoms, which is barely perceptible in the cadmium curve, is well marked in that of tin. The shoulder is somewhat exaggerated in the figure, owing to the fact that the two series of experiments which start from opposite ends of the curve, approach each other here, and through thermometric errors, or loss of metal by oxidation, do not quite meet. We cannot however see, in any feature of the curve, an indication of the existence of chemical compounds such as the $SnZn_4$ that Alder Wright believed to exist.

Considered from the point of view of the physical theory of solution, it would appear that, as the solution becomes more concentrated, the atoms of tin tend to form larger aggregates to a greater extent than do those of cadmium. In fact, zinc-tin approximates more to the condition of zinc-bismuth than does the cadmium alloy. We are perhaps too much in the habit of regarding as a perfect solution any liquid mixture which does not separate into conjugates. On the contrary, there is probably an infinite series of gradations between that perfect state of solution in which the dissolved body, whatever may be its relation to the solvent, is divided into single atoms or molecules, and that in which it is on the point of separating in drops from the solvent liquid. We may expect to see these degrees of dissolution reproduced in the freezing point curves as well as in other physical properties.

In connection with this subject, it is not without interest to compare the preceding curves with Figure 5, which is the ideal f. p. curve for zinc containing another metal in solution. This curve is calculated from Le Chatelier's equation,

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

where x is the concentration of zinc (the atomic percentage divided by 100), λ is the latent heat of fusion of an atomic weight of zinc, and θ_0 and θ are the freezing points, reckoned from absolute zero, of pure zinc and of the alloy respectively. The equation assumes that the molecular

condition of both metals remains the same throughout as it was in the dilute solution, and that the heat of solution of the zinc in the alloy at the lower temperature remains the same as the heat of fusion of the pure zinc at 419°. The rapid divergence of the real curves from Figure 5 shows how far these assumptions are from being true.

Thallium, Lead, Antimony, Magnesium, and Nickel in Zinc.

We have (No. 2) carried our experiments on the addition of thallium or lead to zinc very far, for Figures 8 and 9 and Tables VII and V show that these two curves, if completed, would closely resemble that of zinc-bismuth. In all three cases, the addition of the second metal soon causes the alloy to separate into two conjugates, and we have the phenomena of the long upper flat repeated. So far as our experiments enable us to decide, we see from Figure 9 that zinc is saturated with thallium at the freezing point, when 0·45 atomic per cents. of the latter metal are present, and that the f. p. of the zinc is thereby lowered by 2·3°.

Similarly, Figure 8 shows that the zinc-lead alloy, at its freezing point, is saturated with lead when 0·26 atomic per cents. of lead are present, the temperature on the flat being 1·6° below the f. p. of pure zinc.

The zinc-antimony curve of Figure 7, although similar in appearance to the two preceding, records a different phenomenon. Here, the angle at 412·6° and 1·25 atomic per cents. of antimony gives the lower eutectic f. p. and the composition of the eutectic alloy, and, as in the case of zinc-aluminium, there must be another branch starting from the eutectic angle and running up towards the f. p. of pure antimony. This curve would probably be worth completing.

In drawing the antimony curve, but little weight is given to the second reading at 0·365 atomic per cents., as the atomic fall deduced from it is obviously inconsistent with the others. Similarly, the second and third readings at 0·799 atomic per cents., taken after a night's interval, and after re-melting and heating the alloy to a red heat, have not so much value attached to them as the first.

Zinc-Magnesium.

This curve was not traced to saturation ; in fact, the part examined is nearly a straight line. A peculiarity of this curve lies in its steepness. From the beginning to the last experiment, the atomic falls caused by magnesium are greater than those due to any other metal. This is more remarkable, as the magnesium might be expected to oxidise more readily than the other metals, and losses from this cause would make the observed depressions too small.

Zinc-Nickel.

A very small addition of nickel to zinc lowers the f. p., but the limit is soon reached, and further additions of nickel produce no effect. The depression was too small to admit of trustworthy measurement.

Dilute Solutions and the Heat of Fusion of Zinc.

In Figures 6 to 12 (p. 404), the dilute solutions of the metals, whose alloys with zinc we have discussed above, are given on a larger scale than the complete curves   This plan enables us, as in the case of antimony, to reject unsatisfactory observations and to read off the mean atomic fall.

If we wish to deduce from our results the latent heat of fusion of zinc, we are warned, by the rapid way in which the curves of Figures 1 and 4 rise above Figure 5, that it is useless to consider solutions containing more than one or two atomic per cents. of dissolved metal. But dilute solutions present special difficulties.   We have first the difficulty that the temperature differences measured are small com-pared with the probable error of experiment.   This shows itself in the irregularity of the atomic falls for very dilute solutions ; but when the conditions are favourable, as in the bismuth, the lead and the last of the tin series, we think the temperature differences of the early parts of each series, found probably within an hour of each other, may be trusted to within a very few hundredths of a degree.

A more serious difficulty is the tendency for the observed atomic falls in very dilute solutions to be abnormally large.   This peculiarity is evident in the tin experiments, Table IVA (p. 392).   Series 3 of this table was carried out much later than the others to verify the fact. We have here to deal with a phenomenon that has been one of the main causes of error in modern cryoscopic work, and which was first dis-cussed in a systematic manner by Nernst and Abegg.*   As we do not in our work surround the alloy by a bath of constant temperature, a "convergence temperature" does not, strictly speaking, exist, but since the furnace and the other bodies which are in thermal communication with the alloy are at a lower temperature than it at the moment of reading the f. p., we may regard the quantity $t' - t_o$ in their formula †

$$t' = T_o - \frac{k}{K}(t' - t_o)$$

as necessarily positive. It follows that t', the observed f. p., is lower than T_o, the true f. p. or equilibrium temperature. This applies to pure zinc as well as to the alloys, but Nernst and Abegg found that K for pure water was much greater than for a solution, while k was probably the same for both.   For similar reasons, K for a pure metal would probably

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* *Zeit. physik. Chem.*, 1894, **15**, 681.

† Where t_o is the convergence temperature, and K and k are constants depending on the nature of the substance.

be greater than for an alloy. In other words, our observed depressions must be greater than the true ones. The resulting error appears to affect the atomic falls of dilute solutions most seriously. It is clear, therefore, that we cannot hope to obtain a very accurate value of the latent heat from the experiments we have hitherto made. But it would not be impossible, by modifying our arrangements, to find K and k, and so largely increase the accuracy of the results.

The question now arises how to deduce the most probable value of the atomic fall from the numerous observed values. If we take the arithmetical mean of the atomic falls given in the tables, we attach undue importance to the experiments on very dilute solutions where the experimental error is large. We think it a good plan to divide the arithmetical mean of the depressions, taken from column 3 of the tables, by the arithmetical mean of the atomic percentages taken from column 2. We thus give to each experiment a weight in the result proportional to the temperature interval measured in it. We must confine ourselves to those early experiments for which the f. p. curve is a straight line. Thus, for bismuth, we have, from Table IIIA (p. 390), Series 1 and 2, the following.

Atomic per cents.	Depressions of f. p.
0·139	0·70°
0·262	1·27
0·386	1·86
0·063	0·34
0·187	1·09

This gives a mean depression of $1·052°$ for a mean concentration of 0·2075 atomic per cents., or an atomic fall of 5·07.

Applying this method to each of the other metals, we get the following table.

Metal.	Extreme atomic per-centage.	Mean atomic percentage.	Mean depres-sion.	Mean atomic fall.
Bismuth	0·386	0·2075	1·052°	5·07
Antimony *	0·799	0·4377	2·247	5·13
,, from curve	0·500	0·500	2·60	(5·20)
Lead	0·200	0·150	0·78	5·20
Thallium	0·393	0·2595	1·285	4·95
Tin	1·187	0·655	3·497	5·34
Magnesium	0·975	0·655	3·572	5·45
Cadmium	1·464	0·732	3·377	4·61
Aluminium	0·99	0·99	4·10	(4·14)

* Here we have taken the *mean* reading at 0·365, and also the mean reading at 0·799, otherwise too much weight would have been given to these concentrations.

Atomic Percents.

FREEZING POINT-CURVES OF:

Zn — Cd............Fig. 1
Zn — Al............Fig. 2
Zn — Bi............Fig. 3
Zn — Sn............Fig. 4
Ideal ....Fig. 5

Temperatures.

Atomic Percents.

Atomic Percents.

Fig. 6

Bi — Zn

Fig. 8

Pb — Zn   Fig. 7

Sb — Zn

Fig. 9

Tl — Zn

Mg — Zn

Sn — Zn

Cd — Zn

Fig. 11

Fig. 10

Fig. 12

FREEZING POINTS OF DILUTE
SOLUTIONS.

ZINC AS SOLVENT.

The numbers immediately below
the line of each curve give the F. P.
Centigrade Temperature.

The numbers at the top and bottom
of the page give the composition.

Atomic Percents.

The last column in this table shows a good deal of discrepancy between the mean atomic falls for the various metals, the most divergent being the cases of magnesium, cadmium, and aluminium. The large atomic falls shown by magnesium in zinc have a different character from those of tin. It will be seen from Table VIII (pp. 395–6) that they have been verified by repeated experiment, and that, instead of diminishing, they are either constant or increase with increasing concentration. A possible explanation is that the magnesium is combining with the zinc, but we do not feel satisfied that we have here the true explanation. In our early experiments, in which tin was used as a solvent, cadmium gave a smaller atomic fall than most other metals, so that we may perhaps regard it as a peculiarity of this metal to do so. But, in some experiments in which cadmium was dissolved in zinc which had been contaminated with about 1 per cent. of platinum, we obtained for cadmium the atomic falls 4·8 and 4·9, which are not very far from the average for other metals. The case of aluminium is different, in tin it gives only half the normal depression, and here it deviates so much from the others that we think we are justified in rejecting its value as, from some unknown cause, too low.

In the above table, we have placed a bracket round the atomic falls that we do not propose to use in getting the final mean.

The remaining numbers must be regarded as *a priori* equally probable, and therefore their mean ought to be found by the method of least squares, but their accuracy hardly justifies so refined a method. We have, therefore, taken their arithmetical mean, which is $5\cdot11^{\circ}$. As this is at a mean concentration of half an atom, we may use the equation for dilute solutions

$$\delta\theta = 0\cdot0198\ \theta^2/\lambda$$

to obtain the latent heat. Here, $\delta\theta = 5\cdot11^{\circ}$ the atomic fall, $\theta = 273^{\circ} + 419^{\circ} = 692^{\circ}$ the melting point of zinc on the absolute scale, and λ is the latent heat of fusion of an atomic weight of zinc.

From these data, we find that the latent heat of fusion of a gram of zinc is 28·33 calories. This number agrees very well with Persons' value of 28·13, but it would have been easy, by leaving out cadmium or magnesium, or by using the numbers from rather more concentrated solutions, to obtain a result which differed by several per cents. from the above.

Section II.

Metals which raise the Freezing Point of Zinc.

We have found that silver, gold, copper, and perhaps platinum, in however small a quantity they are added to zinc, at once raise the f. p. and apparently cause the whole mass of metal to solidify above the f. p. of pure zinc.

In the case of gold, copper, and platinum, we have only studied dilute solutions, but all alloys of silver and zinc have been examined. We shall, therefore, begin by discussing the experiments with zinc-silver. The results are given in Table IX, and in Figures 13, 14, and 15 (p. 422).

In the first four series, in which the temperature rarely rose so high as 600°, we determined the composition of each alloy by calculation from the weights of metal which had been placed in the crucible, but this method began to be untrustworthy in series 3 and 4, on account of the oxidation of the zinc. In series 9, also, which, chronologically, was an early series, the composition was deduced from the weights added, and it is a little curious that when once the zinc has been stirred into the molten silver, there is, in dilute solutions of zinc in silver, very little further oxidation. But in the middle part of the curve, the burning away of the zinc was continuous, and it became quite clear that the composition of the alloy must be determined by analysis ; we therefore, at first, after every few readings of the f. p., and finally just before each reading, extracted samples of the alloy for analysis. This was done by means of pipettes made from somewhat thick-walled Jena glass tubes. One end of the tube was thickened and drawn out to an almost capillary opening. The lower part of the pipette was heated to a faint-red heat, and dipped in the alloy at a moment when the latter was 20 or 30 degrees above its f. p. The necessary amount of alloy was then sucked up into the pipette and withdrawn. The glass became very soft at the higher temperatures if left long in the alloy, but by carrying out the operation rapidly this method of extraction was possible even at the melting point of silver. The samples of alloy were in the shape of thin rods of a very convenient form for examination.

A portion of each sample was weighed, dissolved in nitric acid, and its content of silver estimated by ammonium thiocyanate solution which had been carefully standardised on the same silver as that used in the experiments. The graduated instruments employed had been tested

by the Berlin physikalishe Anstalt, and the control analyses agreed, as a rule, to within very nearly 1 in 1000. The percentage of zinc was obtained by subtracting that of silver from 100. It is obvious that this method ceases to be satisfactory when the percentage of zinc is a small one; hence the first result of Series 11 (p. 412) is not more trustworthy than that of Series 9 (p. 410).

TABLE IXA.

SILVER ADDED TO ZINC.

Series 1.   300 *grams of Zinc.*

Percentage of silver present.	Atomic percentage of silver.	Freezing point centigrade.
0	0	418·8
0·164	0·1	419·23
0·328	0·2	419·64
1·14	0·7	421·9*
1·94	1·19	424·35
3·50	2·15	429·70

The silver used in this series was prepared by Stas' method.

* At this stage, the alloy was heated more than 100° above the freezing point of zinc, in order to bring the silver into solution. At the recorded temperature, a precipitate began to form, and at the end of 5 minutes, the temperature having fallen less than a degree, almost the whole mass had become solid from the bottom upwards.

In plotting this series, we have added 0·8° to all the freezing points to make the freezing point of zinc the same as in Series 2 and 3.

Series 2.   200 *grams of Zinc.*

0	0	419·7
4·78	2·96	430·4
9·15	5·76	497·6*
,,	,,	429·8

* A well-marked, unmistakable point.

F F 2

Series 3.　150 *grams of Zinc.*

Percentage of silver present.	Atomic percentage of silver.	Freezing point centigrade.
0	0	419·6
4·11	2·53	441·0*
		430·4†
7·08 ,,	4·42 ,,	478·7
		430·4‡
8·50 ,,	5·33 ,,	495·2 §
		430·0
13·76 ,,	8·83 ,,	538·3 ‖
,,	,,	429·1 ¶

* Here the rate of cooling became twice as slow.

† Here the rate of cooling became three times as slow, and a precipitate began to form. After a fall of two or three degrees below this point, the alloy was a solid mass. The period of constant temperature at the freezing point is not so prolonged as in the case of *eutectic points.*

‡ The alloy becomes a thick paste before this point is reached, but at this point the rate of cooling becomes three or four times as slow as immediately before, to quicken again after the freezing point of zinc is reached.

§ The mass soon gets pasty after this point.

‖ Here the rate of cooling became for a few degrees twice as slow as before, but it gradually became quicker, and attained its previous rate before the lower point was reached.

¶ Here the halt in the cooling, though well marked, was more fugitive than with solutions containing less silver.

Towards the end of this series, we began to notice some oxidation of the zinc.

Series 4.　120 *grams of Zinc.*

19·82	13·04	571·3*
24·84	16·71	593·9

* This is a well-marked point, the rate of cooling becoming nearly three times as slow as before the point. After the freezing point, stirring soon becomes impossible.

All the silver seems to dissolve below 600°, and at this temperature carbon appears to reduce the zinc oxide.

Series 5.　*Silver added to Zinc.*

This series was commenced by melting together 120 grams of zinc and 40 grams of silver. After taking the freezing point, more silver was added, the total weight of silver present being recorded in column 1.

At the end of the series, the percentage of silver in the alloy was

found by analysis to be 37·65 per cent. This corresponds to 26·83 atomic per cents.

If we assume, what is very nearly true, that no silver was lost during the experiments, we can, from the result of the final analysis, calculate the weight of zinc left in the alloy, it is 115·9 grams. Thus 4·1 grams of zinc have been lost by oxidation during the experiments. This loss distributed equally over the four experiments gives us column 2, the probable weight of zinc present at the moment of reading each freezing point.

1	2	3	4	5
Weight of silver present.	Probable weight of zinc present.	Percentage of silver.	Atomic percentage of silver.	Freezing point centigrade.
40	118·97	25·16	16·95	592·3*
50	117·95	29·77	20·47	608·2*
60	116·92	33·92	23·75	619·5*
70	115·90	37·65	26·83	626·8†

* All well-marked freezing points.

† Here the alloy sets to a solid mass at a temperature but little below the freezing point.

Series 6. Silver added to Zinc.

One hundred and fifty grams of zinc and 42·02 grams of silver were melted together, and additional quantities of silver added before each reading of the freezing point.

The composition of the alloy was determined by extracting a sample immediately before each freezing and determining the percentage of silver.

1	2	3
Percentage of silver present.	Atomic percentage of silver.	Freezing point centigrade.
22·16	14·73	580·9
28·88	19·77	606·0
34·19	23·97	620·4
37·27	26·50	626·4
39·76	28·59	630·0
41·80	30·36	636·1
46·73	34·74	654·4*

* Less than a degree below the freezing point, stirring becomes impossible on account of the abundance of precipitate, but in this and the three preceding experiments the alloy is very fluid *at the freezing point.* All the points in this series were well-marked, steady temperatures.

Series 7.

140·1 grams of zinc and 112·0 grams of silver melted together, additional quantities of zinc added, and the percentage of silver determined by analysis as before.

1	2	3
Percentage of silver present.	Atomic percentage of silver.	Freezing point centigrade.
45·15	33·31	649·5
43·72	32·03	644·5
42·17	30·67	638·1
40·69	29·39	631·2

After the last reading, and without re-melting, we extracted some of the still liquid alloy and found in it 40·39 per cent., that is, 29·13 atomic per cents. of silver.

Series 8.   Silver added to Zinc.

This series was carried out in the same way as Series V., beginning with 100 grams of zinc and 70 grams of silver.

The analysis of the alloy at the termination of the series showed that it contained 64·37 per cents. of silver. Hence, assuming no loss of silver, we find a loss of 14·21 grams of zinc. Distributing this loss equally over the experiments, we are able to obtain column 2 and to complete the table.

1	2	3	4	5
Weight of silver present.	Probable weight of zinc present.	Percentage of silver by weight.	Atomic percentage of silver.	Freezing point centigrade.
70	97·97	41·68	30·25	635·8
80	95·94	45·47	33·60	649·7
90	93·91	48·94	36·77	658·3
100	91·88	52·12	39·78	666·4
115	89·85	56·14	43·72	679·8
130	87·82	59·68	47·33	688·3
155	85·79	64·38	52·30	697·4

Series 9.   Zinc added to Silver.
200 grams of Silver.

On each occasion when the zinc was dropped into the molten silver a little zinc was seen to volatilise and burn, but after the molten alloy

had been stirred, no further burning of zinc was noticed while the solution was dilute in zinc. We thought that there was a more rapid and irregular loss of zinc during the latter part of the series. From this cause, *or for some other reason*, the freezing points of this series deduced from the weights of metal used do not lie on a smooth curve. This might be due to a real singularity in the curve, but as the first five points of this series agree very well with Series 10, whilst the later points do not, we are disposed to think that after 21·9 atomic per cents. of zinc there is an experimental error in Series 9, probably due to irregular and more rapid burning of zinc. We, therefore, only use in drawing the curve the first five points of Series 9, and the last point which, being based on an analysis, is trustworthy. This analysis might be used to correct the weight of zinc present at the previous readings, as was done in Series 5 and 8, but owing probably to the irregular rate at which the zinc was lost, this method of correction does not improve matters.

In column 1 we give the nominal weights of zinc in the crucible, assuming no loss. These are, of course, all greater than the true weights, and therefore a curve plotted from them must lie *above* the true curve. The true weight of zinc present at the last reading was 120·35, and it is from this number that the last percentage of zinc is calculated.

Total weight of zinc present.	Percentage weight of zinc.	Atomic percentage of zinc.	Freezing point centigrade.
0	0	0	958·9
6·13	2·97	4·81	926·9
11·22	5·31	8·46	900·7
22·88	10·27	15·86	849·1
34·05	14·55	21·90	808·6
50·20?	20·06	29·26	763·9
57·72?	22·40	32·2	750·9*
65·62?	24·70	35·1	734·5
78·52?	28·19	39·3	711·1
92·67?	31·66	43·3	706·8†
107·87?	35·04	47·06	703·0
132·07?	37·57‡	49·79‡	695·7‡

* A soft precipitate was noticed some little time before the freezing point was read, and this point became here a steadier temperature than with less zinc.

† A very steady temperature.

‡ The composition determined by analysis.

Series 10. *Zinc added to Silver.*

This series contains a number of points *determined* by analysis and marked A in the fourth column of the table, and also a number of points for which the percentage composition is *corrected* by the following

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analysis as in Series 5 and 7.   Each sample taken out of the crucible for analysis was weighed, and hence, assuming that there was no accidental loss of silver, we were able to form column 1 of the table, the weight of silver present at each reading of a freezing point.

Column 2 gives the weight of zinc added to or taken from the crucible immediately before each reading.

Column 3 gives the weight of zinc present, deduced from analysis or corrected by analysis.

Column 4 gives the percentage by weight of zinc, and column 5 the atomic percentage.

Column 6 gives the freezing point.

1.	2.	3.	4.	5.	6.
Weight of silver present.	Weight of zinc added before each experiment.	Weight of zinc present corrected by analysis.	Percentage of zinc by weight.	Atomic percentage of zinc.	Freezing point centigrade.
200·0	0	0	0	0	959·2
,,	+ 48·51	47·51	19·20	28·14	764·0
,,	+ 9·45	55·98	21·87A	31·57	742·0
187·5	− 3·46	52·52	,,	,,	745·1
,,	+ 7·57	58·53	23·79	33·97	728·1
,,	+ 8·60	65·57	25·91	36·56	711·6
,,	+ 6·75	70·76	27·40	38·35	707·6
,,	+10·86	80·06	29·92A	41·31	705·1
168	− 8·32	71·74	,,	,,	705·8
,,	+10·94	80·54	32·41	44·14	702·2
,,	+14·72	93·12	35·66	47·74	697·5
,,	+15·72	106·7	38·84A	51·15	691·2
147·47	−13·05	93·65	,,	,,	692·8
,,	+23·65	115·41	43·90	56·33	679·8
,,	+20·15	133·67	47·55A	59·90	667·5
133·55	−12·61	121·06	,,	,,	669·3
,,	+23·65	142·82	51·69A	63·81	657·2
96·10	−40·05	102·77	,,	,,	658·0
,,	+31·10	132·43	57·95A	69·42	636·5

Series 11.   *Zinc added to* 200 *grams of Silver.*

In the Fletcher blast furnace with coal-gas burning over the surface of the metal.

The composition of the alloy was determined immediately before each reading by extracting a few grams with a Jena glass pipette, and estimating the silver with ammonium thiocyanate.

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Percentage of zinc by weight.	Atomic percentage of zinc.	Freezing point centigrade.	Atomic fall.
0	0	957·6	
1·94	3·16	936·8	6·58
4·77	7·63	904·0	7·02
7·39	11·62	872·3	7·34
12·13	18·54	822·0	7·32
14·06	21·24	805·9	7·15
17·23	25·55	778·5	7·01
17·84	26·36	769·2	7·15
19·72	28·82	755·6	
22·57	32·46	733·3 *	
,,	,,	(705·6)†	
		(705·5)	
24·05	34·30	723·2	
,,	,,	(705·5)	
24·89	35·33	717·9	
,,	,,	(705·4)	
		(705·6)	
25·84	36·48	711·3	
,,	,,	(705·8)	
26·86	37·71	705·6	

* This temperature was known to be a little too low at the time of reading.

† This and the other numbers in brackets are eutectic freezing points, below the first freezing point, and correspond to the moment when that part of the alloy which is still liquid has, through the separation of solid silver, reached the composition of 37·5 atomic per cents. of zinc. These freezing points, especially the last two, were very constant temperatures.

The table, as always, gives the observed freezing points, but in drawing the curve we shall add 1·4°C. to each one in order to make the freezing point of silver 959°C., as in Series 9 and 10.

Series 12. Zinc added to Silver.

Conditions similar to Series 11, composition of alloys found by analysis.

Percentage weight of zinc.	Atomic percentage of zinc.	Freezing point.
41·65	54·06	684·8
42·72	55·14	682·3
44·68	57·11	676·6
46·76	59·16	670·6
47·48	59·84	667·9
52·40	64·48	655·4
56·63	68·28	643·0
,,	,,	636·4 (some indications of a stop here).
57·62	69·13	637·9 very steady.
59·21	70·52	630·6 ditto.
60·70	71·80	628·8

The Zinc-silver Curve.

This curve (Figs. 13, 14, 15, p. 422) presents several peculiarities; indeed, it is the most remarkable curve we have as yet examined.

From pure silver to 37·5 atomic per cents. of zinc, the experiments allow us to draw it as very nearly a straight line; there is a perceptible upward concavity after 20 atoms of zinc, but it is very slight. We are not quite certain, however, that a minute cryoscopic examination of this part of the curve might not reveal further details in it. At 37·5 atomic per cents. of zinc, there is an abrupt angle, and the curve becomes for a short time nearly horizontal, the depression produced by the next few atomic per cents. of zinc being very slight; but the slope slowly increases so that the curve, while always tending downwards, is convex. Near 61 atomic per cents. of zinc there is an obtuse angle, and from this point another, but shorter, convex branch proceeds, ending in a somewhat more pronounced obtuse angle at 70·5 atomic per cents. of zinc. From this last angle, the curve, always convex, sweeps downwards with increasing steepness to near 98 atomic per cents. of zinc, where another obtuse angle occurs. From this angle down to the melting point of zinc, we have drawn it as a straight line, though there are perhaps hardly enough experimental points to justify us in doing so. Figure 14 shows an independent series of experiments, carried out in order to confirm the two middle angles. The points of this series are not plotted on the main curve, but are shifted 25° lower down, so as to distinguish them from the others. It will be seen that Fig. 14 completely confirms the accuracy of the main figure, putting the position of the angle at 70·5 atoms beyond question. Unfortunately, no experiments were made between 60 and 63 atoms, so that the angle near 61 atoms, though both figures show its existence, is not so accurately located.

The curve above described is that of the first freezing points of each alloy, recording the temperature at which the alloy begins to precipitate solid matter. Our figures also show that second freezing points were detected between 32·5 and 36·5 atomic per cents. of zinc. These second freezing points are identical with the first freezing point of the alloy containing 37·5 atomic per cents. of zinc. Each of these was a very constant temperature lasting for a long time without change, so that a large amount of solid matter must form here without change in the composition of the residual liquid. Probably more of these points still further to the left could have been found had they been looked for. These second freezing points occurring long after the first f. p., indicate the moment when, through the separation of matter richer in silver than the liquid, the still liquid part of each alloy attains the composition of 37·5 atomic per cents. of zinc. We looked for such second freezing points to the left of the angles at 61 and

70·5 atomic per cents. of zinc, but, with one doubtful exception, we failed to find any.

From 90 to 98 atomic per cents. of zinc, a well-marked horizontal row of second freezing points is seen. A good deal of solid matter separates before the temperature falls to the level of these second freezing points, but they are well-marked, very stationary temperatures, becoming steadier and steadier with each addition of zinc. They are hardly so steady as a eutectic point, but a degree or two below them the alloy sets to a solid mass.

The first f. p. differs a good deal in character at different parts of the curve. That of pure silver is a very constant temperature, but when a few per cents. of zinc have been added, it is much more fugitive. At about 32 atomic per cents. of zinc, we noticed that the period of constant temperature at the f. p. became longer. On the almost horizontal portions of the curve which occur immediately to the right of each of the first three angles, there is a prolonged halt in the cooling at the f. p. For example, at 65·3 atoms of zinc the alloy appeared to solidify at a constant temperature, and at 73·2 atoms it was noticed that the alloy set to a hard mass at or very near the f. p. At 70·5 atoms of zinc, the f. p. was very steady, and at 40 atoms the period of constant temperature at the f. p. was prolonged. It is clear that, wherever we see the curve to be nearly horizontal, we can predict that the freezing point will be marked by a very steady temperature, for much solid matter must form before the composition of the liquid can alter sufficiently to change the f. p. perceptibly. The converse is not, however, true, for between 98 and 100 atoms of zinc the freezing point curve is a line sloping rapidly downwards, whilst each freezing point is an absolutely constant temperature at which the whole alloy solidifies. We noticed a peculiarity similar to this in the freezing points of cadmium containing a little silver. From 80 to 98 atoms of zinc, the upper freezing point is very fugitive, and it is clear that very little solid matter is formed at the f. p.

Description of the Silver-zinc Alloys.

The samples of alloy extracted for analysis were broken by repeated bending, or, when necessary, by hammering. We thus obtained a rough estimate of the degree of toughness or brittleness of the specimen, and were able to examine the fractured surface with a lens. There was also sometimes a free surface where the alloy had solidified in contact with the air. It is known that the information that can be gained from such an examination is very complicated and much affected by the rates at which the metal has cooled, but a few features struck us as worth recording.

From pure silver to 34·3 atomic per cents. of zinc, the alloy is fairly

malleable, requiring to be bent to and fro a good many times before it breaks, but at 35·3 atoms it is much more brittle, still more so at 36·5, still brittle at 37·7, but at 41·3 it has become tough. At 51·15 it is highly brittle, scarcely bending at all, in fact, becoming still more brittle up to 60 atomic per cents. of zinc, when it crushes like glass. It is still brittle at 64·48, but at 69·5 it is quite tough, and this toughness, while diminishing somewhat, is present up to 72 atoms of zinc.

In other words, with the curve before us we may say that the alloy is malleable or tough up to near the first angle, but that a few per cents. before and up to the angle it becomes brittle. Its character immediately after the angle, we do not know, but at 41·3 it is malleable and tough, thence it gradually becomes more brittle, until a maximum of brittleness is reached at 60, just before the second angle. The brittleness persists, though not so markedly, until near the third angle, but close before this, at 69·5, it is not at all brittle and, as far as we have examined, there is some toughness.

The fractured surfaces were finely grained at first, but at 18·5 atoms of zinc there was a trace of conchoidal fracture. From 25·5 atoms almost up to the angle, most of the alloys showed on the fractured surface, and on any free surface, dendritic crystals, the minor leaflets standing out like the teeth of a comb at right angles to a central rib. At 31·6 atoms of zinc, the whole fracture consisted of such crystals in very high relief. Beyond the first angle, we found no trace of these crystals.

Close to the first angle, at 37·7, the fracture showed an irregular pitted surface, at 41·3 the grain is much finer. At 51·15, the alloy breaks as if the larger units of structure were polyhedra with plane faces a millimetre or more in size. Each of these faces is minutely pitted. Another portion of this alloy, when broken with a hammer, showed red crystals in a cavity.* This alloy does not give one the impression of being homogeneous. At 54 atoms of zinc, the fracture is rocklike, or perhaps more like that of galena. From 59 to 63 atoms, all the alloys we examined had a conchoidal fracture with a brilliant glassy surface, no texture or crystals were visible, and the alloy seemed to be perfectly homogeneous. This is the region of the alloys that are as brittle as glass. At 64·5 atoms of zinc, the conchoidal fracture has quite disappeared, and the fractured surface consists of a confused mass of minute, short, crystal faces. From here up to 69 atoms, the fracture gets coarser and is like cast iron, but just beyond the angle, at 70·5, the conchoidal fracture shows itself again, not, however, so strikingly as at

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* Alloys whose composition is near that indicated by the formula AgZn, although under ordinary circumstances of a silver white colour, become externally bright red when heated to 300° and suddenly cooled. We have discussed this phenomenon in a paper read before the Cambridge Philosophical Society in November, 1896.

the previous angle. We have not examined in this manner the alloys with higher percentages of zinc.

Discussion of the results.

While certain features in this remarkable curve need further experiment before they can be satisfactorily explained, we can arrive at some conclusions from the facts already ascertained. There can be no doubt that the angles at 61 and 70·5 atomic per cents. of zinc indicate the existence of at least two chemical compounds of zinc and silver. But the formulæ of these compounds appear to us very uncertain. The angles show that they are not wholly dissociated into their constituent metals at the melting point of the alloy, but that they are, to a large extent, so decomposed is rendered probable by the absence of eutectic minimum freezing points at the two angles, and by the continual downward trend of the curve, which nowhere shows a maximum freezing point. If the compounds were quite stable at the temperatures at which the alloy melts, a maximum freezing point, or intermediate summit, would occur in each convex branch of the curve, and the composition of the alloy at this summit would tell us the formula of the compound. But the partial dissociation of the alloy degrades the summit, so that it becomes difficult to locate it, although it will probably not shift its position to right or left.* We must, therefore, abandon the hope of reading with certainty from the curve the formulæ of the chemical compounds that the metals can form ; although it is obvious that such formulæ as Ag_3Zn_2, $AgZn$, Ag_2Zn_3, $AgZn_2$, Ag_2Zn_5, $AgZn_3$, are fairly consistent with what we as yet know. In previous papers, we have more than once expressed the opinion that most chemical compounds which metals form with each other dissociate to a very large extent on melting, and the more cases we study the more convinced we are that this is the case.†

The microscopical study of the alloys and the determination of the points on the curve at which the alloy solidifies homogeneously may help us to fix the formulæ of the compounds. The first of these two investigations, we have not yet had time to attack, but should it appear that others are not engaged on it, we hope to attempt it. The somewhat cursory examination of the alloys already made shows that near and on both sides of the angle at 61 atoms of zinc the alloy is strikingly homogeneous, and that this is also the case immediately to the right of the angle at 70·5 atoms. The conchoidal fracture is similar at these two points and absent elsewhere. In fact, without having seen the curve one could, from the physical properties of the alloys, pick out

* See Heycock and Neville, "The Freezing Points of Triple Alloys," Trans., 1894, **65**, p. 70.

† See also Foerster, *Naturwissenschaftliche Rundschau,* 1894.

these two points as similar and specially remarkable. The period of constant temperature at the freezing point is also very prolonged here. But all these features can be explained in at least two ways,—either the angles are eutectic points, in which case the alloy solidifying, though not a chemical compound, is necessarily very homogeneous, or else, in opposition to the simpler theory of the freezing point curve, they correspond to chemical compounds. Assuming dissociation, the occurrence of an angle at the formula of a compound that really exists in the solid state does not contradict the theory.

The fact that an alloy appears to solidify at a constant temperature may be due to one of several causes.

1. The liquid alloy may consist of two conjugate liquids, as in the case of zinc-bismuth. We are not at all sure that the first angle at 37·5, together with the flat to the right of it, may not be due to this cause.

2. The alloy may be an ordinary eutectic alloy, or, to speak more generally, the solid forming may consist of two conjugate solids. These two cases may be brought under one heading, but with this difference, that in case (1) the eutectic alloy occurs above the melting point of the more fusible metal, while in case (2) it occurs at or below this melting point.

3. The solid forming may be a definite compound of the same composition as the liquid from which it is separating. This may be the explanation of the steady temperatures at 61 and 70·5 atoms of zinc. We should expect this to happen at a summit corresponding to a stable compound, but we have not yet found such a case ; gold-aluminium and some other aluminium alloys would very probably afford instances of this.

4. The two substances present in the liquid alloy may be solidifying isomorphously in the same proportion as that in which they are present in the liquid. It has occurred to us that the short line, from 100 to 98 atomic per cents. of zinc, which, if produced, passes nearly through the f. p. of pure silver, may indicate that, in this region, the zinc and silver are separating isomorphously. But this point, like the similar cases of zinc-gold and zinc-copper, is one that needs further investigation. It may be that the isomorphism is not between zinc and silver, but between zinc and a compound of silver and zinc. In the very similar case of dilute solutions of silver in cadmium, we found that the solid separating at first contained more silver than the mother liquid. This rather points to the probability that the substance separating between 100 and 98 atoms of zinc is a solid solution, in which case, as Van't Hoff has pointed out, the straight line of freezing points would prove that Henry's law holds good between the concentrations in the solid and the liquid phases.

TABLE X.

Gold added to Zinc.

In a Fletcher draught furnace, in a cylindrical clay crucible imbedded in a larger Salamander crucible, the space between being filled with broken fragments of crucible. Coal gas burning over the surface of the metal. Hand-stir with clay ring stirrer.

250 grams of Zinc.

Percentage weight of gold.	Atomic percentage of gold.	Freezing point centigrade.
0	0	418·79
0·296	0·098	419·29
0·903	0·302	419·93
4·02	1·374	423·50*
5·94	2·054	425·81
9·40	3·33	430·00†
13·06	4·754	431·75‡
,,	,,	432·27
,,	,,	431·65
16·16	6·015	461·34
,,	,,	431·42§
,,	,,	462·26‖
,,	,,	431·71¶

* No precipitate was noticed at the moment when the f. p. was read, and the liquid seemed very fluid, but after this, at *the same temperature*, the alloy becomes solid.

† No precipitate was noticed for some time after reading the f. p., but finally a precipitate formed while the stirring was still easy. The f. p. is still well-marked here, but not so constant as with less gold.

‡ Also marked decrease in rate of cooling at 444·13°, another time at 444·71°.

§ Marked decrease in rate of cooling accompanied by formation of precipitate at 461·8°

No precipitate could be detected at the point here recorded, but soon after it formed freely and the whole mass became pasty, so that stirring was impossible.

¶ A very steady temperature.

The gold was dropped into the liquid zinc in these experiments. No incandescence was noticed when the gold was dropped in.

As in the similar cases with silver and copper, there is, at the freezing point below the first flat, not merely a temporary halt in the cooling, but the whole mass appears to solidify at or near the recorded temperature.

TABLE XI.

Copper added to Zinc.

Series 1.

The conditions were the same as in the gold-zinc experiments, Table X. The first quantity of copper was added as an alloy, but afterwards the copper was dropped into the molten zinc.

Percentage weight of copper.	Atomic percentage of copper.	Freezing point centigrade.
	0	418·82
0·134	0·139	419·17*
0·364	0·377	419·77
1·042	1·08	421·70
3·11	3·22	423·81†
6·76	6·98	423·96‡

* This f. p. is a stationary temperature for several minutes.

† A considerable amount of precipitate forms even above the f. p.

‡ With this concentration, we thought there was a decrease in the rate of cooling at 561·6°, and much precipitate had formed in the crucible at 541·8°.

Series 2.

Furnace A.

The alloys were made by melting together, in a sealed vacuous tube of Jena glass, weighed quantities of copper with a considerable excess of zinc. When the alloy thus formed had been well melted and shaken, it was allowed to cool, the tube opened, and the alloy added to the remainder of the zinc in the crucible.

0	0	418·93
0·402	0·416	419·77
1·838	1·900	422·79
2·590	2·678	423·60*
,,	,,	435·36
4·033	4·167	423·5
		423·6†

* Very steady temperature.

† Although this is a well-marked f. p., the alloy was pasty before the temperature fell to this point. No higher point could be detected.

Series 3.

250 grams of Zinc.

Dropped the copper into the zinc.

0	0	418·93
5·66	5·846	423·58*
,,	,,	423·55
10·715	11·05	524·88
		422·4 †
15·257	15·70	595·8 ‡
		667·2 §

* At this point there was so much heavy precipitate already formed that stirring was impossible.

† Lower point not so well marked.

A well marked f. p., trustworthy.

§ The point on the lower flat can no longer be detected.

Zinc-Gold and Zinc-Copper.

These curves have only been traced by us for comparatively dilute solutions of these metals in zinc. The completion of the gold-zinc was deferred to a future occasion, on account of the expense of handling the considerable quantities of gold needed, that of copper partly because, when we had carried our experiments to the point given in this paper, we became aware that M. Charpy had completed the copper-zinc curve. We were also influenced by the fact that the numerous analyses that would have been necessary would have required much greater labour than was the case with the alloys containing silver.

It will be seen that these curves closely reproduce the phenomena of the corresponding part of the silver curve. The first angle and flat occur at a different temperature in each case, but in all three we have, starting from pure zinc, a line of steady freezing points, which for gold was very straight. In this region, we have the same phenomenon of almost complete solidification without further fall in temperature when the f. p. has been reached. Just before 2 atoms of copper or 4 atoms of gold, we have a very similar angle, and then the very fugitive upper freezing point, followed by copious precipitation, and, at a constant lower temperature, the steady lower freezing point. In the case of copper, we found that as we progressed to the left, by adding copper, this lower freezing point on the flat became less marked and finally before 16 atomic per cents. was lost. This is a reason for believing that the matter precipitating between the two freezing points was not pure copper, although it clearly contained more copper than the liquid in which it was forming. It is evident that, whenever the explanation of the silver-zinc curve is found, that of the other two will follow.

Zinc-Platinum.

We do not give a table for this pair of metals, but we have made a few experiments on adding platinum to molten zinc. In some cases, the alloys were made in sealed glass tubes, in other cases the platinum was dropped into the molten zinc. Nearly four per cent. of platinum by weight was added in portions to the zinc. It appears to dissolve readily, but it does not appreciably alter the freezing point of the zinc. Each f. p. was a very constant temperature, stirring becoming impossible before the pyrometer indicated any fall. It has occurred to us that the flat of the previous cases may here be at the f. p. of zinc, and that the upper freezing points may have been so high or so fugitive, that we failed to detect them. We hope to examine this point again.

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FREEZING POINT CURVES OF SILVER-ZINC ALLOYS.

Fig. 13.   The complete curve.

Fig. 14.   Series XII. drawn 25° Lower, but on the same scale.

Fig. 15.   Dilute solution of Silver-Zinc on a larger scale.