PHILOSOPHICAL TRANSACTIONS

I. *The Freezing Points, Melting Points, and Solid Solubility Limits of the Alloys of Silver and Copper with the Elements of the B Sub-Groups.*

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INTRODUCTION.

It is well known that both copper and silver, when alloyed with many other elements, are able to form primary solid solutions of the substitutional type, in which the solute atoms replace those of the solvent upon its lattice so that the crystal structure of the parent metal is retained. The solubility limits of many of these solid solutions have been determined experimentally, but little progress has previously been made in discovering general principles or a quantitative theory. In the present paper we confine our attention to the alloys of copper and silver with the elements of the B sub-groups, including those of the two first short periods. These elements are as follows :—

Li	Be	B	C	N	O	F
Na	Mg	Al	Si	P	S	Cl
Cu	Zn	Ga	Ge	As	Se	Br
Ag	Cd	In	Sn	Sb	Te	I
Au	Hg	Tl	Pb	Bi.		

On the experimental side we have made complete determinations of the solubility limits in the following binary systems :—copper-gallium, copper-germanium, copper-antimony, silver-aluminium, silver-gallium, silver-cadmium, and silver-indium. Partial or confirmatory investigations have been made in the following binary and ternary systems : copper-zinc, copper-aluminium, copper-arsenic, silver-tin, copper-zinc-gallium, copper-zinc-germanium, and copper-gallium-germanium.

On the theoretical side we give a general discussion of the factors affecting the solubility limits in this type of alloy, and show that certain definite quantitative principles are now apparent. In this connexion it is desirable to summarize the experi-

mental data in such a way that the different systems can be compared at equi-atomic compositions. For this purpose the experimental data of the present work and those of other investigators were plotted accurately on squared paper, and the solubility lines drawn so as to fit the experimental points in the most probable way. From these diagrams the temperatures of the liquidus (freezing point) and solidus (melting point) curves were read off at 1, 2, 3 . . . , 10, 12, 14 . . . , atomic per cent. of the solute element, and the figures obtained are given in Tables I to VIII. Corresponding data for the solubility lines in the different systems are given in Table IX.

These tables summarize the experimental data at present available, and, except where otherwise stated, all are taken from what appear to us to be reasonably accurate work, as distinct from some of the early preliminary investigations.

It must be appreciated, therefore, that where the data from Tables I to IX are used in connexion with the theoretical work, the points plotted in the figures are not the actual experimental determinations, but are the points taken from the smoothed curves. Since most of the lines in equilibrium diagrams are determined by the bracketing method,* the above procedure seemed the only clear way of comparing the different systems.

Tables I to VIII.

In these tables the liquidus and solidus points of copper and silver alloys are given for different atomic percentages of the solute elements. In general the data are given for the whole range in which the α-phase is in equilibrium with the liquid phase, *i.e.*, as far as the nearest whole number point above the peritectic or eutectic horizontal. Where this is not so it implies that data are not available for more concentrated alloys, or that the experimental points are too irregular to enable the curve to be drawn accurately.

Table I.

System.	Silver-beryllium.		Silver-zinc.		Silver-cadmium.	
Atomic % of solute.	Liquidus.	Solidus.	Liquidus.	Solidus.	Liquidus.	Solidus.
0	961	961	961	961	961	961
1	956	923	954	949	957	956
2	950	903	948	938	953	952
3	944	887	941	927	949	947
4	938	—	934	916	945	942
5	931	—	928	906	941	938
6	923	—	921	896	937	934
7	914	—	914	887	933	929
8	905	—	907	878	928	924
9	895	—	900	869	923	919
10	886	—	892	860	919	914
12	—	—	876	844	910	905
14	—	—	862	829	901	896

* By drawing a line between two points, one representing a homogeneous and the other a two-phase alloy.

TABLE I—*continued.*

System.	Silver-beryllium.		Silver-zinc.		Silver-cadmium.	
Atomic % of solute.	Liquidus.	Solidus.	Liquidus.	Solidus.	Liquidus.	Solidus.
16	—	—	848	814	892	886
18	—	—	833	800	882	876
20	—	—	820	787	871	865
22	—	—	806	775	861	853
24	—	—	793	763	851	841
26	—	—	781	752	841	829
28	—	—	769	741	831	816
30	—	—	757	—	820	801
32	—	—	745	—	809	783
34	—	—	—	—	797	765
36	—	—	—	—	786	746
38	—	—	—	—	775	—
40	—	—	—	—	763	—

TABLE II.

System.	Silver-mercury.		Silver-aluminium.	
Atomic % of solute.	Liquidus.	Solidus.	Liquidus.	Solidus.
0	961	961	961	961
1	955	—	954	950
2	950	Values	947	940
3	944	here	940	929
4	939	are	933	919
5	933	uncertain	926	909
6	927	—	918	898
7	921	—	911	888
8	915	—	904	878
9	909	—	897	867
10	903	—	889	856
12	890	—	872	836
14	876	—	856	815
16	862	—	838	794
18	848	681	816	—
20	834	628	793	—
22	819	568	—	—
24	805	500	—	—
26	789	430	—	—
28	773	350	—	—
30	757	—	—	—
32	741	—	—	—
34	724	—	—	—
36	—	—	—	—
38	—	—	—	—
40	—	—	—	—

TABLE III.

System.	Silver-gallium.	Silver-indium.		Silver-tin.		Silver-lead.
Atomic % of solute.	Solidus.	Liquidus.	Solidus.	Liquidus.	Solidus.	Liquidus.
0	961	961	961	961	961	961
1	940	954	951	953	944	950
2	919	947	941	946	927	940
3	899	941	931	938	910	930
4	880	934	920	930	892	920
5	862	928	909	922	873	910
6	844	921	898	913	854	900
7	825	915	887	904	834	890
8	807	909	876	893	813	880
9	790	902	864	882	792	870
10	773	895	852	871	771	859
12	731	878	825	847	728	837
14	695	859	797	821	—	815
16	659	(837)	766	790	—	—
18	—	—	730	754	—	—
20	—	—	690	—	—	—
22	—	—	—	—	—	—
24	—	—	—	—	—	—
26	—	—	—	—	—	—
28	—	—	—	—	—	—
30	—	—	—	—	—	—

TABLE IV.

System.	Silver-copper.	Silver-antimony.	Silver-bismuth.	System.	Silver-Copper.	Silver-antimony.	Silver-bismuth.
Atomic % of solute.	Liquidus.	Liquidus.	Liquidus.	Atomic % of solute.	Liquidus.	Liquidus.	Liquidus.
0	961	961	961	14	884	763	793
1	955	952	951	16	874	—	—
2	949	943	941	18	864	—	—
3	944	933	930	20	856	—	—
4	939	923	920	22	847	—	—
5	933	912	909	24	838	—	—
6	927	901	899	26	830	—	—
7	921	888	888	28	822	—	—
8	915	873	875	30	815	—	—
9	910	858	863	32	807	—	—
10	904	841	850	34	799	—	—
12	894	802	823				

TABLE V.

System.	Copper-silver.	Copper-gold.	Copper-beryllium.	Copper-magnesium.	Copper-zinc.	
Atomic % of solute.	Liquidus.	Liquidus.	Liquidus.	Liquidus.	Liquidus.	Solidus.
0	1084	1084	1084	1084	1084	1084
1	1076	1079	1076	1072	1080	1079
2	1068	1073	1069	1061	1076	1074
3	1060	1067	1061	1049	1072	1069
4	1052	1062	1053	1037	1067	1064
5	1044	1056	1045	1024	1063	1059
6	1037	1051	1038	1011	1059	1054
7	1030	1046	1030	997	1055	1049
8	1024	1041	1021	982	1051	1044
9	1017	1035	1012	966	1046	1040
10	1010	1030	1003	949	1042	1034
12	998	1025	985	913	1034	1024
14	985	1019	966	—	1025	1014
16	973	—	945	—	1016	1003
18	962	—	926	—	1006	992
20	951	—	905	—	997	980
22	941	—	883	—	987	968
24	931	—	—	—	977	956
26	921	—	—	—	967	943
28	—	—	—	—	957	930
30	—	—	—	—	946	916
32	—	—	—	—	935	—
34	—	—	—	—	924	—
36	—	—	—	—	914	—
38	—	—	—	—	—	—
40	—	—	—	—	—	—

TABLE VI.

System.	Copper-cadmium.	Copper-aluminium.		Copper-gallium.	
Atomic % of solute.	Liquidus.	Liquidus.	Solidus.	Liquidus.	Solidus.
0	1084	1084	1084	1084	1084
1	1072	1083	1081	1079	1075
2	1060	1082	1078	1073	1065
3	1048	1080	1075	1068	1055
4	1037	1079	1072	1062	1045
5	1025	1077	1069	1056	1036
6	1014	1075	1066	1050	1026
7	1003	1073	1063	1044	1016
8	992	1071	1060	1037	1006

TABLE VI—*continued.*

System.	Copper-cadmium.	Copper-aluminium.		Copper-gallium.	
Atomic % of solute.	Liquidus.	Liquidus.	Solidus.	Liquidus.	Solidus.
9	980	1069	1057	1030	996
10	967	1066	1054	1023	986
12	942	1059	1048	1007	965
14	917	1051	1041	990	941
16	891	1041	—	973	917
18	—	—	—	954	—
20	—	—	—	934	—
22	—	—	—	—	—
24	—	—	—	—	—
26	—	—	—	—	—
28	—	—	—	—	—
30	—	—	—	—	—
32	—	—	—	—	—
34	—	—	—	—	—
36	—	—	—	—	—
38	—	—	—	—	—
40	—	—	—	—	—

TABLE VII.

System.	Copper-silicon.		Copper-germanium.		Copper-tin.	
Atomic % of solute.	Liquidus.	Solidus.	Liquidus.	Solidus.	Liquidus.	Solidus.
0	1084	1084	1084	1084	1084	1084
1	1077	1068	1076	1065	1073	1000
2	1069	1051	1067	1045	1061	950
3	1061	1035	1058	1025	1049	920
4	1053	1018	1050	1004	1035	890
5	1044	1000	1042	981	1021	862
6	1034	980	1034	960	1005	835
7	1023	959	1025	938	987	810
8	1010	937	1015	916	968	—
9	997	913	1005	895	949	—
10	981	887	992	873	928	—
11	964	858	978	849	905	—
12	943	—	958	821	881	—
13	925	—	—	—	855	—
14	903	—	—	—	831	—
15	880	—	—	—	806	—
16	852	—	—	—	—	—
17	—	—	—	—	—	—
18	—	—	—	—	—	

TABLE VIII.

System.	Copper-Lead.	Copper-antimony.	Copper-bismuth.
Atomic % of solute.	Liquidus.	Liquidus.	Liquidus.
0	1084	1084	1084
1	1072	1072	1073
2	1061	1060	1062
3	1049	1047	1052
4	1038	1031	1043
5	1028	1015	1034
6	1019	998	1025
7	1010	980	1017
8	1001	960	1009
9	994	937	—
10	987	910	—
11	981	880	—
12	975	847	—
13	970	—	—
14	967	—	—
15	963	—	—
16	960	—	—

TABLE IX.

In this table the solubility limits of the α-solid solutions of copper and silver are given in atomic percentages of the solute elements at different temperatures. Where the values at the lower temperatures are given in brackets it implies that the data are not quite certain, and in such systems the general tendency is for the solubility to diminish slightly with falling temperature.

TABLE IX.

° C.	Silver-cadmium.	Silver-aluminium.	Silver-gallium.	Silver-indium.	Silver-tin.	Copper-zinc.
1000	—	—	—	—	—	—
950	—	—	—	—	—	—
900	—	—	—	—	—	31·9
850	—	—	—	—	—	32·9
800	—	—	—	—	—	33·8
750	—	17·9	—	—	—	34·7
700	37·7	18·85	—	—	11·8	35·5
650	38·7	19·75	—	19·9	11·3	36·2
600	39·7	20·5	18·6	19·8	10·8	36·9
550	40·7	20·7	18·4	19·6	10·4	37·5
500	41·5	20·6	18·3	19·5	10·1	38·0
450	42·1	20·5	18·1	19·5	9·9	38·5
400	42·3	20·3	18·0	19·4	9·7	38·5
300	42·1	17·5	17·7	19·4	9·5	(38·5)
200	42·0	—	—	—	—	—

TABLE IX—*continued.*

°C.	Copper-aluminium.	Copper-gallium.	Copper-silicon.	Copper-germanium.	Copper-tin.	Copper-antimony.
1000	16·1	—	—	—	—	—
950	16·6	—	—	—	—	—
900	17·1	16·5	—	—	—	—
850	17·55	17·6	11·15	—	—	—
800	18·0	18·2	13·7	11·8	—	—
750	18·5	18·9	14·0	11·55	7·9	—
700	18·9	19·4	13·7	11·2	8·2	—
650	19·4	20·1	12·9	10·8	8·6	—
600	19·85	20·2	11·9	10·6	8·9	5·6
550	20·3	20·1	10·9	10·5	9·2	5·6
500	20·38	19·9	10·15	10·4	9·26	5·45
450	(20·38)	19·7	9·5	10·35	(9·26)	5·1
400	(20·38)	19·4	8·9	10·3	—	4·3
300	—	19·0	7·5	10·2	—	3·4
200	—	—	—	—	—	2·8

For the solidus lines, and solubility curves determined by annealing and quenching methods, the error of the temperature measurements is estimated as about ± 10° C. In many investigations the determinations agree among themselves to a much higher degree of accuracy, but, as pointed out by SMITH,* errors of thermocouple calibration, temperature fluctuations within furnaces, etc., make it advisable to admit a considerable possible error.

For the liquidus (freezing point) lines, a clear distinction must be made between actual individual observations, and points taken from the smoothed curves. Since the liquidus curves start from the freezing points of the pure solvent metals (copper or silver), and since these are often used as standard points, the absolute error in the liquidus curve naturally diminishes as the freezing point of the solvent is approached. The possible error in the points taken from the smoothed curves is estimated to increase by about 5°† for each 100° depression of the freezing points from those of the pure solvents, although in some the accuracy is greater. On the other hand, examination shows that even in the most careful work yet available, individual observations may differ by 10° from the smoothed curve. Consequently, when results of individual experiments are compared with theoretical values, the possible experimental error is at least double that when points are taken from smoothed curves.

On the side of the compositions of the alloys the position is less satisfactory. In investigations by several workers where the pyrometry has been of the highest order, the compositions have been estimated from the weights of metals melted together, or

* ' J. Inst. Met.,' vol. 40, p. 359 (1928).

† All temperatures are stated in degrees Centigrade.

small percentages of a solute element have been determined by a difference method of analysis. With cooling curve work, additional complications are met, since the slow rates of cooling necessary in order to obtain accurate arrest points may cause segregation of the part of the ingot which is the last to solidify. In the present work, complete analyses have been given wherever possible, and precautions have been taken to avoid errors from segregation effects, volatilization of one constituent on annealing, etc. Since most of the solubility lines are determined by the method of " bracketing," a possible error of about 0·5 atomic % may be expected, although in many diagrams the accuracy is much greater.*

Part I.—General Principles.

According to recent physical theory we must no longer regard a metallic crystal as an array of neutral atoms, but rather as a lattice of positive ions held together by shared electrons, and, from this point of view, the formation of a solid solution may be regarded as controlled by the following factors.

1. *A Distortion of the Lattice.*—As will be appreciated later, when the difference between the atomic diameters of the solvent and solute exceeds a certain critical limit the lattice distortion is so great that the solid solution is very restricted. Where the atomic diameters are more nearly equal, an appreciable solid solution is usually formed, and the slight lattice distortion exerts a small effect upon the otherwise clear valency laws which govern the solubility limits.

2. *A change in the Relative Number of Valency Electrons and Atoms.*—Thus when a divalent zinc atom is substituted for a univalent copper atom, the number of atoms remains unchanged, whilst the number of electrons is increased by one for each atomic substitution. For convenience we shall call such changes " valency effects."

3. *An effect of the Periods (in the Periodic Table) of the Solvent and Solute Atoms.*—Thus copper, zinc, gallium, and germanium are in the same period, and the solubility relations indicate that the substitution of any of these last three elements for copper to form a solid solution is a much simpler process than the substitution of an element from another period. With silver as solvent the same applies to the formation of a solid solution by cadmium, indium, or tin from the same period. This is analogous to the effects upon electrical resistance discovered by Norbury,† who showed that the increase in electrical resistance produced by 1 atomic % of different elements in solid solution in copper, silver, and gold increased with the distance, both vertically and horizontally, between the solvent and solute atoms in the periodic table.

4. *A Tendency towards Atomic Rearrangement at the Simple Whole Number Ratios of Atoms* Cu_3X (or Ag_3X), CuX (or AgX).—There is a general tendency for an otherwise homogeneous solid solution area to be broken up by an atomic rearrangement in alloys

* The experimental data are discussed in Appendix I.

† ' Trans. Faraday Soc.,' vol. 16, p. 570 (1921) ; ' J. Inst. Met.,' vol. 33, p. 92 (1925).

in the region of 25 or 50 atomic % of the solute element. This tendency increases with increasing difference in the atomic radii of solvent and solute atoms. It is important only in the alloys of copper and silver with univalent or divalent elements, since it is only in these that the α-solubility limit exceeds 25 atomic %. These effects are not discussed in the present paper, since they are best studied by resistance or X-ray methods for which apparatus is not available.

In general, therefore, the solubility limit is determined by the above four factors, and it is their interplay which makes the results so complex.

(1) *The Size Factor.*

The exact " atomic diameter " of an element in the B sub-groups is not always easy to define. It has been shown by one of us,* that except for the heavy elements, there is a tendency for the elements of the B sub-groups to crystallize in such a way that each atom is surrounded by (8 — N) neighbours, where N is the group to which the element belongs. This is due to the partly co-valent nature of the forces in these crystals, and except in Group IV B (diamond structure) results in the atoms having two sets of neighbours at different distances in the crystal. In such atoms we consider the atomic diameter to be given by the closest distance of approach. Apart from this, the elements aluminium, indium, thallium, white (but not grey) tin, and lead are incompletely ionized in the solid crystal of the element,† and in these the atomic diameter in the element is about 0·3 A. greater than the effective atomic diameter when the atom is fully ionized. The evidence on this point is discussed in Appendix II. Thus while an element such as tin has an interatomic distance of 3·07 A. in the crystal of the element in which the atom is incompletely ionized (white tin), the atomic diameter is only 2·8 A. in grey tin with the normal tetravalent diamond structure. The " radius " of an atom is also probably affected by the co-ordination number, or number of close neighbours in the structure. To overcome this difficulty GOLDSCHMIDT‡ has put forward a series of atomic radii for co-ordination number 12, which were deduced from solid solutions or intermetallic compounds with this co-ordination number. Unfortunately, these are not always satisfactory (see Appendix II), but to an approximation they are of value.

In fig. 1 the atomic diameters of the various B group elements are plotted against the atomic numbers with the following notation. Where the crystal structure of the element is such that all the close neighbours of an atom are equidistant, the single atomic diameter is represented ●. Where there are two sets of neighbours the smaller interatomic distance is represented ×, whilst GOLDSCHMIDT'S values are denoted ○.

* HUME-ROTHERY, ' Phil. Mag.,' vol. 9, p. 65 (1930).

† HUME-ROTHERY, *ibid.* ; also " The Metallic State " (Oxford, The Clarendon Press, p. 326).

‡ ' Z. phys. Chem.,' vol. 133, p. 397 (1928).

Where the element is incompletely ionized in the solid state, the interatomic distance in the crystal of the element is denoted ⊙, and an arrow is drawn to the estimated atomic diameter of the element in the fully ionized state, and it is this value which is generally important in connexion with the solid solutions in copper and silver.

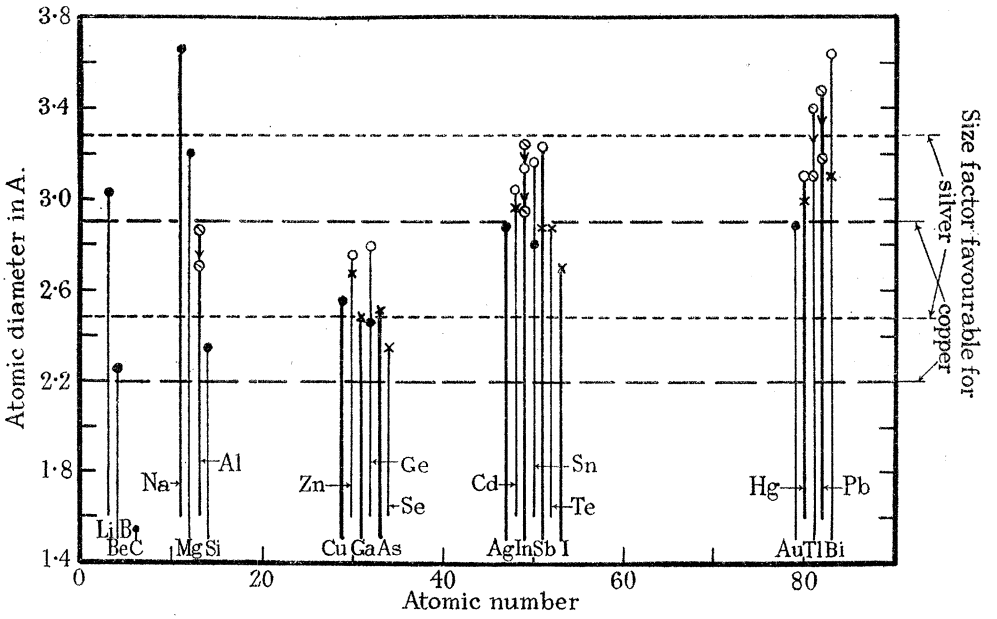

FIG. 1.

It is now our preliminary hypothesis that, *with silver or copper as solvent, where the atomic diameters of the solvent and solute atoms differ by more than about* $13\frac{1}{2}$–14% *of that of the solvent, the size factor is unfavourable, and the primary solid solution is very restricted, whilst when the atomic diameters are within this limit, the size factor is favourable, and considerable solid solutions may be formed, for which in many cases the solubility limits follow the simple valency laws described in the next section.*

Since the atomic diameters of copper and silver are 2·56 A. and 2·88 A. respectively, we have, in fig. 1, drawn two parallel lines at a distance of 0·35 A. from the atomic diameter of copper, and two similar dotted lines at 0·40 A. from the atomic diameter of silver, the values 0·35 A. and 0·40 A. being about 13·8% of the atomic diameters of these two elements

Examination of this figure at once shows that the zones of favourable size factor overlap, and in this way many apparent anomalies are accounted for. Thus with divalent elements, zinc is in the favourable zone for both silver and copper, but magnesium, cadmium, and mercury are outside the favourable zone for copper, but within that for silver, whilst beryllium is just within the favourable zone for copper but outside that for silver. Here we find wide solid solutions in the systems copper-zinc, copper-beryllium, silver-zinc, silver-cadmium, and silver-mercury, but not in the systems copper-cadmium or copper-mercury. Similar principles hold elsewhere. The following

systems are borderline cases in which the differences between the atomic diameters are almost at the critical value :—

Univalent	Copper-silver, copper-gold.
Divalent	Copper-beryllium.
Trivalent	Silver-gallium.
Tetravalent	Copper-tin, silver-germanium.
Pentavalent	Copper-antimony, silver-arsenic.

(2) *Valency Effects.*

The typical solid solution area in a binary system is of the kind shown in fig. 2. Here AL is the liquidus or freezing point curve of the molten alloy, and AS the solidus or melting point curve of the solid solution, the two being related in such a way that at any given temperature, say, t, a liquid of composition x is in equilibrium with a solid of composition y. Above the temperature SL the saturated solid solution is in equilibrium with a liquid phase, and as described later, the equilibrium relations are comparatively simple. Below SL the saturated solid solution is in equilibrium with a second solid phase, and the curve SX generally shows an increase of solubility with temperature, but in some of the copper and silver alloys investigated a different kind of equilibrium is found, and the solubility decreases with temperature.

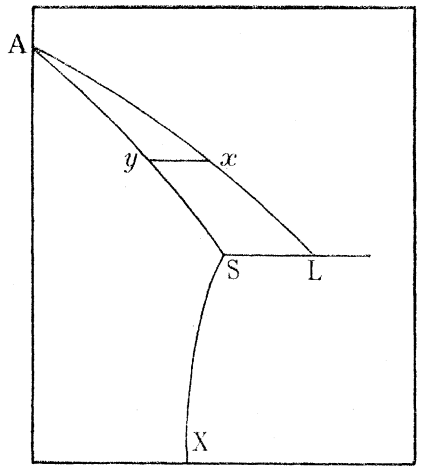

FIG. 2.

In considering the effects of valency we shall, therefore, deal in turn with the liquidus and solidus lines, and then with the two types of solubility curve. Special emphasis is laid on the investigation of the series of alloys, copper-zinc, copper-gallium, and copper-germanium, and silver-cadmium, silver-indium, and silver-tin. In all these alloys the lattice distortion is nearly the same and is relatively small. The fact that the solvent and solute atoms are in the same period means that the quantum numbers of the outer electron shells of solvent and solute are the same, whilst differences due to atomic weights or atomic number are slight, so that everything is favourable for showing the pure valency effects free from complicating factors.

A. *The Liquidus Lines.*

Examination of the liquidus curves shows that, with silver or copper as solvent when solvent and solute are in the same horizontal row of the periodic table, *the atomic compositions of alloys of a given freezing point are inversely proportional to the valencies of the solute elements.* For the range in which the liquidus curve is almost linear, this is

equivalent to saying that *the atomic depression of freezing point is approximately proportional to the valency of the solute.*

This implies that if we plot the freezing point curves, not in terms of simple atomic compositions, but in " equivalent atomic compositions " (*i.e.*, atomic composition × valency) all the curves become superposed. This is shown in figs. 3 and 4 in which

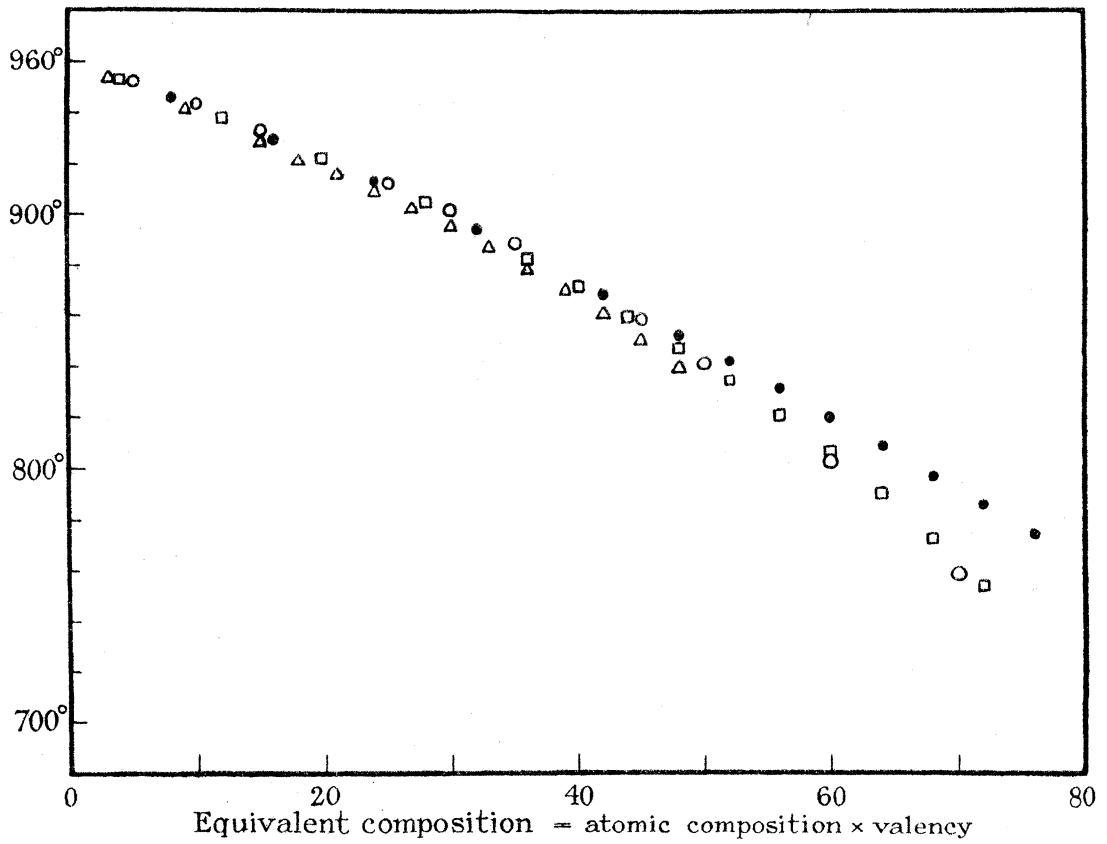

FIG. 3.—Liquidus points: ● Ag-Cd; △ Ag-In; ⊡ Ag-Sn; ⊙ Ag-Sb.

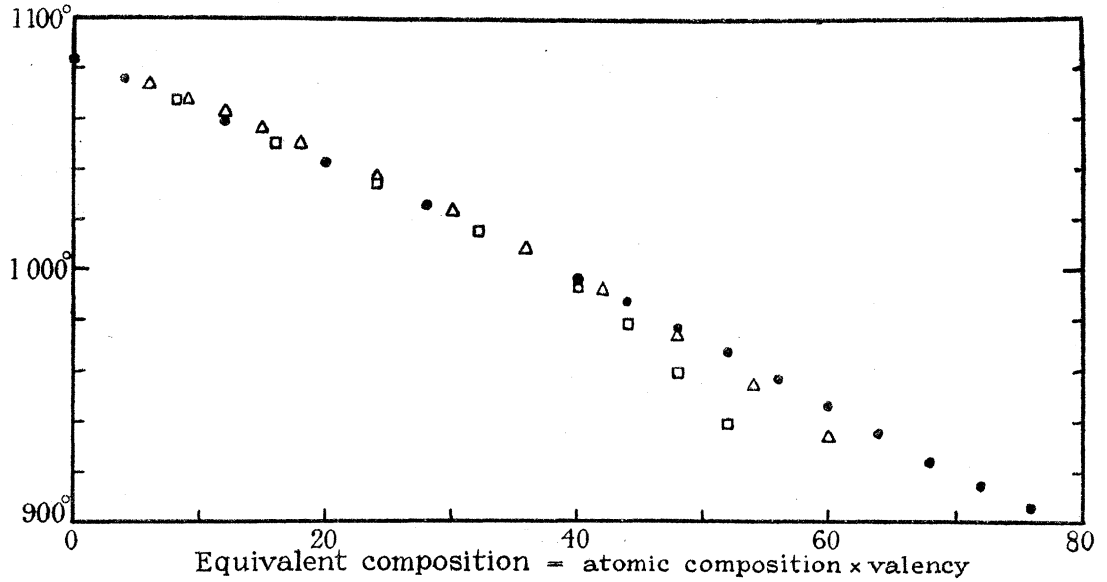

FIG. 4.—Liquidus points: ● Cu-Zn; ▲ Cu-Ga; □ Cu-Ge.

the ordinates are temperatures, and the abscissæ are equivalent compositions so that a point, say, 36, on the equivalent composition scale represents $36/2 = 18$ atomic % of a divalent element, $36/3 = 12$ atomic % of a trivalent element, and $36/4 = 9$ atomic % of a tetravalent element. The agreement is within the limits of experimental error to equivalent compositions of about 35, although errors of a few degrees prevent proof of the whole number law. For the silver series the relation holds as far as antimony in Group V, but in the copper series the position as regards arsenic is less certain, because the cooling curve work of FRIEDRICH* was carried out at a rate of cooling of 10° in 8 seconds in order to avoid errors from volatilization, and at this rate of cooling the freezing points would almost certainly be some degrees too low, which is exactly what is found in the dilute solutions.

The discovery of such simple laws for the binary freezing point curves naturally suggests that the same kind of relation may hold for ternary or quaternary alloys provided that no mutual interaction occurs between the different solute atoms. The rarity of the metals gallium, germanium, and indium prevents any complete investigation, but the freezing points of a few ternary alloys were determined, and the results are given in Table X, together with the freezing points deduced from the curves in fig. 4, on the assumption that the solute elements exert their normal valency effects. Thus in an alloy of composition 90 atomic % copper, 5 atomic % zinc, and 5 atomic % gallium, the total equivalent composition of the solute atoms is taken as $(5 \times 2) + (5 \times 3) = 25$. In calculating the freezing points which should be given by an alloy of this equivalent composition we have to decide which of the curves in fig. 4 shall be taken for comparison, since they do not all exactly coincide. For this purpose we have used as our standard the freezing point curve of the copper-zinc alloys as given by the figures in Table V, and all "calculated" values for copper alloys are deduced from this curve. It must be admitted that the exact position of the curve is subject to an error of a few degrees. As explained later, the experimental values of PARRAVANO agree

TABLE X.

Composition of the ternary alloy.								Total equivalent composition.	Freezing point deduced from fig.	Observed freezing point.
Weight %.				Atomic %.						
Cu.	Zn.	Ga.	Ge.	Cu.	Zn.	Ga.	Ge.			
87·21	8·82	3·97	—	87·71	8·62	3·63	—	28·1	1024°	1025°
91·35	4·76	3·89	—	91·79	4·65	3·56	—	20·0	1042°	1042°
86·82	9·04	—	4·14	87·48	8·86	—	3·66	32·4	1015°	1012°
90·58	4·35	—	5·07	91·25	4·26	—	4·49	26·5	1028°	1027°
92·20	—	3·64	4·16	92·96	—	3·35	3·69	24·8	1032°	1029°

* 'Metallurgie,' vol. 5, p. 529 (1908).

with those of TAFEL, and of RUER and KREMERS, and also with most of those of JITSUKA, but there are the inevitable deviations found in this class of work, so that an exact curve cannot be constructed. We have thought it advisable to use this curve for the following reasons :—(1) There are three independent investigations in close agreement with each other, and in reasonable agreement with a fourth ; (2) the commonness of zinc has enabled many more alloys to be investigated than for gallium or germanium, and has permitted the use of larger cooling curve ingots ; (3) the deviation from the simple valency law given above is greater as the valency increases, so that the divalent metal is more likely to give the fundamental equivalent freezing point curve. For the silver alloys dealt with later we have taken as standard the liquidus of the system silver-cadmium for which our own results are in good agreement with those of PETRENKO and FEDEROW.

As will be seen from Table X, the agreement is satisfactory for the five alloys included, all of which were prepared from virgin metals. Two additional copper-gallium-germanium alloys were examined, but, for reasons of economy, they had to be prepared from ingots which had been remelted several times. Their freezing points were distinctly low, and it seems reasonable to suppose that contamination had occurred (see p. 86). But, taken as a whole, the agreement is satisfactory and suggests that the freezing points of these ternary alloys are given by the above simple whole number laws to within an accuracy of 5° up to a total equivalent composition of 35.

When we come to apply these principles to elements where the solvent and solute are in different periods, the position is naturally more complicated, since the quantum numbers of the outermost electron shells of the two atoms are no longer the same, and the atomic diameters are much more variable. In such cases the systems are found to divide themselves into three classes.

Class I.—The solute element exerts approximately its normal valency effect in dilute solutions.

Examples of this kind are :—copper-silicon, silver-aluminium, copper-bismuth, silver-bismuth.

The points for these are shown in fig. 5, together with the standard equivalent composition—freezing point curves for copper-zinc and silver-cadmium. It will be seen that, for the silver alloys, the silver-bismuth curve shows the normal valency effect, whilst with silver aluminium the freezing point depression is slightly but systematically greater. In the copper alloys there are deviations in either direction in the concentrated solutions, but in the dilute solutions the curves approach asymptotically to the standard equivalent composition curve. The copper-silicon curve is, in fact, almost indistinguishable from that for copper-germanium. We do not, of course, suggest that any direct comparison can be made between an alloy such as copper-bismuth where there is practically no solid solution, and an alloy such as copper-zinc,

where a wide solid solution is formed, but the important point is that the initial depression of freezing point corresponds to the normal valency effect. In such cases there is again the prospect of applying these rules to ternary alloys, as may be seen from the following example.

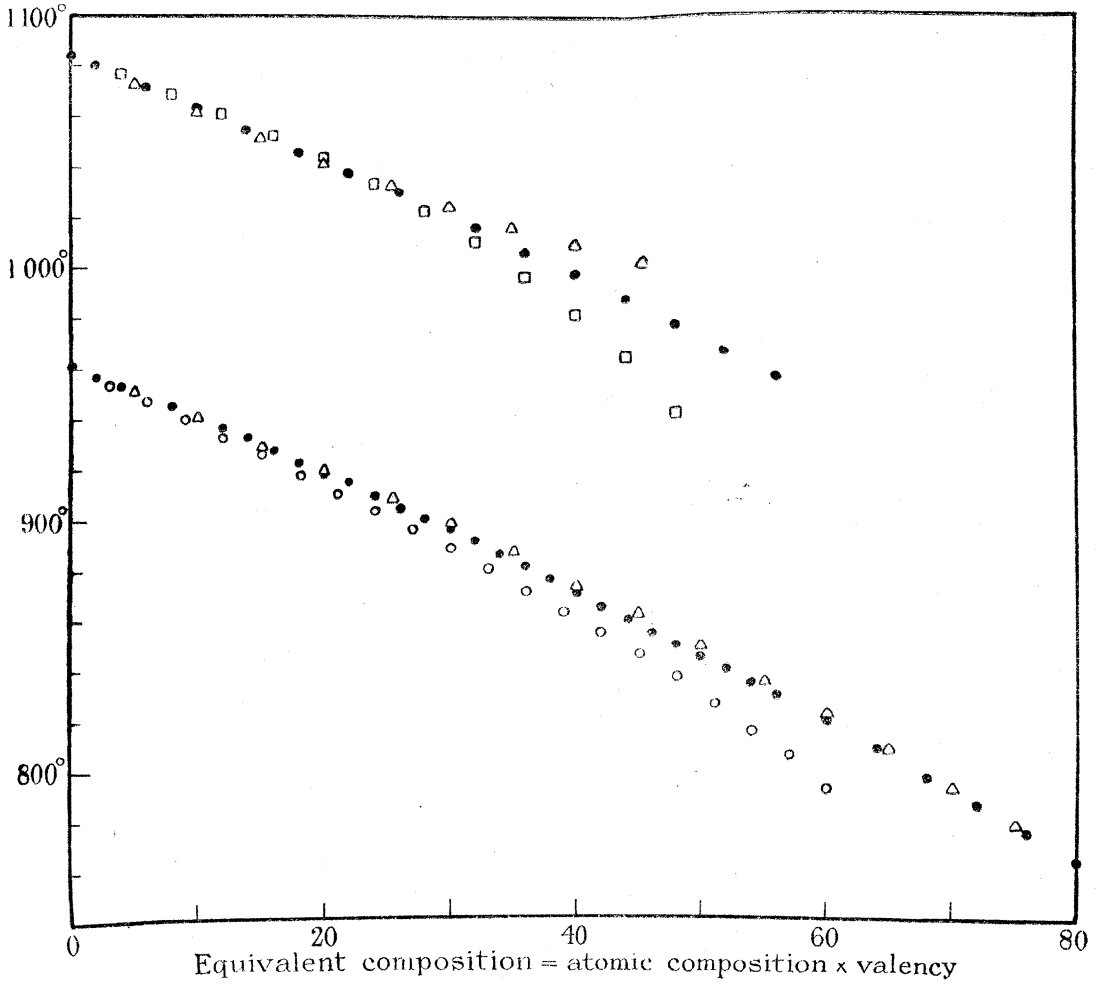

FIG. 5.—Liquidus points: upper curve, ● Cu-Zn; □ Cu-Si; Δ Cu-Bi; lower curve, ● Ag-Cd; ○ Ag-Al; Δ Ag-Bi.

Copper-zinc-silicon.—Approximate data for a few of these alloys have been given by VADER* and are shown in Table XI. The compositions of these alloys were unfortunately sometimes only estimated from the weights of metals used, and slight loss of both zinc and silicon is to be expected at the higher temperature. The calculated and observed freezing points are in agreement within the obvious experimental error except for the first alloy, and for that Dr. VADER† has kindly told the author that the high value is probably due to losses on melting. As will be appreciated from the next section, the

* 'J. Inst. Met.,' vol. 44, p. 369 (1930). In Table III of this paper there is a misprint, the liquidus point of the third alloy being 960° as shown by the cooling curve in fig. 12, and not 950° as in the table.

† In a private communication.

freezing points of more concentrated alloys can probably be calculated by the methods described later.*

TABLE XI.

Composition of the ternary alloy.						Total equivalent composition.	Calculated freezing point.	Observed freezing point.
Weight %.			Atomic %.					
Cu.	Zn.	Si.	Cu.	Zn.	Si.			
90	8	2	88	7·6	4·4	32·8	1014	1031
88	8	4	83·9	7·4	8·6	49·2	974	970
87·2	9·73	2·96	84·4	9·1	6·5	44·2	986	980
86·2	9·30	3·97	82·4	9·1	8·6	52·6	965	960

Class II.—The solute element lowers the freezing point by an amount which in dilute solution is a simple multiple or fraction of that to be expected from its normal valency.

Since the general form of all these freezing point curves is the same, it is not surprising that they can be made to fit the standard equivalent composition curves of figs. 3 and 4 by means of an arbitrary factor. It is, however, most significant that some of the factors are simple whole numbers or fractions. In other words, as regards their effects upon the freezing points, some elements act as though they had, so to speak, fictitious valencies which were whole numbers. Since the cause of this remains unknown, we propose to call these fictitious valencies "liquidus factors," and by the "adjusted equivalent composition" we mean the atomic per cent. of the solute element multiplied by the liquidus factor. In considering these results we have, of course, to realize fully the possible errors in the experimental data. In the following systems the agreement seems so close over such a wide range that it can hardly be a coincidence :—

System.	Normal valency of solute.	Liquidus factor in alloy.
Silver–zinc	2	3
Copper–beryllium	2	4
Copper–magnesium	2	6

* Data for more of these alloys have been given by GOULD and RAY ("Metals and Alloys," vol. 1, p. 456 (1930)), but their results seem inaccurate. In particular they give the freezing points of simple copper–zinc brasses containing 40% and 14·4% of zinc respectively as 925° and 1040°. Since the copper–zinc liquidus meets the 905° peritectic line at approximately 39% Zn, this alloy cannot melt above 905°, and their other values appear too high.

The freezing points of these alloys in terms of adjusted equivalent compositions are plotted graphically in fig. 6, from which it will be seen how the agreement is almost exact over two hundred degrees. In these diagrams the abscissæ are atomic compositions multiplied by the liquidus factor, and the normal copper-zinc and silver-cadmium curves are included for comparison. For copper-magnesium, for example, the liquidus factor is 6, so that the adjusted equivalent composition of an alloy containing 10 atomic % of magnesium is $6 \times 10 = 60$. It will be seen that within the limits

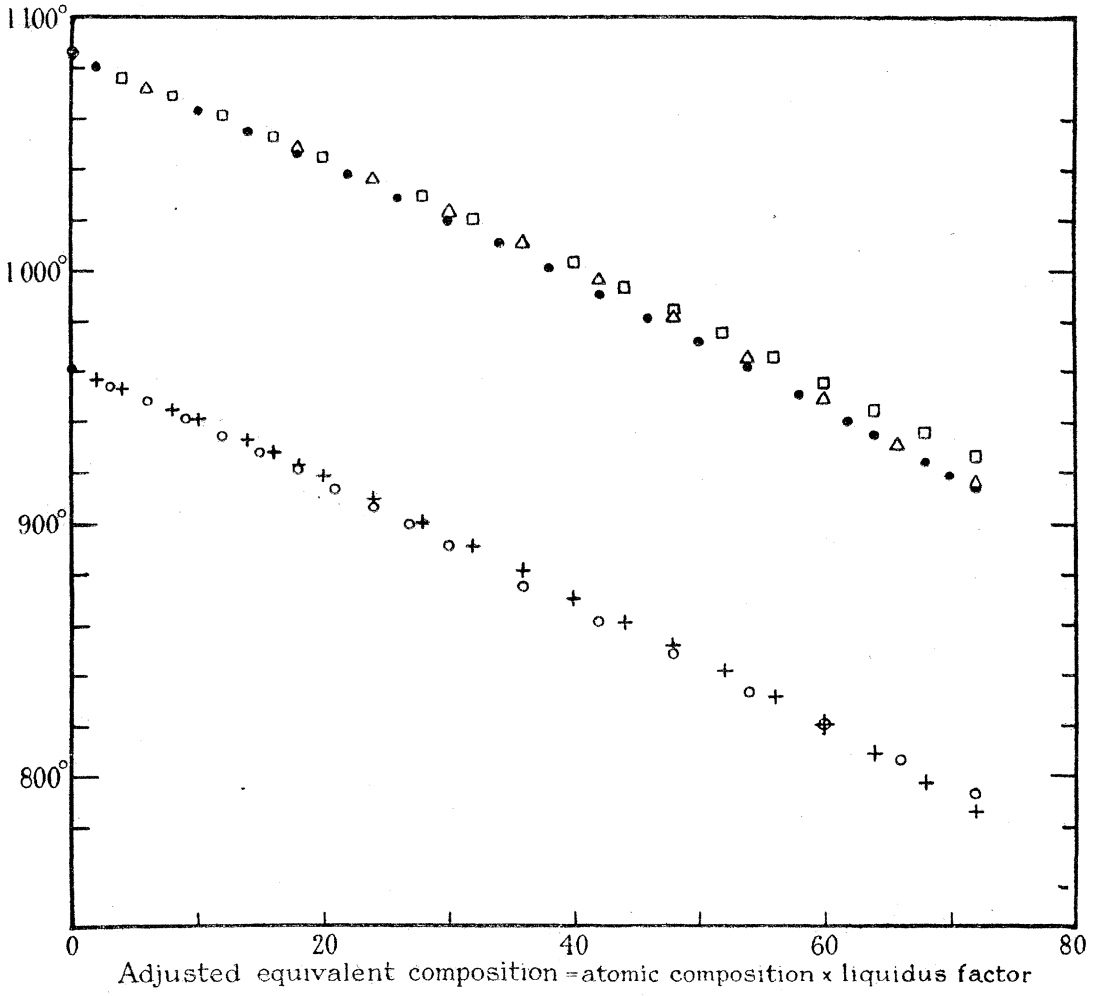

FIG. 6.—Liquidus points : Upper curve : ● Cu-Zn normal valency 2; □ Cu-Be liquidus factor 4; Δ Cu-Mg liquidus factor 6. Lower curve: + Ag-Cd normal valency 2; O Ag-Zn liquidus factor 3.

of the experimental error the copper-magnesium and copper-zinc points lie on the same curve, so that the magnesium is depressing the freezing point as though one magnesium atom were equivalent to three zinc atoms. Similarly, in the copper-beryllium alloys, the liquidus factor is 4, and the depression of freezing point is as though one beryllium atom were equal to two zinc atoms, whilst in the silver-zinc series the zinc acts as though it had a valency of three.

It will be noted that in the more concentrated solutions slight deviations occur, and, whilst in the above systems these deviations are probably within the experimental error over a wide range, there are many alloys in which this is not so. In some systems, however, we still find that the initial depressions of freezing point are again those to be expected from whole number liquidus factors. Owing to the smallness of freezing point depressions in the dilute solutions only the most accurate work can be considered in this connexion, but in the following systems the evidence seems very suggestive :—

System.	Normal valency of solute.	Liquidus factor.
Silver-copper	1	3
Silver-beryllium	2	3
Silver-thallium	3	5
Silver-lead	4	5
Copper-silver	1	4
Copper-cadmium	2	6
Copper-lead	4	6

The adjusted equivalent composition freezing point curves for these alloys are shown in fig. 7, together with the standard copper-zinc and silver-cadmium curves. It will

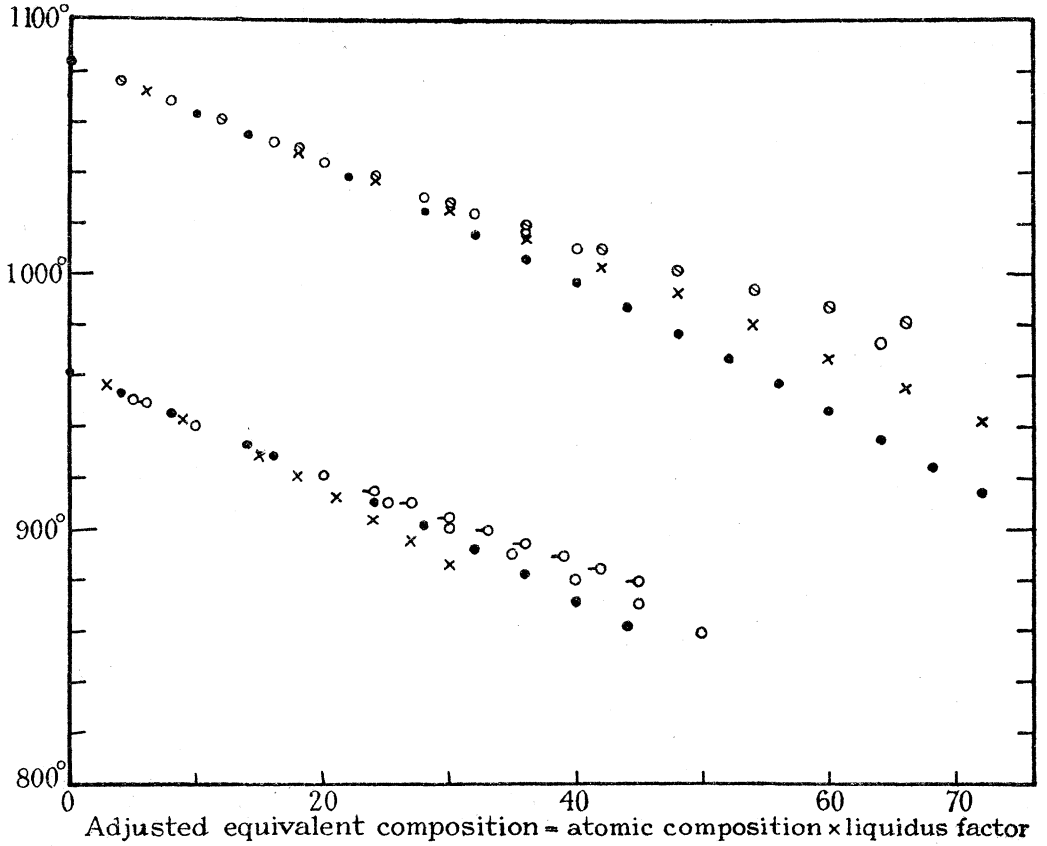

FIG. 7.—Liquidus points: Upper curve: ● Cu-Zn normal valency 2; ○ Cu-Ag liquidus factor 4; × Cu-Cd liquidus factor 6; ⊘ Cu-Pb liquidus factor 6. Lower curve: ● Ag-Cd normal valency 2; × Ag-Be liquidus factor 3; -○ Ag-Cu liquidus factor 3; ○ Ag-Pb liquidus factor 5.

be seen that all the curves approach asymptotically to a common tangent, although in the more concentrated solutions there are divergencies in either direction. These points are all from work of the highest quality yet available, and the error in the temperatures is not likely to be more than 1° or 2° (see Appendix I).

In the following systems the evidence is not so conclusive, but in dilute solutions the curves again appear to correspond to whole number liquidus factors, although in the copper-antimony and copper-tin series there is an increasing divergence in the more concentrated alloys.

System.	Normal valency of solute.	Liquidus factor.
Silver-mercury	2	3
Silver-gallium	3	4
Copper-gold	1	3
Copper-tin	4	6
Copper-antimony	4	6

We may summarize these conclusions by saying that the depression of freezing point of silver and copper by some elements agrees over a wide range with the conception of liquidus factors which are whole numbers, whilst in other systems there is a distinct suggestion that the initial depression of freezing point is that to be expected from a whole number liquidus factor, although the experimental error* of 1° or 2° does not enable us to say conclusively that the factor is an exact integer. If, however, the factors are not exact whole numbers there seems little doubt that the liquidus curves of the different systems divide themselves into groups in each of which the initial depression of freezing point is approximately the same. Further, we may point out that if later work shows that the factors are not really whole numbers, the general methods of calculation which we now suggest will not be invalidated.

From the point of view of the binary systems these factors are of little practical value since they can only be determined when the freezing point curve is known. But if it can be shown that the same factors hold in ternary systems, the progress will be considerable, since we shall have, in effect, a method for calculating the ternary freezing point surfaces from a knowledge of the binary curves. Fortunately, it is possible to do this in many cases. It will be seen from fig. 6 that the adjusted equivalent composition freezing point curves in the more concentrated solutions deviate in either direction from the standard equivalent composition curve. For this reason it is advisable to divide our calculations into two parts: the first referring to the more dilute

* We would emphasize here that attempts to measure the freezing points of alloys to within less than $\pm 1°$ involve a large number of minor precautions and corrections which have been taken by very few investigators.

solutions in which the simple liquidus factors can be used, and the second dealing with more concentrated solutions in which a correction factor is required, but where this correction factor can be deduced from the binary curves.

Copper-zinc-cadmium.—In this system the simple liquidus factor of 6 for cadmium, and the normal valency of 2 for zinc, enable the freezing points to be calculated over a very considerable range. The system has been investigated by JENKINS* in great detail. The tables unfortunately only give the exact data for one alloy containing 3·2% Cd, and 9·54% of zinc, the corresponding atomic composition being 9·14 atomic % zinc and 1·78 atomic % cadmium. This gives an adjusted equivalent composition of $(9{\cdot}14 \times 2) + (1{\cdot}78 \times 6) = 29{\cdot}96$, and the freezing point deduced from the equivalent composition curve is 1021° as compared with the experimental value of 1027°. The remaining data for the copper-rich alloys are only given in the form of a triangular diagram with isothermal intervals of 25° for the liquidus.

TABLE XII.

Composition of alloy.						Adjusted equivalent composition.	Estimated freezing point.	Observed freezing point.
Weights %.			Atomic %.					
Cu.	Zn.	Cd.	Cu.	Zn.	Cd.			
—	7·5	1·25	—	7·35	0·71	19·0	1044	1050
—	5	2·3	—	4·92	1·32	17·8	1046	1050
—	10	2·5	—	9·86	1·43	28·3	1024	1025
—	5·1	4·9	—	5·08	2·84	27·2	1027	1025
—	15	2·5	—	14·81	1·44	38·3	1001	1000
—	10·2	5·0	—	10·17	2·90	37·7	1002	1000
—	5·8	7·5	—	5·84	4·39	38·0	1002	1000
—	15·7	5	—	15·67	2·90	48·7	975	975
—	8·6	8·9	—	8·72	5·25	49·9	972	975

Fortunately these isothermals intersect the triangular lines at convenient points and from these the data in Table XII have been read off, the compositions being accurate to a few tenths per cent. It will be seen that the measured freezing points agree very well with those deduced from the adjusted equivalent compositions.

Copper-zinc-tin.—This system has been investigated in detail by HOYT,† whose results are given in the form of a comparatively large scale triangular diagram with liquidus isothermals at intervals of 20°. From these the figures given in Table XIII have been read off, the compositions being accurate to within a few tenths per cent. by weight. It will be seen that the observed freezing points are in very good agreement with those

* 'J. Inst. Met.,' vol. 38, p. 391 (1927).

† 'J. Inst. Met.,' vol. 10, p. 235 (1913).

deduced from the adjusted equivalent compositions. Later data by HANSEN and TAMMANN* are also in good agreement, but the work does not seem to have been carried out so carefully,† and is therefore not considered in detail here. Calculations for more concentrated solutions are given later (p. 27).

TABLE XIII.

Composition of alloy.				Adjusted equivalent composition.	Estimated freezing point.	Observed freezing point.
Weights %.		Atomic %.				
Zn.	Sn.	Zn.	Sn.			
5·25	3·4	5·19	1·85	21·5	1039	1040
10	3·21	9·90	1·75	30·3	1019	1020
3·52	6·48	3·53	3·58	28·54	1024	1020
10	5·60	10·01	3·09	38·56	1001	1000
15·10	4·90	15·00	2·70	46·2	982	980
10	7·59	10·11	4·23	45·6	983	980
5·23	10	5·34	5·62	44·4	986	980

We may now consider the calculation of the freezing points of more concentrated solutions where correction factors have to be introduced. In these copper-rich and silver-rich alloys we consider that the equilibrium between the liquid and solid phases is the result of two distinct factors, the one electronic and the other atomic. We suggest, further, that, when proceeding along the same horizontal row of the periodic table, *i.e.*, in a series such as copper-zinc, copper-gallium, and copper-germanium, the atoms, or more properly the ions, are so similar in structure that, to a first approximation, the atomic factor is negligible, and the equilibrium is the result of the electronic factor alone. This suggestion that neighbouring atoms are almost indistinguishable or identical in the B sub-groups (the A sub-groups behave quite differently), is supported by many facts, such as the readiness with which one atom will replace the other in certain crystal structures, the almost constant atomic diameters‡ in the crystals of the elements, etc. From this point of view the simple valency laws for the freezing point curves are the result of the electronic factor, and the deviations in more concentrated solutions are due to the increasing effect of the atomic factor. The probability of such an explanation is greatly strengthened by the fact that, as we show in the next section,

* 'Z. anorg. Chem.,' vol. 138, p. 143 (1924).

† The rate of cooling used was 1° in 2·5 seconds.

‡ In passing from copper to germanium the extreme variation in atomic diameter is from 2·67A to 2·44 A. In the A group elements of the same period the atomic diameters from potassium to titanium vary from 4·54 A to 2·90 A.

the solidus lines and solid solubility limits also obey simple valency laws where deviations related to atomic diameters are clearly shown.

The fact that in the binary alloys, in which the solvent and solute are in different periods, the freezing point curves in dilute solutions give depressions corresponding to "liquidus factors," which are whole numbers, suggests that we have again to deal with some kind of electronic quantum relation, and we again suggest that the deviations in more concentrated solutions are the result of the atomic factor. Reference to fig. 7 will show that these deviations may be in either direction from the standard equivalent composition curve, and we suggest that this characteristic of the solute atom is retained in ternary or more complex alloys provided that no mutual interaction takes place between the different solute atoms.

Suppose a given ternary or more complex alloy has a total adjusted equivalent composition E, and that there is x atomic % of one particular solute element A whose liquidus factor is a. If the alloy were a simple binary alloy of copper with A, our adjusted equivalent composition E would correspond to a binary alloy containing (E/a) atomic % of A. Let us suppose that the actual freezing point curve of the system Cu — A shows that an alloy containing (E/a) atomic % of A freezes at a temperature θ_A, whilst according to the standard equivalent composition curve an alloy of equivalent composition E should freeze at θ_E. Let this deviation $\theta_A - \theta_E = \Delta\theta_A$, where $\Delta\theta_A$ may be positive or negative.

Now in our ternary alloy we have again a total adjusted equivalent composition E, but the particular element A is only present to the extent of x%. We now assume that a direct proportionality exists, so that, whilst in the binary alloy of adjusted equivalent composition E, the (E/a) atoms of A produced a deviation $\Delta\theta_A$, in the ternary alloy of total adjusted equivalent composition E, the x atoms of A will produce a deviation equal to

$$\Delta\theta_A \times \frac{x}{(E/a)}.$$

Similarly, if there is y atomic % of the solute element B, of liquidus factor b, the deviation will be given by a corresponding term

$$\Delta\theta_B \times \frac{y}{(E/b)},$$

and in a complex alloy of copper with solute elements A, B, C, . . . the total deviation from the standard adjusted equivalent composition curve will be given by the algebraic sum of all these terms.

We may make this more clear by means of the following example from the system copper-silver-lead. Reference to fig. 7 shows that in both the binary systems copper-silver and copper-lead, the adjusted equivalent composition—freezing point curves in the more concentrated solutions are higher than the standard curve, although in the more dilute solutions they agree well with liquidus factors of 4 for silver and 6 for lead.

In this system, therefore, both correction terms are positive, and we expect the liquidus points of the more concentrated ternary alloys to be at higher temperatures than those expected from the simple adjusted equivalent composition curve.

Consider an alloy containing 1·66 atomic % silver, 5·20 atomic % lead, 93·14 atomic % copper.

The total adjusted equivalent composition is

$$E = (1{\cdot}66 \times 4) + (5{\cdot}20 \times 6) = 37{\cdot}84.$$

The corresponding liquidus point from the standard equivalent composition curve is $\theta_E = 1001°$ C.

If the alloy were a simple copper-silver alloy, an adjusted equivalent composition of 37·84 would mean an alloy containing $\frac{37{\cdot}84}{4} = 9{\cdot}46$ atomic % silver, and this would freeze at 1014°, or 13° higher than indicated by the standard curve (θ_E). The actual ternary alloy has also a total adjusted equivalent composition of 37·84, but only contains 1·66 atomic % of silver. Hence

$$\Delta\theta_{Ag} = \frac{13 \times 1{\cdot}66}{9{\cdot}46} = +\,2°.$$

A binary copper-lead alloy of adjusted equivalent composition 37·84 would contain $\frac{37{\cdot}84}{6} = 6{\cdot}31$ atomic % of lead, and this would freeze at 1016°, or 15° higher than indicated by the standard curve (θ_E). The actual ternary alloy of total adjusted equivalent composition 37·84 only contains 5·20 atomic % of lead. Hence

$$\Delta\theta_{Pb} = \frac{15 \times 5{\cdot}2}{6{\cdot}31} = +\,12°.$$

The total correction term is thus

$$\Delta\theta_{Ag} + \Delta\theta_{Pb} = 2 + 12 = 14,$$

and we expect the liquidus point to be at 1001 + 14 = 1015° C. The experimental value is 1011°. In this way we have made calculations for the following ternary alloys, and, as can be seen from the tables, the results are, on the whole, encouraging, and for some very good indeed.

Copper-silver-zinc.—The liquidus points of this system have been determined by UENO.* The alloys are not analysed in all cases, but test analyses showed that zinc was lost to the extent of about 0·3%, and we have therefore deducted this amount from the compositions determined from the weights of metals used, and have added a proportional amount to the figures for the percentages of copper and silver.

The accuracy of the work has been tested by comparing the values given by UENO with those of HEYCOCK and NEVILLE, and of PARRAVANO and TAFEL. A satisfactory

* 'Mem. Coll. Sci. Kyoto Imp. Univ.,' vol. 12, p. 347 (1929).

agreement is shown for the copper-zinc binary alloys, but for the silver-zinc series the three points given by UENO are systematically 5°–10° higher than those of HEYCOCK and NEVILLE,* possibly owing to loss of zinc by volatilization, since several volatile metals are more readily lost from silver than from copper.

The results for the copper-rich alloys are given in Table XIV, from which it will be seen that the agreement is satisfactory. In this table the fifth column gives the total adjusted equivalent composition, whilst the sixth column gives the simple uncorrected freezing point, θ_E, deduced from the standard equivalent composition curve. Here,

TABLE XIV.

Composition of alloy.				Adjusted equivalent composition.	θ_E.	$\Delta\theta_{Ag}$.	Corrected calculated freezing point.	Observed freezing point.
Weight %		Atomic %						
Ag.	Zn.	Ag.	Zn.					
					°	°	°	°
2·0	9·7	1·19	9·54	23·8	1034	+ 1	1035	1035
5·0	9·7	3·02	9·66	31·4	1018	+ 3	1021	1022
7·0	9·7	4·26	9·74	36·5	1005	+ 5	1010	1013
10·0	9·7	6·14	10·14	44·8	985	+10	995	999
20·1	9·7	12·95	10·3	72·4	913	+34	947	948
2·0	19·7	1·20	19·42	43·6	988	+ 2	990	990
5·0	19·7	3·03	19·6	51·3	969	+ 5	974	975
7·0	19·7	4·27	19·8	56·7	955	+ 8	963	966
10·0	19·7	6·18	20·1	64·9	933	+15	948	952
2·0	29·7	1·21	29·6	64·0	935	+ 3	938	936
5·0	29·7	3·03	29·7	71·5	915	+ 8	923	920

since our standard curve is that of the copper-zinc alloys, the correction term is required for the silver alone, and the seventh column gives the values of $\Delta\theta_{Ag}$ calculated by the methods just described.

The next column gives the corrected freezing point ($\theta_E + \Delta\theta_{Ag}$) as calculated, and the final column gives the experimental values.

A few results were also given for the silver-rich alloys. For these the simple liquidus factor of 3 for zinc in the binary silver-zinc alloys gives results so near to the standard curve that the corrections for the zinc are very small, and are hardly justified in view of the uncertainty of the exact composition. We have therefore corrected only for the copper with liquidus factor 3. The results are shown in Table XV, from which it will be seen that a good agreement is obtained, although in view of the point previously mentioned concerning the discrepancy between the results of HEYCOCK and NEVILLE, and of UENO for the binary silver-zinc alloys, the figures are not quite so reliable as those for the copper-rich alloys in Table XIV.

* 'Phil. Trans.,' A, vol. 202, p. 1 (1903).

TABLE XV.

Composition of alloy.				Adjusted equivalent composition.	θ_E.	$\Delta\theta_{Cu}$.	Corrected calculated freezing point.	Observed freezing point.
Weight %.		Atomic %.						
Cu.	Zn.	Cu.	Zn.					
					°	°	°	°
7·5	2·2	11·9	3·4	45·9	856	+17	873	873
6·0	3·7	9·55	5·73	45·84	856	+14	870	871
5·0	4·7	7·96	7·28	45·7	857	+11	868	870
2·5	7·2	3·98	11·16	45·4	857	+ 6	863	868

Copper-tin-antimony.—Liquidus points for this ternary system have been determined by TASAKI*, who used an electrical resistance method in which the temperature variations of resistance of rods of the alloys were measured. The compositions of the alloys given in the tables are from the weights of metals used, but analyses showed that the desired composition was obtained, although it is not clear whether the analyses referred to the specimens after the actual resistance measurements had been made. The accuracy of the method may be estimated from the fact that figures given for binary copper-antimony alloys agree well with those of CARPENTER,† whilst for binary copper-tin alloys, some of TASAKI'S figures differ by 5°–10° from those of HEYCOCK and NEVILLE, others being in good agreement.

TABLE XVI.

Composition of alloy.				Adjusted equivalent composition.	θ_E.	$\Delta\theta_{Sb}$.	$\Delta\theta_{Sn}$.	Corrected calculated freezing point.	Observed freezing point.
Weight %.		Atomic %.							
Sb.	Sn.	Sb.	Sn.						
					°	°	°	°	°
5	5	2·74	2·81	33·3	1013	—	—	1013	1020
5	10	2·81	5·76	51·4	969	— 8	— 8	953	954
10	5	5·62	2·88	51·0	970	—14	— 4	952	954
5	15	2·88	8·86	70·4	917	—15	—22	880	890
10	10	5·76	5·92	70·1	919	—30	—15	874	885
15	5	8·65	2·96	69·7	920	—44	— 8	868	880

In this case both tin and antimony have liquidus factors of 6 in dilute solution, and in more concentrated solutions their adjusted equivalent composition-freezing point

* 'Mem. Coll. Sci. Kyoto Imp. Univ.,' vol. 12, p. 249 (1929).

† 'Int. Z. Metallog.,' vol. 4, p. 300 (1913).

curves lie below the standard curve, so that both $\Delta\theta_{Sb}$ and $\Delta\theta_{Sn}$ are negative. As will be seen from Table XVI, the corrected calculated values below 900° are systematically lower by 10°–12° than those determined experimentally, whilst above 900° the error is less. In view of the slight uncertainty in composition the agreement is fairly satisfactory.

Copper-zinc-tin.—On p. 22 we have already given the calculated and observed values for the freezing points of the copper-rich alloys of this system, and Table XVII

TABLE XVII.

Composition of alloy.				Adjusted equivalent composition.	θ_E.	$\Delta\theta_{Sn}$.	Corrected calculated freezing point.	Observed freezing point.
Weight %.		Atomic %.						
Zn.	Sn.	Zn.	Sn.					
9·56	10·0	9·35	5·39	51·0	970°	−7°	963°	960°
20	4·14	19·9	2·27	53·5	963	− 3	960	960
20	6·23	20·14	3·46	61·0	944	− 6	938	940
13·02	10	10·56	5·82	56·0	957	− 9	948	940
6·79	13·21	7·05	7·55	59·4	949	−14	935	940
20	8·04	20·3	4·50	67·6	925	−10	915	920
10	13·64	10·4	7·82	67·7	925	−18	907	920

gives similar values for more concentrated solutions in which the correction term, $\Delta\theta_{Sn}$, is negative. The observed values are again taken from the work of HOYT (*loc. cit.*). It will be seen that the agreement is good as far as the 940° isothermal, but below this point the calculated values become too low.

Copper-zinc-cadmium.—The results for the copper-rich alloys of this system have already been given in Table XII, and Table XVIIIA gives the calculated and observed freezing points for the more concentrated alloys in which the correction term

TABLE XVIIIA.

Composition of alloy.				Adjusted equivalent composition.	θ_E.	$\Delta\theta_{Cd}$.	Corrected calculated freezing point.	Observed freezing point.
Weight %.		Atomic %.						
Zn.	Cd.	Zn.	Cd.					
20·0	5·0	20·0	2·91	57·5	953°	+5°	958°	950°
12·5	10·0	12·75	5·93	61·1	943	+11	954	950
15·0	12·5	15·5	7·51	76·1	905	+17	922	925
24·14	5·86	24·3	3·42	69·0	921	+ 8	929	925

$\Delta\theta_{Cd}$ is positive. The experimental values are again from the work of JENKINS (*loc. cit.*), and the agreement is satisfactory.

Copper-silver-lead.—This system has been investigated by FRIEDRICH and LEROUX†, and although the compositions given are synthetic, their work appears reasonably accurate, since comparison shows that their figures for copper-lead alloys are in good agreement with those of HEYCOCK and NEVILLE, whilst for copper-silver alloys their liquidus points are too low by an amount which gradually increases until at 1000° it is about 10°. For copper-rich alloys both $\Delta\theta_{Ag}$ and $\Delta\theta_{Pb}$ are positive, and as can be seen from Table XVIIIB a fair agreement is obtained. Data for a few silver-rich alloys are also included, and as can be seen from Table XVIIIC the agreement is again satisfactory.

TABLE XVIIIB.

Composition of alloy.				Adjusted equivalent composition.	θ_E.	$\Delta\theta_{Ag}$.	$\Delta\theta_{Pb}$.	Corrected calculated freezing point.	Observed freezing point.
Weight %.		Atomic %.							
Ag.	Pb.	Ag.	Pb.						
					°	°	°	°	°
1	5	0·61	1·60	12·0	1059	—	—	1059	1049
5	5	3·05	1·62	21·9	1038	+ 2	+ 2	1042	1043* (? + 3°)
5	15	3·27	5·26	45·0	985	+ 8	+15	1008	998
2·5	15	1·66	5·20	37·8	1001	+ 2	+12	1015	1011
5	25	3·65	9·51	71·7	915	+10	+48	973	963
10	10	6·63	3·45	47·2	979	+11	+10	1000	989

* This alloy showed 3° of super-cooling, and we are uncertain whether the temperature should be 1043° or 1046°.

TABLE XVIIIC.

Composition of alloy.				Adjusted equivalent composition.	θ_E.	$\Delta\theta_{Cu}$.	$\Delta\theta_{Pb}$.	Corrected calculated freezing point.	Observed freezing point.
Weight %.		Atomic %.							
Cu.	Pb.	Cu.	Pb.						
					°	°	°	°	°
5	5	8·39	2·57	38·0	877	+ 9	+ 2	888	890 or 894
5	8	8·51	4·18	46·4	855	+12	+ 5	872	870 or 873

Note.—These alloys showed slight supercooling and we are uncertain whether the amount of this should be added in order to give the highest point of the arrest.

† 'Metallurgie,' vol. 4, p. 293 (1907).

Copper-zinc-lead.—In this system difficulty exists in estimating the value of the experimental work. A few determinations have recently been made by HANSEN,* but the alloys are all essentially brasses with very small additions of lead, so that a critical test of the method of calculation is not obtained.

The system has also been investigated by PARRAVANO,† who took a large number of cooling curves, but on account of segregation only alloys with very small lead contents could be analysed, and in other cases only the synthetic compositions are given. We find here a fairly good agreement between the calculated and observed results for those alloys which were analysed, but, for the others, the calculated results are too low, which is what would be expected if loss of zinc took place; further critical comparison does not, therefore, seem justified.

Copper-zinc-silicon.—In more concentrated solutions the value of $\Delta\theta_{Si}$ is negative, and the corrected calculated values would therefore be slightly lower than those given in Table XI, and this would give a better agreement with the observed values. But since the alloys examined by VADER (*loc. cit.*) were not analysed after the cooling curve, we have thought it unjustifiable to make such a critical comparison.

From these examples it may be suggested that the method detailed above will permit the calculation of the liquidus points of ternary or more complex alloys where the binary freezing point curves are known, provided that no mutual interaction occurs between the different solute atoms. But with copper-magnesium-silicon, for example, we may well expect the rules to break down owing to the formation of the very stable compound Mg_2Si. Further, as will be appreciated from the next section, the rules will fail where the solute atom is liable to undergo a change in its electronic state or valency, and they should not be applied indiscriminately to the transition elements of the A sub-groups. But experiments with a comparatively few alloys will show whether a given ternary or quaternary system follows the general principles, and in the event of confirmation being obtained, we may not unreasonably use the methods described above to calculate the liquidus points over a wide range, with a great saving of very tedious experimental work.

The following complex alloys examined by HANSEN‡ may serve to illustrate these principles, although they were not analysed after the cooling curves had been made:—

(1) *Alloy containing* 86·17% Cu; 9·49% Sn; 1·05% Pb; 3·05% Zn; 0·12% Sb, with traces of Fe and Ni.

Atomic composition, 5·37% Sn; 0·34% Pb; 3·14% Zn; 0·07% Sb.

* 'Z. Metallk.' (1929).

† 'Gazz. Chim. Ital.,' vol. 44, p. 475 (1914).

‡ 'Z. Metallk.,' vol. 24, p. 63 (1932). Dr. HANSEN has kindly told us in a private communication that the alloys were not analysed after the cooling curves, so that a little loss of zinc is to be expected, although as the alloys were melted under borax, the loss is small. Any decrease in the zinc content will of course raise the freezing point.

Adjusted equivalent composition = $(6 \times 5{\cdot}37) + (6 \times 0{\cdot}34) + (2 \times 3{\cdot}14) + (6 \times 0{\cdot}07) = 40{\cdot}9$.

θ_E = simple uncorrected liquidus point from equivalent composition curve = 995°.

Correction factors, $\Delta\theta_{Sn} = -3°$; $\Delta\theta_{Pb} = +1°$.

Corrected calculated freezing point 993°.

Observed freezing point 1000° C.

(2) *Alloy containing* 85·19% Cu; 4·76% Sn; 4·27% Pb; 5·73% Zn, with traces of Fe.

Atomic composition, 2·69% Sn; 1·39% Pb; 5·89% Zn; 90·03% Cu.

Adjusted equivalent composition $(6 \times 2{\cdot}69) + (6 \times 1{\cdot}39) + (2 \times 5{\cdot}89) = 36{\cdot}3$.

$\theta_E = 1005°$.

Correction factors, $\Delta\theta_{Sn} = 0$. $\Delta\theta_{Pb} = +3°$.

Corrected calculated freezing point, 1008°.

Observed freezing point, 1016°.

Class III.—The Freezing Point Curve becomes nearly Horizontal at Infinite Dilution.

In the systems which we have been considering the liquidus lines are definitely curved, although in dilute solutions they approximate to straight lines. These lines approach the freezing point of the pure solvent at a definite angle, the smallest atomic depression of freezing point being roughly 4° per 1 atomic % for the systems copper-zinc and silver cadmium. There are, however, one or two systems where the depression is very much less.

The first of these is silver-gold, where both metals are univalent, and both solvent and solute have almost exactly the same atomic diameters (2·88 A). In this system the freezing point curve passes continuously from the melting point of silver (961°) to that of gold (1065°).* According to ROBERTS-AUSTEN and KIRKE-ROSE† the gold-rich alloys have freezing points which are almost indistinguishable from those of pure gold, so that the initial depression of freezing point is zero. This has been disputed by RAYDT,‡ but this investigator only examined a very few alloys, so that the evidence is incomplete. In any case, however, the initial depression of freezing point at the gold end of this system is less than 1° per 1 atomic % of silver, whilst the work of HEYCOCK and NEVILLE (*loc. cit.*) shows that the rise of freezing point at the silver end of this system is also less than 1° per 1 atomic %. In our opinion this is a fact of great significance. In the systems copper-silver and copper-gold, the two metals are of the same valency, but of different atomic diameters, and here we have steep falls of freezing point

* The alloys of gold with the B group element are not considered in this paper, but in general they exhibit many of the characteristics of the corresponding alloys of silver.

† 'Chem. News,' vol. 1 (1903).

‡ 'Z. anorg. Chem.,' vol. 75, p. 59 (1912).

at each end of the diagrams, and the same applies to systems like copper-gallium or silver-antimony, where the atomic diameters are almost the same, whilst the valencies are different. But in the one case where both valency and atomic diameter are identical, the initial depression or elevation of freezing point is exceedingly small. This, of course, is completely in agreement with the hypothesis that the equilibrium is a dual one involving an electronic or valency effect on the one hand, and an atomic effect on the other. The same characteristic is rather unexpectedly shown by the system copper-aluminium. As will be seen from fig. 8, the depression of freezing point is abnormally small, the liquidus point of the alloy containing 15 atomic % of aluminium being 1046°, as compared with 980° for an alloy containing 15 atomic % of gallium. Further, as will be seen from fig. 8, the liquidus becomes almost horizontal in dilute solutions, the initial depression of freezing point being less than 1° per 1 atomic %.

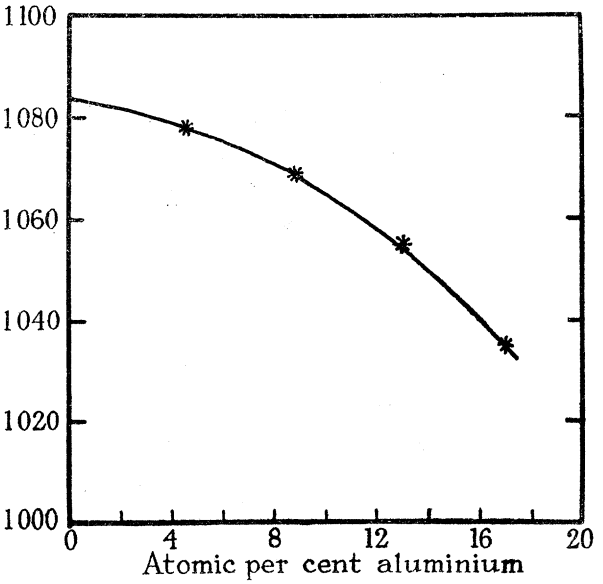

FIG. 8.—The liquidus curve of the system copper-aluminium.

As one of us has shown,* there is considerable evidence that aluminium is univalent in the crystal of the element, and we suggest that this very small depression of freezing point is due to the fact that the aluminium in the molten alloy is also univalent. There is, however, considerable evidence (see p. 37) that the aluminium is trivalent in solid solution in copper. If this be so, we have a case involving an equilibrium between different states of the same atom, and a simple relation is not to be expected. Examination shows that the binary copper-aluminium curve cannot be made to fit the standard equivalent composition curve by means of an arbitrary factor. The ternary system copper-aluminium-tin has been investigated in great detail by STOCKDALE,† whilst the system copper-zinc-aluminium has been studied by CARPENTER and EDWARDS‡

* HUME-ROTHERY, *loc. cit.*

† 'J. Inst. Met.,' vol. 35, p. 181 (1926).

‡ 'Z. Metallk.,' vol. 2, p. 209 (1912).

and by HANSEN and BAUER.* We have made an exhaustive examination of this work, but the methods of calculation previously described are unsuccessful, and we conclude that, as is only to be expected, the methods must not be used where changes of valency, which may be influenced by additional metals, are concerned.

B. *The Solidus Lines.*

The Solidus Curves.—Examination of the equilibrium diagrams shows that *when proceeding along the same horizontal row of the periodic table, the atomic compositions of alloys of a given melting point are approximately inversely proportional to the squares of the valencies of the solute elements.* Since the solidus curves are almost linear, this is equivalent to saying *that the atomic depression of melting point is proportional to the square of the valency of the solute.*

This implies that if we plot the equilibrium diagrams in terms of atomic compositions multiplied by the square of the valency the solidus lines should be superimposed, and, as can be seen from figs. 9 and 10, this is very nearly so. In this diagram the ordinates are temperature, and the abscissæ atomic compositions × (valency)², so that a point,

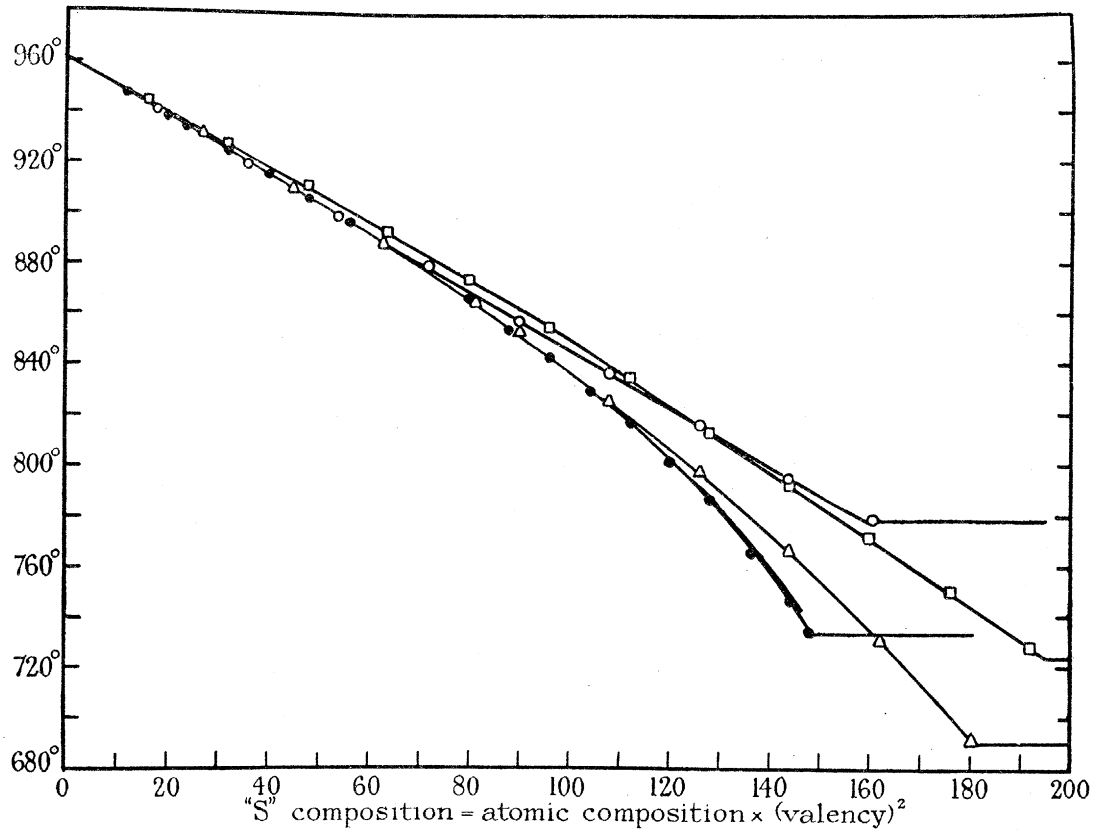

FIG. 9.—Solidus points: ● Ag-Cd with peritectic at 733°; O Ag-Al with peritectic at 779°; Δ Ag-In with peritectic at 690°; □ Ag-Sn with peritectic at 724°.

* 'Z. Metallk.,' vol. 24, p. 73 (1932).

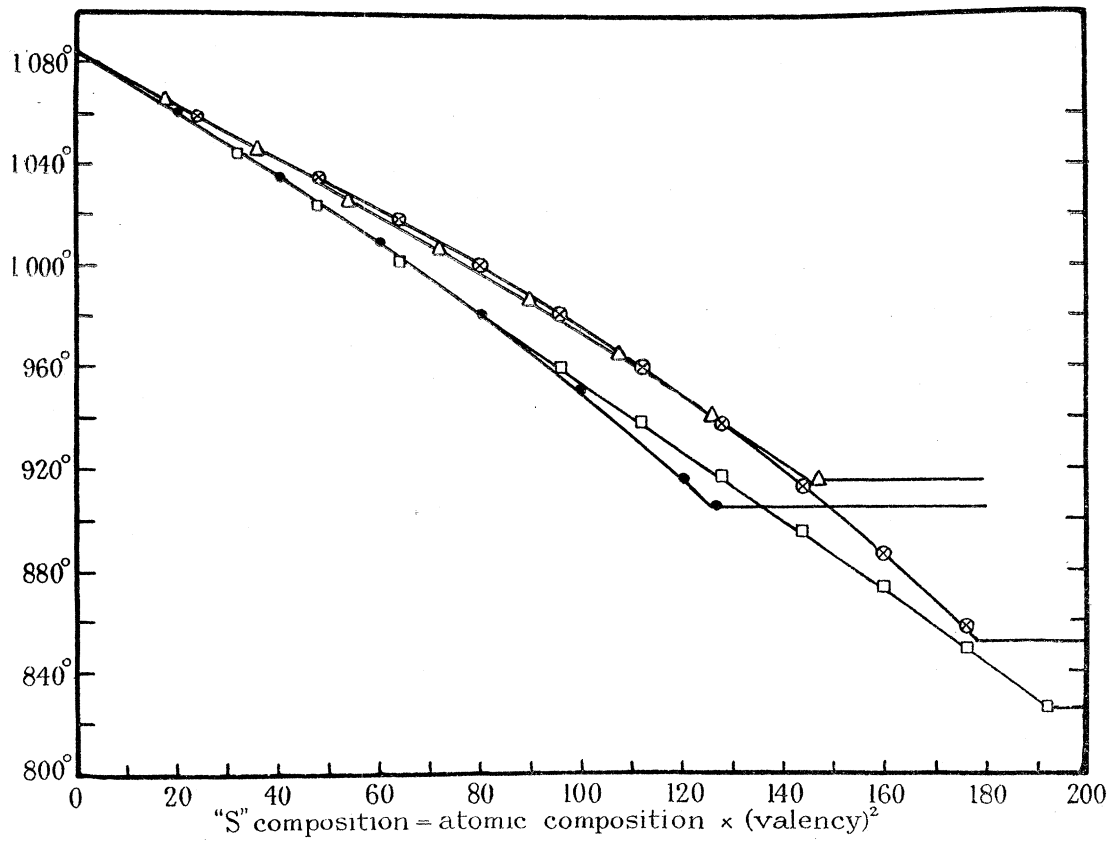

FIG. 10.—Solidus points: ● Cu-Zn with peritectic at 905°; Δ Cu-Ga with peritectic at 914°; □ Cu-Ge with peritectic at 821°; ⊗ Cu-Si with peritectic at 850°.

say, 72, on the " S " composition* scale represents 72/4 = 18 atomic % zinc, 72/9 = 8 atomic % gallium, and 72/16 = 4·5 atomic % germanium. The effect of this is to stretch out very greatly the scale of the 3 and 4 valent elements so that a small difference in composition is greatly magnified. It will be noted that the different lines are not so accurately superimposed as those in the liquidus diagrams, and these differences appear to be closely connected with the relative sizes of the atoms in the crystals of the elements, and the lattice distortion in the solid solution, but as these effects involve a consideration of the effect of co-ordination number we do not deal with them here.

The almost exact agreement of the solidus points with the laws involving the squares of whole numbers again suggests the possibility of their application to ternary or quaternary alloys. We have therefore investigated a few ternary copper alloys, and the results are given in Table XIX. In this Table the first two columns give the percentage composition of the alloys, whilst the third column gives the total " S " composition calculated on the assumption that the solute atoms exert their normal valency effects. Thus in an alloy containing 5 atomic % zinc, and 5 atomic % gallium, the total " S " composition is taken as $(5 \times 2^2) + (5 \times 3^2) = 65$. In this system, since the binary

* The term " S " Composition is used here as an abbreviation for atomic composition × (valency)².

curves do not exactly coincide, we take the theoretical value of the solidus point for the ternary alloy as lying between the two binary curves in fig. 10, at a point which is in proportion to the " S " composition of each constituent. Thus the solidus point for a binary copper-zinc alloy of " S " composition 65, is 1001°, and that for a binary copper-gallium alloy of ionic composition 65 is 1013°, so that the difference is 12°. In the alloy containing 5 atomic % of each element, the ionic compositions of zinc and gallium are 20 and 45 respectively, and we take the theoretical solidus point as being $1001° + 12 \times \frac{45}{65} = 1009°$.

TABLE XIX.

Composition of alloy.						Total " S " composition.	Calculated solidus point.	Quenching temperature and micro-structure.
Weight %.			Atomic %.					
Zn.	Ga.	Ge.	Zn.	Ga.	Ge.		°C.	
8·20	3·75	—	8·02	3·44	—	63·0	1010	1002° homogeneous α. 1013° α + chilled liquid.
4·19	—	5·08	4·11	—	4·50	88·4	969	963° homogeneous α. 973° α + traces of chilled liquid.
9·03	—	4·02	8·85	—	3·56	92·4	962	963° homogeneous α. 968° α + trace of chilled liquid. 973° α + chilled liquid.
—	3·43	4·24	—	3·16	3·76	88·6	975	963° homogeneous α. 973° α + traces of chilled liquid.

As will be seen from the Table the results obtained in this way are satisfactory.

When the solvent and solute are not in the same period the position is more complex and we find that the following general types can be recognized :—

(1) In a few systems where the atomic size factors are favourable the same principles hold and the depression of melting point is again proportional to the square of the valency. Examples of this kind are : copper-silicon, silver-aluminium. The points for these are included in figs. 10 and 11. In the copper series the ionic composition curve for copper-silicon is slightly above the remaining curves, and it is significant that the lattice distortion in the copper-silicon alloys is the smallest of the whole series.*

(2) Where the atomic size factor is unfavourable, the solid solution is very restricted, and the depression of melting point is correspondingly great, and is apparently controlled chiefly by lattice distortion. Such systems include the following, but as the present

* In the copper-silicon alloys the lattice distortion (the increase in α, the side of the unit cube) is about 0·00057 A. per 1 atomic %, as compared with 0·0036 A. per 1 atomic % of germanium.

paper deals essentially with valency effects, we have not considered them in detail, or given the solubility data in the collected tables. The inclusion of the systems silver-thallium and silver-lead in this group is subject to the assumption that the thallium and

silver-beryllium.	silver-thallium.	copper-magnesium.	copper-thallium.
silver-silicon.	silver-lead.	copper-cadmium.	copper-lead.
		copper-mercury.	copper-bismuth.
		copper-indium.	

lead exist in the alloy in the incompletely ionized state in which they exist in the crystals of the elements. In the fully ionized state the atomic diameters would be within the favourable zone for silver, but the stability of the incompletely ionized form is relatively much greater in the third long period, so that the incompletely ionized state may persist in the alloys.

(3) Where the atomic diameters of solvent and solute are near the critical limit, the solidus lines are very sensitive to other factors. In some systems the solidus depression, instead of corresponding to the normal valency effect, is that to be expected from an adjusted valency which is the same as the liquidus factor for the liquidus curve, *e.g.* :—

silver-gallium	normal valency 3,	adjusted valency 4
silver-zinc	,, 2	,, 4

These are not represented graphically, but if reference is made to Table II it will be seen that the solidus of the system silver-gallium is nearly the same as that of the system silver-tin over a wide range. With silver-zinc the initial depression of solidus is almost exactly that of the trivalent silver-indium, although in more concentrated solutions the silver-zinc curve flattens and the solidus points are higher than those in a typical trivalent system.

In other systems the solidus curve is markedly convex towards the axis, so that the initial atomic depression of melting point is much greater than that in more concentrated solid solutions. An example of this kind is the system copper-tin. This type of curve can readily be understood qualitatively if the depression of melting point is due both to an electronic and an atomic factor. Preliminary investigations kindly made by Dr. A. J. Bradley on some of the alloys which we have been examining, appear to indicate that, where the size factors are favourable, the substitution of an atom of higher valency for one of copper produces an expansion of the lattice. In other words, an increase in the ratio of valency electrons to atoms tends to make the lattice expand. Consequently, if an atom such as that of tin is just too large to fit conveniently on to the lattice of copper, the first few atoms of tin may cause a rapid fall in melting point owing to the distortion produced by the atomic factor. But the introduction of the tin atoms increases the ratio of valency electrons to atoms, and this increase will itself cause an expansion of the lattice, so that if anything like a sharp critical atomic size limit exists, the relative part played by the atomic factor will rapidly become less.

Where the solute atom is smaller than that of the solvent (copper or silver), but of higher valency, the atomic and electronic factors will be in opposition, and the resultant effects will depend upon their relative magnitude. Where solvent and solute are in different periods, the two systems, silver-aluminium and copper-silicon, which we have found to behave normally as regards liquidus and solidus depression, are both ones in which, although the size factor is favourable, the solute has a smaller atomic diameter,* but a higher valency than the solvent. Thus the two effects act in opposition, with the result that the lattice distortion is small, and the pure valency effect is left undisturbed.

The full interpretation of these curves will thus require an accurate knowledge of the lattice distortion at high temperatures, and it is hoped to be able to present a study of this later.

The Solid Solubility Curves.

In the preceding sections we have seen how, even for solute elements of favourable size factor, the simple valency relations for the solidus lines are more sensitive to slight variations of atomic diameter and lattice distortion than are the relations for the liquidus curves. For the solid solubility curve where the equilibrium is with a second solid phase, it is only natural that this effect of size factor and lattice distortion should be more prominent. A study of the equilibrium diagrams now reveals the fact that *where the atomic size factors are favourable, the maximum α- solid-solubility, to a first approximation, corresponds to a constant electron concentration.* To a higher degree of accuracy correction factors are required to allow for differences in atomic diameters and lattice distortions. By the electron concentration is meant the ratio of valency electrons to atoms, so that for pure copper or silver the value is 1·0, whilst for an alloy containing x atomic % of a solute element of valency v, the electron concentration is $1 + x\frac{(v-1)}{100}$. Thus for an alloy containing 20 atomic % of aluminium, and 80 atomic % of copper, each 100 atoms of the alloy contain $(20 \times 3) + (80 \times 1) = 140$ valency electrons, and the ratio of valency electrons to atoms is $\frac{140}{100} = 1{\cdot}4 = 1 + \frac{20\,(3-1)}{100}$.

In Table XX we give the maximum solid solubility for the alloy systems of favourable size factor, and for some of those at the edge of the critical size limits. It will be seen that, except for beryllium and mercury, the maximum solid solubility for systems of favourable size factor is for all within 1–2 atomic % of that required to give an electron concentration of about 1·40. In the copper series the maximum electron concentration of 1·42 is given by the copper-silicon alloys, and, as we have already explained, it is in this system that the lattice distortion is the least. For copper and tin the atomic diameters are at the edge of the critical zone, with the result that the maximum solid solubility has fallen to an electron concentration of 1·27. With solvent and solute in the same

* For aluminium the atomic diameter referred to is of course that for the 3-valent state, and is not that taken from the crystal of the element, where the atom is incompletely ionized.

TABLE XX.

Alloy system.	Valency of solute.	Maximum α solid solubility in atomic %.	Electron concentration of maximum solubility.
Copper-beryllium	2	16·6	1·166
Copper-zinc	2	38·4	1·384
Copper-aluminium	3	20·38	1·408
Copper-gallium	3	20·3	1·406
Copper-silicon	4	14·0	1·42
Copper-germanium	4	12·0	1·36
Copper-tin	4	9·26	1·27
Silver-cadmium	2	42·5	1·425
Silver-zinc	2	37·8	1·378
Silver-mercury	2	35·0	1·35
Silver-indium	3	20·0	1·40
Silver-aluminium	3	20·4	1·408
Silver-gallium	3	19·0	1·380
Silver-tin	4	12·2	1·366

period, the 4-valent elements give slightly lower maximum electron concentrations, and are also those which give the greatest lattice distortion per atom of solute. Whilst the effect of the size factor can be seen in a general way, a quantitative comparison will only be possible when the lattice constants are known for the whole series of alloys over a wide range of temperature.

As explained later, we suggest that the maximum solid solubilities in the different systems occur at approximately the same electron concentration because the crystal lattices of the univalent elements silver and copper are founded essentially upon a ratio of one valency electron to one atom, and there is a limit to the extent to which additional electrons can be introduced into the structure. When this limit is exceeded a phase with a new crystal structure is formed, and as one of us originally* showed, this new phase frequently occurs at a composition corresponding to an electron concentration of 1·5, *i.e.*, a ratio of 3 electrons to 2 atoms. WESTGREN† has confirmed our original suggestions that there are many alloys in which these new phases of electron concentration 1·5 have body-centred cubic structures. This, however, is not always so, and close packed hexagonal or β- manganese structures are sometimes found with the ratio of 3 electrons to 2 atoms, particularly when the size factors are favourable, whilst in some alloys (*e.g.*, silver-aluminium, silver-cadmium) there are both high temperature and low temperature modifications each of electron concentration 1·5.

The predominant part played by electron concentration naturally indicates that this principle can be applied to determine the α- solid-solubility limits in ternary or quaternary alloys where the size factors are favourable. For accuracy we have, of course,

* HUME-ROTHERY, 'J. Inst. Met.,' vol. 35, p. 295 (1926).

† 'Metallwirtschaft,' June (1928), *cf.* 'Ann. Rep. Chem. Soc.' (1928), p. 300.

to consider the solubility limit at different temperatures, and for this purpose we have to distinguish between the parts of the equilibrium diagrams in which the solubility decreases with rising temperature from those in which it increases. Since the solubility limit represents the composition at which the solid solution is in equilibrium with a second solid phase, we have to consider the nature of these phases. A survey of the equilibrium diagrams shows that in cases where the solubility first increases, and then decreases with rising temperature, the change in direction of the curve takes place at the temperature of a change or transformation in the second phase with which the α-solid solution is in equilibrium. Thus, in the silver-aluminium series, the α-solubility increases up to 608°, and then diminishes, and 608° is the temperature at which the β-phase, with which the α is in equilibrium, undergoes a transformation. In some systems (*e.g.*, copper-aluminium) the β-phase is stable only above a critical temperature below which it splits up into a mixture of α and a new phase ; in other cases (*e.g.*, silver-aluminium) the β-phase undergoes a polymorphic transformation, whilst in a third class (*e.g.*, copper-zinc) the change is little understood, and involves an evolution of heat, and change of volume, but no change in the type of crystal structure. In some cases (*e.g.*, copper-tin, silver-cadmium) the β-phase may undergo two successive transformations. As regards the solubility limit of the α-phase, it seems probable that there are three types of equilibrium, one in which the solubility increases with rising temperature, one in which it decreases, and one in which it is approximately constant.

The equilibrium in which the solubility decreases with rising temperature appears to be highly characteristic, and in fig. 11 we have plotted the solubility curves of this type for the copper and silver alloys of favourable size factor, and for the copper-tin alloys in which the favourable size limit is nearly reached. The diagram is drawn in terms of electron concentration, so that the concentration 1·36 means $36/1 = 36$ atomic % of a divalent element, $36/2 = 18$ atomic % of a trivalent element, and $36/3 = 12$ atomic % of a tetravalent element. For each alloy system the temperature at the top of the curve is that at which the solubility curve meets the solidus line, and at which the peritectic reaction α + liquid $\rightleftharpoons$ β takes place. The temperature at the bottom of the curve is that at which it changes direction, and, as previously explained, this corresponds to a transformation in the β-phase with which the α is in equilibrium.

For the alloys of favourable size factor it will be seen that the curves differ by an amount equivalent to 1 or 2 atomic % in a total solubility of 38 and 20 atomic % for the divalent and trivalent elements respectively, these differences being due to the atomic factor. For the tetravalent elements this kind of curve is only found in the copper-silicon series over a small range at high temperature, and the conditions are clearly erratic.

The application of these principles to the calculation of solubility limits in ternary alloys may be shown by means of the work of HANSEN and BAUER* on ternary copper-

* Z. Metallk., vol. 24, p. 73 (1932).

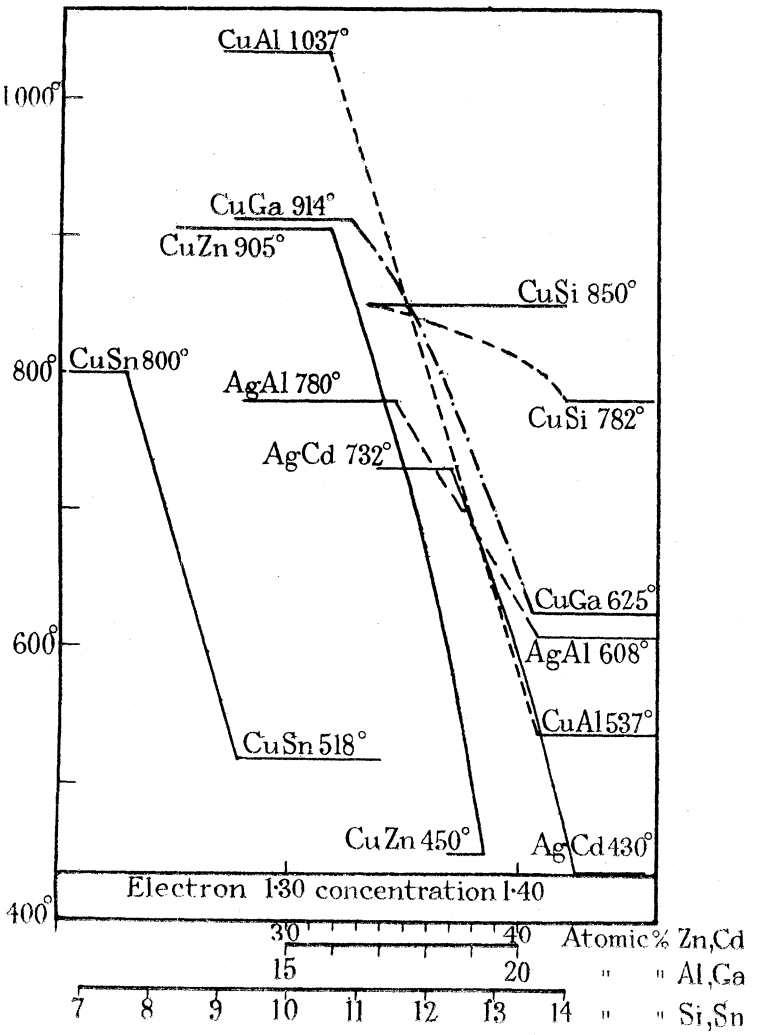

FIG. 11.—In this figure the solid-solubility curves are plotted against the electron concentration for those alloys in which the solubility diminishes with rising temperature.

zinc-aluminium alloys. These investigators did not anneal their alloys for very long periods, but at the higher temperatures their results should be reliable, and we have made the following calculations :—

800° *Solubility Isothermal.*—In copper-zinc alloys the solubility limit at 800° is 33·8 atomic %, giving an electron concentration of 1·338. The corresponding values for the copper-aluminium systems are 18 atomic % and 1·36 respectively. From figs. 14, 15, and 16 of HANSEN and BAUER'S paper, alloys of the following composition lie on the 800° isothermal of the α-solid solution area :—

(1) Cu 71·5%, Zn 26·5%, Al 2%.
Atomic composition = Zn 25·3 atomic %, Al 4·63 atomic %.
Total electron concentration = 1·346.

(2) Cu 77·7%, Zn 18·3%, Al 4%.
Atomic composition = Zn 16·96 atomic %, Al 9·00 atomic %.
Total electron concentration = 1·350.

(3) Cu 83·3%, Zn 10·7%, Al 6%.
Atomic composition = Zn 9·65 atomic %, Al 13·12 atomic %.
Total electron concentration = 1·359.

700° *Solubility Isothermal.*—In the copper-zinc binary alloys the solubility limit is at 35·5 atomic %, giving an electron concentration of 1·355. In the copper-aluminium alloys the corresponding values are 18·9 and 1·378. From the diagrams the following alloys lie on the 700° α solid-solubility isothermal :—

(1) Cu 69·9%, Zn 28·1%, Al 2%.
Atomic composition Zn = 26·8 atomic %, Al 4·63 atomic %.
Total electron concentration = 1·361.

(2) Cu 76·0%, Zn 20·0%, Al 4·0%.
Atomic composition, Zn 18·5 atomic %, Al 9·00 atomic %.
Total electron concentration = 1·365.

(3) Cu 81·6%, Zn 12·4%, Al 6·0%.
Atomic composition, Zn 11·2 atomic %, Al 13·12 atomic %.
Total electron concentration = 1·374.

It will be seen that the electron concentrations of the ternary alloys at the solubility limits are approximately constant at any one temperature, and that at each temperature their exact values move systematically from those of the binary copper-zinc alloys to those of the binary copper-aluminium alloys as the percentage of aluminium increases. This implies that we have in effect a method for calculating the solubility limits of ternary alloys in this kind of equilibrium, since the small difference between the curves for the divalent and trivalent alloys can readily be allowed for by an empirical correction term such as we have used for the solidus calculations on p. 34. The equilibrium is essentially an electron concentration equilibrium, as was suggested by BERNAL,* and in some ways resembles the results of BRADLEY and GREGORY,† who found that in the complex "γ-phases" the characteristic "γ" structure occurred in ternary copper-zinc-aluminium alloys as long as the ratio of electrons to atoms was maintained at 21 : 13.

In fig. 11 it will be noted that, although in the system copper-tin the difference in atomic diameters has reduced the solubility considerably, the solubility curve is still almost parallel to the curves for the copper-zinc and copper-aluminium alloys. This naturally suggests that the atomic factor enters the equilibrium in the form of a simple multiplying

* 'Trans. Faraday Soc.,' vol. 25, p. 376 (1929).
† 'Mem. Manch. Phil. Soc.,' vol. 72, p. 91 (1927–8).

term, and it is desirable to see whether this same term can be used for ternary alloys. As we have already explained, the electron concentration is given by the expression

$$1 + \frac{x\,(v-1)}{100},$$

where x is the atomic % of solute element of valency v. The normal valency of tin is 4, and, as can be seen from fig. 11, the difference in size factors prevents the solubility from reaching its normal value. The copper-tin curve can, however, be made to coincide with that for copper-aluminium by assuming tin to have an adjusted valency of 5·7, which, it will be noted, is very nearly equal to the liquidus factor of 6 which we deduced from the liquidus curves. If now this same factor can be shown to give the solubility limits in ternary copper-aluminium-tin alloys we shall have what is practically a method for deducing the ternary solid solubility limits from the binary curves even where the atomic size factors are no longer favourable. The ternary system copper-aluminium-tin has been investigated in detail by STOCKDALE,* and, although the annealing times were not as long as is now considered desirable, the results are probably substantially correct at the higher temperatures in which the α-solid-solubility diminishes with temperature. The method of calculation may be illustrated by considering an alloy containing 13·26 atomic % of aluminium, and 1·51 atomic % of tin, which STOCKDALE'S results show to lie on the α-solubility surface at 875°.

If the tin acts as though it possessed the adjusted valency of 5·7, which we have deduced from a study of the binary Cu–Sn curve, the total " adjusted electron concentration " of the alloy may be written as

$$1 + \frac{13{\cdot}26 \times (3-1)}{100} + \frac{1{\cdot}51 \times (5{\cdot}7-1)}{100} = 1{\cdot}336.$$

In the copper-aluminium alloys the solubility limit at 875° is 17·2 atomic % of aluminium, which gives an electron concentration of

$$1 + \frac{17{\cdot}2 \times (3-1)}{100} = 1{\cdot}344.$$

The difference between the two values 1·336 and 1·344 is 0·008, which is equivalent to 0·4 atomic % of aluminium or 0·17 atomic % of tin. In this way we have made the calculations shown in Table XXI, and it will be seen that the method permits the calculation of the ternary solubility surface to within an accuracy of 0·5 atomic % aluminium, or 0·2 atomic % of tin. The solubility limits predicted by this method are slightly greater than those given in STOCKDALE'S paper, and part of this difference may be the result of insufficient annealing.

In fig. 12 we have drawn the low temperature portions of the solubility curves for the different systems in terms of electron concentration. From this it will be seen that,

* ' J. Inst. Met.,' vol. 35, p. 181 (1926).

TABLE XXI.

Composition of alloy.				Temperature of solubility limit.	Total "adjusted electron concentration" of ternary alloy.	Electron concentration of solubility limit in binary copper-aluminium alloy at the same temperature.
Weight %.		Atomic %.				
Al.	Sn.	Al.	Sn.			
7	3	15·28	1·49	660°*	1·376	1·386
6	3	13·26	1·51	875	1·336	1·344
5·78	5	12·92	2·54	650	1·378	1·388
5	5	11·29	2·56	822	1·346	1·355
4	7	9·23	3·67	765	1·357	1·367

* For this alloy, the smooth curve in the diagram gives the solubility limit as beginning at 660°, whilst the tables state that the alloy contained a trace of the β constituent at 660°.

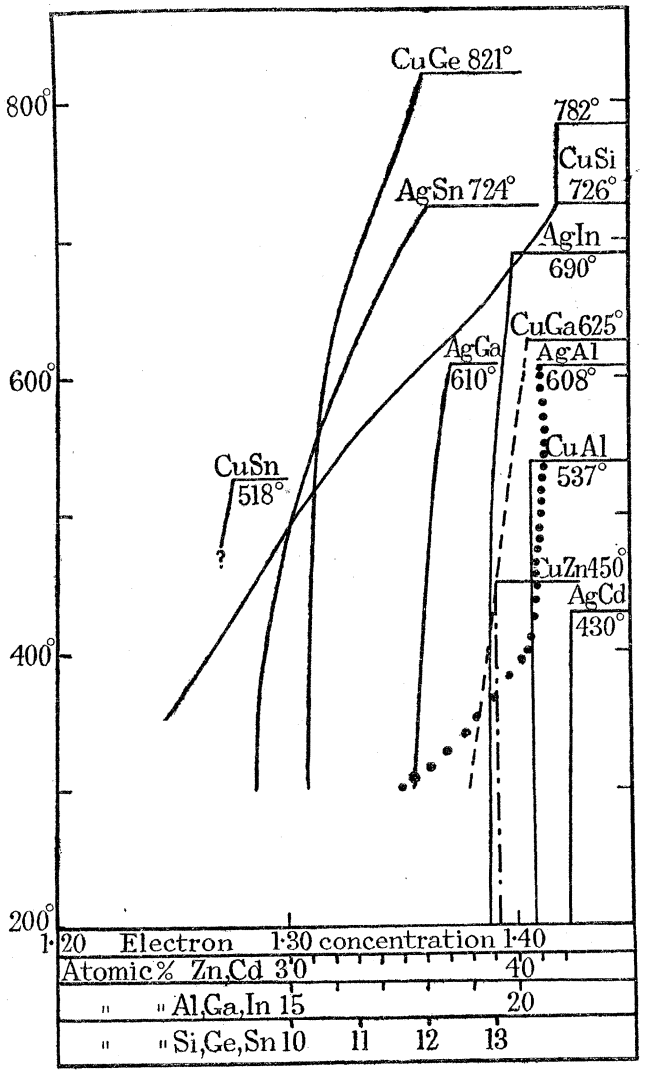

FIG. 12.

where the atomic size factors are favourable, the curves are essentially of the same nature as regards the maximum electron concentration, but there are characteristic deviations which are due to differences in the phases with which the α-solid-solution is in equilibrium. Generally speaking, the more electronegative the solute element, the greater is the tendency for the formation of stable intermediate compounds at the expense of the α-solution, and it is for this reason that in systems such as copper-arsenic, or copper-selenium, the α-solid-solution is very restricted in spite of the fact that the atomic size factors are favourable. This tendency which may be called the "electronegative valency effect," is probably the cause of the rapid diminution of the solubility limit in the copper-silicon alloys at low temperatures, since silicon is the most electronegative of the tetravalent elements.

At present there do not appear to be any accurate determinations of ternary diagrams at the lower temperatures by means of which a critical test can be made, but the general application of the preceding electron concentration methods of calculations with appropriate correction terms is obvious.

We may further suggest that it is this electron concentration principle which forms the real justification for the original views of GUILLET* concerning the "zinc equivalents" of different elements in complex brasses. As shown by BAUER and HANSEN,† this theory in its original form is not in agreement with the facts at true equilibrium, and the "zinc equivalent coefficients" which GUILLET determined from cast alloys have little real significance. But when translated from weight percentages into electron concentrations, the idea of GUILLET is essentially true for elements of favourable size factor.

The above methods of calculation are, of course, semi-empirical so far as they depend upon correction factors deduced from the binary curves, but, even so, it is hoped that they may be of value in determining some of the solubility limits of complex alloys of copper and silver. For if it can be shown that the solubility limits of a few suitably chosen alloys in a particular ternary or quaternary system agree with the above kind of calculation, the method may reasonably be used for intermediate alloys until a theory has been developed which takes into account both the electron concentration and the atomic size factor.

DISCUSSION.

From the preceding sections it seems clear that the fundamental valency relations are shown only when the atomic size factors are favourable, and, particularly, when the solvent and solute are in the same period. In such conditions we have the three main principles :—

(1) The atomic compositions of alloys of a given freezing point are inversely proportional to the valency of the solute.

* 'Rev. Met.,' vol. 2, p. 97 (1905); vol. 3, p. 243 (1906).

† 'Z. Metallk.,' vol. 5–6 (1929).

(2) The atomic compositions of alloys of a given melting point are approximately inversely proportional to the square of the valency of the solute.

(3) The maximum solubility of the α-solid-solution, and the part of the solubility curve in which the solubility diminishes with temperature, are determined mainly by the electron concentration.

To a higher degree of accuracy all these relations require slight correction factors to allow for the difference in atomic diameters, and the lattice distortion, these corrections becoming more important as we pass from the liquidus to the solidus, and then to the solubility curve.

As previously explained, we suggest that the third relation indicates that the lattices of copper and silver are built up essentially on a ratio of one valency electron to one atom, and that there is a limit to the extent to which additional electrons can be introduced. We may note that this also explains why the solid-solubility process is not necessarily reciprocal. In a system such as copper-silicon, for example, the element silicon crystallizes in the diamond type of structure in which each atom has four close neighbours. Here the structure depends upon a ratio of four valency electrons to one atom, every atom taking four neighbours, and sharing one of its electrons with each to form simple co-valent bonds. If an atom of silicon is replaced by one of copper, which has only one valency electron, there will be insufficient electrons to form the co-valent bonds, and we shall expect the solid solubility to be very small. But there is not the same objection to having a slight excess of electrons, and so we can understand how tetravalent silicon atoms can be taken up by the copper lattice to a certain extent. This principle, which may be called the "relative valency effect," has already been noted by BERNAL in connexion with "γ-phases" of copper, silver, and gold alloys which obey the valency rule.*

The freezing point and melting point relations are more difficult to explain. JEFFERY† has attempted to apply the principles of thermodynamics to liquidus-solidus equilibria, and also to the equilibrium between a saturated solid solution and the second solid phase with which it is in equilibrium at the temperatures where the whole alloy is solid. JEFFERY uses a simplified form of the VAN'T HOFF equation connecting the compositions of phases in equilibrium with the latent heats of fusion or solution. He then makes different assumptions concerning the condition of the solute element in the various phases, *e.g.*, whether present as monatomic molecules, diatomic molecules, or compound molecules of particular formulæ, and finds which assumptions give the best agreement with experiment. Taken as a whole his results show that in

* The "γ-phases" have formulæ such as Cu_5Zn_8, Cu_9Al_4, and are based on a ratio of 21 valency electrons to 13 atoms. They do not form appreciable solid solutions on the copper-side of the 21 : 13 ratio, but do form solid solutions with slightly more zinc, aluminium, etc. See BERNAL, 'Trans. Faraday Society,' vol. 25, p. 376 (1929), and 'Ann. Rep. Chem. Soc.,' p. 294 (1931),

† 'Trans. Faraday Soc.,' vol. 26, p. 86 (1930).

systems where the equilibrium diagram is simple (*e.g.*, silver-copper, lead-tin) the equations indicate that the solute is present in the form of single atoms, and this is in agreement with the X-ray evidence that primary solid solutions are formed by the substitution of one atom for the other. In the class of alloy which we have been considering the position is more complicated and some of the conclusions are improbable. Thus in copper-tin alloys it is necessary to assume that the tin exists as Cu_4Sn molecules in the liquid phase, and that these molecules exist as such in the α-solid-solution, but that the β-solid-solution contains monatomic tin in an allotropic form of monatomic copper.

It is well known that the VAN'T HOFF equation can be written in the form

$$\Delta\theta = \frac{R\theta_0^2}{L} \cdot \frac{C_L - C_S}{C_L},$$

where $\Delta\theta$ is the depression of freezing point produced by 1 molecule per kg. of solvent, and θ_0 is the freezing point of the solvent, L its heat of fusion per kg., and C_L and C_S the concentration of liquid and solid which exist in equilibrium in a dilute solution.

We have applied this equation to the liquidus and solidus lines of our copper alloys, and find that the results for latent heats of fusion are variable.

We suggest that these discrepancies are due to the existence of equilibria involving both electronic and atomic factors. The equations involving the terms $R\theta_0^2$ are valid only for systems which obey the classical gas laws, whereas the electrons will form a degenerate system to which the classical laws cannot be applied, and the complete equilibrium will be explained only by the application of the quantum statistics to partly degenerate systems. It does not seem probable, however, that thermodynamics alone will lead to an explanation of the valency relations unless additional assumptions are made, and the following general line of approach is suggested tentatively.

In the gaseous state of matter the atoms are free to move in three dimensions, whilst in the solid state this freedom is lost and they can only oscillate about fixed centres. Between these two extremes we have the liquid and liquid-crystal states. In the latter the atoms (or molecules) are regarded as being partly restrained, but free to move in one or more dimensions. For the liquid state the condition is less certain, but there is increasing evidence, from magnetic and other properties, that some kind of a structure exists.* We may assume, therefore, that in molten silver or copper there is still some kind of a structure, and that this depends essentially on a ratio of one valency electron to one atom. We assume further that when the size factors are favourable, and particularly when solvent and solute are in the same period, the atomic factors are negligible, and the essential cause of changes in freezing point, melting point, solubility limit,

* We have to thank Mr. J. D. BERNAL for much information on this point. The structures to which we refer are quite distinct from the existence of seed crystals in the liquid just above the melting point which have been shown to occur for bismuth and a few other metals.

etc., is the introduction of electrons above the ratio of one electron to one atom. Thus we can at once understand why the freezing point depression is so very small in the system silver-gold, where the valency is the same, and the atomic diameters almost identical. It is clear that the freezing point depression is not a simple function of the excess electrons alone, for then the same depression of freezing point should be produced by the introduction of the same number of extra electrons. This would require one atom of tin to be equivalent to three atoms of cadmium in the silver alloys, whereas the actual proportionality factor is two. This suggests that the effect of the metal ions must also be taken into account, but here again we can understand why the freezing point depression is so small in the system silver-gold where the ions have the same charge.

If the above general idea is accepted, there will be two extremes in this kind of equilibrium. Where the atomic size factors are markedly unfavourable, the atomic factor is predominant, and the classical methods may be applied as in the work of JEFFERY. At the other extreme, when the atomic size factors are favourable, and the solvent and solute are in the same period, the equilibrium is essentially electronic and ionic, and the classical equations require modification* to allow for the fact that the electrons form a degenerate system. In between these extremes are systems such as copper-tin and silver-gallium, where the size factors are near the critical limit, and the whole position becomes more confused. The fact that in these and other systems the experimental work leads to the conception of liquidus and solidus factors which are whole numbers suggests clearly that there is some kind of electronic quantum equilibrium. It is this fact which makes us consider a purely *ionic* explanation to be improbable. An assumption that the depression of the freezing point was proportional to the repulsion between an ion of the solvent and one of the solute, and the depression of the melting point proportional to the repulsion between two solute ions would account for the relations in the periods, but would give no reason for the whole number factors in other relations. An electronic explanation, on the other hand, does not suffer from this disadvantage, since the electrons in different atoms are in different energy states.

It may be noted that, since this work was finished, a paper has appeared by LINDE,† in which it is shown that with silver as solvent, the increase in electrical resistance caused by 1 atomic % of cadmium, indium . . ., etc., in solid solution is proportional to $(v - 1)^2$, where v is the valency of the solute, thus giving further evidence for the existence of simple valency relations in this type of alloy.

* We would emphasize here that the application of the older thermodynamical equations to metallic equilibria is much more complicated than is assumed by many writers. Apart from the fact that the electrons will form a degenerate system, the existence of contact potentials between different phases may require the introduction of terms for electrical work done in the various cycles which are assumed.

† 'Ann. Physik.,' vol. 10, p. 52 (1931); vol. 14, p. 353 (1932).

PART II.—EXPERIMENTAL.

General Methods.

For the more common metals the ordinary methods of preparation, annealing, microscopic examination, etc., could be used, but with the alloys of the rare metals gallium, germanium, and indium only very small quantities were available, and a special technique had to be developed.

These alloys were prepared in quantities of about 3 grams in miniature salamander crucibles, usually lined with alundum cement. These were heated in a small electric crucible furnace in an atmosphere of nitrogen.* The two metals were usually melted together under a thick layer of powdered charcoal, but in some of the earlier experiments the copper or silver was melted first and the second metal then added. The alloy was then well stirred with a preheated fireclay rod, the preheating being essential with the small quantities concerned. The copper alloys were then quickly cast into a $\frac{1}{4}$-inch diameter mould bored in a heavy copper block. This gave very rapid cooling and a correspondingly fine microstructure. The small crucibles cooled rapidly on removal from the furnace, so that the whole operation had to be carried out in a few seconds, and, if this was done successfully, the alloy was obtained in the form of a small cylinder about $\frac{1}{2}$ inch long by $\frac{1}{4}$ inch diameter. If the directing of the molten metal was inaccurate, part or all of the alloy solidified as an irregular lump on the top of the copper mould, but even here the cooling was sufficiently rapid for a fine structure to be obtained. Since silver alloys show a tendency to inverse segregation, the alloys of this metal were cast in $\frac{1}{4}$-inch diameter sand moulds.

* In a few of the earlier experiments the nitrogen was omitted.

In order to avoid undue loss in the form of filings, the alloys were cut up with fine jewellers' saws mounted in a lathe. They were then sealed in partially evacuated hard glass tubes, and were heated in an electric resistance tube furnace controlled by a Foster Temperature-Regulator. The fluctuations in temperature were greatly reduced by placing the regulating thermocouple against the wall of the tube furnace, and then fixing a second silica tube in the furnace, the space between the silica tube and the furnace being partly lagged up with asbestos wool. The sealed tube containing the specimen was then placed inside the second silica tube, and the whole packed with asbestos wool, the temperature of the specimens being measured with an alumel-chromel thermocouple, the sheath of which was in contact with the specimen tube. In this way, as in the Haughton-Hanson thermostat, the gap between the inner tube and the furnace wall served to protect the specimen from the usual "temperature hunting." As finally arranged, the accuracy of the temperature control was of the order $\pm 2^\circ$ at 500° C., decreasing to $\pm 4^\circ$ at 800° C., for long periods, although for short periods, as in the determination of solidus points, an accuracy of $\pm 1^\circ$ could be obtained at 800° by suitable adjustment of the resistances. In the early part of the work, on the copper-germanium and copper-gallium alloys, however, the accuracy was not so good, and fluctuations of the order 1% of the temperature occurred, but fortunately, the solubility lines concerned are so nearly vertical that the temperature fluctuations are within the limits of accuracy with which the compositions could be determined.

Temperature Fluctuations in the Furnace.—The annealing furnace was 19 inches long, and for 3 inches at each end the winding was slightly more closely spaced than over the middle portion, in order to counteract the end cooling effect. With from 3 inches to 4 inches of asbestos lagging at each end of the inner furnace tube, the middle part was at a satisfactorily constant temperature, but at temperatures of 800° a somewhat sharp drop of 5° or even 10° was sometimes found over the 1 or 2 inches nearest the lagging at each end. This meant that, in order to obtain the best results, the specimen tube had to be in the middle of the furnace, and not pushed into the furnace from one end until it touched the lagging at the far end. This particular source of error was only discovered during the work on the copper-gallium and copper-germanium alloys, and was guarded against in all the later experiments. Fortunately, nearly all the earlier experiments were at the lower temperatures, so that it is unlikely that appreciable errors have been introduced in this way.

The Solidus Experiments.—Some of the solidus quenching experiments were carried out in the automatically controlled furnace, whilst for others hand control was used. The alloy was always kept at the quenching temperature for 30 minutes, and was then quenched in water. The accuracy of the temperature control varied with the exact adjustment of the resistances, and the deviation from the mean temperature was of the order $\pm 1^\circ$ C. in a good experiment, and $\pm 4^\circ$ C. in a very bad one. That the period of 30 minutes was sufficient to ensure true equilibrium was shown by annealing

a sample just above the solidus temperature and then quenching it, when the micro examination showed the presence of chilled liquid. On re-annealing this alloy for 30 minutes just below the solidus temperature, the chilled liquid was entirely absorbed, and the alloy became homogeneous.

The Liquidus Experiments.—Where too little of the rare metal existed for a cooling curve to be taken, points on the liquidus were determined by a quenching method. For this purpose small portions of the alloy were wrapped in covers of alundum cement. After drying the cement, the pellet was sealed in a partially evacuated tube, and quenched after heating for 30 minutes at a constant temperature. A complete section was then cut and examined microscopically after polishing and etching. If quenched from above the liquidus point, the alloy would show only a fine structure of chilled liquid, whilst if quenched from below the liquidus point, the structure consisted of coarse crystals of the α-solid-solution embedded in the much finer chilled liquid. Such specimens were always analysed after the high temperature anneals. The method has obvious limitations, but, with non-volatile metals, it enables liquidus points to be determined to a fair degree of accuracy with very small quantities of material.

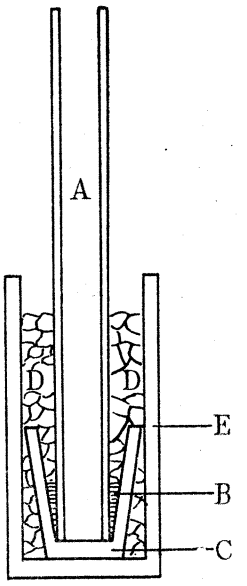

FIG. 13.—Apparatus for taking Cooling Curves. A, $\frac{3}{8}$-inch silica tube; B, alundum cement; C, inner salamander crucible; D, charcoal packing; E, outer fireclay crucible.

Wherever possible, cooling curves were taken in the apparatus shown in fig. 13. The inside of the $\frac{3}{8}$-inch diameter silica tube was coated with alundum cement, and embedded in alundum cement in a small crucible, which was placed in a much larger crucible filled with charcoal. The whole was then heated in an electric crucible furnace, and the alloy, which was melted under charcoal or borax, was thoroughly stirred with a silica rod. The thermocouple of 30 S.W.G. wire in a thin silica sheath was then lowered, and the cooling curve taken with a current still running through the furnace, so that the rate of cooling at the arrest point was from 3° to 8° per minute. With this apparatus it was possible to obtain sharp and reproducible arrest points with from 4 to 10 grams of alloy, provided that the rate of cooling was slow and regular, and that supercooling was prevented.*

In view of the small size of the cooling curve ingots, a thin and sensitive thermocouple was essential, and specially drawn 30 S.W.G. alumel-chromel wires were used. Below the melting point of silver (961°) these were very satisfactory, but at higher temperatures they underwent slight changes. When sealed off, a thermocouple would generally last for about four or five cooling curves above 1000°, and would

* Attempts to prevent supercooling by stirring with the thermocouple sheath were unsatisfactory, because, with the small quantities of the alloys, the stirring caused temperature fluctuations. Supercooling could generally be prevented by tapping the furnace, but in one experiment this was unsuccessful, and the curve was repeated.

then break. The brittle portions of the wires were then cut off and the wires again fused, so that one long thermocouple could be used for a long time without having to remake the cold junctions. The first thermocouple showed a slow and progressive change of roughly 1° C. for each time it was heated above 1000° C., the electromotive force at the silver point rising slowly from 38·2 to 38·7 millivolts. The reason for this is unknown, but it may have been due to a slow ageing process at the cold junction, since the second thermocouple made from the same batch of wire had an initial value of 38·8 for the silver point, which slowly rose to 39·15.

It was not considered advisable to standardize these thermocouples against the melting point of copper, because heating to this high temperature not only greatly shortened the life of the thin wires, but also tended to change the electromotive force during the actual calibration. For the high temperature curves the thermocouples were, therefore, re-calibrated against the freezing point of silver after every one, two, or three experiments. Other standard points used were those of the silver-copper eutectic (778°), aluminium (658°), and zinc (419°), whilst two thermocouples were standardized against the freezing point of copper (1084°) in order to obtain the temperature factor (*i.e.*, the average number of degrees per millivolt) between the silver and copper points. The temperature factors increased with rising temperature so that the temperature-e.m.f. relation was really a curve, but the degree of curvature was so slight that it could be ignored for the region near to a calibration point, and the temperatures calculated from the temperature factor between two calibration points.

For the whole range of the three thermocouples used the extreme values for the silver point were 38·2 and 39·15, whilst the temperature factors between 778° and 961° varied from 26·2 and 25·3. If, therefore, in this range we had assumed a constant temperature factor of 26·2, we should have introduced a maximum error of roughly 1° for each 25° from a calibration point. The actual error was much less than this, because the changes in the temperature factors ran roughly parallel to the changes in the calibration points, and could be allowed for in this way. The policy of checking the thermocouple against the freezing point of silver naturally meant that the possible error increased as the measured temperature differed from the silver point. On reviewing the data, and comparing the values with those of other alumel-chromel thermocouples, we conclude that below 1000° the calibration errors are negligible, and that it is only above 1040° that they may exceed 3° in a few of the earliest experiments, and, wherever possible, these have been tested by later work.

Etching Methods.—In general the pieces of alloy could be ground down by hand, but where they were very small they were mounted in Bakelite cement, which was hardened by heating in a steam oven.

The structures of the copper alloys quenched from the higher temperatures were readily revealed by a number of reagents, and it was only where slight precipitation of one constituent had occurred at low temperatures in a much twinned alloy that any difficulty was encountered. The most suitable reagent was found to be a mixture

of ammonia and hydrogen peroxide used either directly or by means of polish attack.

The silver alloys were more difficult to etch, particularly when homogeneous, or when containing only traces of a second constituent. For two-phase alloys, satisfactory results were obtained by a dilute freshly-prepared solution of chromic and sulphuric acids, but this did not always reveal traces of chilled liquid or of a second constituent. In these alloys the best results were obtained by first etching them in more concentrated chromic-sulphuric acid so as to form a deposit of silver chromate, which was wiped off with cotton wool. The specimen was then very lightly polished, dipped for one second in the dilute chromic-sulphuric acid, and then washed and immersed in a solution of ammonia and hydrogen peroxide. This reagent appears very suitable for revealing the presence of chilled liquid, but sometimes does not seem sufficiently powerful to remove the surface layer produced by polishing.

The microstructures of all the homogeneous alloys investigated consisted of the typical twinned α-solid-solution of silver or copper. Alloys just within the two-phase area showed the second constituent present in the grain boundaries and corners, whilst alloys well within the two-phase area showed structures of the $\alpha\beta$-brass or $\alpha\beta$-silver-aluminium type. As all these structures are quite typical we have not thought it necessary to reproduce photomicrographs.

Materials used.—In the work on the silver alloys the silver used was granulated metal of 99·95% purity, supplied by Messrs. Johnson, Matthey & Co., Ltd., whilst for the copper alloys the metal was best quality electrolytic copper, supplied by Messrs. Hopkin & Williams, Ltd.

Analysis of Alloys.—Unless otherwise stated, the analytical work was carried out by Mr. R. G. Johnston, of the Midland Laboratory Guild, Ltd., Birmingham, and by his chief assistant, Miss U. F. Willis, and the experimental details are given in the individual sections. With the alloys of the rare metals the amounts available were in general too small to enable duplicate determinations to be made, and a complete analysis of both constituents was therefore carried out. The percentages of the constituents thus determined added up very satisfactorily, and suggested that the analytical technique was of the highest order.

The experimental methods detailed above have been developed over a period of five years, during which the accuracy has been greatly increased, and when possible we have endeavoured to confirm the results of the early work. For the liquidus and solidus points we think that the most accurate results have been obtained for the silver alloys and for the ternary copper alloys. For the solubility curves we hope that the results above 500° are substantially correct. The determination of the solubility curve below 350° is the least certain, because the microscopic method is not well suited for the detection of slight precipitation of a second constituent unless a wide area can be examined, and, with the rare metals, we have often had to work with pieces of about 3–4 mm. We hope it may be possible to check these results later by means of X-ray measurements.

Unless the weight percentage composition is expressly stated, all alloys are referred to by their atomic compositions.

Silver-Cadmium.

Previous Work.—The system silver-cadmium was first investigated by PETRENKO and FEDEROW,* who gave the temperature of the peritectic horizontal (corresponding to the reaction α + liquid $\rightleftharpoons$ β) as 722° to 724°. More recently FRAENKEL and WOLF† have investigated the part of the diagram surrounding the β-phase. Their diagram gives the peritectic horizontal as lying at about 730° to 740°, and shows that the β-phase undergoes two transformations which, as regards their equilibrium with the α-phase, take place at 430° and 211° respectively.

Materials used.—The cadmium used in the present work was kindly presented by the Metropolitan-Vickers Electrical Company, Ltd., and we must express our thanks to Dr. G. MCKERROW for his interest in this connexion. The metal was described as being of 99·95% purity with traces of oxide.

Experimental Methods.—For the determination of the solidus line and solubility limits, alloys were very kindly prepared from the above metals by the British Non-Ferrous Metals Research Association.

For this purpose an approximately 50% alloy was first cast and then used for the preparation of $\frac{1}{4}$-inch diameter sand castings. We must express our very warm thanks to Dr. O. F. HUDSON for his help in this matter, as his experience of casting alloys of volatile metals to the desired composition has saved us a great deal of time and trouble. Experiment showed that, on annealing at the higher temperatures in partially evacuated tubes, cadmium was lost in amounts which varied from a few tenths per cent to as much as 1·5%, and for this reason it was essential to analyse the specimens after they had been annealed. The solubility curve is such that the limit of the α-solid-solution reaches a maximum at 430°, and diminishes with rising temperature. The alloys were, therefore, first given a preliminary anneal of 12 days at 430° in order to remove the bulk of the cored structure without appreciable loss of cadmium. They were then hammered, and re-annealed at the higher temperatures for times which varied from 4 days at 500° to 24 hours at 705°. Since the solubility curve bends backwards above 430°, one analysis after the high temperature anneal was sometimes sufficient. If, for example, an alloy was found to be homogeneous and to contain x% of cadmium after quenching from 600° C., but to be two-phase after quenching from 625° C., a second analysis was not always considered necessary. For the higher temperature would result in a slightly greater loss of cadmium, so that if the alloy which actually contained a little less than x% of cadmium at 625° C. was in the two-phase region, then *a fortiori* the alloy containing x% of cadmium would have exceeded the α-solid-solubility

* 'Z. anorg. Chem.,' vol. 70, p. 157 (1910).

† 'Z. anorg. Chem.,' vol. 189, p 145 (1930).

limit. This procedure was, of course, only justified if the preliminary annealing treatments were the same, and if the temperatures of the second anneals were reasonably close together.

For the determination of the liquidus, cooling curves were taken, using about 40 grams of alloy for each experiment. The alloys were prepared under a very thick layer of fused borax in crucibles lined with alundum cement, and placed inside a larger crucible, the space between the two being filled with charcoal and the whole heated in an electric crucible furnace fed with nitrogen. The borax was first fused, and lumps of the 50% cadmium alloy and of pure silver added alternately, so that unnecessary overheating of the furnace was prevented. After thorough stirring, the thermocouple, in a thin silica sheath, was inserted and the cooling curve taken, the rate of cooling at the liquidus point being from 4·5° to 6° per minute. As soon as the arrest was noted, the current was switched off, and the furnace opened in order to complete the cooling as quickly as possible. Under these conditions the loss of cadmium was comparatively slight, and very little can have occurred after the solidification began. The determination of the exact composition of the cooling curve ingot was, however, not easy, since the slow cooling sometimes gave rise to segregation effects. The policy finally adopted was to cut two complete vertical sections of the ingot. One of these was analysed for both cadmium and silver in order to ensure that no contamination or oxidation had occurred,* whilst the other was analysed for silver only, and the cadmium determined by difference. In five ingots the two values for the cadmium content agreed within 0·35%, and the mean values were taken. In four others, however, the two values differed by more than 0·5%,† and here additional analyses were carried out, using as large a portion of the ingot as was available. The mean cadmium content was then obtained by adding together the total quantity of alloy used in all the determinations, and dividing this into the total weight of cadmium found. The segregation difficulties were greatest for the first two alloys in Table XXII, and the compositions given may be a few tenths per cent too high, the mean compositions by analysis being greater than the intended compositions.

Analysis.—For the analysis the silver was determined as chloride, and the cadmium by electrolysis in oxalate solution. Twenty-three complete analyses were made, and the extreme values for the sum of the percentages of silver and cadmium were 99·80 and 100·12, except in one where an accident occurred.

Experimental Results.

The results of the liquidus determinations are given in Table XXII and are plotted in fig. 14, together with the points obtained by PETRENKO. For the silver rich alloys the values from the two determinations are indistinguishable, but for alloys

* The extreme values for the sum of the direct figures for silver and cadmium were 99·87 and 100·08.

† The extreme variation was 1·1%.

containing more than 25 atomic % of cadmium, the present figures are about 10° higher than those of PETRENKO. If a smooth curve is drawn through the present liquidus values, it cuts the 733° peritectic horizontal, at a composition of 45 atomic % cadmium. PETRENKO's values for this point were 44 atomic % of cadmium and 722° whilst according to the diagram of FRAENKEL and WOLF (*loc. cit.*) the point is at about 44·2 atomic % of cadmium, and between 730° and 740°, so that the agreement is satisfactory.

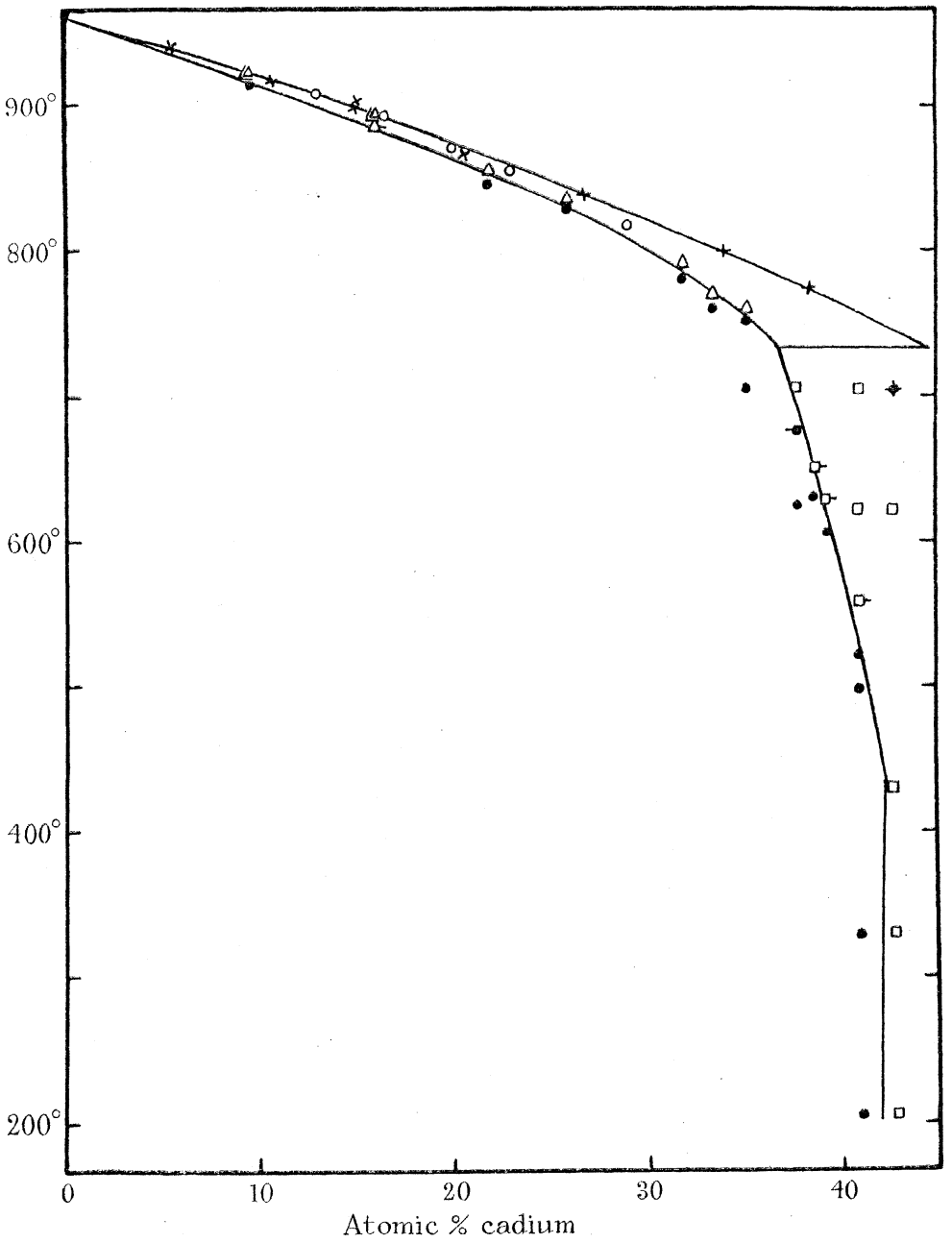

FIG. 14.—Silver-Cadium. × points from cooling curves, authors; ○ points from cooling curves, PETRENKO; ● homogeneous α; ◿ α + much liquid; △ α + liquid; △- α + traces of liquid; □ α + β; □- α + trace of β; -◆- Homogeneous β.

TABLE XXII.—Liquidus Points.

Composition of alloy.		Liquidus point.
Weight % Cd.	Atomic % Cd.	
5·79	5·57	941°*
5·78	5·56	940
11·16	10·8	914
15·62	15·1	902
15·52	15·0	896
21·33	20·65	863‡
27·59	26·8	839
34·92	34·0	799
39·46	38·5	773†

* This alloy weighed only 25 gm. and the thermocouple sheath was at the side of a rather shallow ingot.

† This alloy gave a second arrest at 733°, the temperature of the peritectic horizontal. Quenching experiments gave this temperature as lying between 726° and 732° C. ± 2°.

‡ With this alloy the arrest was much less pronounced than for the others.

Solidus Points.—The results of the solidus determinations are given in Table XXIII. These experiments were carried out on specimens which had received a preliminary

TABLE XXIII.

Composition of alloy.		Quenching temperature.	Microstructure.
Weight % Cd.	Atomic % Cd.		
9·88	9·52	922°	α + much chilled liquid.
—	—	914	α*
16·70	16·13	893	α + very much chilled liquid.
—	—	885	α + traces of chilled liquid at edges.
22·61	21·91	854	α + chilled liquid.
—	—	845	Homogeneous α.
26·79	25·99	833	α + small amount of chilled liquid.
—	—	828	α with a trace of chilled liquid in the centre.
32·81	31·92	790	α + chilled liquid.
—	—	780	Homogeneous α.
34·57	33·65	769	α + a little chilled liquid.
—	—	760	Homogeneous α.
36·13	35·20	760	α + chilled liquid.
—	—	752	α*

* These alloys may have contained a trace of chilled liquid in one place at the edge.

anneal of 5 days at 426°. When allowance is made for the relative quantities of solid and liquid present, a satisfactorily smooth curve can be drawn through the solidus points for the seven alloys examined, and this cuts the 733° peritectic horizontal at approximately 37·3 atomic % cadmium, in almost exact agreement with the value (37·0%) obtained by prolongation of the solubility curve (see below).

The results for the determination of the solubility curve above 430° are shown in Table XXIV, which requires little explanation. All the alloys were hammered between the preliminary and final heat treatments so as to cause recrystallization during the final annealing. Alloy 42·78, after quenching from 705°, was found to consist of homo-

TABLE XXIV.—The α-Solubility Curve above 430°.

Composition of alloy.		Previous heat treatment.	Time and temperature of final anneal and quench.	Microstructure.
Weight % Cd.	Atomic % Cd.			
38·85	37·89	12 days 430° 12 days 430° 12 days 430°	24 hours 705° 41 hours 677° 2 days 625°	α + small amount of β. α + traces of β at edges. Homogeneous α.
39·71 39·89	38·75 38·92	None 12 days 430° and slowly cooled	2 days 630° 42 hours 651°	Homogeneous α. α + traces of β.
40·41	39·43	12 days 430° and 2 weeks at 205° 12 days 430° and slowly cooled	41 hours 605° 44 hours 628°	Homogeneous α. α + a little β.
42·06	41·07	12 days 430° 12 days 430° 12 days 430° 12 days 430° 12 days 430°	24 hours 705° 2 days 622° 2 days 557° 2 days 521° 4 days 498°	α + β. α + β. α + a little β. Homogeneous α. Homogeneous α.
43·79	42·78	12 days 430° 12 days 430° 12 days 430° and then well hammered	24 hours 705° 2 days 622° 7 days 430°	Homogeneous β. α + β. α + β.

geneous β, in agreement with the diagram of FRAENKEL and WOLF (*loc. cit.*). After repeated annealing and hammering at 430°, the alloy 42·78 consisted principally of α with some β, and the solubility limit of the α-phase is estimated as about 42·4 atomic % cadmium at 430°. The solubility diminishes with rising temperature, and the solubility curve cuts the 733° peritectic horizontal at about 37·3 atomic % cadmium in good agreement with the intersection of the solidus curve. These results and those for the lower temperatures are plotted in fig. 14.

The Solubility Curve below 430°.—In order to determine whether there is any change in the α-solubility-limit below 430° (the temperature of the transformation of the β-phase), two series of alloys which had received previous heat treatment of 12 days at 430° were re-annealed for two weeks at 330° and 205° C. respectively. In order to save the present authors' time these annealings were carried out in furnaces at the National Physical Laboratory, and we must express our very warm thanks to Dr. C. H. DESCH, F.R.S., for his extremely kind help in this connexion.

After treatment at 330°, alloy 43·78, which was two-phase at 430°, showed minute traces of further precipitation of the second constituent in the grain boundaries. At 205° further precipitation had occurred in the grain boundaries, but the total amount precipitated was very small compared with the relative amount of the β-phase present in the alloy quenched from 430°. From this we conclude that the α-solubility-limit diminishes slightly between 430° and 205° (the second transformation of the β-phase is at 211°), but that the change is not more than a few tenths of an atomic per cent. Alloy 41·07 remained homogeneous after the above treatments, and also after cooling from 300° to 100° over a period of two weeks, and being maintained at 100° for a further eight days.

Discussion.—The figures given in the collected tables are taken directly from the above work. As will be appreciated from the data in Tables XXIII and XXIV, a few of the alloys showed slight inverse segregation in spite of the fact that they were sand castings. But the liquidus and solidus and the α and β solid solubility curves respectively are so close together that very little error can have been introduced on this account. The cross-section of alloy 39·43 in Table XXIV, quenched from 628°, showed traces of the β-constituent except in the immediate centre (inverse segregation). In this section the centre of the flat disc was drilled away and the outside portion analysed so as to give the composition of the part which was two-phase. At 605° the entire section was homogeneous.

Silver-Indium.

Materials used.—For the determination of the solidus and the solubility curve H.S. indium, supplied by Messrs. Adam Hilger, Ltd., was used. The purity of this metal was 99·74%, with 0·22% of lead, and 0·15% of cadmium as the chief impurities. Five grams of this metal were obtained by means of a grant made by the Imperial Chemical Industries, Ltd., to whom the authors must express their sincere thanks. At a much later stage in the research, some specially pure metal was obtained, for which the authors must express their thanks to the Council of the Royal Society for a grant. This metal, which was also supplied by Messrs. Adam Hilger, Ltd., had an indium content of approximately 99·97%, with 0·025% of lead as the chief impurity, and was used for the freezing point determinations.

Preparation of Alloys.—The alloys were prepared in quantities of about three grams by melting under charcoal, using the methods previously described. The desired composition was generally obtained to within a few tenths per cent.

Analysis of Alloys.—For the analysis the alloy was dissolved in nitric acid, and the silver precipitated as chloride. The precipitate was dissolved in ammonia, and then reprecipitated and weighed as chloride. The combined filtrates were made slightly alkaline with ammonia, and boiled until no longer alkaline, when the whole of the indium was precipitated, and was then filtered off, dried, and ignited. The indium oxide appeared to be hygroscopic, and the final weighings were, therefore, carried out as quickly as possible. The total of the silver and indium percentages determined in this way lay between 99·88 and 100·13 in all but two experiments. In one of these the analysis was repeated with a specimen of the same alloy which had had a different heat treatment, whilst in the other, where an obvious mistake had occurred, a difference value was taken.

Experimental Results.

Liquidus Points.—Cooling curves were taken in the apparatus shown in fig. 13 for six alloys containing up to 15% of the specially pure indium, some being melted under charcoal and some under borax. A section of each cooling curve ingot was then analysed in order to ensure that no contamination had occurred. When the indium contents determined by analysis were used to plot the liquidus curve, it was found that the points did not lie accurately on a smooth curve, but, if the best possible curve were drawn, the points lying above it were those for alloys for which the indium contents by analysis were greater than those estimated from the weights of the metals used, whilst for the points below the curve the analytical values were less than the synthetic values. This clearly suggested that the analytical results were again affected by segregation effects, since the tubular arrangement of the apparatus shown in fig. 13 made it impossible for silver to splash out during stirring, and there seems no way of accounting for an indium content greater than that calculated from the weights of metals used.

Duplicate analyses also gave direct evidence of segregation, but since it was desired to save the alloys made from the very pure metal, it was not thought advisable to dissolve all the ingots for analysis, and we have, therefore, plotted the liquidus curve from the synthetic composition of the alloys. This policy appears justified in view of the fact that the annealing experiments gave no indication of loss of indium by volatilization, and that in the preparation of the chill castings the desired composition was usually obtained very closely in spite of the small quantities used. As will be seen from Table XXV, the synthetic compositions, and those determined by analysis, agree within 0·36%, except for one specimen, where there is a very large difference.* The liquidus points from the synthetic compositions lie well on a smooth curve, which is about 3° lower than the curve which would be drawn if the analytical compositions were used (omitting the one alloy in which the analysis is clearly wrong). The arrest

* It is perhaps significant that the slice of the ingot sent for analysis was from the extreme outside, but, as explained above, it was not thought justifiable to destroy the whole ingot in order to see whether the error was due to segregation, or to the analysis of a wrong sample.

point of alloy 4·95 showed very slight supercooling, and it is probable that the liquidus points for this region are really a little higher than those given in the collected tables, since for this, and also alloy 10·0, the rate of cooling was accidentally as great as 8° per minute.

An additional point on the liquidus was obtained by the quenching method, using two pieces of alloy F (p. 62). When quenched from 798° the cross-section of the alloy showed principally the fine dendritic structure of the chilled liquid with occasional large crystals of the α-solid-solution. The relative amounts of the chilled liquid and undissolved α-crystals showed that the alloy had been quenched from very near to the liquidus point. A second experiment, in which the alloy was quenched from 809° was not quite so successful, since the alundum covering cracked, and a little of the liquid alloy ran into the cracks. A cross-section through the irregular mass showed that a few α-crystals were still present, and from this we place the liquidus point as about 810°–820°, and as being definitely above 800° The analysis of a portion of the alloy after these experiments gave the composition as 20·1 atomic % (21·1% indium by weight), in very good agreement with the value (20·04 atomic % of indium) for the composition before the experiment.

TABLE XXV.

Composition of alloy.		Liquidus point.
Weight % In.	Atomic % In.	
3·15 (3·66)	3·0	941·5°
5·24 (4·90)	4·95	926
8·45 (8·90)	8·0	910
10·6 (10·56)	10·0	893
15·4 (11·49 ?)	14·6	848
15·9 (16·32)	15·0	850

The Solidus.—The solidus experiments are shown in Table XXVI, which is self-explanatory. The first two alloys were made by remelting pieces of alloys B and C

(see p. 61) with more silver, and the analyses showed that no contamination had occurred.

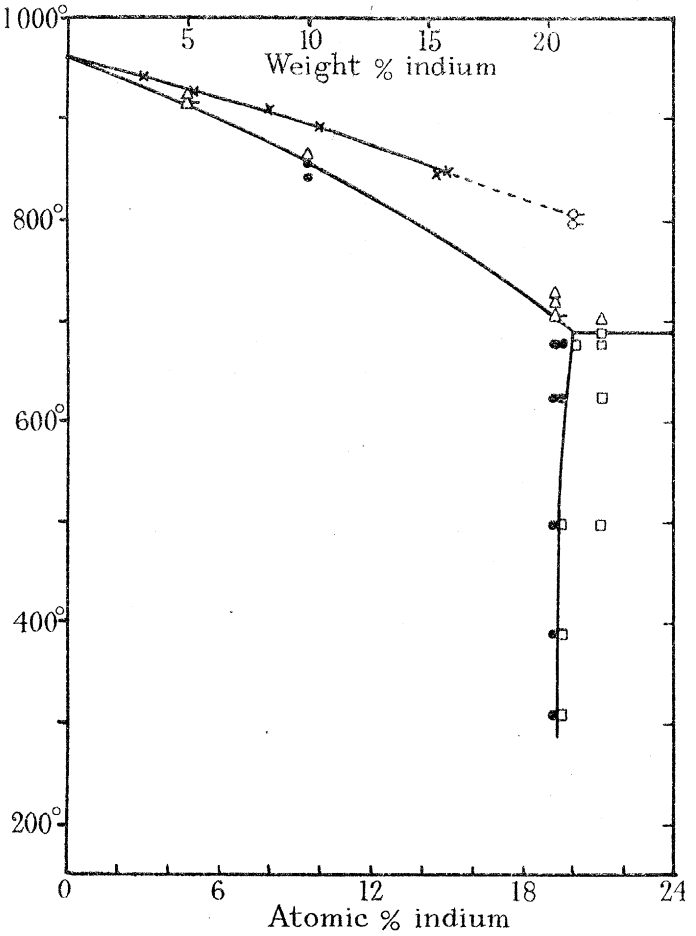

FIG. 15.—Silver-Indium. ● homogeneous α-solid-solution; □ α + β; Δ α + chilled liquid; Δ- α + traces of chilled liquid; × points from cooling curves; O- chilled liquid + a little α (quenching experiment).

The Solubility Curve.—The determination of the solubility curve was difficult on account of the small size of the ingots available. Many of the same specimens had to be used for annealing at different temperatures, and for this reason it is more convenient to describe the results for each alloy separately, since it is difficult to give the previous heat treatments conveniently in tabular form.

(*a*) *Alloy A.*—Intended composition 19·9% indium by weight. Composition by analysis :—

(1) After annealing at 625° for 5 days : 20·21% indium by weight.
(2) After 5 days at 625°, followed by 5 days at 498°, and 30 minutes at 728° : 20·26% indium by weight.

Mean composition 20·24% indium by weight = 19·26 atomic % indium.

This alloy remained homogeneous at all temperatures between 678° and 308°, after a

TABLE XXVI.

Composition of alloy.		Previous heat treatment.	Quenching temperature.	Microstructure.
Weight % In.	Atomic % In.			
4·98	4·69	16 hours at 825°	922°	α + Chilled liquid.
		,, ,,	915°	α + Traces of chilled liquid.
10·08	9·53	16 hours at 825°	863°	α + Chilled liquid.
		,, ,,	856°, 843°	α.
20·26	19·28	5 days at 624° + 5 days at 498°	728°, 718°	α + Chilled liquid.
		,, ,,	706°	α + Traces of chilled liquid.
22·19	21·14	5 days at 624° + 5 days at 498°	701°	α + Liquid.
		,, ,,	689°	α + β with a little chilled liquid in some places.*
		,, ,,	678°	α + β.

* This alloy appeared to have been quenched from nearly the peritectic temperature, since in some places the β had melted to form α + liquid, whilst in others it had not.

variety of annealing and quenching treatments. The low temperature treatment consisted of two weeks' annealing at 308° with a specimen which had previously been annealed for five days at 678° and five days at 390°. This alloy is, therefore, definitely in the homogeneous area, and is the same alloy used for the solidus determination given in Table XXVI.

Alloys B and C.—These alloys were intended to have indium contents of 22·0 and 22·6% by weight of indium respectively. The microstructures, however, indicated that their compositions were nearly the same, and this was confirmed by the analyses which gave the indium contents as 22·19 and 22·22% by weight respectively. Some of the specimens used for analysis had been annealed for 5 days at 678°, and others for 5 days at 624°, followed by 5 days at 500° and 30 minutes at 678°. The two alloys have so nearly the same composition that we may take a mean value of 22·21% indium by weight, or 21·15 atomic % indium.

Both these alloys were clearly in the two-phase region at all temperatures between 390° and 678°, after a variety of treatments, including anneals of 5 days at 678° and 9 days at 624 to 627°. The microstructures were very like those of an αβ-silver-aluminium alloy.

Alloys D and E.—These alloys were intended to have compositions of 20·5 and 21·0% by weight of indium respectively, but their microstructures were almost indistinguishable, and the analysis confirmed that their compositions were identical. Using a specimen which had been annealed for 5 days at 624° and then for 5 days at 498°, alloy D was found to contain 20·60% indium by weight, whilst alloy E contained 20·57% indium

according to the analysis of a specimen which had had the same heat treatment, together with an additional 30 minutes at 678°. The two alloys have, therefore, so nearly the same composition that we may consider them together, taking a mean value of 20·59% indium by weight or 19·59 atomic % indium.

After annealing for 5 days at 678°, both alloys were homogeneous. After annealing for 5 days at 624°, alloy E contained slight traces of a second constituent, whilst alloy D was homogeneous in some places where recrystallization and grain growth had occurred, but was still just two-phase in other parts. After hammering (to cause recrystallization) and annealing for a further 4 days at 624°, alloy E became homogeneous. On hammering the above specimens and re-annealing at 498°, both alloys became two-phase, and further precipitation of the second phase occurred on annealing again at 390° and 308°.

Alloy F.—Attempts were made to prepare two alloys containing between 19·5 and 20·5 atomic % indium, but the ingots were not sound, and the two constituents were unevenly distributed, whilst analyses of different portions of one ingot showed that the composition was not uniform. These defects were probably due to casting from too low a temperature. The unused portions of these alloys, together with some of alloy C, were then melted together under borax in a small crucible surrounded by charcoal, and heated in the electric crucible furnace, which was fed with nitrogen. The sand-cast ingot was annealed for 24 hours at 666°, and then quenched, well hammered, and re-annealed for 3 days at 676°, and again quenched. The resulting alloy was just two-phase with a few particles of the β-constituent uniformly distributed. The composition by analysis was 21·05 % indium by weight or 20·04 atomic % indium.* The maximum solid solubility limit may therefore be taken as 20·0 atomic % at the peritectic temperature.

Discussion.—The points given in the collected tables are taken directly from the above work. The solubility limit is clearly that of a typical trivalent element, but, as for the system silver-tin, the solubility increases continuously with temperature up to the peritectic horizontal, and does not show the decrease at high temperatures which is so characteristic of the systems copper-gallium, copper-aluminium, and silver-aluminium.

Silver-tin.

Previous Work.—The equilibrium diagram of the system silver-tin was first satisfactorily established by MURPHY† in 1926, but the boundary of the silver-rich α-solid-solution was not determined within very exact limits. Through the kindness of Mr. MURPHY and the staff of the National Physical Laboratory the present authors were

* The sum total of the percentages of silver and indium determined by analysis was 99·94, so that the remelting did not introduce impurities.

† 'J. Inst. Met.,' vol. 35, p. 107 (1926).

given some of the actual specimens used by Mr. MURPHY and the limits have been determined more accurately.

The Solidus.—The experiments for the determination of the solidus are summarized in Table XXVII, which is self-explanatory. It will be seen that the agreement between the two investigations is excellent where the determinations overlap. One or two of the ingots of which the cross-section was of the shape shown in fig. 16, showed slight inverse segregation in the hollow in the middle of the upper surface, and alloys were obtained in which this portion contained chilled liquid, whilst the remainder was homogeneous. Such alloys are marked * in Table XXVII, and are classed as homogeneous.

FIG. 16.

TABLE XXVII.

Composition of alloy.		Preliminary treatment.	Quenching temperature.	Structure.	Investigator.
Weight % Sn.	Atomic % Sn.				
4·0	3·65	4 days 700° ,, —	907° 899° 895°	α + liquid α* α	Authors. Authors. Murphy.
6·0	5·49	4 days 700° ,, —	871° 866° 852°	α + liquid α + trace liquid α	Authors. Authors. Murphy.
8·0	7·32	— 4 days 807°	836° 807°	α + liquid α	Murphy. Murphy.
10·0	9·17	4 days 807° 4 days 784°	807° 784°	α + liquid α	Murphy. Murphy.
11·0	10·10	4 days 700° ,,	785°, 775° 770°	α + liquid α + trace liquid	Authors. Authors.
12·0	11·03	—	750° 728°	α + trace liquid α	Murphy. Murphy.
14·0	12·89	—	725°	α + liquid	Murphy.

The Solubility Curve.—The data for the solubility curve are given in Table XXVIII, which is self-explanatory and needs no comment. The results of these two tables are plotted in fig. 17, together with the liquidus curve drawn from the data in the collected tables.

Discussion.—The liquidus points given in the collected tables are from the results of MURPHY (*loc. cit.*) and of HEYCOCK and NEVILLE,† which are in very good agreement

† 'Phil. Trans.,' A, vol. 189, p. 25 (1897).

TABLE XXVIII.

Composition of alloy.		Preliminary treatment.	Time and temperature of anneal and quench.	Structure.	Investigator.
Weight % Sn.	Atomic % Sn.				
13·5	12·42	—	14 days 707°	α + β	Murphy.
13·0	11·96	—	1 hour 721°	α	Murphy.
13·0	11·96	—	3 days 706°	α + β	Authors.
12·0	11·03	—	40 hours 672°	α	Murphy.
12·0	11·03	3 days 706°	2 days 640°	α	Authors.
12·0	11·03	—	7 days 602°	α + β	Murphy.
11·0	10·10	3 days 706°	3 days 544°	α	Authors.
11·0	10·10	—	14 days 456°	α + β	Murphy.
10·0	9·17	14 days 450°	Slowly cooled	α	Murphy.

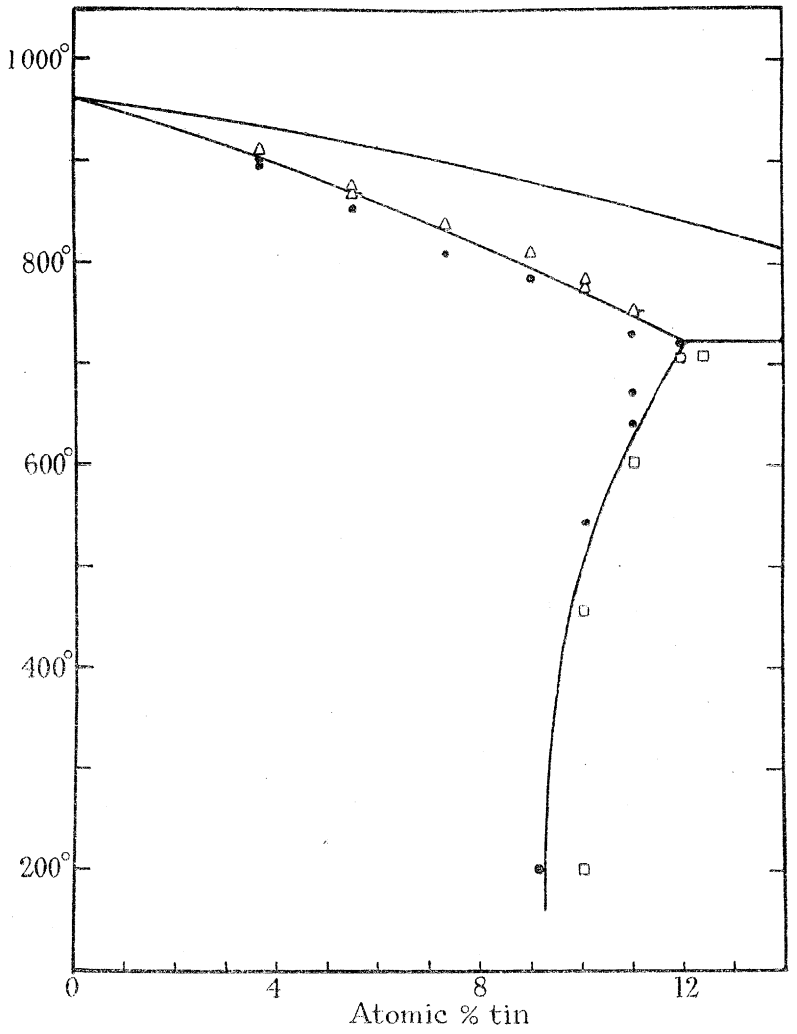

FIG. 17.—Silver-tin. ● Homogeneous α-solid-solution; Δ α + liquid; Δ- α + trace of liquid; □ α+ β.

over a wide range. For the solidus and solubility curves we have used the combined results of MURPHY and of the present authors given in Tables XXVII and XXVIII. As regards the α-solid-solution the diagram bears a remarkably close resemblance to that of the system copper-germanium.

Silver-zinc.

General.—The liquidus of the system silver-zinc was determined accurately by HEYCOCK and NEVILLE,† whilst the general equilibrium diagram, including the α-solid-solubility limit, was investigated by CARPENTER.‡ We have already shown in Part I of this paper that the liquidus gives a freezing point depression which corresponds to that of a normal trivalent element, and for this reason it was thought of great interest to see whether the solidus depression also corresponded to a valency of three.

Experimental.—The alloys used for this work were kindly prepared by Messrs. Johnson, Matthey & Co., Ltd., and were supplied in the form of small sand castings of $\frac{3}{8}$-inch diameter. They were given a preliminary anneal of 24 hours at 500° in order to remove the bulk of the cored structure, and were then used for the solidus determinations. The specimens were analysed after the quenching experiments because a little zinc was lost during the heat treatments; both silver and zinc were determined. The results are shown in Table XXIX, and the solidus points given in the collected tables have been taken from a smooth curve drawn so as to fit the present data. The results indicate that the initial depression of freezing point is that of a normal three-valent element, but that the curve subsequently flattens so as to give solidus points which are higher than those for the solidus of the trivalent system silver-indium.

TABLE XXIX.

Composition of alloy.		Quenching temperature.	Microstructure.
Weight % Zinc.	Atomic % Zinc.		
		°	
2·98	4·82	913	α + a little chilled liquid.
6·05	9·61	871	α + chilled liquid.
6·05	9·61	859	Homogeneous α.
9·26	14·41	830	α + chilled liquid.
9·26	14·41	818	Homogeneous α*.
12·51	19·1	797	α + a little chilled liquid.
12·51	19·1	786	Homogeneous α*.
16·95	25·2	764	α + chilled liquid.
16·95	25·2	754	Homogeneous α.
19·28	28·27	742	α + chilled liquid.
19·28	28·27	736	Homogeneous α.

* These alloys may have contained a trace of chilled liquid.

† 'Trans. Chem. Soc.,' p. 413 (1897).

‡ 'Int. Z. Metallogr.,' vol. 3, p. 145 (1913).

*Silver-aluminium.**

Previous Work.—Whilst this investigation was in progress a paper appeared by HOAR and ROWNTREE,† who determined the liquidus and the α-solid-solubility limit above 600°. An X-ray determination of the α-solid-solubility limit was made by WESTGREN and BRADLEY,‡ who used specimens annealed for some minutes at about 100° below the melting point in order to relieve strains, but no special precautions were taken to ensure slow cooling, so that it is not possible to state the temperature to which their solubility limit of 19 atomic % corresponds. Further X-ray investigations have been made by PHELPS and DAVY§ and by AGEEW and SHOYKET.‖

Materials used.—The aluminium used was of German origin and was obtained by Messrs. Hopkin and Williams. Analyses carried out by the British Aluminium Company gave the following composition :—

Copper, 0·030% ; silicon, 0·032% ; iron, 0·024% ; aluminium, 99·906%.

Preparation of Alloys.—The alloys were prepared under charcoal in crucibles lined with alundum cement, and were cast in $\frac{1}{4}$-inch diameter sand moulds. Only very slight signs of inverse segregation were noted, but slight vertical segregation was found in some of the ingots, the compositions of different sections varying by amounts of the order 0·1 to 0·2% by weight. This difficulty was overcome by the analysis of the exact sections used for the microscopic examination.

TABLE XXX.

Composition of alloy.		Quenching temperature.	Microstructure.
Weight % Al.	Atomic % Al.		
		°	
1·48	5·67	910	α + chilled liquid.
		900	α.
2·75	10·16	860	α + chilled liquid.
		852	α.
4·21	14·96	810	α + chilled liquid.
		800	α.

These analyses are by one of the authors (K. M. C. E.).

* This work is taken mainly from the thesis of one of us (K. M. C. E.) for Part II of the Honours Course in Chemistry, and for the degree of B.Sc. in the University of Oxford. The analyses have been repeated by Mr. R. G. Johnstone, and further annealing experiments carried out at low temperatures.

† ' J. Inst. Met.,' vol. 45, p. 119 (1931).

‡ ' Phil. Mag.,' vol. 6, p. 280 (1928).

§ ' Amer. Inst. Min. Met. Tech.' Publ. No. 443.

‖ ' J. Inst. Met.,' vol. 52, p. 119 (1933).

Analysis of the Alloys.—Owing to the small aluminium content of the alloys, both aluminium and silver were at first determined, the former by the α-hydroxy quinoline method and the latter as chloride. The values so obtained added up so nearly to 100·00 that it was considered justifiable to determine only the silver and to estimate the aluminium by difference.

The Solidus.—The results of the solidus determinations are shown in Table XXX, and refer to specimens which had received a preliminary annealing treatment of two days at 700° C.

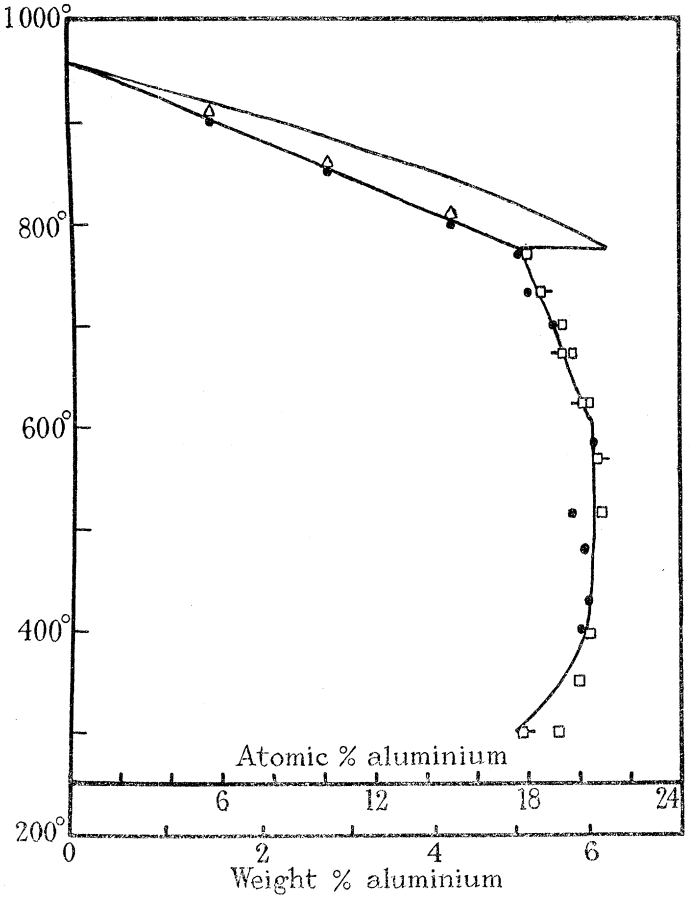

FIG. 18.—Silver-aluminium. ● Homogeneous α; Δ α + liquid; □- α + a little β; □ α + β.

The Solubility Curve above 600° *C.*—Preliminary experiments showed that the solubility of aluminium in silver decreased above 600° C., and the points on this portion of the curve were determined by re-annealing specimens which had previously been made homogeneous. The results obtained are shown in Table XXXI and are in almost exact agreement with those of HOAR and ROWNTREE.

The Solubility Curve below 600°—The high temperature modification of the silver-aluminium " β-phase " undergoes a transformation at about 600°, and below this temperature the solubility of aluminium in silver no longer increases markedly with falling temperature, but becomes almost constant until about 400°, below which

TABLE XXXI.

Composition of alloy.		Previous heat treatment.	Time and temperature of anneal and quench.	Micro-structure.
Weight % Al.	Atomic % Al.			
5·10	17·70	2 days at 700° and hammered	12 hours 770°	α.
5·21	18·03	2 days at 700° and hammered	12 hours 770°	α + β.
5·22	18·05	2 days at 700° and hammered	24 hours 734°	α.
5·39	18·57	2 days at 700° and hammered	24 hours 734°	α + a little β.
5·56	19·06	None	4 days 700°	α.
5·66	19·36	None	4 days 700°	α + β.
5·66	19·36	None	4 days 671°	α + trace of β.
5·80	19·76	None	4 days 671°	α + β.
5·95	20·20	5 days at 604° plus 2 days at 623° and then hammered	4 days 623°	α + trace of β.
6·00	20·35	5 days at 604° plus 2 days at 623° and then hammered	4 days 623°	α + β.

point the solubility diminishes. This second bend in the solubility curve is accompanied by a change in the microstructure of the alloys, the relative amount of the second constituent increasing markedly below 400°. Since the present paper refers to the α-solid-solubility limits, we have not dealt with this point in detail, and for convenience all two-phase alloys are referred to as " α + β " in the Tables, but it seems probable that the α-phase is really in equilibrium with three different phases, one below 400°, one between 400° and 600°, and a third at higher temperature.

Inconsistent results were at first obtained at 400°, one early annealing experiment placing the α-solubility limit at approximately 19 atomic % of aluminium, whereas later experiments gave the limit at about 20 atomic %. Unfortunately no record was kept of the previous heat treatment of the specimens used in the first experiment, but it seems probable that they had been annealed above 700° If so, they would have acquired a coarse two-phase structure instead of being made homogeneous before the low temperature anneal. These results have therefore been discarded, since they were not confirmed by three later series of experiments. The results for the low temperature anneals are given in Table XXXII, which is self-explanatory. Alloys containing from 6·10 to 6·20% aluminium by weight (20·6 to 21·0 atomic % aluminium) were not obtained homogeneous below 569°, and the maximum solubility is estimated at about 20·6 to 20·7 atomic % aluminium in the range 580°–600°.

Comparison with Previous Work.—At high temperatures the results of the present work are in very good agreement with those of HOAR and ROWNTREE. The limiting solubility given by PHELPS and DAVY was 5·4% aluminium by weight for alloys annealed for 24 hours between 650° and 700°, and then cooled to room temperature during 24–48 hours. Examination of their data for the lattice constants of the homogeneous alloys shows that the points given deviate so much from the straight line

which they assume that the experimental error in the X-ray measurements readily accounts for the difference between their value and the lower solubility found in the present work. According to the work of AGEEW and SHOYKET, the Ag-Al β-phase stable at high temperatures decomposes at 600° into a mixture of $\alpha + \gamma$, but at low temperatures there is a second modification β^1 stable up to about 400°. This type of diagram would, of course, be in complete agreement with the double bend in the solubility curve found in the present work.

TABLE XXXII.

Composition of alloy.		Previous heat treatment.	Time and temperature of anneal and quench.	Micro-structure.*
Weight % Al.	Atomic % Al.			
6·10	20·62	5 days at approximately 600°	6 days 585°	α.
6·15	20·77	4 days 450° plus 2 days 400°	3 days 569°	α + trace of β.
5·80	19·76	5 days at approximately 600°	5 days 515°	α.
6·22	20·98	5 days at approximately 600°	5 days 515°	α + β.
5·95	20·20	5 days at approximately 600°	4 days 480°	α.
6·02	20·39	Specimens from 397° below given 2 days at 600°	2 days 427°	α.
5·91	20·12	5 days at approximately 600°	5 days 403°	α.†
5·40	18·60	2 days at approximately 700°	5 days 403°	α + ? trace of β.‡
6·02	20·39	Specimens from 671°, Table II, re-annealed for 2 days at 600°	3 days 397°	α + a little β.
6·07	20·54	Specimens from 671°, Table II, re-annealed for 2 days at 600°	3 days 397°	α + β.
5·88	20·0	Specimen from 397° above	2 days 350°	α + a little β.§
5·57	19·10	2 days 700°‖	3 weeks 300°	α + β.
5·14	17·81	2 days 700°‖	3 weeks 300°	α + a little β.

* In this table, as explained in the text, the second phase is called " β " throughout, although there are probably three modifications or different phases.

† This alloy was homogeneous over the whole of the cross-section except in one place where a trace of β was noted.

‡ This alloy was examined several times and was described as homogeneous, but after repeated etching it was noted as showing what appeared to be traces of a second constituent. It is thought that these must have been cracks caused by hammering after the preliminary anneal. Alternatively the preliminary annealing treatment at approximately 700° may have exceeded the α-solid-solubility limit at this temperature, and so left β-particles which were not absorbed at 403°.

§ This alloy was homogeneous at 397°.

‖ A little doubt exists as to the temperature of the previous heat treatment of these alloys, but as the alloy 17·81 is homogeneous at temperatures up to 760° this is immaterial.

These workers also give values for the α-solid-solubility limit obtained by X-ray measurements, but unfortunately the curve assumed for the homogeneous alloys is taken from only three points. AGEEW and SHOYKET give values which are systematically higher than those of the present work, but the difference is within the experimental error of the X-ray methods.

Discussion.—The solubility curve of aluminium in silver is clearly that of a typical trivalent element, and it may be noted that this accounts for the contraction in the lattice constant of the alloys since the radius of the aluminium atom in the trivalent state is smaller than in the incompletely ionized form in which the aluminium atom exists in the element.

Silver-gallium.

Materials used.—The gallium employed for this investigation was the metal of German origin used for the work on copper-gallium alloys (see p. 76).

Preparation of Alloys.—The alloys were melted under charcoal in an atmosphere of nitrogen. Slight inverse segregation was detected in one or two specimens, but fortunately it was possible to prevent this affecting the determination of the solubility limit. The desired composition of the alloys was not obtained so accurately as in the copper-gallium series, as in nearly all there was a slight loss of gallium.

Analytical Methods.—For the analysis, the alloy was dissolved in nitric acid, and the solution diluted to a considerable volume, after which the silver was precipitated as chloride, and the gallium determined by the method described later (p. 76). Twenty determinations were made in all, and the extreme values for the sum of the silver and gallium figures were 99·82 and 100·11, whilst in eleven cases the totals lay between 99·9 and 100·04.

Change of Composition on Annealing.—In this system, in contrast to the copper-gallium alloys, distinct evidence was obtained of loss of gallium on annealing in sealed tubes at temperatures of 500° and above, but below this point no change occurred with small lumps of alloy.*

The gallium vapour appeared to be absorbed by the glass, which turned milky in some cases. The times of annealing were so long that alloys were never obtained in which the outside was homogeneous and the interior two-phase. The specimens appeared uniform throughout, and the policy was therefore adopted of analysing the alloys of critical composition after each annealing treatment above 500°. The changes were such as to affect the composition by amounts of the order 1 %. These repeated analyses used up so much of the rare metals that a fully detailed examination was impossible.

The Liquidus.—Since the solidus curve (see p. 71) showed a depression of melting point almost exactly the same as that in the system silver-tin, it was of great importance

* With filings used for X-ray analysis, loss of gallium probably continues to lower temperatures.

to see whether the liquidus curve was also that of a normal 4-valent element. Unfortunately the amount of gallium available did not enable a detailed examination to be made, but a satisfactory cooling curve was taken for an alloy containing 11·47 atomic % gallium,‡ the liquidus point for which was determined as 850°. The corresponding liquidus point for a silver-tin alloy containing 11·5 atomic % tin is 853°, so that at this point the gallium has depressed the freezing point of silver by almost exactly the amount to be expected from a normal 4-valent element.

An additional point in the neighbourhood of 20 atomic % gallium was obtained by the quenching method. After quenching from 737°, an alloy containing 18·8 atomic % of gallium showed both chilled liquid and undissolved α-crystals. An experiment in which an alloy containing 19·4 atomic % of gallium was quenched from 754° was not entirely successful because some of the liquid alloy entered cracks in the alundum cover, but a complete section through the middle of the irregular mass showed a few α-crystals in a large amount of chilled liquid. From these experiments we estimate the liquidus point of an alloy containing 19 atomic % gallium as approximately 760°. The corresponding values for silver alloys containing 19 atomic % of tin and 38 atomic % of cadmium are 730° and 765° respectively,§ so that the gallium is again resembling a tetravalent element rather than the normal trivalent indium, for which the liquidus point of an alloy containing 19 atomic % indium is approximately 820°.

The Solidus.—The results for the solidus determination are given in Table XXXIII.

TABLE XXXIII.

Composition of alloy.		Previous heat treatment.	Annealing temperature.	Structure.
Weight % Ga.	Atomic % Ga.			
2·50	3·82	5 days 600°*	901°, 890°	α + chilled liquid.
		5 days 600°*	879°	α + trace of liquid.
6·37	9·53	4 days 600°	801°	α + liquid.
6·37	9·53	4 days 600°	792°	α + a little liquid.
6·42	9·60	4 days 600°	779°	α.
9·81†	14·41	4 days 600°	690°	α + a little liquid.
9·81†	14·41	4 days 600°	677°	α.
11·37	16·57	4 days 624°	654°	α + traces of liquid.
11·11	16·21	5 days 627°	645°, 635°	α.

* The preliminary annealing of this alloy extended over 7 days, but the tube was removed occasionally for a few hours to enable the furnace to be used for other purposes.

† The composition of this alloy was determined by difference owing to an accident in manipulation.

‡ In view of the critical nature of this experiment, the whole of the cooling curve ingot was used for analysis to avoid segregation effects.

§ In the silver-tin series the 19 atomic % alloy is almost at the peritectic temperature (724°), and the freezing point is lower than the cadmium alloy of the same equivalent composition.

In this work one alloy was ignored entirely. It was intended to contain 4 atomic % of gallium, but the melting point lay completely off the curve given by the other alloys. The analysis of two samples which had had almost the same heat treatment gave different results, which were much lower than the intended composition, and it could only be concluded that the specimen was of uneven composition. The experiment was repeated by making a new casting, and in this the alloy had almost the intended composition (3·82 atomic % gallium instead of 4·0); this alloy is included in Table XXXIII. The analysis indicated that the differences of 10° to 20° between the solidus quenching temperatures did not influence the composition to any marked extent, provided the preliminary heat treatment was the same. For this reason the compositions of the solidus alloys were usually taken from specimens quenched from one of the critical temperatures, or from a mixture of the two, and specimens from each

TABLE XXXIV.

Composition of alloy.		Previous heat treatment.	Time and temperature of anneal.	Structure.	Remarks.
Weight % Ga.	Atomic % Ga.				
13·91	20·01	5 days 498°, 3 days	2 days 595°	α + β	—
13·40	19·32	587°–592°	2 days 595°	α + β	—
12·99	18·77	5 days 500°	4 days 601°	α + β	—
12·76	18·46	5 days 498° 3 days 587°–592°	2 days 595°	α	—
13·06	18·86	None	5 days 561°	α + β	—
15·29	21·83	None	5 days 498°	β + trace of α	Hammered before annealing.
14·61	20·95	None	5 days 498°	α + β	,, ,,
14·09	20·24	None	5 days 498°	α + β	,, ,,
13·93	20·03	None	5 days 498°	α + β	,, ,,
13·06	18·86	None	5 days 500°	α + small amount of β	,, ,, See page 73.
12·51	18·12	None	5 days 498°	α	Hammered before annealing.
14·61	20·95	2 days at 500° and then hammered	10 days 390°	α + β	Compositions assumed the same as those of specimens having 5 days at 498°.
14·09	20·24	2 days at 500° and then hammered	10 days 390°	α + β	,, ,,
13·93	20·03	2 days at 500° and then hammered	10 days 390°	α + β	,, ,,
13·06	18·86	5 days 561°	5 days 401°	α + β	Analysed after 401°.
12·39	17·96	2 days at 500° and then hammered	14 days 390°	α	See page 74.
12·39	17·96	2 days 500° and 14 days 390°	2 weeks 308°	α + β	See page 74.

temperature were not analysed separately. But where the solidus specimens of any one ingot had received different preliminary heat treatments, greater care was necessary, and each specimen was analysed.

The temperature of the peritectic or eutectic horizontal was determined as lying between 606° and 625°, by quenching alloys in the two-phase area. It will be seen that the system is remarkable for the relatively steep fall in the solidus as compared with the corresponding lines in the systems silver-indium, silver-aluminium, and copper-gallium. Reference to the collected tables will show that the solidus depression is, in fact, almost exactly equal to that of the normal 4-valent system silver-tin.

The Solubility Curve.

Table XXXIV gives the results of the experiments for the determination of the solubility curve, and is self-explanatory except for the following points: Alloy 18·86,

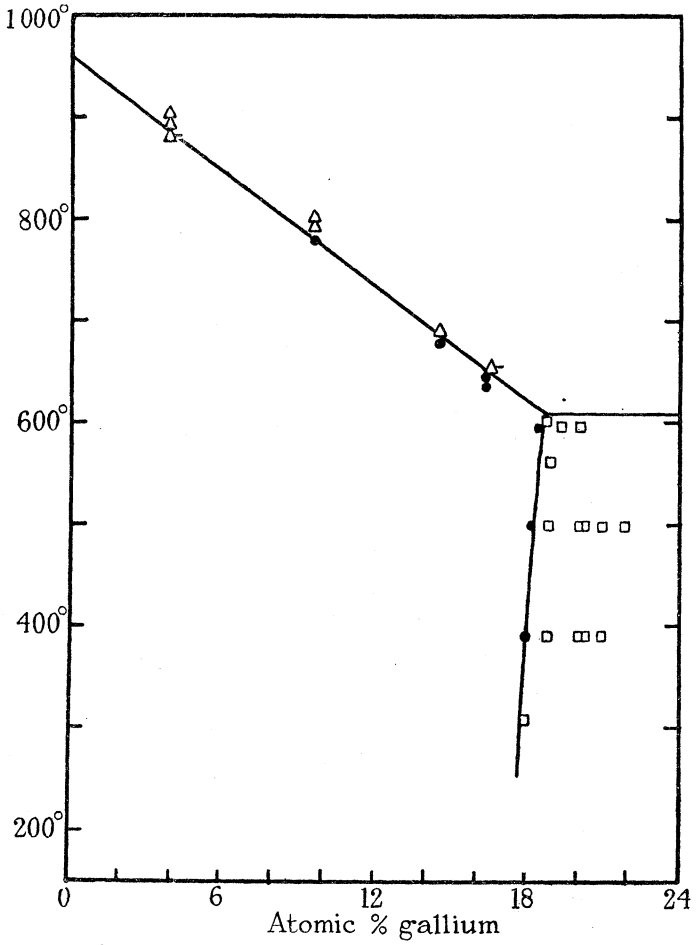

FIG. 19.—Silver-gallium. ● Homogeneous α-solid-solution; □ α + β; Δ α + liquid. Δ- α + trace of liquid.

after 5 days at 500° and 5 days at 561°, showed slight signs of inverse segregation, but was two-phase throughout. Alloy 17·96 was given a preliminary anneal at 500° and

then hammered and annealed for 10 days at 390°, after which it was homogeneous in some parts, but two-phase in others near the outside of the ingot. As the grain size was rather variable, this alloy was given a further anneal of 4 days at 400°, after which it was still just two-phase at the outside for a depth of about 0·4 mm. in a specimen of width 6 mm. This suggested slight inverse segregation in the original casting and the annealed sample was, therefore, filed so as to remove the outer layer, and the inner portion was analysed so as to give the composition of the alloy which was homogeneous at 390°. After a further anneal at 308° this alloy was two-phase throughout the whole of its cross-section.

The experimental results are plotted in fig. 19, and it will be seen that the maximum solid solubility is slightly less than that of the typical trivalent systems copper-aluminium, silver-aluminium, copper-gallium, and silver-indium. This difference is probably due chiefly to the fact that the atomic diameter of gallium lies just outside the zone of favourable size-factor for silver.

Copper-zinc.

Previous Work.—The previous work on copper-zinc alloys is very extensive and has been exhaustively reviewed by BAUER and HANSEN.† The solidus alone does not seem to have been determined conclusively, and we have therefore determined a few points by the quenching method in order to make sure of the position of this line.

Materials used.—The alloys used were kindly presented by the British Non-Ferrous Metals Research Association, and were in the form of cast strip ingots made from the purest metals. The authors must express their thanks to Dr. O. F. HUDSON for his kind interest in this connexion.

Experimental Details.—The alloys used for the solidus quenches were given a pre-

TABLE XXXV.

Composition of alloy.		Quenching temperature.	Microstructure.
Weight % Zn.	Atomic % Zn.		
		°	
30·40	29·81	930	α + chilled liquid.
		918	α + trace of chilled liquid.
24·8	24·3	958	α + small amount chilled liquid.
		949	α.
19·79	19·34	992	α + liquid.
		981	α*.
14·57	14·23	1012	α + trace of chilled liquid.
9·99	9·74	1040	α + chilled liquid.
		1030	α.

* This specimen may have contained a trace of chilled liquid at one edge.

† " Die Aufbau der Kupfer-Zink Legierungen."

liminary anneal of 10 days at 400° in order to remove the greater part of the cored structure before the quenching experiments, a duplicate series of experiments being made with alloys which had not received the preliminary anneal. The appearance of chilled liquid was quite sharp and clear. The alloys were analysed after the quenching experiments because a slight loss of zinc always occurred.

These observations are plotted in fig. 20, together with the end points of the thermal arrests of RUER and KREMERS,* and the uppermost portion of the solubility curve of GENDERS and BAILEY,† and it will be seen that the agreement is satisfactory. The solidus curve is some 6° higher than that of JITSUKA,‡ suggesting that the rate of cooling

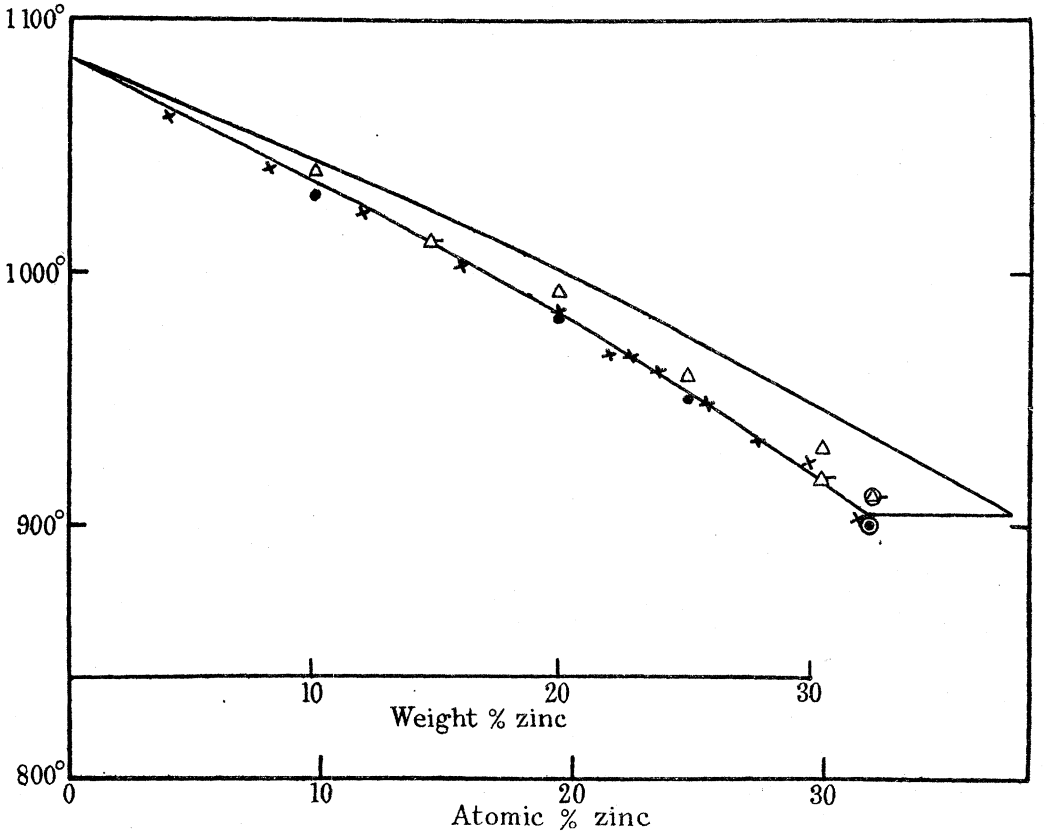

FIG. 20.—Copper-zinc. Δ α + liquid (Authors); Δ- α + trace of liquid (Authors); ● homogeneous α (Authors); (Δ)- α + trace of liquid (GENDERS and BAILEY); (●) homogeneous α (GENDERS and BAILEY); × end points of arrests (RUER and KREMERS).

employed by this investigator was not sufficiently slow for true equilibrium to be obtained, but the end points of the arrests obtained by RUER and KREMERS are in very good agreement with those of the present quenching methods.

If the best curve through the solidus points in fig. 20 is extrapolated to 905°, the

* 'Z. anorg. Chem.,' vol. 184, p. 196 (1929).

† 'J. Inst. Met.,' vol. 33, p. 213 (1925).

‡ 'Mem. Coll. Sci., Tokyo Imp. Univ.,' vol. 8, p. 179 (1925).

temperature of the peritectic horizontal, it indicates a limiting solubility of 31·5 atomic % zinc. This is in almost exact agreement with the work of GENDERS and BAILEY, whose solubility curve indicated that the limiting solubility of zinc in copper at this temperature was a little less than that of an alloy containing 32·3% zinc by weight or 31·69 atomic % zinc.

Copper-gallium.

Materials used.—For the preliminary part of this work " H.S." gallium from Messrs. Adam Hilger, Ltd., was used, the purity being approximately 99·8%, with zinc (0·19%), tin (0·003%), sodium (0·02%) as the chief impurities, together with traces of calcium, lead, antimony, and iron. At a later date gallium was obtained from a German source, together with a certificate of analysis of a similar batch, indicating a purity of approximately 99·875%, with zinc (0·07%), copper (0·04%), lead (0·01%) as the chief impurities. The particular metal used in the present work was slightly less pure than this ; a spectroscopic report from the Midland Laboratory Guild stated that the metal was remarkably pure, except for zinc, which was present in amounts of the order 0·15 to 0·20%.

Preparation of Alloys.—The alloys were prepared under charcoal by the methods previously described, and no evidence of segregation effects was obtained. The intended composition was usually obtained to within two or three-tenths of 1%, but differences up to as much as 0·6% were found in one or two alloys, and in these the analytical values were confirmed by the microstructure.

Analyses.—For the analysis the alloys were dissolved in nitric acid and, after evaporation to a very small bulk, concentrated hydrochloric acid was added, and the whole boiled until no further chlorine was evolved. The solution was well diluted, boiled, and treated with hydrogen sulphide. The copper sulphide was filtered, thoroughly washed, dissolved in dilute nitric acid, and the copper determined electrolytically.

For the determination of the gallium, the filtrate was boiled free from hydrogen sulphide, oxidized with a little bromine water, made faintly ammoniacal, and boiled until just acid. Under these conditions the gallium, which readily formed a very sticky and adherent precipitate, was precipitated in a crystalline or semi-crystalline form, which was filtered, washed, and ignited to oxide.

Twenty-four determinations were carried out and, apart from the two referred to below, the extreme values for the sum of the percentages of copper and gallium were 99·81 and 100·15, whilst in thirteen determinations the totals lay between 99·86 and 100·06. In two determinations the copper values were ignored owing to obvious accidents in manipulation.

The analytical values agreed well with the microstructures for all except four alloys. In alloys 20·09 and 20·32 the microstructures indicated that the former contained very slightly more gallium than the latter, whilst, at the lower temperatures, alloy 19·23 appeared to precipitate more of a gallium-rich constituent than alloy 19·49. These

differences may be due to slight segregation effects, or may indicate the limits of the methods employed.

The Liquidus.—Two preliminary points were obtained by the quenching method, but, when more gallium became available, the cooling curve method alone was used. The results are given in Table XXXVI. The analyses were carried out on complete vertical sections of the ingot, and, in three out of five, the analytical value for the gallium content was within 0·13% of the synthetic value. For alloy 19·05, two analyses gave different results, one nearly agreeing with the synthetic value and the other giving a higher gallium content. We have preferred the synthetic value, since there seems to have been no means by which gallium could have been gained.* In alloy 5·87 the cooling curve ingot was cut into three pieces, one of which was analysed for both constituents, and the other two for copper only. The maximum difference between the figures for the copper contents was 0·15%, and it is possible that the gallium content is really about 0·2% less than that given in the table, since the analytical value was greater by this amount than that intended. In alloy 5·85 the metals were melted under powdered charcoal in a closed silica tube embedded in charcoal, and the composition given is synthetic. The arrest point was 1050° or 1052° according to the exact calibration of the thermocouple, but the former value is more probable since it refers to a calibration made immediately after the cooling curve for this alloy when the thermocouple had settled down to a steady value. In alloy 4·74 the rate of cooling was accidentally 10° per minute.

TABLE XXXVI.

Composition of alloy.		Arrest points.	Remarks.
Weight % Ga.	Atomic % Ga.		
		°	
5·18	4·74	1059	Prepared by melting alloy 9·66 with copper.
6·38	5·85	1050	Prepared from virgin metals.
6·40	5·87	1053	Prepared from virgin metals.
10·50	9·66	1021	Prepared from virgin metals.
15·13	13·99	994	Prepared from virgin metals.
20·5	19·05	942, 914	Prepared from virgin metals. The 914° arrest is that of the peritectic horizontal.

* Owing to an uncertainty in the thermocouple calibration, the ingot of this alloy was remelted, and the cooling curve repeated. The two curves gave identical arrest points. The analysis which gave the higher gallium content was from the ingot after the remelting, which suggests clearly that the effect is due to segregation, since any loss of gallium by oxidation, volatilization, etc., would affect the composition in the opposite direction.

The Solidus.—Table XXXVII gives the results of the quenching experiments used for the determination of the solidus, all these being for specimens which had previously been annealed. All the analyses were carried out on the specimens after the annealing and quenching treatment. With alloy 3·69, chilled liquid was clearly present in the specimen quenched from 1059° C. The specimen from 1052° showed slight traces of chilled liquid in the grain boundaries, but at one side near a contraction cavity a small patch of chilled liquid was also apparent. It was concluded that there must have been slight segregation or irregularity in the neighbourhood of the cavity, and this portion was ignored, and not used for the analysis. The temperature of the peritectic horizontal was found from the quenching experiments to lie between 906° and 925°, in agreement with the value of 914° for alloy 19·05 in Table XXXVI.

TABLE XXXVII.

Composition of alloy.		Quenching temperature.	Structure.
Weight % Ga.	Atomic % Ga.		
4·03	3·69	° 1059 1052	α + liquid. α + trace of liquid (see above).
7·82	7·17	1023 1010	α + liquid. α.
10·54	9·70	1004 994 986	α + liquid. α + trace of liquid. α.
14·49	13·38	952 941	α + liquid. α.
17·83 19·41	16·52 18·01	906 925	α + β. α + liquid.

The Solubility Curve.—The experiments showed that the solubility reached a maximum in the neighbourhood of 620°, and decreased considerably at high temperatures, and slightly at low temperature. In order to minimize the risk of loss of gallium* by volatilization, the high temperature portion of the curve was determined by heating previously annealed samples for periods of 30 minutes at successive temperatures above 700°, after which they were quenched and examined microscopically. In order to test whether the period of 30 minutes was sufficient to ensure precipitation,

* Later work showed that, actually, loss by volatilization did not occur, in marked contrast to the silver-gallium alloys where considerable loss was found.

an additional experiment was carried out in which previously annealed samples were heated at 800° for 6 hours, and then quenched, and, as can be seen from fig. 21, the points obtained in this way agree well with those obtained by the other method. These results are summarized in Table XXXVIII; all the analyses were carried out on specimens after annealing at the high temperature anneals.

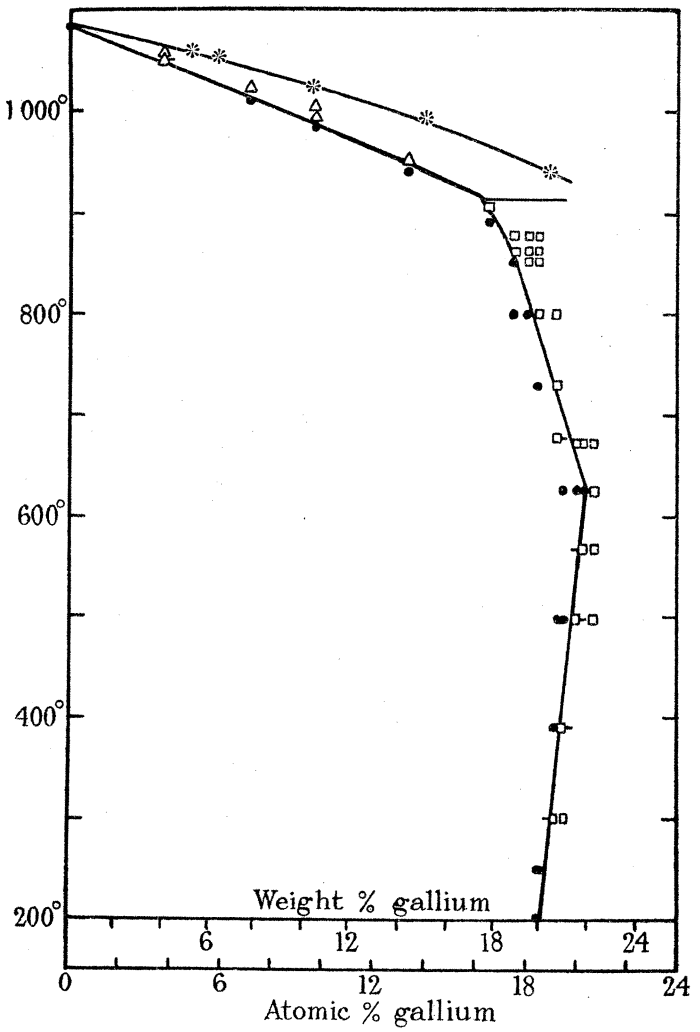

FIG. 21.—Copper-gallium. * Points from cooling curves; ● homogeneous α; Δ- α + trace of liquid; Δ α + liquid; □ α + trace of β; □ α + β.

Prolonged annealings and heat treatments were given in order to determine the solubility in the region of its maximum value at about 620°, and these are summarized in Table XXXIX. These observations are plotted on a larger scale in fig. 22, and it will be seen that, apart from the two points mentioned before, the results are consistent, and the solubility reaches a maximum value of approximately 20·25 atomic % gallium.

TABLE XXXVIII.

Composition of alloy.		Previous heat treatment.	Annealing temperature and time.	Micro-structure.
Weight % Ga.	Atomic % Ga.			
17·83	16·52	5 days 627° ,,	30 mins. 906° 30 mins. 893°	α + β α
18·87	17·49	2 days 700° ,, ,,	30 mins. 877°, 862° 30 mins. 852° 6 hours 800°	α + β α α
19·41	18·01	2 days 700° ,,	30 mins. 877°, 862°, 852° 6 hours 800°	α + β α
19·92	18·49	2 days 700° ,, None	30 mins. 877°, 862°, 852° 6 hours 800° 2 days 730°	α + β α + β α
20·69	19·21	2 days 700° ,,	6 hours 800° 2 days 730°	α + β α + β

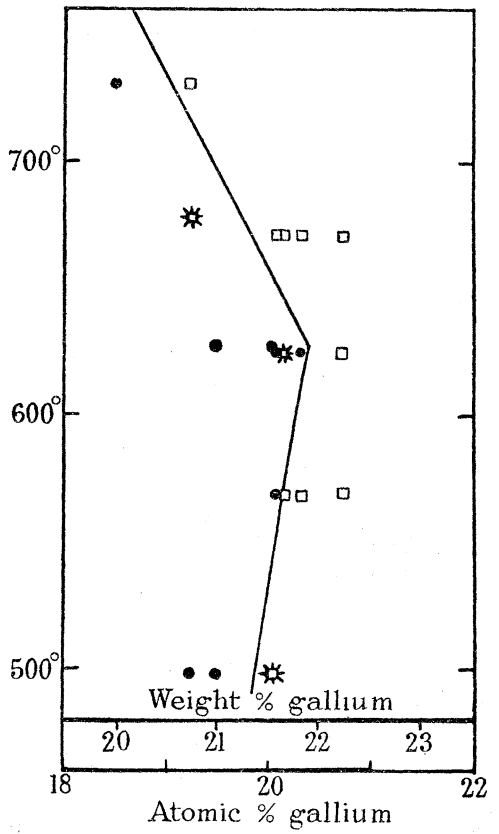

FIG. 22.—Copper-gallium; region of maximum α-solid solubility. ● Homogeneous α; * α + trace of β; □ α + β.

TABLE XXXIX.

Composition of alloy.		Previous heat treatment.	Time and temperature of anneal.	Micro-structure.	Remarks.
Weight % Ga.	Atomic % Ga.				
20·71	19·23	Hammered and then 5 days at 678°	4 days 678°	α + trace of β	Hammered again before the final anneal at 678°.
20·69	19·21	5 days 625°	5 days 498°	α	—
20·98	19·49	2 days 700° 5 days 625°	5 days 627° 5 days 498°	α α	—
21·55	20·03	4 days 491° ,,	5 days 627° 5 days 498°	α α + trace β	— Hammered after the 491° anneal.
21·61	20·09	24 hours 625°–730° 5 days 625° ,,	5 days 625° 2 days 569° 1 day 671°	α α α + β	—
21·66	20·13	24 hours 625°–730° 5 days 625° ,,	5 days 625° 2 days 569° 1 day 671°	α + trace β α + β α + β	Specimen hammered and then given 2 more days at 625°, after which it still showed traces of β. — —
21·86	20·32	24 hours 625°–730° 5 days 625° ,,	5 days 625° 2 days 569° 1 day 671°	α α + β α + β	May have contained a trace of β, but after 2 more days at 625° it was homogeneous. — —
22·26	20·71	4 days 624° 24 hours 625°–730° and then 9 days 625°	5 days 625° 2 days 569° 1 day 671°	α + β α + β α + β	Hammered after the 624° anneal. — Also 2 constituent at 500°.

The results for the low temperature portion of the curve are summarized in Table XL, which is self-explanatory. The solubility was always determined by the re-annealing of specimens which had been made homogeneous by previous treatment at a higher temperature. In alloy 19·21, annealed and quenched from 390°, the main alloy was homogeneous, but a few particles of a second constituent were present round a contraction cavity at the top of the ingot. At 300°, however, occasional particles of the second constituent had precipitated in the main bulk of the alloy. This alloy is there-

TABLE XL.

Composition of alloy.		Previous heat treatment.	Time and temperature of anneal.	Structure.	Remarks.
Weight % Ga.	Atomic % Ga.				
20·98	19·49	5 days 624° 5 days at 624° + 10 days at 390°	10 days 390° 2 weeks 300°	α + trace of β α + β	—
20·71	19·23	9 days 678° 9 days at 678° + 10 days at 390°	10 days 390° 2 weeks 300°	α + trace of β α + β	—
20·69	19·21	5 days at 625° + 5 days at 498°	10 days 390° 2 weeks 300°	α α + trace of β	See below.
19·92 19·41	18·49 18·01	2 days 730° 2 days 700°	3 weeks 200° 3 weeks 200°	α α	— —

fore described as homogeneous at 390° and two-phase at 300°, since abnormal results are known to be found when contraction cavities occur.

Discussion.—The figures in the collected tables are taken directly from the above work, and call for little comment. Owing to the smallness of the specimens available, the low temperature portion of the solubility curve is the least reliable, although the precipitation was clear at 300°. The general shape and position of the solubility curve are remarkably like those in the system copper-aluminium.

Copper-germanium.

Materials.—The germanium used for this work was kindly presented by Professor Dennis, of Cornell University ; it was described as the purest available, and no indication of impurity was found during the chemical analyses. Nine grams of metal were set aside for this research.

Preparation of Alloys.—The alloys were prepared, in the usual way, under charcoal. The greatest difference between the intended composition of the alloy and that determined by analysis was 0·23%, and in 11 out of 15 cast alloys the difference was within 0·1%.

Analysis.—For the analyses the alloys were dissolved in nitric acid, the solution neutralized with ammonia, made faintly acid with nitric acid, after which the copper was separated electrolytically. Owing to the fact that the first deposit tended to carry down a little germanium, the copper was redissolved and redeposited, then dried and weighed. The combined filtrates and electrolytes were evaporated and ignited to constant weight in a weighed silica crucible. Since the oxide, GeO_2, is very hygroscopic,

the weighing must be rapid. The oxide was tested for copper, and any traces of this metal estimated colorimetrically. Twenty-one determinations were carried out, and the extreme values for the sum of the percentages of copper and germanium were 99·80 and 100·10, whilst in twelve determinations the totals lay between 99·95 and 100·05. In one alloy the germanium had to be determined by difference owing to an accident in manipulation.

Segregation Effects.—Segregation effects were not observed in alloys containing less than 11·7 atomic % germanium, but in alloys 11·92 and 12·26 distinct traces of inverse segregation were noted, the relative amount of the second (β) constituent being greater at the outside of the ingot. This does not affect the determination of the solubility line, since no alloy was found in which one part was homogeneous and another part two-phase, but for alloys containing higher percentages of germanium, sand castings would be advisable.

The Liquidus.—Points were obtained on the liquidus by the quenching method, and also by means of cooling curves, and, as will be seen from Table XLI, a fair agreement has been obtained between the results from the two methods. In the quenching experiments all the specimens were analysed after the high temperature treatment, except alloy 10·91. The loss in germanium content caused by annealing in the semi-liquid area was about 0·2 to 0·3%, so that the points for alloy 10·91 are not likely to be seriously wrong. For the cooling curve ingots the composition was determined by the analysis of the whole ingot for the alloy marked * in Table XLI.

In alloy 2·72 we have taken the synthetic composition in preference to the value given by the analysis of a section, since a later analysis indicated that segregation had

TABLE XLI.

Composition of alloy.		Temperature.	Structure or arrest point.	Remarks.
Weight % Ge.	Atomic % Ge.			
3·01*	2·66	1058	Arrest point	Remelted ingot.
3·07	2·72	1057°	Arrest point	2° super cooling.
2·94	2·59	1071°	Chilled liquid	Quenching method.
2·94	2·59	1065°	Chilled liquid + a little solid α	Quenching method.
3·96	3·49	1053°	Arrest point	Cooling curve.
5·67	5·02	1054°	Chilled liquid	Quenching method.
5·67	5·02	1043°	Chilled liquid + a little solid α	Quenching method.
6·90	6·10	1032°	Arrest point	Cooling curve.
10·19	9·06	1004°	Chilled liquid	Quenching method.
10·19	9·06	990°	α + chilled liquid	Quenching method.
10·21	9·08	1005°	Arrest point	Cooling curve.
12·24	10·91	981°	Chilled liquid	Quenching method.
12·24	10·91	959°	α + chilled liquid	Quenching method.
14·14	12·64	936°, 921°	Arrest point	Cooling curve.

occurred. In this alloy some super-cooling occurred and the arrest is probably a little too low. Alloy 2·66 is the same ingot remelted, but owing to an accident it had to be melted twice (making three meltings in all) before the curve was taken, and the ingot only weighed about $3\frac{1}{2}$ grams.*

In other alloys the composition was determined by the analysis of a complete vertical section. At this stage in the work the dangers of segregation effects had not been fully appreciated, but the analytical values agree so closely with the intended compositions that it is improbable that appreciable errors have been introduced.

The Solidus.—The points found for the solidus are given in Table XLII, and a reasonable curve can be drawn through them, with the exception of the one point for alloy 8·30. The peritectic horizontal was determined as lying between 818° and 826° by the quenching method, and at 821° by the cooling curve of alloy 12·64 (Table XLI).

TABLE XLII.

Composition of alloy.		Temperature.	Structure.	Remarks.
Weight % Ge.	Atomic % Ge.			
2·94	2·59	1055°	α + chilled liquid	—
2·94	2·59	1040°	α + trace of chilled liquid . .	—
5·47	4·83	990°	α + chilled liquid	—
5·47	4·83	979°	α	—
5·92	5·23	974°	α + chilled liquid	Germanium estimated by difference.
5·92	5·23	959°	α	—
7·83	6·94	941°	α + a little chilled liquid . .	—
7·83	6·94	932°	α	—
9·35	8·30	934°	α + chilled liquid	—
9·35	8·30	920°	α	—
10·44	9·28	897°	α + chilled liquid	—
10·44	9·28	885°	α	—
11·98	10·68	850°	α	—
12·70, 13·04	11·33, 11·64	850°	α + chilled liquid	—
12·70, 13·04	11·33, 11·64	826°, 818°	α	—
14·14	12·64	821°	Peritectic temperature . . .	Cooling curve arrest.
13·35	11·92	826°	α + chilled liquid	Quenching method.
13·35	11·92	818°	α + β	Quenching method.

The Solubility Line.—The early experiments showed that the solubility increased with temperature, and that prolonged annealing was necessary for equilibrium to be attained at the lower temperatures. Thus at 562° C. a direct anneal of 5 days placed

* The ingot was cut into three slices, and the centre portion and the two outside slices analysed separately, the result being 3·10 and 2·92 by weight. The mean value 3·01 is given in the table, but the true value may be more nearly 3·10 since difficulties in manipulations affected the value 2·92 for the outside portions.

the solubility limit between alloys 10·19 and 10·37, but with specimens previously made homogeneous at 700°, and then re-annealed at 561°, the limit at the latter temperature was found to lie between alloys 10·37 and 10·68, so that the change is of the order 0·3% (atomic).

These results are summarized in Table XLIII.

TABLE XLIII.

Composition of alloy.		Time and temperature of anneal and quench.	Structure.	Previous heat treatment and other remarks.
Weight % Ge.	Atomic % Ge.			
11·63	10·37	3 hours 853°	α	3 days 700°
11·98	10·68	3 hours 853°	α	3 days 700°
12·24	10·91	3 hours 853°	α	3 days 700°
12·70	11·33	3 hours 853°	α + chilled liquid	3 days 700°
13·04	11·64	3 hours 853°	α + chilled liquid	3 days 700°
12·70	11·33	5 hours 800°	α	42 hours 680°
13·04	11·64	5 hours 800°	α	42 hours 680°
13·35	11·92	5 hours 800°	α + β	42 hours 680°
13·73	12·26	5 hours 800°	α + β	42 hours 680°
12·70	11·33	18 hours 741°	α	5 days 680°–760°
13·04	11·64	18 hours 741°	α + β	5 days 680°–760°
11·98	10·68	5 days 682°	α	—
12·24	10·91	5 days 682°	α	—
12·70	11·33	42 hours 681°	α + β	3 days between 680° and 760°
13·04	11·64	42 hours 681°	α + β	3 days between 680° and 760°
11·43	10·19	2 days 570°	α	18 hours 700°
11·63	10·37	2 days 570°	α + ? trace of β	18 hours 700°
11·98	10·68	2 days 570°	α + β	18 hours 700°
12·24	10·91	2 days 570°	α + β	18 hours 700°
11·43	10·19	4 days 491°	α	3 days 700°
11·63	10·37	4 days 491°	α	Possibly a trace of β
11·98	10·68	4 days 491°	α + β	3 days 700°
11·98	10·68	5 days at 368°	α + β	15 hours at 700°
11·63	10·37	5 days at 368°	α + trace β	plus 6 hours at
11·43	10·19	5 days at 368°	α	750° to 780°

The results of these experiments are shown in fig. 23, from which it will be seen that the solubility of germanium in copper reaches a maximum of 12·0 atomic % at 821° C., and decreases to 10·5% at 200° C. The general nature of the diagram is very similar to that of the system silver-tin.

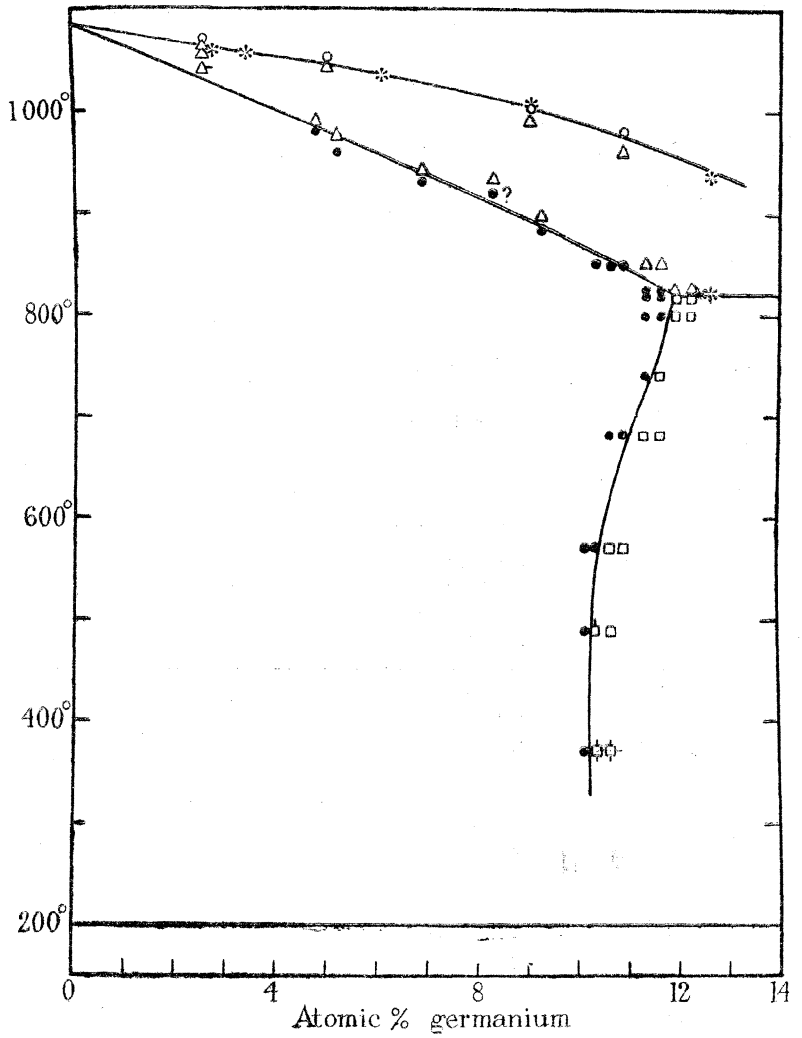

FIG. 23.—Copper-germanium. ● Homogeneous solid solution; □ α + β; Δ α + liquid; Δ- and traces of liquid; -□- α and traces of β; ○ totally liquid by quenching method.

Ternary Copper Alloys.

The copper-zinc-germanium and copper-zinc-gallium alloys were prepared by melting germanium or gallium with some of the specially pure brass used for the work on copper-zinc-alloys, whilst the copper-gallium-germanium alloy was prepared by melting the pure metals with copper. All the melting was carried out under borax in the cooling curve apparatus, fig. 13, and the cooling curve was then taken immediately.

The compositions of the cooling curve ingots were determined by the analysis of a complete vertical section. The analysis of the copper-gallium-germanium alloy gave almost exactly the same composition as that calculated from the weights of metals used.*

* In contrast to the results for the remelted ingots (see p. 15) in which both the gallium and germanium contents by analysis were lower than those intended. These were the first ternary alloys analysed, and the analytical technique was greatly improved for all remaining alloys.

In the remaining alloys the analyses indicated that a little zinc was lost in melting, whilst the germanium and gallium contents by analysis were slightly greater than those intended. This may be due to the fact that borax takes up a little of the copper during the melting, or alternatively to segregation effects. In only one alloy did the difference exceed 0·25%, and in this the higher germanium content was confirmed by the analysis of a further portion of the cooling curve ingot, which was cut off and used for the solidus determination. It does not seem probable that the results are substantially in error on account of segregation, because the analyses of the portions cut off for the solidus experiments gave analytical values for gallium and germanium which were within a few tenths of a per cent. of those obtained from the analysis of the complete sections, although the zinc contents diminished slightly on account of volatilization during the annealing at high temperatures.

For the solidus experiments the pieces from the cooling curve ingots were annealed for a few hours at 700° C., and heated to the quenching temperature, and held there for 30 minutes in the usual way. The appearance of chilled liquid was quite clear, and no marked segregation was noticed. This is in contrast to the results found with slowly-cooled copper-antimony and silver-indium alloys.

The results of these experiments have already been given in Tables X and XIX.

Copper-aluminium.

General.—The system copper-aluminium has been investigated by STOCKDALE,* who determined the liquidus and the boundary of the α-solid-solution, and stated that the liquidus and solidus were very close together. Two points on the solidus curve have been determined by one of us (K. M. C. E.). These experiments place the solidus points of alloys containing 8·08 and 11·57 atomic % of aluminium at 1060° and 1050° respectively. These points agree well with STOCKDALE'S values of 15·85 atomic % for the limit of the α-solid-solution at the peritectic horizontal at 1031° and it is noteworthy that the depression of the solidus is almost exactly one-third of that in the normal trivalent system copper-gallium. The alloys used were prepared from electrolytic copper and some specially pure aluminium of German origin containing 99·90% of aluminium.

Copper-arsenic.†

General.—The solubility of arsenic in copper has been determined by HANSON‡ as being almost exactly 7·25% of arsenic by weight, or 6·21 atomic %, and was found to be independent of temperature. In view of the results which we obtained for the

* 'J. Inst. Met.,' vol. 28, p. 273 (1922).

† These experiments were carried out by one of us (G. W. M.) as part of a thesis for Part II of the Honours Course in Chemistry, and for the B.Sc. degree of the University of Oxford.

‡ 'J. Inst. Met.,' vol. 37, p. 140 (1927).

solubility limit in copper-antimony alloys, it was thought of interest to confirm that there was no decrease in the solubility of arsenic at low temperatures.

We therefore prepared a series of alloys containing from 6·5 to 8% of arsenic by weight; the melting was carried out under borax and the alloys cast in the heavy copper moulds in order to give the finest possible structure. Portions of the castings were then annealed for one week at 550° one and two weeks at 500° and specimens from the 500° anneal were then re-annealed for one week at 400°, 350°, and 200° respectively. These experiments showed that the solubility limit at 550° lay between 5·91 and 6·40 atomic % of arsenic, and that no change occurred on re-annealing at the lower temperatures. These results are in complete agreement with those of HANSON.

Copper-antimony.

General.—The system copper-antimony has previously been investigated by CARPENTER,* who determined the liquidus accurately by cooling curves, the results of which are in good agreement with those of TASAKI,† who used a resistance method. In a further paper by REIMANN‡ the results are only given in the form of a small-scale diagram. According to CARPENTER, whose alloys were annealed for periods of six weeks, the solubility limit of alloys annealed to equilibrium was about 4 atomic % of antimony or nearly 8% by weight. More recently ARCHBUTT and PRYTHERCH§ have given the solubility limit as lying between 9·5 and 10·0% antimony by weight at high temperatures.

The present investigation‖ was the first of the series described in this paper, and was carried out before an electric crucible furnace was available. The alloys were melted under charcoal in a small Fletcher injector furnace worked by a foot-bellows and were cast in chill moulds. After the work was completed the paper of ARCHBUTT and PRYTHERCH appeared, and suggested that the above methods of preparation might have introduced small amounts of oxygen owing to the existence of stable ternary compounds of copper, antimony, and oxygen which are able to enter into the alloy. A few of the alloys were, therefore, analysed completely for both copper and antimony, and the sum of the two percentages was of the order 99·4 to 99·5. The separation of copper and antimony is a difficult one, so that a little loss may be expected, but the difference is outside the limits of this error, and suggests that about 0·3 to 0·4% of oxygen was present in our alloys, and for this reason we present our results in brief outline only.

* 'Int. Z. Metallog.,' vol. 4, p. 300 (1913).

† 'Mem. Coll. Sci. Kyoto Imp. Univ.,' vol. 12, p. 249 (1929).

‡ 'Z. Metallk.,' vol. 12, p. 321 (1920).

§ 'J. Inst. Met.,' vol. 45, p. 265 (1931).

‖ The experiments in this paper were carried out by one of us (G. W. M.) for a research thesis for Part II of the Honours Course in Chemistry, and for the B.Sc. Degree at the University of Oxford.

Materials used.—Great difficulty was found in obtaining antimony of sufficient purity, and the metal finally used was 99·818% pure with 0·076% of arsenic, and 0·035% of sulphur as the chief impurities.

Experimental Methods.—The alloys were cast in $\frac{1}{4}$-inch and $\frac{3}{8}$-inch cylindrical chill moulds made of copper, so as to give a very fine structure, the remainder of the metal being poured into iron moulds. For the solubility determinations the specimens from the copper moulds were used almost exclusively, since they possessed the finer structure. Alloys prepared in this way were free from segregation effects, but some contained minute pinholes which could be seen under the microscope.

Owing to the breakdown of a thermostat, the preliminary annealing experiments were carried out by hand control for periods of ten hours, after which the specimen was quenched and either examined microscopically or given a further period of annealing. During this work the temperature was kept within 5° of the desired value. For the final work the Foster Temperature Regulator was used.

Analytical Methods.—The alloys used contained comparatively small amounts of antimony and in order to obtain the required degree of accuracy the antimony was determined directly by a modification of FINKENER'S* method. Its principle is the precipitation from acid solution of a basic ferric carbonate, which carries down the antimony. In the original method this is followed by the distillation of the antimony from the acid solution of the precipitate, but it was found more convenient to dissolve the iron precipitate containing the antimony as sulphide, and then to precipitate the antimony in hydrochloric acid. The precipitate of pentasulphide was allowed to settle for an hour or two, filtered through a Gooch crucible, washed with very dilute acetic acid saturated with hydrogen sulphide, and then heated for 2–3 hours in a current of carbon dioxide at 270°–280°, after which it was cooled in the stream of gas, and the antimony weighed as in sulphide. A second heating seldom gave any alteration in weight.

The Solubility Curve.—The results for the solubility curve are shown in Table XLIV. The solubility at the lower temperatures was determined by first annealing the specimens for 108 hours between 550° and 600° C. in order to render them homogeneous. They were then re-annealed at the lower temperatures for a period of 30 hours, and experiments showed that above 200° C. this was sufficient to ensure precipitation in those alloys which were outside the homogeneous area at the lower temperatures. At the higher temperatures the solubility limit was determined by annealing specimens for one week at 500°, 550°, and 600° C.

The results indicated that the solubility is practically unchanged between 625° and 550°, but shows a slight decrease at 500°, followed by a much more marked decrease below 450°. It is noteworthy that the β phase with which the α is in equilibrium undergoes a transformation in the neighbourhood of 450°, and the bend in the α-solubility

* 'J. Soc. Chem. Ind.,' vol. 8, p. 733 (1889).

curve is probably connected with this. Alloys which became two-phase on annealing at 200° and 300° showed patches with a very fine pearlitic structure, but at higher temperatures the antimony rich phase was precipitated as bluish-white lozenge-shaped particles in the grain boundaries, or, alternatively, in the cleavage planes.

TABLE XLIV.

Composition of alloy.		Final annealing temperature.											
Weight % Sb.	Atomic % Sb.	200°	300°	350°	400°	410°	440°	460°	470°	500°	550°	608°	625°
5·10	2·76	O	—	—	—	—	—	—	—	—	—	—	—
5·41	2·94	X	—	—	—	—	—	—	—	—	—	—	—
5·94	3·23	X	O	—	O	O	O	—	—	—	—	—	—
6·35	3·46	X	X	O	O	O	O	—	—	—	—	—	—
6·94	3·80	—	X	X	O	O	O	—	—	—	—	—	—
7·19	3·94	X	X	X	O	O	O	—	—	—	—	—	—
7·80	4·28	X	X	X	O	O	O	—	—	—	—	—	—
8·25	4·40	—	—	—	X	O	O	—	O	O	—	—	—
8·57	4·73	X	X	X	X	X	O	—	O	O	—	—	—
8·63	4·76	X	X	—	X	X	O	—	O	O	O	—	—
8·99	4·97	X	X	—	X	X	X	O	O	O	O	—	—
9·60	5·32	—	X	—	X	X	X	X	O	O	O	—	—
9·89	5·49	—	X	—	X	X	X	X	X	X	O	O	O
10·43	5·80	—	—	—	—	—	—	X	X	X	X	X	X

O = alloys which were homogeneous after annealing and quenching from a particular temperature.
X = Two-phase alloys.

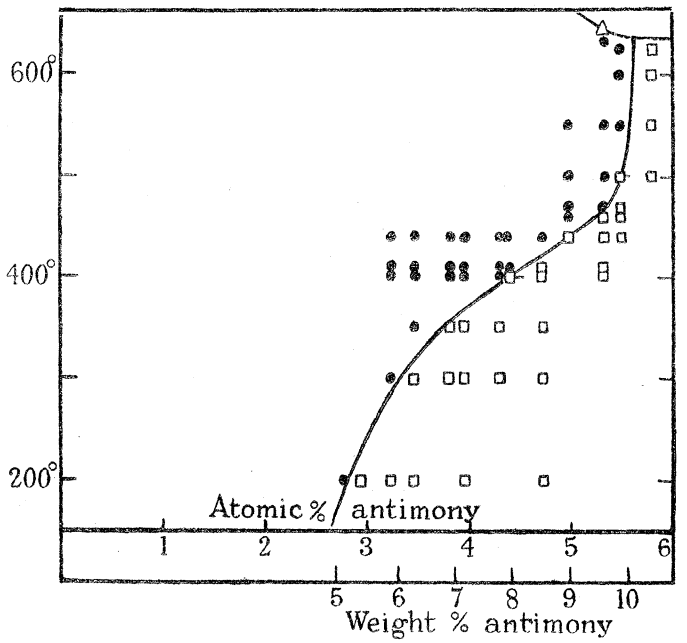

FIG. 24.—Copper-antimony; Δ α + liquid; □ α + β; □· α + traces of β; ● homogeneous α.

When compared with the early data given by CARPENTER, the present results indicate a higher solubility above 400°, but a smaller solubility at lower temperatures. The present value for the solubility at high temperatures is in very good agreement with that of ARCHBUTT and PRYTHERCH, although these investigators did not obtain a fall in solubility at the lower temperatures. Unfortunately, ARCHBUTT and PRYTHERCH did not anneal their alloys at temperatures below 400°, and although at this temperature the difference, according to our diagram, should be noticeable, it is not very great, and the discrepancy may possibly be due to the slight oxygen content of our alloys. Mr. BOWEN, of the University of Swansea, very kindly attempted to make X-ray measurements of the lattice constants of some oxygen-free alloys given to us by Mr. ARCHBUTT after we had annealed these at 600°. The results suggested that our diagram was correct in indicating a fall in solubility at low temperatures, but the coarse structure of the slowly-cooled vacuum-melted metals appeared to make it impossible to obtain satisfactory " powder " of uniform composition.

APPENDIX I.

Review of the experimental data used in the collected tables.

For the systems dealt with in the experimental section of the present paper we have already indicated the sources of the experimental data used in preparing the collected tables, and, except for the point mentioned below in connexion with the freezing point determinations of HEYCOCK and NEVILLE, little further comment is necessary. The following points may, however, be noted in order that the relative accuracy of the data may be appreciated.

For the liquidus curves the results of HEYCOCK and NEVILLE* have been used in the following systems :—

silver-copper.	copper-silver.
silver-zinc.	copper-gold.
silver-tin.	copper-tin.
silver-lead.	copper-lead.
silver-antimony.	copper-bismuth.
silver-bismuth.	

In spite of its early date this work is probably as accurate as any later determinations, except in a few systems where the purity of the second metal has been improved. The only point to be noted is that, presumably owing to differences in the calibration of their pyrometer, HEYCOCK and NEVILLE give slightly different values for the freezing

* ' Phil. Trans.,' A, vol. 189, p. 32 (1897) ; ' Trans. Chem. Soc.,' p. 413 (1897).

points of pure silver and copper in the different alloy systems. In each particular series of alloys, the points lie accurately on a smooth curve passing through the value which is given for the freezing point of the solvent (copper or silver) in that particular series, so that the differences for the values in the different systems appear to be systematic errors in each system. An alternative explanation would be that slight oxidation occurred in some systems, but this does not seem probable because some of the solute metals concerned undoubtedly act as deoxidisers, so that if oxidation were the cause of the low freezing point of the solvent, we should expect a slight flattening of the liquidus as the freezing point of the pure solvent was reached. Many of the points lie so accurately on a smooth curve that a flattening of this kind would be noticed even if it were only 2° or 3°. A general review of this and later work suggests that it is very rarely that the other factors concerned (*e.g.*, exact composition of alloy, calibration errors, impurities, etc.), make it justifiable to read the temperatures to more than 1°, and we have therefore read the temperatures given by HEYCOCK and NEVILLE to the nearest 1° and then applied a systematic correction in each alloy system so as to refer all the results to standard values of 1084° and 961° for the melting points of copper and silver respectively.

If, for example, in a particular series of alloys the freezing point of copper is given as 1081·7°, we have called this 1082°, and have added 2° to bring this up to the standard value of 1084°, and have then added 2° to all the liquidus values given in the same series. The corrections of this kind rarely exceed 2° or 3°, the extreme difference being for the copper-bismuth alloys, where the correction is 7°.

The majority of other investigators have taken values of 1084° or 1083° for the melting point of copper (more usually 1084°) and 960° or 961° for the melting point of silver as thermocouple calibration points, and we have again referred all determinations to the standard values of 1084° and 961° respectively.

Where this method of correction is valid probably most of the values taken from smoothed curves through HEYCOCK and NEVILLE'S points, are not liable to errors of more than 1° for every 20°–25° depression of freezing point. In an alloy of copper, for example, the points in the neighbourhood of 1060° are probably accurate to 1°, those at 1035° are accurate to within 2°, and so on.

In the present work with the comparatively small quantities of the rare metals, the errors in pyrometry tend to make the experimental liquidus points slightly too low, except above 1040° where the calibration error may counterbalance this effect. Unless large quantities of metal are used for the cooling curves, the general tendency in all work is for the arrest points to become too low for the more concentrated alloys in which the thermal arrests caused by the deposition of the α-solid-solution are slight. But with volatile metals, and frequently where the compositions have been determined by analysis, it is often the knowledge of composition which determines the accuracy unless the whole ingot is dissolved for analysis, since, as we have shown, the effect of segregation may be considerable.

The data for the following systems are from the sources indicated :—

Silver-beryllium.—The liquidus values used have been given to us by Dr. DESCH, to whom we must express our thanks. They are from unpublished work which has been carried out with very pure beryllium under the best possible experimental conditions.

Silver-zinc.—The maximum solubility value has been taken from the work of CARPENTER,* but the diagram given is not sufficiently large to enable the points on the solubility curve to be read off accurately. Sir HAROLD CARPENTER has since told us that, although reasonably correct, the solubility curve is probably not as accurately determined as those for others we have quoted, and we have not therefore included the figures in the tables or diagrams.

Silver-mercury.—The data here are from the work of MURPHY,† and the cooling curves were carried out under pressure. On account of the volatility of the metal, the points do not lie so accurately on a smooth curve as for HEYCOCK and NEVILLE'S work, but the values from the smoothed curve are not likely to be wrong by more than 5° above 850°. The solidus was determined by three points between 350° and 650°, but not above this temperature, whilst the shape of the solubility curve was not conclusively established.

Silver-aluminium.—The liquidus points used are from the work of HOAR and ROWNTREE (*loc. cit.*), and lie fairly well on a smooth curve, so that the points are not likely to be in error by more than 5° above 800°. The solidus points are from the work of one of us (K. M. C. E.).

Silver-tin.—The liquidus points of MURPHY‡ and of HEYCOCK and NEVILLE are in almost exact agreement over a very wide range.

Copper-beryllium.—The data used are from the work of BORCHERS,§ in which the cooling curves were carried out in an atmosphere of hydrogen under low pressure. The alloys were not analysed, but as the melting was carried out in crucibles lined with beryllium oxide, there is not likely to have been much contamination or change in composition. We have read the temperatures from a diagram, because the exact figures are not given, and errors of a few degrees may have been introduced in this way.

Copper-magnesium.—The freezing point data have been taken from the very extensive work of JONES,‖ who examined a large number of alloys ; a smooth curve can be drawn from which points do not differ by more than about 5°. The points are uniformly scattered about the smooth curve so that there are unlikely to be errors of more than 2° or 3° in the values given in the collected tables for the points above 980°.

* ' Int. Z. Metallogr.,' vol. 3, p. 145 (1913).
† ' J. Inst. Met.,' vol. 46, p. 507 (1931).
‡ ' J. Inst. Met.,' vol. 35, p. 107 (1926).
§ ' Metallwirts., vol. 11, p. 317 (1932).
‖ ' Inst. Met. ' (1931). Advance copy No. 574.

Copper-cadmium.—The liquidus points in this system are from the work of JENKINS and HANSON.* For the copper-rich alloys the points lie on a satisfactory smooth curve, the initial depression of freezing point being almost exactly 12° per 1 atomic %, which is the same as that in the system copper-magnesium within the limits of the experiments. In the more concentrated alloys the points of JENKINS and HANSON do not lie so accurately on a smooth curve, and here we have drawn a curve with the points scattered evenly on either side. For some reason which is not clear, JENKINS and HANSON drew their curve through the highest points, and thus obtained a curve which passed through some of the points, but lay above all the others. This appears to us to be unjustified, since with a volatile metal the errors are likely to be in connexion with the compositions as well as the temperature measurements. This difference between the two curves does not affect the results in the copper-rich region.

Copper-aluminium.—The data here are from the work of STOCKDALE,† and, except that the aluminium was not of the highest purity, the results for the liquidus are probably correct to within a few degrees. The solubility curve above 537° is also accurately determined, but there may be a slight fall in solubility below this point.

Copper-silicon.—The data for liquidus, solidus, and solubility curve are from the very careful work of SMITH,‡ who examined a large number of alloys. A smooth curve can be drawn from which no liquidus point differs by more than 5°, and the whole work appears of the highest quality.

Copper-tin.—The data for the liquidus are from the work of HEYCOCK and NEVILLE, and for the solidus and solubility curve from that of STOCKDALE.§ The solubility curve is accurate above 518° (the portion where the solubility decreases with rise of temperature), but below this point work by other investigators suggests that a slight fall in solubility may take place.

Copper-zinc.—The freezing point data have been taken from a smooth curve through the points obtained by PARRAVANO,|| TAFEL¶, JITSUKA (*loc. cit.*), and RUER and KREMERS (*loc. cit.*), the greatest weight being given to the results of the last-named investigators. The difficulties caused by the volatility of the zinc make the values uncertain by a few degrees. The solidus points are taken from the present work, and the solubility curve data have been taken from the results of GENDERS and BAILEY (*loc. cit.*) and GAYLER,** and appear satisfactorily accurate above 400°.

* ' J. Inst. Met.,' vol. 31, p. 268 (1924).
† ' J. Inst. Met.,' vol. 28, p. 273 (1922).
‡ ' J. Inst. Met.,' vol. 40, p. 359 (1928).
§ ' J. Inst. Met.,' vol. 34, p. 111 (1925).
|| ' Gazz. Chim. Ital.,' vol. 44, p. 478 (1914).
¶ ' Metallurgie,' vol. 5, pp. 349, 375 (1908).
** ' J. Inst. Met.,' vol. 34, p. 235 (1925).

APPENDIX II.

As indicated in Part I of this paper, we have taken the atomic diameter of elements such as zinc or antimony to be that given by the closest distance of approach in the crystal of the element, rather than the " atomic diameter " as given by GOLDSCHMIDT. Our reason for this is that, in the first place, in trying to find the principles which determine whether one element will form a solid solution with another, it is clearly more satisfactory to use a value which is a constant of the element itself, rather than one which can only be deduced when the structure of an alloy has been determined.

In the work of GOLDSCHMIDT the idea was to find a series of atomic diameters which could be used in different crystal structures when allowance had been made for the different co-ordination numbers (*i.e.*, the number of close neighbours in the crystal). Where metals such as zinc or antimony were dealt with, two principles were used in order to obtain an atomic diameter for a standard co-ordination number of 12. In the first method the lattice expansion or contraction in, say, the copper-antimony α-solid-solution was studied, and if this was found to be a linear function of the composition, it was assumed that the atomic diameter of the solute could be estimated by extrapolation of the straight line. The defect of this method is that in some of the simplest systems (*e.g.*, copper-silver or silver-gold, where solvent and solute have the same valency and crystal structure), the lattice expansion or contraction is not given by a straight line. Consequently it seems very arbitrary to assume that in other more complex systems a true " atomic diameter " can be obtained by extrapolation of a straight line. In the second method the crystal structure of a compound with co-ordination number 12 was investigated. Thus the atomic diameter of antimony was deduced from the structure of the compound Ag_3Sb, which has a close packed hexagonal structure with co-ordination number 12. The objection to this method is clearly that many of these substances are co-valent compounds rather than normal metals, and it again seems rather arbitrary to deduce atomic diameters in this way. The general idea of GOLDSCHMIDT is undoubtedly correct, but it appears to us that for the α-solid-solutions the true answer will be more complicated than GOLDSCHMIDT has assumed, and will involve both electronic and atomic factors. An additional factor which has influenced us to use the closest distances of approach in the crystal of the elements is that we have shown elsewhere that many of these values obey comparatively simple whole number relations which do not involve large corrections for co-ordination number. Thus in the carbon series the atomic diameters of carbon, silicon, titanium, zirconium, hafnium, and thorium obey a relation $\frac{d}{n} = \frac{1}{aZ} n$, where Z is the atomic number and n the quantum number of the outermost shell of electrons in the *ion* of the element. In passing from silicon with co-ordination number 4 to titanium with co-ordination

number 12 there is no indication that a correction of the order 10–12% is needed as GOLDSCHMIDT'S values would suggest, so that it appears that the closest distance of approach in the crystal of the element is a very fundamental constant.

The only other point to be noted is the change in atomic diameter caused by incomplete ionization in the elements of the B sub-groups. In tin we can compare the closest distance of approach in the grey tin (diamond structure with normal co-valency of 4) with that of the incompletely ionized white tin, and the difference is of the order 0·3 A, and we have therefore used this value for other elements such as indium, where the values are approximately the same. In aluminium the atomic diameter in the element which is incompletely ionized is 2·87A. We have shown elsewhere that at the beginning of this period the atomic diameters of the completely ionized sodium, magnesium, and silicon vary as $1/Z^2$. Taking the atomic diameters of magnesium as 3·2 A., and of silicon as 2·35 A., these give the atomic diameter of the normal trivalent aluminium as 2·72 A, which, it will be noted, is within the zone of favourable size limit for both copper and silver, and is very nearly equal to the closest distance of approach (2·77 A.) of two aluminium atoms in the δ Cu_9Al_4 phase where the aluminium atom is certainly in the trivalent state.

ACKNOWLEDGMENTS.

The experimental work on copper-antimony alloys was begun at the Dyson Perrins Laboratory, where temporary accommodation was kindly arranged by the late Professor W. H. PERKIN, F.R.S. The remainder of the work has been carried out at the Old Chemistry Department, the University Museum, Oxford, and we must express our thanks to Professor F. SODDY, F.R.S., for his kindness in giving both laboratory accommodation and many other facilities which have encouraged us.

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available was too small to enable the analyses to be repeated. That, under these conditions, the analytical work could always be relied upon was one of the principal factors which enabled us to determine the solubility limits successfully with such small quantities of material.

Summary.

(1) The factors affecting the formation of primary (α) substitutional solid solutions in silver and copper by the elements of the B sub-groups have been investigated. Complete experimental determinations of the solidus curves and solid solubility limits of the α-solid-solutions are given for the systems silver-cadmium,* silver-indium,* silver-gallium,* silver-aluminium, copper-gallium,* copper-germanium,* and copper-antimony. Partial or confirmatory determinations are given for the systems silver-zinc, silver-tin, copper-zinc, copper-aluminium, copper-arsenic, and for ternary alloys of copper* with zinc, gallium, and germanium.

(2) The formation of a considerable solid solution is determined first by the atomic diameters of solvent and solute. If these differ by more than about 14 per cent. of that of the solvent A., the solid solution is restricted to a few atomic per cent., but, where the " size factor " is favourable a considerable solid solution is usually formed, and the solubility limits generally obey clear valency rules.

(3) Where solvent and solute are in the same period (*e.g.*, silver, cadmium, indium . . .) the atomic compositions of alloys of a given freezing point vary inversely as the valency of the solute as far as Group V, whilst the compositions of alloys of a given melting (solidus) point are approximately inversely proportional to the square of the valency of the solute as far as Group IV. Both these laws apply to ternary alloys.

(4) When solvent and solute are in different periods the initial depression of freezing point is usually greater than that to be expected from the normal valency effect. But many of the solute atoms act as though they possessed a fictitious valency which is a whole number, and to which the name " liquidus factor " is given. It is shown that these same liquidus factors apply to many ternary alloys, and methods are given for the accurate calculation of liquidus points in ternary and quaternary alloys where the binary curves are known.

(5) Where the size factor is favourable the maximum solid solubility is determined mainly by the concentration of valency electrons, and this principle is shown to permit the approximate calculation of the solubility limits in certain ternary alloys.

* Liquidus determinations were also made.