[CONTRIBUTION FROM THE MANUFACTURING DEVELOPMENT BRANCH OF THE WESTERN ELECTRIC COMPANY, INC.]

THE RELATION BETWEEN PSEUDO BINARY LINES AND SOLID SOLUTIONS IN METALLIC TERNARY SYSTEMS

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General Discussion

It is customary, in treating ternary metallic systems, to assume that a compound between two of the components behaves toward the third component as if it were an entirely new substance. This relationship undoubtedly holds in a good many cases, but should not be accepted as a universal axiom. Metallic compounds do not follow the ordinary rules of valence, so it is not surprising that they should vary in other ways.

Let us consider the hypothetical system (Fig. 1) composed of the metals A, B and C, in which a compound, BC, is known to exist in the solid phase, but dissociates in the liquid phase. The pseudobinary line is made by connecting the point BC with A. Ordinarily one would expect that mixtures of the composition indicated by this line BC–A would behave like any common binary system, providing that there was no compound formation between BC and A. Small additions of A to BC should lower the freezing point in which the primary crystals would still be BC. Like results should be obtained on the addition of small amounts of BC to A, giving a true eutectic freezing-point diagram (Fig. 2). Freezing-point curves of melts taken on such a line should show only two distinct breaks, such as are found in ordinary binary systems. The first break corresponds to the separation of one of the constituents, and the second to the eutectic mixture of the two. Since B and C are always separating in the ratio in which they exist in the compound, there can be no break corresponding to the separation of pure B or C and, further, on *analysis* the *ratio of B to C must remain constant* in all parts of the melt.

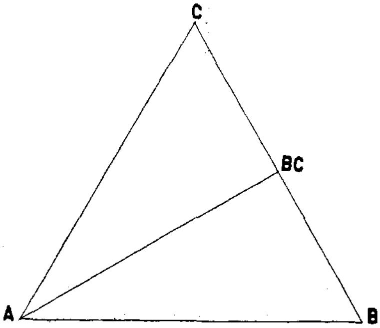

Fig. 1.

Now, permitting Melt K to cool slowly, according to Fig. 2 it should remain entirely liquid until the point L is reached. At this time pure A should separate and the liquid change composition along the line L–E. The lowering of the freezing point of A has been due to the addition of a certain amount of B and a certain amount of C and not to the compound BC, since it has been assumed that BC dissociates in the liquid stage. The result is that the freezing-point depression is greater than would be calculated for the number of moles of BC indicated by the diagram. The formation of a solid solution of either B or C in A would have a tendency to decrease the freezing-point lowering. Therefore a solid solution would separate at a temperature greater than that indicated by Point L (Fig. 2). As soon as a solid solution separated as the primary crystal, the ratio of B to C would be altered and the composition would no longer remain on the pseudobinary line. As solid solution of B in A continued to separate, the liquid would become richer in C so that eventually C must separate in some other form than as BC. The pseudobinary line under these conditions loses all resemblance to a binary system and becomes just a series of compositions on the surface of a ternary diagram.

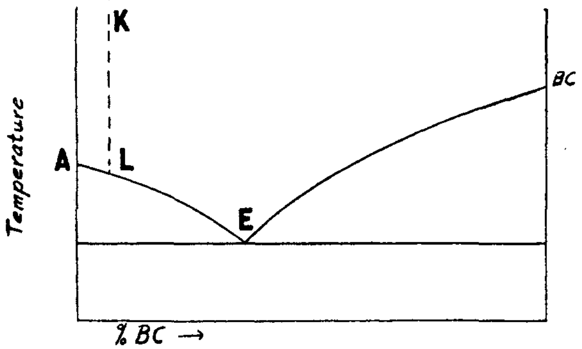

Fig. 2.

Experimental Procedure

In order to test the validity of these assumptions, the Cu_2Sb–Pb line in the lead–antimony–copper system was used. The eutectic point on this line must be near the lead end as evidenced from consideration of the ternary diagram.[1] Accordingly a mixture was made up corresponding to a composition of 99.9% of lead and 0.1% of Cu_2Sb by weight. The melt was heated to a high enough temperature to insure melting and thoroughly agitated to give uniform composition. The mixture, was then allowed to cool very slowly in the furnace so as to approximate, as closely as possible, equilibrium conditions. After complete solidification, careful analyses of different portions of the melt were made; the results are tabulated in Table I. If this composition were close to the eutectic between Cu_2Sb and Pb, the ratio of Pb to Cu_2Sb should remain constant

TABLE I

ANALYSES OF 0.1% Cu_2Sb SAMPLE

Place of sampling	Side surface	Center	Halfway from center	Top surface
Sb, %	0.02	0.05	0.01	0.23
Cu, %	.05	.05	.05	

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[1] Morgen, "The System Copper–Lead–Antimony" (not yet published).

in all parts of the sample. At any rate if the pseudobinary line exists as such in this region, the ratio of copper to antimony should be constant in all parts of the sample. The fact that the copper content was constant while the antimony varied 1000% was rather surprising. As a result, another melt was made containing only 0.05% of copper and no antimony. Both samples were then studied microscopically. Two unusual photomicrographs (Figs. 3 and 4) were obtained. The samples were prepared by cutting with a microtome and etching with a mixture of acetic acid and hydrogen peroxide. In both cases fine needles having a distinct copper color, were found sticking up from the surface. The needles seemed to be always sticking up from the surface regardless of the place of sampling. This is explained on the basis that the needles were so fine that those lying down were washed away when the etching reagent attacked the surface of the lead. That the same type structure was found in both cases, one of which contained no antimony, confirmed the belief that the needles were copper. These results also check with facts of ordinary refining practice. Copper can be removed from molten lead down to about 0.06% of copper. Our results indicate that the actual copper-lead eutectic contains 0.05% of copper by weight.

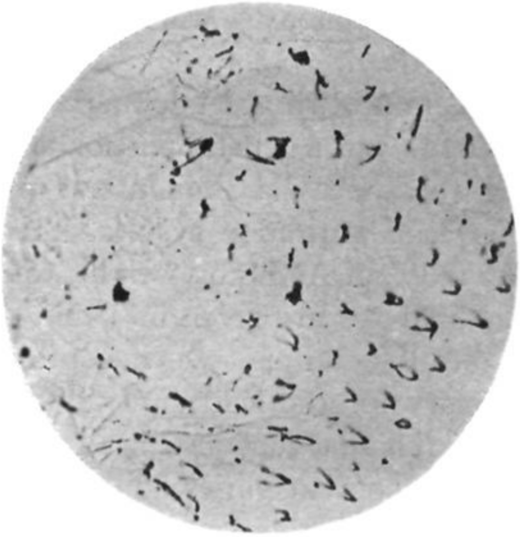

Fig. 3.—99.9% of Pb, 0.05% of Sb, 0.05% of Cu, showing needles sticking up from surface.

Fig. 4.—99.95% of Pb, 0.05% of Cu, showing needles sticking up from surface.

Fig. 5.—98.95% of Pb, 1.0% of Sb. 0.05% of Cu, showing primary blue-violet needles of Cu_2Sb.

An attempt was next made to see if the location of the pseudobinary line could be found in the lead corner. A photomicrograph (Fig. 5) of a sample containing 98.95% of lead, 1% of antimony and 0.05% of copper was made. In this case the very characteristic, blue-violet needles of Cu_2Sb were found. Therefore, the Cu_2Sb line hits the lead-antimony axis somewhere between 0.05 and 1.0% of antimony. This is within the range of solid solubility of antimony[2] in lead.

In order to prove that the change of direction of the pseudobinary line was not a specific property of these components, but a general phenomenon in the presence of solid-solution-forming substances, a similar test was made on the Ag_3Sb–Pb line in the silver–lead–antimony system. Two samples, one containing 3% and the other 0.3% of Ag_3Sb by weight, were melted and cooled slowly as before. The analyses are given in Table II. The segregation is more noticeable in the 3% sample, which contains approximately the amount of silver necessary for the lead–silver binary eutectic. In this case the amount of silver remains constant in all parts of the melt to within 1%, while the antimony content varies 30%. This is exactly the same sort of behavior obtained with the copper alloys, so the results can hardly be called accidental.

TABLE II

ANALYSES OF MELTS ON Ag_3Sb LINE

Sample	1	1	1	1	2	2	2	2
Source	Top surf.	Side surf.	Bottom	Center	Top surf.	Side surf.	Bottom	Center
Sb, %	0.90	0.64	0.62	0.76	0.21	0.12	0.11	0.10
Ag, %	2.28	2.30	2.28	..	.21	.16	.16	..

Conclusions

The results in this paper show that pseudobinary lines are not always made by connecting the point representing the binary compound with the third component. The formation of a solid solution of either of the constituents of the compound with the third component changes the directions of the line. The amount of change depends on the relative stability of the solid solution and the compound. It is to be expected that this effect would be more pronounced in the case of a compound which dissociates in the liquid phase than in the case of a compound which gives stable molecules in the liquid state. At the present time, it has not been possible to demonstrate conclusively whether the solute atoms are distributed at random through the solvent crystal structure or whether the solute atoms appear at definite intervals in the solvent structure. If the solute atoms are placed regularly in the solvent lattice, there probably is no more sharp a distinction between stable solid solutions[3] and weak compounds which dis-

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[2] Dean, Zickrick and Nix, *Trans. Am. Inst. Mining Met. Eng.*, preprint (1926). Morgen and Roberts (not yet published).

[3] Tammann, *Ann. Physik*, **79**, 81 (1926). von Laue, *ibid.*, **78**, 167 (1925).

sociate completely on melting than there is between metals and non-metals in the periodic table.

The writer wishes to thank Mr. E. F. Salchow, who took the photomicrographs, and Mr. R. S. Dean, under whose direction the work was performed and whose advice and suggestions made the paper possible.

Summary

A pseudobinary line is defined as the line connecting the point, representing a compound between two constituents, with the third constituent in a ternary system. Experimental evidence is given to show that mixtures corresponding to compositions on this line do not behave like an ordinary binary system. Photomicrographic as well as analytical evidence is used to show that solid-solution formation may proceed at the expense of a weak metallic compound.

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THE RATE OF RACEMIZATION OF PINENE. A FIRST-ORDER, HOMOGENEOUS GAS REACTION

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During a recent discussion by Professor G. N. Lewis and the author it was suggested by Professor Lewis that a racemization reaction would present novel features from the standpoint of theories of chemical reaction. Thus it is a reaction without heat effect and is perfectly symmetrical, the corresponding forward and reverse rates being equal. Also, the mechanism of inversion from one optically active isomer to its mirror image is easy to interpret in terms of our ideas of activated molecules, an active molecule in this case presumably having an equal chance of changing to the one or the other isomer. The course of the reaction is easily followed by measuring the rotation of the plane of polarized light produced by the mixture of the isomers.

Most racemizations that have been studied have been of polar substances (acids or bases in many cases) whose inversions usually are subject to catalysis or other complications due to ionization. Moreover, a racemization *rate* in the gas phase has to my knowledge never yet been measured. The type of reaction most interesting from the standpoint of the development of theories of reaction rate is a first-order homogeneous, gas reaction which is uncatalyzed by the walls of the containing vessel or otherwise. Thus far we have only two reactions approximating to this type.[2,3]

[1] National Research Fellow in Chemistry.

[2] (a) Daniels and Johnston, THIS JOURNAL, **43**, 53 (1921). (b) Lueck, *ibid.*, **44**, 757 (1922).

[3] Smith, *ibid.*, **47**, 1862 (1925).