

medium, and which simply occupy the spaces left by the earlier formed crystals of other constituents. This criterion must, however, be used with great caution. Thus in Fig. 20, p. 48, certain off-shoots of the eutectic into the dark ground mass might readily suggest that they were idiomorphic. But, on closer examination, we see that these spines really follow the orientation of the dark crystals, so that the eutectic, instead of having sent out early spines which have persisted, has simply occupied certain spaces left within the crystals of the earlier formed constituent.

### CHAPTER III.—FREEZING-POINT CURVES

40. PHYSICAL PROPERTIES OF SERIES OF ALLOYS, OR THE GENERAL SYSTEM IN WHICH THE CHANGES IN ANY GIVEN CRITICAL POINT OR CRITICAL COMPOSITION OCCUR AS WE PASS FROM ONE END OF A SERIES TO ITS OTHER END.—The importance and indeed the meaning of this class of studies can best be seen after we have examined an individual case, of which the “freezing-point curve” is probably the most important.

41. FREEZING-POINT CURVE.—In the cooling curves in Figs. 8, 9, 11, and 28 *B, C, D* and *F*, pp. 18 and 60, we may note two critical temperatures, *B* at which the freezing of the excess-substance begins, and *CD* at which it ends and the freezing of the eutectic occurs. For brevity we may call these the two freezing-points, *e. g.*, for each alloy of lead with tin. Now, to bring together and compare the teaching of all these cooling curves and to see in what manner these freezing-points vary, as we pass from pure lead through the lead-tin alloys to pure tin, we may plot, as in Fig. 24, p. 54, with temperature as ordinate and percentage of tin as abscissa, the position of these two freezing-points, when we find that the upper freezing-points fall into a V-shaped curve, *ABC*, underscored by a horizontal line *aBc*, the freezing-point of the eutectic.\* Let us here

\*Let the reader clearly impress on his mind at the outset that each point in this and like diagrams represents both a specific temperature through its vertical distance from the horizontal axis, and a specific composition through its horizontal distance from the vertical axis. For instance, the point *B* represents the temperature of 180° through its height, and it also represents the composition lead 31 per cent, tin 69 per cent, through its distance to the right of the axis *OA*.

at once recognize this, the essential feature of this family of curves, the underscored *V*. The line *AB* is the locus of the temperature at which lead begins to freeze out from molten lead-tin alloys which contain an excess of lead over the eutectic ratio of 31 per cent, starting with 326° C., the melting-point of pure lead, and ending with 180°, the freezing-point of the eutectic. So, too, *BC* is the locus of the temperature at which the freezing of tin begins in case of all alloys of lead with tin containing less than 31 per cent of lead, or in other words containing an excess of tin over the eutectic ratio. The line *aBc* represents the temperature at which the eutectic freezes in each alloy.\*

42. TWOFOLD ASPECT OF THE V-CURVES.—We saw in § 29, p. 33, that during selective freezing the mother-metal was at every

\*To make perfectly clear the relation between the freezing-point curve and the individual cooling curves, of the two freezing-points of which it gives the loci, let us follow the cooling of some one alloy, say that of 55 per cent of lead, and hence with 24 per cent excess of lead over the eutectic ratio. Let us assume that the molten alloy has been first superheated above its melting-point, say to 350°, G. Following the course of its cooling along the line *GHJK*, it cools past 326°, the freezing-point of lead, without undergoing any freezing; the lead remains molten at a temperature below its own freezing-point, because the new substance, the molten solution, which its integration with the tin forms, has a lower freezing-point; the tin dissolved in the lead lowers the freezing-point of the lead. Only when the temperature falls to about 225° C. does any lead begin to freeze. As the temperature further falls from *H* to *J*, crystals of lead continue freezing out within the molten metal, while the mother-metal, or part still remaining molten, thereby grows correspondingly and progressively richer in tin and leaner in lead. This continues until the temperature has reached 180°, when the molten mother-metal will have become so far impoverished in lead as only to contain 31 per cent of that metal; in short, it will have reached simultaneously the freezing-point of the eutectic and the composition of the eutectic. At this point further cooling is arrested by the heat liberated through the solidification of the eutectic; and only when the whole of the mother-metal shall have frozen, yielding the well-known interstratified plates of the eutectic, only then will the temperature again begin to fall. In this line then, *GH* corresponds to the part *AB* of the cooling curve in Fig. 28 *D*; *HJ* represents the excess-freezing period and corresponds to *BC*; the point *J* represents the jog *CD*, the eutectic-freezing period; and *JK* represents the part *DE*. The fact that the line *aBc* is horizontal represents the fact that the jog *BD* has the same ordinate, *i. e.*, that the eutectic freezes at one and the same temperature, no matter what the initial percentage of lead and of tin in the molten alloy is.

instant at its then freezing-point; that as the temperature progressively fell, so the composition of the mother-metal shifted through selection, in such a manner that its composition at any instant was that for which the freezing-point was the then existing temperature. Now, since *AB* is the locus of the freezing-points for all different compositions between lead 100 and lead 31 per cent, it follows that during this selective freezing it is also the locus of the temperature and composition of the mother-metal throughout selective freezing. Thus starting with a given composition, say lead 55, tin 45, *GK*, Fig. 24, freezing begins at 225° (*H*), and as freezing proceeds, both the composition and the tem-

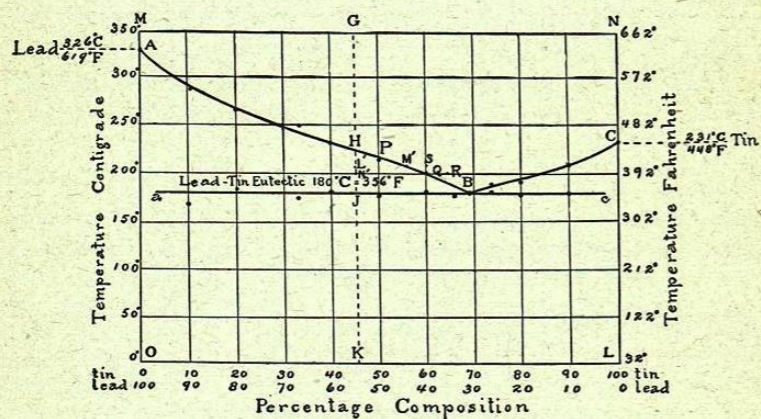


Fig. 24. Freezing-point Curve of the Lead-tin Alloys.

Roberts-Austen, *Fourth Rept. Alloys Research Committee*, Fig. 5, Plate 4, 1897.

perature of the mother-metal are continuously represented by points on *AB*; or in other words the temperature and composition of the mother-metal slide along *AB* from *H* to *B*.

The lines *AB* and *BC* then have a twofold meaning; for varying initial composition of the molten mass they are the loci of the temperature at which freezing begins; while for given initial composition they are loci of the temperature and composition of the mother-metal during selective freezing.

43. PROLONGATION OF THE V-CURVES BEYOND THEIR APEX. — In certain cases the V-branches *AB* and *CB* of the freezing-point curve have been traced beyond their intersection, as shown in

Fig. 25. This has been done independently by Le Chatelier,\* Dahms,† and Roberts-Austen.‡ Fig. 26 gives the cooling curve of the alloy of tin 64 per cent, lead 36, represented by the points

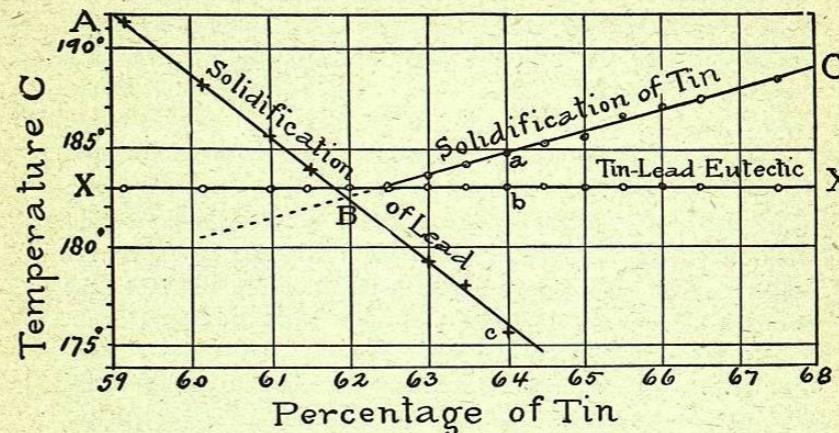


Fig. 25. Freezing-point Curve of Lead-tin Alloys. Roberts-Austen, *Proc. Royal Soc.*, LXIII, p. 452.

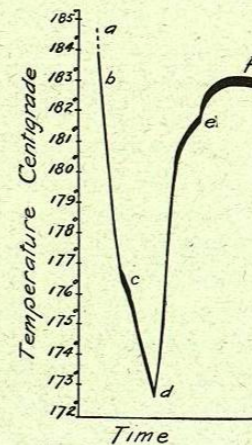


Fig. 26. Cooling Curve of Surfusation in Lead-tin Alloys; Tin 64 per cent; Lead 36 per cent.

Roberts-Austen, *Proc. Royal Soc.*, LXIII, Pl. 9.

\* Le Chatelier, *Comptes Rendus*, April 9, 1894.

† Dahms, *Ann. Phys. Chem.*, LIV, p. 386, 1895.

‡ Roberts-Austen, *Proc. Royal Soc.*, LXIII, p. 452, 1898.

*a*, *b* and *c* in Fig. 25. The lettering on these two figures is made to correspond.

This phenomenon we refer to surfusion. That surfusion should occur is in agreement with what we have already seen in § 30, p. 35. That the point *d*, at which it is arrested, should lack connection with the freezing-point curves, should in fact be a temperature taken at random, needs no explanation. That, once surfusion is arrested and freezing sets in, the heat liberated should raise the temperature to the eutectic freezing-point, *bf*, is natural enough. But why does the retardation *c* come in the prolongation of the line *AB*, *i. e.*, why is it thus related to the normal freezing-point curve, and how comes it that these V-branches can thus be traced beyond their intersection? The interpretation of such phenomena should be cautious; the following explanation is offered tentatively.

Assume that in the molten state a solution of tin in lead is a different and distinct thing from a solution of lead in tin; witness the fact that in the freezing-point curve of the former, *AB*, instead of being a smooth prolongation of the freezing-point curve of the latter *CB*, instead of being joined to *CB* by means of a smoothly curved line, cuts *CB* sharply, as if the two lines *AB* and *CB* related to different bodies.

Assume that these two molten solutions are soluble in each other, each in some sort preserving at least a potential existence, although thanks to the conditions of reciprocal solution, they cannot be separately detected, nor distinguished from each other.

Assume that in the present case the molten alloy of tin 64 lead 36 consisted of two distinct solutions, reciprocally dissolved, each solution dissolved in the other:

Solution 1, large in quantity, consisting of lead dissolved in tin in the ratio of 64 of the solvent (tin) to 36 of the solute (lead).

Solution 2, small in quantity, consisting of tin dissolved in lead in the ratio of 36 of the solvent (lead) to 64 of the solute (tin).

The normal freezing-point of solution 1 is temperature *a*.

The normal freezing-point of solution 2 is temperature *c*, in the direct continuation of the line *AB*.

Assume that in normal freezing without surfusion, when, on cooling to temperature *a*, solution 1 begins to freeze, solution 2

is converted into solution 1 by contact with the solid particles of solution 1, somewhat as one of two allotropic modifications can be transformed into the other by contact with a crystal of that other. Hence the absence of any retardation at temperature *c* in normal freezing unaccompanied by surfusion.

Assume that in the present surfusion it is simply solution 1 which surfuses; that when the temperature falls to *c*, the freezing-point of solution 2, this naturally freezes out, causing the retardation *c* in the cooling curve. The slightness of this retardation corresponds to the assumed small quantity of solution 2.

Assume that, for whatever reason, so strong is the tendency of solution 1 to surfuse, that it persists unfrozen even through this freezing out of solution 2.

Here then we have an explanation of the fact that the retardation *c* comes in the prolongation of *AB*, which is what we started out to explain.

44. OTHER CRITICAL CURVES FOR TEMPERATURE AND COMPOSITION. — Digressing for a moment, let us notice that, just as the freezing-point curve shows the relation between the composition of the alloy as a whole and the position of these two critical freezing-points, so on this same temperature-composition diagram we may show simultaneously various other critical matters.

Thus, in § 98, p. 116, we shall see how the relation between temperature and solvent power is shown by what are usually called "critical curves," but are called in this work "saturation-point" curves.

Again, in § 114, p. 135, we shall see how the course of selection in freezing is expressed by the temperature-composition curves of the frozen part, on the assumption that diffusion has made this part homogeneous.

Finally, in § 121, p. 144, we shall see how the course of selection in freezing is expressed by the temperature-composition curves of the layers in the act of freezing at each instant.

From these curves themselves further inferences can be drawn, can as it were be read on the diagram itself. For instance, from the freezing-point curves we read also the course of selective freezing as it is expressed in the composition of the remaining molten mother-metal at each instant; and the constitution of the frozen mass, as related to the composition of the alloy as a whole. Again, the saturation-point curves also teach this relation

between constitution on one hand and temperature and composition of the alloy as a whole on the other hand.

By placing two or more of these curves on the same diagram, we may see how these various critical matters are related to one another.

To sum up, we have

- (1) the freezing-point curves,
- (2) the saturation-point curves,
- (3) the temperature-composition curves of the frozen part,
- (4) the temperature-composition curves of the freezing layers.

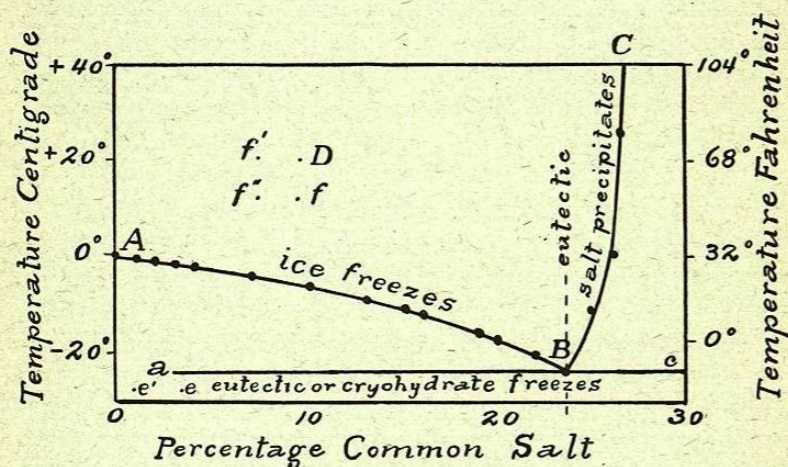


Fig. 27. Freezing-point Curve of Solution of Common Salt in Water.  
Guthrie, *Phil. Mag.*, 5 Ser., I, p. 359, 1876.

Let us now return from this digression to consider the first of these sets of curves, the freezing-point curves.

45. FREEZING-POINT CURVE OF SALT WATER. — If, now, proceeding as we did in §§ 41 and 42 with the freezing-points of the lead-tin alloys, we assemble as in Fig. 27 the freezing-points of all possible solutions of salt and water as shown in Figs. 7 to 11, p. 18, and plot them in a freezing-point curve, we find that we get a curve of the same general family, the underscored V. One branch  $AB$  of the V represents the points at which the water begins freezing out from solutions containing an excess of water over the eutectic ratio of 23.6 per cent, and the other branch

$BC$  represents the points at which salt begins freezing out or precipitating from solutions containing initially an excess of salt above the eutectic ratio. The horizontal branch or line  $aBc$  underscoring the V, represents the freezing of the eutectic of 23.6 per cent of salt and 76.4 per cent of ice. We see that we have an exact correspondence between the behavior of alloys of the lead-tin class in freezing and that of aqueous solutions, in the shape and meaning of the freezing-point curve, and in the constitution of the frozen mass.

46. COOLING AND FREEZING-POINT CURVES SHOWN SIMULTANEOUSLY. — Fig. 28, pp. 60, 61, represents an attempt to show simultaneously the cooling and the freezing-point curves of the lead-tin series of alloys. First we have the cooling curves for various compositions, Figs. 28 A to 28 G, the several curves being so spaced apart that the horizontal position of the axis  $OA$  in each corresponds to the percentage of tin in the alloy to which the curve applies. Suppose that we now pass a black tape through all the points  $B$ , and another through all the points  $C$ . Suppose that each cooling curve is hinged at its axis  $OA$ , and is now rotated  $90^\circ$  to the left, so that, instead of lying in the plane of the paper as in Figs. 28 A to 28 G, each curve stands out at an angle as in Fig. 28 H. The two tapes now reproduce the freezing-point curve  $ABC$  and  $aBc$  of Fig. 24, while the several cooling curves remain visible.

#### CHAPTER IV. — CONSTITUTION OF BINARY ALLOYS WHICH FORM NO DEFINITE CHEMICAL COMPOUND

47. CONSTITUTION TO BE EXPECTED IN CERTAIN TYPICAL CASES. — Let us next consider what constitution we should expect in certain typical cases, premising that this sort of forecast may have to be modified considerably by later investigations. In the present chapter we will for simplicity consider cases in which the two metals form no definite chemical compound with each other, and we will see how their constitution should be affected by the assumptions (1) that (when solid) they are wholly insoluble in each other, (2) that they are reciprocally soluble in all proportions, and (3) that their reciprocal solubility,