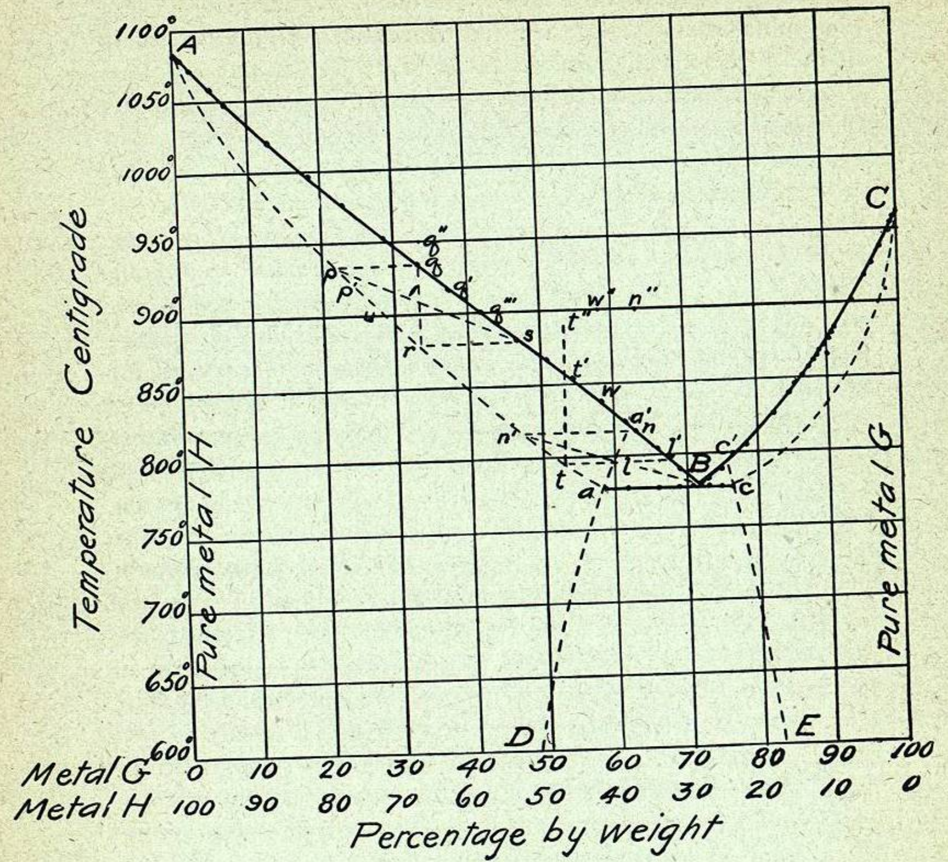

Fig. 49. Freezing-point and other Thermal Curves, Mainly Suppositious, of a Series of Alloys Eutectiferous in the Middle but not at the Ends.

The underscored V-curve, *ABCaBc*, is plotted by the author from the actual data of Heycock and Neville, *Phil. Trans. Roy. Soc.*, CLXXXIX, A, pp. 32–36, 1897, for the freezing-point curves of the silver-copper alloys. The other curves here given are purely conjectural.

The data of Heycock and Neville have naturally led many to believe that the eutectiferous region is the very short one between points *a* and *c*. The author knows of no series of alloys in which the eutectiferous region is so short. In general it extends much more nearly completely across the diagram. Actually Osmond found indications of a eutectic both in argentiferous copper containing only 1 per cent of silver and also in cupriferous silver containing only 1 per cent of copper. I have found a large quantity of what was undoubtedly eutectic in pure argentiferous copper containing 3.30 per cent of silver and 96.4 per cent of copper.

same line, beginning at *w* and likewise running towards *B*. For each initial composition, then, the temperature-composition curve of the mother-metal is some one fragment of this line *AB*; and if we select initial compositions near enough together, manifestly their fragments of this line *AB* must overlap, and where they overlap they coincide.

The reason why it is a single line of which these several temperature-composition curves are simply fragments is a simple one. At each instant during selective freezing (assuming equilibrium) the mother-metal is at its freezing-point; and as the freezing-point for any given momentary composition of mother-metal is quite the same no matter what the initial composition of the molten mass was, so for each momentary composition of mother-metal one and the same point represents its temperature and composition no matter what the initial composition of the alloy. So too of any series of temperatures, *i. e.*, of any fragment of the freezing-point curve. If two alloys have initially so nearly the same composition that in freezing a certain part of the range of composition, through which the mother-metal of the first passes, overlaps part of the range of composition through which the mother-metal of the second passes, then at each temperature in that part which the two have in common each mother-metal must have the same composition as the other, since for each of them this composition is that for which this temperature is the freezing-point. But this is simply saying that where these two temperature-composition curves overlap they are identical. And so on for every other fragment of the line *AB*.

Now, always assuming that the conditions throughout are those of equilibrium, just as one and the same line *AB* is the temperature-composition locus for the mother-metal during freezing, for all initial compositions of the molten alloy between *A* and *B*, so there is a second line, *Aa*, Fig. 49, which is the temperature-composition locus for the part already frozen, the frozen continent, which line holds true for all initial compositions of the molten alloy between *A* and *B*. No matter what the initial composition of the molten alloy as a whole before freezing begins, the temperature-composition locus for the resultant frozen part is, during selective freezing, some one fragment of this line *Aa*. In short, as during selective freezing the composition and temperature of the mother-metal slide along the line *AB* towards

B, so simultaneously do the temperature and composition of the frozen part slide along *Aa* towards *a*. And, because the temperature of frozen mass and mother-metal are assumed to be identical, so the temperature-composition point for the frozen part must at each instant be the point on *Aa* having the same ordinate as the temperature-composition point on *AB* for the molten mother-metal, at that same instant; in short, at any instant the frozen-part point on *Aa* must be horizontally opposite the mother-metal point on *AB*.

Let us temporarily assume that the two extremities of this temperature-composition curve for the frozen part in equilibrium, are *Aa* for alloys at the left of *B* and *Cc* for alloys at the right of *B*. In § 118, p. 141, we shall see that this must be true.

These assertions, be it understood, assume that equilibrium exists. In particular the temperature is assumed to be absolutely uniform throughout the mass, both molten and frozen; and it is assumed that diffusion has completely effaced the heterogeneousness which freezing sets up both in the solid and in the molten parts (Fig. 42, p. 96), so that the frozen continent has become uniform throughout in composition, and that the mother-metal also has. During freezing itself, the outer layers of the frozen part, those through which the heat escapes from the system, are cooler than the inner ones, and these in turn than the molten mother-metal. Manifestly this condition of equilibrium for any given temperature could be reached only by holding the temperature constant at that point until this equalization both of temperature and of composition could effect itself through diffusion and conduction, aided in the molten part by convection; in short, only by completely arresting the freezing and the removal of heat from the system. This condition of equilibrium, then, is one which would not actually be reached in any given freezing unless it were thus artificially arrested. But it is of importance as showing the condition towards which affairs tend.

115. REASONS FOR THIS CURVE. — How comes it, now, that the temperature-composition curve of the frozen continent is a fragment of one and the same line, no matter what the initial composition of the molten alloy is when it is all molten? Simply because, for given temperature and composition of the molten mother-metal, there is only one temperature and composition which the frozen part can have if, as we assume, it is to be in equilibrium with that mother-metal. The temperature of the two parts in any given case is clearly identical for equilibrium, since were one hotter than the other, heat would quickly flow from it to that other and continue flowing until they reached the same temperature. Hence the temperature-composition point representing the frozen layers must, at any given instant during freezing, be on the same horizontal line as the point representing the mother-metal.

And since the temperature-composition curve of the mother-metal during freezing is a fragment of one and the same line *AB* or *CB*, no matter what the initial composition of the alloy when it is all molten; and since for *any given point* on *AB* or *CB* represented at any moment during freezing there is only *one point* which can represent temperature and composition of a frozen part in equilibrium with the mother-metal at that point on *AB* or *CB*, no matter what the initial composition of the alloy; so there can be only *one series of points, i. e., one line,* which for equilibrium represents temperature and composition of the frozen part, *i. e., one line only corresponding to line AB for the molten part,* and only one line corresponding to the line *CB*. Just what the position of these lines is must be determined in each case; but that there is one line somewhere to the left hand of *AB* and one to the right hand of *CB*, representing the temperature and composition of the frozen part in equilibrium with the mother-metal represented by the horizontally opposite points on *AB* or *CB*, is thus clear on reflection.

116. TEMPERATURE AND COMPOSITION OF THE FROZEN PART AND THE MOLTEN MOTHER-METAL DURING SELECTIVE FREEZING.

NON-EUTECTIFEROUS ALLOY, METALS *G* AND *H*. — First let us, to fix our ideas, consider a specific case in Fig. 49, that of the alloy 32 per cent of metal *G* and 68 per cent of metal *H*, and let us assume that we begin cooling it slowly from say 950°, *q''*. The alloy begins to freeze when the temperature falls to *q* (say 933°), and the very first layer to freeze out has composition *p*, horizontally opposite *q*, (here sketched by eye as 22 per cent *G* and 78 per cent *H*). This follows because this first smallest incipiency of a flakelet may be considered as the smallest quantity which, in view of the size of the molecules themselves, can possibly exist; a quantity not infinitesimal but of the same order of size as the molecules themselves; in other words, consisting of the smallest possible number of molecules, and therefore of uniform composition throughout. As regards the composition of the frozen part, equilibrium exists, as it clearly must whenever that frozen part is of uniform composition throughout. Thus, as regards the first particle to freeze out, we have only to assume uniformity of temperature, and the other conditions of equilibrium exist. This then places the first frozen particle at *p* without awaiting diffusion.

During the further fall say to *q′* (say 918°) a succession of layers will freeze out each richer in *G* than the preceding. If, now, the temperature is held constant at 918° until the diffusion of metal *G* in these different onion peels has completed itself, so that their composition has become the same throughout, and equilibrium has thus been reached, then as already pointed out, the composition of this frozen mass will be represented by the point *p′* on *Aa* horizontally opposite the point *q′* which represents the composition of the remaining molten mother-metal with which it is in contact.

Clearly, when the whole of the alloy has solidified and its composition has by diffusion become uniform, that composition must be the same as that of the original alloy when molten; for the frozen alloy is that same initial alloy simply changed from a homogeneous molten to a homogeneous solid, without adding to or taking away from its initial composition. Its composition, therefore, must be on the same ordinate as the initial composition, *q″* and *q*; and since, because it has now become homogeneous it is on *Aa,* it must be *r,* the point on *Aa* vertically under *q″* and *q*.

If just before the very last flakelet froze, and when the molten mother-metal had thus been reduced to its smallest possible quantity, the temperature, which would now be substantially that of *r,* were held constant until the whole of the frozen mass became homogeneous through diffusion, so that its composition, following the reasoning in the last paragraph, had become substantially *r*; then, since the composition of the mother-metal at any instant when the frozen mass has become homogeneous is the point on *AB* horizontally opposite the composition-point on *Aa* of the frozen part, the composition of this last particle of molten mother-metal must be the point opposite *r, i. e.,* it must be *s*.

In short, the temperature and composition of the mother-metal at the beginning and end of the freezing are *q* and *s* respectively, and those of the frozen mass *p* and *r,* of which *p* is horizontally opposite *q, r* vertically under *q,* and *s* horizontally opposite *r*.

117. Barely Non-eutectiferous Alloy of Metals *G* and *H*. — Let us next consider the cooling of the molten alloy of composition *w″*. This is on the same ordinate as *a*. But *a* is the western boundary of the eutectiferous range (see § 105, p. 121). In other words, it represents metal *H* exactly saturated when solid with *G*. Were the molten alloy to contain more of metal *G* than this, be that excess of *G* ever so small, that would supersaturate the freezing metal *H,* and consequently in the course of selective freezing the enrichment in metal *G* of the freezing layers would reach the saturation-point before the whole of the mother-metal had frozen; and the remainder of this mother-metal would in freezing split up into the eutectic (see § 64, p. 72). In short, our present alloy of composition *w″*, from considerations with which we have already become familiar, is barely non-eutectiferous.

118. Position of the Extremities of Temperature-Composition Curve for the Frozen Part. — The temperature at which the freezing ends in case of any eutectiferous alloy, and of an alloy which is barely non-eutectiferous in the sense of being of the composition which exactly bounds the eutectiferous range, is the eutectic freezing-point, through which the line *aBc* runs. Such an alloy which bounds this range we may call a boundary alloy. If, now, such a boundary alloy is frozen, and, on reaching the lower freezing-point at which its freezing would end, it is held at stationary temperature until diffusion has completed itself, it will be wholly in equilibrium, and on this account it will be a point on the temperature-composition curve for the frozen part under conditions of equilibrium. Its temperature and composition will both be represented by point *a*. Hence point *a,* which represents the boundary of the eutectiferous-range and also the eutectic freezing-point, is one extremity of this curve.

Clearly the other extremity is the point *A*. For, if our initial molten mass is not an alloy at all but simply pure metal *H,* then when it freezes no selection can take place; throughout the freezing both mother-metal and frozen part are pure metal

H; and also throughout the freezing the temperature is A. This point A, then, is one point representing equilibrium for both temperature and composition for both the mother-metal and the frozen part during freezing. It is the extremity of the temperature-composition curve for both molten mother-metal and frozen part, for alloys at the left of B.

So, *mutatis mutandis*, C and c are the extremities of this same curve for alloys at the right of B.

119. EUTECTIFEROUS ALLOY OF METALS G AND H. — Let us next consider the cooling from 900° of an alloy of 37 per cent of metal H and 63 per cent of metal G, represented initially by the point n''. When the alloy in cooling reaches temperature n, say 818°, it begins to freeze, and the first frozen particle will have composition n', horizontally opposite n on the line Aa, or say 52 per cent of H and 48 per cent of G. As the temperature further falls and freezing progresses the composition of the frozen part, assuming always that diffusion has made it homogeneous, will slide along Aa from n' towards a, while the composition of the remaining mother-metal will slide along AB from n towards B. When the temperature reaches B the frozen mass will have composition a, or say 42 per cent of H and 58 per cent of G, while that of the remaining mother-metal will have reached B, or 28 per cent H, 72 per cent G.

As the frozen mass at this instant contains only about 58 per cent of G, a, whereas the initial mass contained 63 per cent of G, n, it is evident that the difference between these two amounts must be represented by the existence of a still considerable quantity of mother-metal. Now begins the eutectic-freezing period.

Up to this point the freezing has been selective, *i. e.*, the layers freezing out have been richer in metal H than the mother-metal from which they freeze, so that this mother-metal has been growing continuously richer in metal G and hence more fusible. But at this point selection ceases for the reason already explained, that the mother-metal has now reached the composition of lowest freezing-point, and consequently no further selection can further lower the freezing-point. Hence the remaining mother-metal now freezes without selection, but in freezing splits up into a conglomerate of separate flakes of G saturated with H and of H saturated with G.

But as the mother-metal is now of the eutectic composition, the conglomerate into which it now splits up will be the true eutectic, as we saw in § 74, p. 84. We have thus three bodies in this conglomerate: (1) the excess or previously frozen part, metal H saturated with metal G, saturated because we now are assuming that equilibrium has been reached; (2) the flakes of metal H, forming part of the eutectic, also saturated with G (§ 74, p. 84); and (3) the flakes of metal G, forming the remainder of the eutectic and saturated with H. Manifestly (1) and (2) cannot diffuse into or otherwise react on each other, because they are of identical composition; and (3) cannot diffuse into either of the others, for the reason given in § 73, p. 80. Hence, in short, the eutectic which forms through the freezing and splitting up of the mother-metal at temperature B remains as the eutectic, and is not absorbed into the previously frozen part.

This, as before, is on the assumption that the previously frozen part has become uniform through diffusion.

The fact that the composition of the mother-metal remains constant during the remainder of the freezing implies that the temperature at which the freezing now completes itself is constant; and this part of the freezing is therefore represented by point B.

During the eutectic-freezing period, the conglomerate of which the now frozen part consists is the saturated solid solution of G in H formed during the excess-freezing period, and called substance (1) above, which remains constant in quantity, plus a progressively increasing quantity of eutectic.

120. SUMMARY OF THE FOREGOING. — In short, in Fig. 49 the loci for temperature and composition are as follows:

	FOR THE MOLTEN METAL	FOR THE FROZEN PART
During the excess-freezing, or solid-solution generating, or selective period	AB	Aa
During the eutectic-freezing period.	B	aB

During the former period the frozen mass, assuming that diffusion completes itself, becomes homogeneous; during the latter it remains a conglomerate of (1) the eutectic and (2) the saturated solid solution of metal H saturated with metal G, the saturation of this solution preventing diffusion of the eutectic into it.