and temperature *T*, when its temperature sinks to *F* it will, as in case α, split up into two saturated molten solutions, the composition of which during further cooling travels from *F* to *M*, and from *F* to *J*; so that on reaching this temperature *MJ* we have the same condition of affairs as in case α. With further removal of heat from the system, it tends to freeze, generating solid alloys *f* and *P*.

But here again, just as in case α, it is the more infusible of these two solid alloys that should actually freeze first by preference. Let us assume that it is alloy *P* which is the more infusible of the two. It therefore begins freezing out, and the average composition of the residual molten mother-metal in consequence travels to the left until, as in case α, this average composition finally reaches *M*, *i. e.*, until by the rearrangement of the components of the mother-metal and the freezing out of alloy *P*, the whole of molten alloy *J* has been removed and only molten alloy *M* remains. Then, as before, this molten alloy *M* should freeze like any other eutectic, splitting up into alternate particles of solid alloys *f* and *P* respectively.

In short, the whole proceeds exactly as in case α, except that when freezing begins, that which freezes out first is not pure metal *G*, but *G* saturated with *H*, and that when the composition of the residual mother-metal eventually reaches *M*, the alternate particles of the eutectic into which it now in freezing splits up are, not pure metals *H* and *G*, but saturated solid solutions of *G* in *H* and of *H* in *G*.

109. Relative Position of the Saturation-point Curve for the Solid and Molten States. — Since the solubility of each metal in the other should naturally be much less when both are solid than when both are molten, the saturation-point curves for the two states should be related to each other as shown in Fig. 47; that is to say, the curve for the solid state should lie to the left of *M* and to the right of *J*. In other words, there should be a sharp jog like *f′M* and *QJ* between these curves for the solid and molten states respectively.

110. Subcase 5 *B*, the Saturation-point Curve Cuts the two Upper or V-Branches of the Freezing-point Curve at Different Temperatures. — α. *The two metals when solid are wholly insoluble in each other.* In this case the freezing-point curve assumes the peculiar shape shown in Fig. 48. Here the upper freezing-points for alloys containing between 70 and 100 per cent of *H* are represented by *AM*, and those for alloys between 0 and 20 per cent of *H* by *BJ*; and the lower freezing-points for these two regions will be on the lines *DM* and *J′E*. For alloys of intermediate composition, containing between 20 and 70 per cent of *H*, the upper freezing-point is *JK′M* and the lower freezing-point is *J′M*.

To test this let us follow the cooling of a few different alloys containing respectively *I*, *F*, *T* and *Q* per cent of metal *G*.

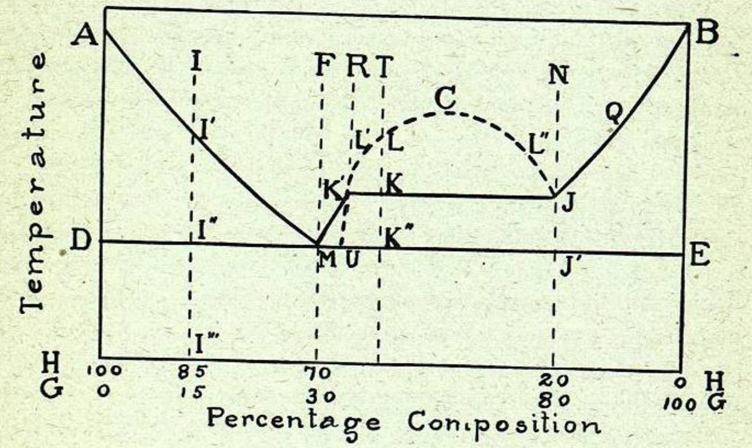

Fig. 48. Freezing-point Curve of Alloys of two Metals of Limited Reciprocal Solubility when Molten, but Complete Reciprocal Insolubility when Solid. Subcase 5*B*, the Solubility Curve Cuts the Upper Branches of the Freezing-point Curve at Different Temperatures.

Alloys I and F. The shape of the freezing-point curve at *M* and at the left of *M* is shown by the same reasoning that established the corresponding part of Fig. 45. (See alloys *R* and *S* of Fig. 45.)

Alloy T is a molten solution of *G* in *H*, which on cooling to the saturation-point curve becomes saturated, and on passing below it splits up into two saturated molten solutions (1) a large quantity of a solution of *G* in *H*, and (2) a small quantity of a solution of *H* in *G*. When the temperature has fallen to *L*, alloy 1 will contain L' per cent of G dissolved in $100 - L'$ per cent of H, and alloy 2 will contain $100 - L''$ per cent of H dissolved in L'' per cent of G. When the temperature falls to K, alloy 1 will contain K' per cent of G dissolved in $100 - K'$ per cent of H, and alloy 2 will contain $100 - J$ per cent of H dissolved in J per cent of G. In short, the composition of these two alloys will be K' and J respectively. Alloy J, however, will now be at its freezing-point, and on further removal of heat, but without further fall of temperature, it will begin freezing.

In the freezing which now takes place alloy J should in effect deposit only metal G, as we see on trying to imagine the contrary. Suppose that the first flake of alloy J in freezing at temperature J does so without selection, *i. e.*, that it deposits a flake of composition J. As metals H and G by assumption are insoluble in each other, this first flake must (if equilibrium is reached), break up into particles of pure G and separate particles of pure H. But these pure particles of H, exposed as they are in the very act of freezing to alloy K', which is a saturated solution of G in H, should immediately remelt and reënter alloy K', since the alloy which this reëntering would create is fusible at the existing temperature, because it has more than K' per cent of H, *i. e.*, because its composition lies to the left of K'. This remelting then would give us two molten alloys, alloy J, and an alloy with composition to the left of K'.

But as the mean composition of the mother-metal would still be between J and K' it would immediately rearrange itself into a mechanical mixture of two alloys of composition J and K' respectively (§ 73, p. 80). The effect of the freezing and remelting which have taken place at temperature J thus would be to eliminate from the molten mass a small quantity of metal G, and so to shift the average composition of the mother-metal from K toward K'.

But this shifting will leave the mother-metal as before in the condition of a mechanical mixture of molten alloys J and K', because at temperature J this is the constitution of any mother-metal the average composition of which lies anywhere between J and K'. So that, as regards farther freezing, on farther removal of heat from the system, we have exactly the same condition of affairs that we had when the first flake began to freeze. Hence,

for the same reason as before, the next step in the freezing is in effect to eliminate from the mother-metal a second small quantity of metal G, to be followed by a second rearrangement of the residual mother-metal so that it contains a smaller proportion of alloy J and a larger proportion of alloy K'. Thus, its average composition travels a second step to the left. Following this, flake by flake, what really happens is that metal G begins freezing out at constant temperature, and that the composition of the mother-metal progressively travels from K to K', which means that the proportion of alloy J is constantly diminishing and that of alloy K' is constantly increasing until, when the average composition of the now residual molten mother-metal reaches K', the whole of alloy J has been removed by the freezing out of the metal G, and the mother-metal now consists exclusively of alloy K'. The temperature will thus remain constant during this freezing out of alloy J.

Now that the molten mother-metal has been reduced to a single constituent, alloy K', the condition of things is practically the same as in any simple case of selective freezing; for instance, it is parallel with the condition which exists when, in Fig. 24, p. 54, the alloy of composition G has cooled to temperature P. In cooling from H to P part of the excess-metal (lead) has frozen out, so that the composition of the residual mother-metal has traveled from H to P. With further fall of temperature the lead continues freezing out, and the composition and temperature of the mother-metal slide along the line PB.

So, in our present case, Fig. 48, with further fall of temperature, metal G continues freezing out, and its freezing bears such a relation to the fall of temperature that the composition and temperature of the mother-metal for every successive degree of temperature reached remain on the line $K'M$; in short, the temperature and composition of the mother-metal slide along $K'M$, there reaching the freezing-point of eutectic, and of course simultaneously reaching the eutectic composition.

At K' the mother-metal is H exactly saturated with G. As the temperature begins to descend below K' some of G begins freezing out, thus leaving in the mother-metal less G than suffices to saturate it at temperature K', assuming that the continuation of the saturation-point curve $K'U$ is inclined to the right of the freezing-point curve $K'M$, as drawn in Fig. 48.* But with the simultaneous incipient fall of temperature from K' the solubility of G in H simultaneously falls. For simplicity let us assume that this fall of the solubility is not so great that the proportion of G now in the mother-metal suffices to saturate it; in other words that the freezing-point curve $K'M$ is more strongly inclined than the continuation of the saturation-point curve $CK'U$, so that, as the composition and temperature of the mother-metal slide along $K'M$ the mother-metal first ceases to be saturated with G and then progressively falls farther and farther short of being saturated with G, *i. e.*, grows farther and farther unsaturated with G. In this case the mother-metal throughout the remainder of the freezing remains a single unsaturated solution, quite as in Fig. 24.

We may actually sketch the part $K'U$ of the saturation-point curve for the molten state to indicate that it actually lies to the right of the section $K'M$ of the freezing-point curve. Indeed, this prolongation $K'U$ can sometimes be determined by the phenomena of surfusion.

Once the temperature has fallen to M, the mother-metal will begin to freeze unselectively,† like any eutectic, simply because no selective form of freezing can (normally) postpone complete freezing. In freezing the eutectic will, like any other, split up into its components H and G, assumed to be insoluble in each other when solid, and, therefore, each pure.

---

[*] The angle between lines $K'M$ and $K'U$ may vary and conceivably might fall to zero, so that $K'M$ would coincide with $K'U$. In this case the line should be drawn double, a solid line to indicate this section of the freezing-point curve and a broken line to indicate this section of the saturation-point curve.

[†] That the freezing at M will be unselective is seen readily on trying to suppose the opposite, *i. e.*, that it is selective. Selective freezing can occur only through a selection which gives to the mother-metal a freezing-point lower than the existing temperature. But such selection cannot occur through freezing out of part of metal G, because that would move the composition to the left and would make the mother-metal more infusible. The freezing on the other hand cannot be made selective in the sense that metal H freezes out, because that would in like manner shift the composition of the mother-metal to the right, and this also would make it more infusible, and in particular infusible at the existing temperature M.

Thus, for initial composition T we have two freezing-points, K and K''. The same would be true of any alloy of composition between R and N. For alloys between R and F, the upper freezing-point will be on the line $K'M$ and the lower freezing-point will be on the line MJ'.

This then gives us the freezing-point curves between F and N, *viz.*, for the upper freezing-point $MK'J$ and for the lower freezing-point MJ'.

Alloy Q. The series of alloys between N and B will have for the upper branch of the freezing-point curve $BJK'M$, and for the lower branch $J'E$. Take for instance alloy Q; it will begin freezing selectively by the solidification of the excess or solvent metal G, and the composition and temperature of the mother-metal will, as in all like cases, slide from Q to J. But as the temperature starts to descend below J, the composition of the mother-metal crosses the solubility curve, and the mother-metal therefore splits up into a mechanical mixture of two alloys of compositions K' and J respectively.

But the molten mother-metal has now reached the same condition that it reached when, starting initially with composition T, it had cooled to temperature K, in that it is now a mechanical mixture of molten alloys J and K'. And, just as in that former case, with further removal of heat metal G in effect begins freezing out, and consequently the average composition of the mother-metal travels to the left from J to K'. Then, the freezing out of G still continuing, the temperature and composition of the mother-metal, quite as before, slide from K' to M. Finally at M the temperature again remains constant while the whole of the residual mother-metal freezes without selection, splitting up in freezing into the conglomerate eutectic of alternate particles of metal G and metal H.

Alloys intermediate in composition between Q and B will, in freezing, follow the same course as Q, and in particular they will all have a second or lower freezing-point on the line $DMJ'E$; in other words this line will extend clear to the right-hand side of the diagram. The reason for this is that, thanks to the assumed complete insolubility of H in G when solid, at whatever point between J and B the initial composition of the molten alloy lies, when on cooling to the line BJ freezing begins, it is metal G alone which freezes out; so that, no matter how little of H

is present, *i. e.*, no matter how little to the left of B the initial composition of the whole lies, that quantity of H unimpaired will continue to accumulate in the mother-metal. Hence, when the temperature of the mother-metal falls as low as J, there will still be that same quantity and hence a finite quantity, of metal H present; in short, the mother-metal will now have temperature and composition J.

But in that it thus has this composition and temperature, it is in the same condition that alloy Q was when it reached temperature J; and therefore its further behavior, on further abstraction of heat, will be the same as that of alloy Q from this same time. The temperature of the molten mother-metal will remain constant as its composition gradually slides from J to K', and its temperature and composition will then slide from K' to M. And since up to this time nothing but metal G has frozen out, the same original quantity of metal H will now be present in the mother-metal; so that this, in now freezing unselectively, will yield the conglomerate eutectic, containing the whole of the initial metal H.

In short, no matter how little H is initially present, that whole quantity will be found in the eutectic conglomerate formed at M; or in other words there will be a conglomerate eutectic freezing-point at temperature M, no matter how little H is present, so that the line representing this lower freezing-point extends clear to the right-hand end of the diagram.

Comparing Figs. 45 and 48, we see that the essential difference is that in Fig. 45 the distance JJ' is reduced to nil. We may therefore regard subcase 5A as simply a special example of subcase 5B.

111. SUBCASE 5 $B\ \beta$, THE TWO METALS WHEN SOLID ARE SOMEWHAT SOLUBLE IN EACH OTHER. — Comparing §§ 107 and 108, pp. 121 and 125, and in particular comparing Figs. 45 and 47, we see that the effect of changing the assumed condition for the solid state from complete insolubility to limited solubility, was, as regards the diagram, to shorten the eutectic freezing-point line so that instead of running completely across the diagram it is bounded by the points f and P, and to create the saturation-point lines Off' and NPQ. As regards the procedure in freezing the effect of this change was that, instead of pure metal H, it was H saturated with G that froze out, up to the time when the mother-metal reached composition J; and that during the remainder or eutectic part of the freezing, the conglomerate eutectic which froze consisted of alternate particles of H saturated with G and of G saturated with H, instead of pure H and pure G.

Applying the same reasoning to the present case would lead to the same changes, both in the diagram and in the course of the freezing which that diagram depicts.

112. DETERMINATION OF THE SATURATION-POINT CURVES FOR THE SOLID STATE. — While these saturation-point curves for the solid state are not readily determined, we may yet reach an approximation to them in some cases. Thus, to find the solubility θf of G in O (Fig. 44) at given temperature θ°, we may heat to θ° a very thin strip of O in contact with an excess of G, and hold them at θ° for several different periods, cooling them and then determining after each heating and cooling what percentage of G has been absorbed by O by diffusion, and thus determining how much of G can thus be forced into O.

Conversely, how much of G can be retained by O at θ° may next be determined. The alloy which we should treat in this case should contain rather more of G than our foregoing absorption test succeeded in forcing into O, because an absorption test cannot pass saturation θf, and is likely not to reach it, while our present retention test will leave O at least saturated and probably much supersaturated with G, *i.e.*, will leave more than θf of G in O. We heat this alloy well above θ°, or better above its melting-point, then cool it to θ°, hold it there for a long period, then quench it in water to retain the degree of concentration retained at θ°.

We then examine the alloy under the microscope, to see whether under these favorable conditions any excess of G has separated out within the solid alloy; and if possible we try to get an approximate idea of the proportion of G that has thus separated out, remembering that it should not be pure G but G saturated with gH per cent of O that should thus separate out. Should any separation of G be detected, we infer that the percentage of G in the alloy is greater than θf, and we make a second approximation, using an alloy containing less of G, *etc.*

If, as will probably be the case, the results of the absorption and retention tests do not closely agree, the former ones representing undersaturation or less than θf, and the latter ones supersaturation or more than θf, we at least establish limits between which the true saturation-point lies. Sharply defined results are hardly to be hoped for, because the approach to the saturation-point from either direction is likely to be asymptotic, or at least extremely slow towards the end, in a solid and relatively cool alloy.

113. Determination of the Saturation-point Curves for the Molten State. — To determine the two points of the saturation-point curve for a given temperature T we might proceed as follows.

The two metals should be melted in a crucible under some protecting coating, such as potassium cyanide, and heated to a temperature T' considerably higher than T, and very thoroughly mixed. In deciding on the temperature T' the question of loss by volatilization should be considered. In no case should the temperature T' approach the boiling-point of either metal.

The mixed metals should then be poured into a narrow clay tube, perhaps 8 inches long, preheated to T', closed at one end and capable of being stoppered tightly at the other. While at T' the tube should be agitated so as to mix the metals further. Though we may hardly hope to saturate these two metals with each other for temperature T', yet we may hope that at this temperature each will take up at least as much of the other as would suffice to saturate it at the lower temperature T.

The molten mass should now be cooled to T in the tube, and held there for say eight or ten hours, or as much longer as experience shows to be necessary. Should each metal have dissolved more of the other than corresponds to the saturation-point for T, each will tend now to expel this excess; and the object of allowing the temperature to remain stationary is both to allow the two alloys to separate into two distinct masses, and to perfect the separation of this excess by gravity.

As a convenient source of stationary temperature, we may use a vertical cylinder a little larger than the clay tube, heated by means of plantinum wires themselves raised to incandescence by an electric current; lacking this, a bath of molten lead or other molten metal may be used. Great care must be exercised to keep the different parts of the tube at the same temperature, lest convection currents interfere with the separation by gravity, and all agitation of the tube must be avoided.

In case either metal is liable to oxidize, a reducing atmosphere, or at least a neutral one, should be provided.

After allowing time for this separation by gravity, and with as little agitation as possible, the two ends of the columns of metal, which are the parts where separation should be most complete, should be cooled as rapidly as practicable, for instance, by holding "chills," *i. e.*, chilled pieces of iron against them. For this purpose the iron might previously have been cooled in a freezing-mixture. The object of this rapid cooling is to prevent the approach to equilibrium which has been reached at T from being disturbed by long exposure to any lower temperature in cooling.

Provision should be made for giving access to the upper and lower end of the tube so that the chills may be brought in contact with them without removing the tube from the furnace. To this end the upper section of the furnace may be movable, and the lower one may be provided with a suitable aperture.

After the whole has solidified and been thus cooled, borings from the two ends should be analyzed so as to give an approximation to the saturation-points. The ends should further be examined under the microscope, to see whether any particles of the excess dissolved at T' has failed to remove itself by gravity at T, and to obtain an approximate idea of the quantity of this excess.

This observation should enable us to apply a correction to the direct results of our chemical analysis.

The method here described is a modification of that of Dr. C. R. Alder Wright.*

114. The Course of Selection. Temperature-composition Curve of the Frozen Continent during Selective Freezing. — We have seen that the curve which represents the temperature and composition of the mother-metal during selective freezing, say of bismuth-bearing tin, is a fragment of one and the same line, whatever may be the initial composition. Thus if the molten alloy has composition q'', Fig. 49, p. 136, this curve is a fragment of the line AB, beginning at q and running towards B. For molten alloy of composition w'' it is also a fragment of this

---

* *Proc. Royal Soc.*, XLV, pp. 465 and 471, 1889.