crease.* This is in sharp contrast with the progressive enrichment in bismuth of the layers deposited during the subsaturation period. It does not, however, invalidate any of the inferences which we have thus far drawn.

CHAPTER V. — OTHER SERIES-CURVES OF BINARY ALLOYS FORMING NO CHEMICAL COMPOUND

98. SATURATION-POINT OR SO-CALLED CRITICAL CURVES.† — *General Assumption.* Throughout the discussion of this subject, §§ 98 to 111, pp. 116 to 132, it is assumed that the conditions are those of complete equilibrium, and the influence of lag, surfusion, supersaturation, and every form of disturbance is ignored.

In order to understand what is meant by a saturation-point curve let us consider the case of a molten alloy of two metals, forming no chemical compound with each other. Here, as in case of two aqueous liquids, while the two generally dissolve in all proportions to form homogeneous solutions with each other, yet in certain cases they dissolve only within certain limits, and the same is true of certain molten binary alloys. In certain cases the molten alloy is not one homogeneous mass, because the two metals are in such proportions that neither can dissolve the whole of the other. They therefore exist as independent saturated solutions

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*On account of this fall of the saturation-point, the layers which are saturated with bismuth at the time of their deposition, would become supersaturated as the temperature descends farther; and a point to be investigated is whether, to relieve this supersaturation, part of the excess of bismuth separates itself in minute grains within the solid metal. The condition which would favor this separation would be very long exposure to a temperature far enough below the freezing-point (at which the deposited layers were just saturated) to cause the supersaturation to be pronounced, yet high enough to permit such molecular transformation, such escape of the excess of bismuth from the state of solution, and its aggregation into particles large enough to be detected.

† These curves are called "critical curves," though the appropriateness of this name may be disputed, since it is not evident that the mutual solubility of two metals is a more critical matter than the freezing-points of their alloys. To the name "saturation-point curves," which is here proposed, no such objection applies.

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of each in the other. These solutions may be mechanically mixed as an emulsion, but on long standing they tend, as in the case of the lead-zinc alloys, to separate into two layers, plumbiferous zinc (the lighter) floating above, and zinciferous lead (the heavier) lying beneath.* (Cf. § 73, p. 83.)

The abscissa OD in Fig. 43 represents the proportion of molten metal G which molten metal O can dissolve at temperature O, and the curve DF indicates how the solubility of G in O increases as the temperature rises. In the same way, the intercept GE represents the proportion of metal O which metal G can dissolve at temperature O, and the curve EF represents the increase in the solubility of O in G with rise of temperature. At given temperature θ, O can dissolve θf per cent of G, and G can dissolve gH per cent of O. Hence at this temperature, an alloy
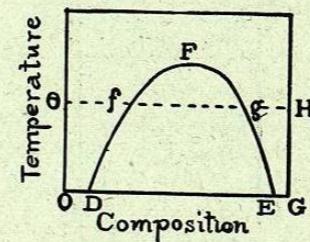

Fig. 43.   Saturation-point Curve of Molten Binary Alloys.

consisting of metal O with less than θf per cent of metal G is an unsaturated solution of G in O; one with θf per cent is a saturated solution of G in O; one with less than gH per cent of metal O is an unsaturated solution of metal O in metal G; one with gH per cent is such a solution but saturated; and alloys between θf and gH are a mixture of saturated solutions, (1) of θf per cent of G in O, and (2) of gH per cent of O in G.

The alloys represented by different points along the line fg will be mechanical mixtures of these two saturated solutions, in different proportions.

At F these two curves meet, so that at this temperature and at all higher ones the two metals dissolve in each other in all proportions. And in general, any point outside the line DFE rep-

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*Alder Wright, *Jour. Soc. Chem. Indust.*, XI, p. 492, June 30, 1892.

resents an unsaturated solution of one metal in the other; any point on that line represents a saturated solution of one metal in the other, and any point within it a mechanical mixture of the two saturated alloys, (1) O saturated with G and (2) G saturated with O, saturated that is to say for the existing temperature. That each of these alloys should be saturated, assuming equilibrium to have been established, has already been shown in § 73, p. 80, where we saw that "if there is more of each metal than suffices to saturate the other, the condition of equilibrium is that of a mechanical mixture of particles of the two metals, each saturated with the other; in other words, that of a pair of saturated solutions. Manifestly this is as true of the molten as of the solid state."
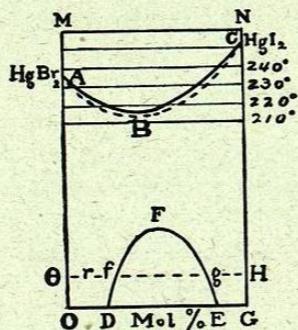

Fig. 44.

Saturation-point and Freezing-point Curves of Mercuric Bromide and Iodide.

Roberts-Austen and Stansfield, *Rapports Présentés au Congrès International de Physique*, I, Paris, 1900, p. 382; from Reinders, *Kon. Akad. van Wetens.* te Amsterdam, p. 146, 1899.

99. Saturation-point Curves in Solid Metal. (1) Non-eutectiferous Alloys. — Turning now to the solid state, the simplest case is that of two metals which, like gold and silver, are soluble in each other in all proportions at and even somewhat below their freezing-points. But two such metals thus soluble without limit, may at still lower temperatures be of limited solubility, when the condition is like that of the iodide and bromide of mercury, shown in Fig. 44, in which the freezing-point curve ABC of these substances also is given. Here, as before, DF and EF represent the solubility of each substance in the other for temperatures from O to F; and, as before, any point

outside this curve (and below the freezing-point curve) represents an unsaturated solid solution of one in the other. Any point on DFE represents a saturated solid solution. The normal condition represented by any point inside the line DFE, the condition towards which equilibrium tends, is that of a mechanical mixture or conglomerate of two solid solutions, one of iodide in bromide, the other of bromide in iodide, each saturated for the existing temperature. The reasons why such a state of affairs is true of molten alloys as explained in § 98, p. 116, apply equally to the case of the solid state.

What has now been said of the solid iodide and bromide of mercury applies with equal force to the solid alloys of any two metals, of which the reciprocal solubility, while unlimited at the freezing-point and even somewhat below it, becomes limited at some still lower temperature. Only, such an alloy, when it cools past the line DFE, Fig. 44, instead of obeying this tendency to break up into two saturated solid solutions may remain as a single supersaturated solution. Or if the solvent metal, instead of becoming supersaturated, actually does expel from itself in the solid alloy the excess of the dissolved metal as fast as, by fall of temperature, its solubility in the solvent metal decreases; yet the particles in which this excess thus separates itself may well be so extremely minute, thanks to the rigidity of the solid alloy, as to be invisible under the microscope. Further investigation is needed to throw light on this question.

Position of the Saturation-point Curve under Various Conditions, and its Relation to the Freezing-point Curve

100. Case 1, The Saturation-point Curve Lies Wholly Below the Freezing-point Curve, *i. e.*, the reciprocal solubility is complete for the molten state at all temperatures, and for the solid state for a certain distance below the freezing-point of the eutectic, but not at still lower temperatures. This is the case which we have considered in the last section (Fig. 44).

101. Case 2, The Two Metals are Completely Insoluble in Each Other at All Temperatures, both When Solid and When Molten. — In this case the saturation-point curve really corresponds to the axes say OM and LN of Fig. 24, p. 54, both below and above the freezing-point curves.

102. CASE 3, THE TWO METALS ARE WHOLLY INSOLUBLE IN EACH OTHER AT ALL TEMPERATURES WHEN SOLID, BUT SOLUBLE IN EACH OTHER IN ALL PROPORTIONS AND AT ALL TEMPERATURES WHEN MOLTEN. — In this case, for the solid state the saturation-point curve as before corresponds to the axes *OM* and *LN* of Fig. 24; while for the molten state it can hardly be said to exist.

103. CASES IN WHICH THE SATURATION-POINT CURVE MEETS OR CUTS THE FREEZING-POINT CURVE. — In the three cases which we have now considered (§§ 100 to 102) the reciprocal solubility for each state, molten and solid, is, in the freezing-point range of temperature, either nil or unlimited. In these cases the two curves (saturation and freezing-point) can hardly be said to meet each other; but a class of cases remains in which, in this freezing-point range, there is limited reciprocal solubility either (Case 4) in the solid state, or (Case 5) in the molten state, or (Case 5 β) in both states. In each of these cases the saturation-point curve meets the freezing-point curve, and in Case 5 it affects the shape of this latter curve in a way which varies with the attendant conditions, as we shall see in §§ 107 and 111, pp. 121 and 132. Table 3 recapitulates these conditions:

TABLE 3

FOR THE MOLTEN STATE RECIPROCAL SOLUBILITY IS COMPLETE	THE SATURATION-POINT CURVE CUTS THE TWO V-BRANCHES OF THE FREEZING-POINT CURVE	RECIPROCAL SOLUBILITY FOR THE SOLID STATE IS
Case 4. At all temperatures		Limited
Case 5. Only above a certain temperature	A, at the same temperature	α, Nil, (*i.e.*, the two metals when solid are wholly insoluble in each other)
		β, Limited (*i.e.*, the two metals when solid are somewhat soluble in each other)
	B, at different temperatures	α Nil
		β Limited

104. CASE 4, FOR THE MOLTEN STATE RECIPROCAL SOLUBILITY IS UNLIMITED AT ALL TEMPERATURES, BUT IN THE

FREEZING-POINT RANGE IT IS LIMITED FOR THE SOLID STATE. — In this case there can hardly be said to be any saturation-point curve for the molten state; while for the solid state this curve is like that sketched at *Daa'* and *Ecc'* in Fig. 49, p. 136. This is sketched only by eye, to give a general idea of the family to which such curves belong.

105. IN THIS AND ALL LIKE CASES THE SATURATION-POINT CURVES PASS THROUGH THE NORMAL OR EQUILIBRIUM BOUNDARIES OF THE EUTECTIFEROUS RANGE. — This we have already established in § 96, p. 114. For limit *a* of the eutectiferous range represents the composition at which solid metal *H* is just saturated with solid metal *G* (Fig. 49) at that temperature, so that any further increase of metal *G*, by tending to supersaturate metal *H*, would give rise to a eutectic. So with point *c, mutatis mutandis.*

106. CASE 5, FOR THE MOLTEN STATE RECIPROCAL SOLUBILITY IS COMPLETE ONLY ABOVE A CERTAIN RANGE. — In this case the saturation-point curve will be found above the freezing-point curve, *i. e.*, extending into the part of the diagram which represents the molten state. If there is a certain degree of reciprocal solubility for the solid state also, then the saturation-point curve will be found below the freezing-point also. If there is not, then the saturation-point curve for the solid state is represented by the axes, as in Case 3.

It remains to consider the influence of the saturation-point curve on the freezing-point curve for subcases 5 *A* and 5 *B*; and also to consider the relative position of the saturation-point curve for the solid and molten states respectively. The former of these subjects we will now consider in §§ 107, 108 and 110, pp. 121, 125 and 126, the latter in § 109, p. 126.

107. SUBCASE 5 *A*, THE SATURATION-POINT CURVE CUTS THE TWO UPPER OR V-BRANCHES OF THE FREEZING-POINT CURVE AT THE SAME TEMPERATURE.*

α *The two metals when solid are wholly insoluble in each*

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* The assumption on which this case rests, that the saturation-point curve cuts the two branches of the freezing-point curve at exactly the same temperature, is, of course, an extremely improbable one, and, mathematically speaking, presumably an impossible one. It may be regarded as a limiting case, and is given here first, only because it is somewhat simpler than the other case in which the saturation-point curve cuts the freezing-point curve at different temperatures.

other. On this assumption, the freezing-point and saturation-point curves are of the family shown in Fig. 45.

Let us test the shape of *AMJC* by following the freezing of three different alloys, those with *R, S* and *T* per cent respectively, of metal *G*.

(1) *Alloy R.* This in cooling would begin freezing at *r* with the solidification of metal *H* and enrichment of the mother-metal in metal *G*, as in the common course of selective freezing; so that the temperature and composition of the mother-metal at successive instants would be represented by a series of points between *r* and *M*. In short, the temperature and composition of the mother-metal slide from *r* to *M*. But on reaching *M* this sliding is arrested, and the mother-metal will now freeze without further fall of temperature as the eutectic, breaking up in freezing into separate particles of the two metals *G* and *H*.

The reason why selective freezing should cease on reaching *M*, and that the mother-metal should there freeze without further selection, *i. e.,* as a whole, is of course the same which leads to the freezing of the eutectic as a whole in any ordinary alloy as soon as the eutectic composition and freezing-point are reached. At each instant during the selective freezing from *r* to *M* the mother-metal has been at its then freezing-point, and it has avoided freezing as a whole by ejecting from itself part of the excess or solvent metal *H*, and so becoming enriched in the dissolved metal *G*, and thereby acquiring a lower freezing-point. This can go on only so long as selective freezing is capable of leading to an alloy of a lower freezing-point. Now this possibility ceases when the temperature and composition of the mother-metal reach *M*, for that is by assumption the freezing-point of the most fusible alloy of the series. Indeed, no possible shifting of composition of the mother-metal could further defer freezing. Moving it to the left would make it still more infusible; moving it to the right would simply split it up into a mechanical mixture of (1) an alloy of composition *M* and (2) another alloy of composition *J*, both infusible at the existing temperature.

(2) *Alloy S.* On cooling to *M*, this alloy would be in the condition in which the mother-metal was at temperature *M* in the case of alloy *R,* and would freeze there as a whole for the same reason.

(3) *Alloy T.* On cooling past *F*, the molten alloy splits up

into two saturated solutions (1) of *G* in *H*, and (2) of *H* in *G*; the composition of these shifts during further cooling, following the curves *FM* and *FJ*, till on reaching temperature *M* these
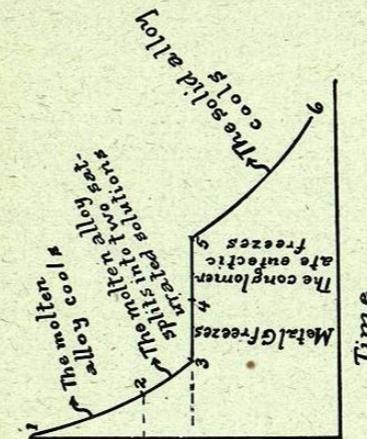
Fig. 46. Cooling Curve of Alloy *T*, of Fig. 45.

Fig. 45. Freezing-point Curve of Alloys of two Metals of Limited Reciprocal Solubility when Molten, but Complete Reciprocal Insolubility when Solid.
Subcase 5*A*, the Solubility Curve cuts both upper Branches of the Freezing-point Curve at the same Temperature.

alloys have respectively composition *M* and composition *J*, and each is therefore at its freezing-point.

At first we might suppose that both these molten alloys would now freeze simultaneously, because they are both at their freezing-point; and that in freezing they would split up simulta-

neously into separate particles of metal G and of metal H. But we must here note that, while the two molten alloys have by assumption the same melting-point, the two component metals have different ones. What would actually happen, we therefore infer, is that the more infusible metal G would begin freezing in preference to metal H, since G is now farther below its freezing-point C, and the temperature lever-arm, so to speak, of the tendency to freeze is therefore greater for G than for H. But the removal of some of metal G from the molten mass taken as a whole, would shift the composition of the remainder of that mass to the left, which means that the components of the two molten alloys would rearrange themselves somewhat as in § 73, p. 80; *i. e.*, that as metal G froze out progressively, so progressively would the proportion of molten alloy J decrease and that of molten alloy M increase.* This would continue until, by this removal of metal G from the molten mass, the residual molten alloy had reached composition M. In short, the composition of the residual molten mother-metal, *i. e.*, the average of its two components M and J, which average initially was F' (the same as T), would gradually travel to the left until it reached M. Once this composition is reached, all further differentiation of the mother-metal ceases; it has now reduced itself to a single molten component M, and this should freeze without further differentiation or selection, like any other eutectic, splitting up into alternate particles of the two component metals H and G.

The cooling curve for such a case is shown in Fig. 46. From 1 to 2 the molten alloy cools without change; from 2 to 3 it splits up into two saturated solutions, the composition of which travels progressively from F to M and from F to J of Fig. 45.

From 3 to 4 metal G freezes out, and the composition of the residual molten mother-metal as a whole (Fig. 45), *i. e.*, the

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* For the benefit of those already familiar with the phase rule it may here be pointed out that this rule leads us to expect the procedure here indicated at temperature MJ, rather than that both metals H and G should freeze out simultaneously. This it does because this latter supposition implies the simultaneous presence of four "phases," molten alloys M and J, solid H and solid G, four phases with only two components. In the procedure which I have sketched there are at no instant more than three phases.

average of its two component saturated solutions, travels to the left from F' to M.

At 4 further differentiation of the remaining molten mother-metal ceases, and from 4 to 5 it freezes as a whole like any other eutectic, splitting up into alternate particles of metal H and metal G.

From 5 to 6 the solid alloy cools.

We here see how the fact that the saturation-point curve extends above the freezing-point curve changes the shape of the latter. In this particular case it simply cuts off the apex of the

Fig. 47. Freezing-point Curve of Alloys of two Metals of Limited Reciprocal Solubility, both when Molten and when Solid.

V, which lines AM and CJ if produced would form, as they do in Figs. 24, 27, 28, 33 and 49.

108. SUBCASE 5 $A\beta$. — *The two metals when solid are somewhat soluble in each other.* Next let us suppose that the two metals, instead of being absolutely insoluble in each other when solid, are somewhat soluble reciprocally, but much less so than when molten. This assumption calls for saturation-point curves for the solid state, but it also implies that they lie respectively to the left-hand of M and the right-hand of J, as shown in Fig. 47.

Considering the cooling of an alloy initially of composition