

a stationary temperature slightly below the freezing-range for a time approximately that which we have gained by the rapid passage through the freezing-range. For in this range below the freezing-point, the equalizing tendency of diffusion is not thus offset by the opposing differentiating tendency of the freezing process. Hence, for given total time occupied by freezing-plus-cooling below the freezing-point, the greatest net equalization, *i. e.*, the minimum segregation, should be had by rapid freezing, followed by slow cooling or long sojourn at stationary temperature below the freezing-point.

This opinion, however, we cannot hold firmly, (1) because we do not know the relative force of effects (1) and (2) of Table 2, and (2) because we do not know how greatly the rate of diffusion is lessened in passing from the freezing-range to some point even slightly below it.

93. CASE 2, THE RATE OF COOLING IS NATURAL, *i. e.*, NOT ARTIFICIALLY VARIABLE. — Up to this point we have considered separately the effects of the rate of cooling in these distinct ranges of temperature, (1) the freezing-range and (2) the range between the lower or eutectic-freezing end of the freezing and the cold. For convenience the results of our study are grouped in Table 2, p. 112. To the manufacturing metallurgist, however, it would generally be so inconvenient to introduce any artificial change in the rate of cooling at the end of the freezing-period that, unless it offers some very great advantage, he will not, but will treat both ranges jointly as one whole. He will either cool through both ranges quickly, or through both ranges slowly, or through both ranges at some consistent intermediate rate, which will not involve artificially changing the rate of cooling at the end of the freezing-range and the beginning of the subfreezing-range.

Our next question, then, is which of the two, (1) natural rapid or (2) natural slow freezing-plus-cooling will give the least residual segregation, or in other words the greatest final uniformity? Clearly natural slow cooling should. If the whole cooling is to be very slow, this in both ranges leads towards equalization. If it is to be moderately slow, we may indeed think that, as far as the freezing-range is concerned, it would work less for uniformity than sudden freezing. But, on examining Table 2, and reflecting that principles (1) and (2) of that table are opposed to each other, we naturally infer that, in general,

the effect of the rate of cooling through the freezing-range will be less than the effect of the rate of cooling below that range; and hence that rapid freezing-plus-cooling will probably give more segregation than slow freezing-plus-cooling. This Roberts-Austen found true in his experiments on the influence of the rate of freezing-plus-cooling on the segregation of copper-silver alloys;* and such other direct evidence as is available points in the same direction.

To this conclusion the metallurgist may naturally object that, whereas in large steel ingots, which cool slowly, segregation is marked, it is insignificant in small steel ingots, or is generally thought to be. The answer is a simple one. It may well be that it is the size of the large steel ingot which, in spite of its slow cooling, causes its segregation to be very serious; and it is diffusion which alone can undo the segregation which freezing induces. We can easily see how this should come about. Diffusion of course is the only agency that in the slowly cooling ingot can remove the initial segregation already set up in freezing. But the great width of a large ingot in itself throws a serious obstacle in the way of thoroughness of diffusion, because of the implied great distance through which diffusion must transport the particles in order to efface initial heterogeneity.

But from this apparent slightness of segregation in small steel ingots we may draw an important inference. It is that principle 1 of Table 2 is probably a powerful one; for, except for this influence, we should expect that small ingots, because their size leads them to cool quickly, would be much segregated. The slightness of their segregation, then, we refer to the powerful influence of principle 1 (column 3, line 1 of Table 2), that rapidity of cooling in the freezing-range lessens segregation through lessening the initial heterogeneity.

As has already been pointed out, this discussion aims to consider only the non-eutectiferous alloys. Unfortunately, the data at hand, such as the segregated steel ingot, are those of eutectiferous alloys. This, of course, greatly lessens their value as evidence.

In the case of eutectiferous alloys there may be an agency,

* *Proc. Roy. Soc.*, 23, pp. 490-493, 1875.

and a powerful one, opposed to the equalizing action of diffusion. Every such alloy is a conglomerate of at least two distinct bodies. In slow cooling each of these bodies may tend to draw together, to coalesce, as in liquation processes; and this tendency one of these bodies may obey to a greater extent than the others, and may thus segregate during slow cooling. The effect of this segregating action is exactly the opposite of that of diffusion, on the degree of residual segregation. Space forbids going farther into this matter, than to point out this additional complication, and to warn the student that our deductions as to the probable course of events in non-eutectiferous alloys cannot be applied to eutectiferous ones without taking this additional influence into account. (See § 35 A.)

TABLE 2

RANGE	EFFECT OF RAPIDITY OF COOLING		FOR THE LEAST RESIDUAL SEGREGATION THE COOLING SHOULD BE
In the freezing-range	In that it lessens the initial heterogeneity	(1) It lessens segregation	Either extremely rapid or very slow
	In that it restrains diffusion in this range	(2) It increases segregation	
From the end of the freezing-range downwards	In that it restrains diffusion in this range	(3) It increases segregation	Very slow
Freezing-plus-cooling, i.e., both ranges successively	Case 1, the rate is variable artificially		Sudden freezing, with slow cooling thence
	Case 2, the rate is natural		Slow cooling

94. OTHER MODES OF GROWTH.—In § 78, p. 88, we saw that, besides the pine-tree mode of growth, there were others, some cube-wise, some sheet-wise. But in the present discussion, from § 78, p. 88, to the present section, we have, to fix our ideas, considered only the broad-branched pine-tree type.

To consider fully how far substituting these other types of growth would modify the conclusions at which we have arrived would carry us too far. But we may in general hold that, while the degree of landlocking and its consequences would vary from type to type, yet this would not affect our general inferences, which are based on the idea that the growth is partly onionwise and partly landlocking. For in each of these other modes of growth it seems clear that more or less landlocking and more or less onion-peel growth should be expected.

95. DIFFUSION IS IN BOTH DIRECTIONS FROM THE SHORE LINE.—Let us here note the fact, which tends to fasten the whole scheme in our memory, that diffusion takes place in both directions simultaneously, landward from the shore layer of the frozen or shore region, and seaward from the littoral layer of the still unfrozen or open sea. We have already noted in § 84, p. 100, this landward migration from the shore layer; and in §§ 82 and 89, pp. 97 and 106, this seaward migration from the littoral layer.

96. THE RATE OF FREEZING AND THAT OF SUBSEQUENT COOLING MAY SHIFT THE APPARENT BOUNDARIES OF THE EUTECTIFEROUS RANGE.—Turning to Fig. 33, p. 75, the ordinates passing through the points *a* and *c* give the composition of the two alloys which bound the eutectiferous range (§ 67, p. 74). By definition, alloys to the left of *a* when cold are simply bismuth-bearing tin, a solid solution of bismuth in tin; those to the right of *c* are simply stanniferous bismuth, a solid solution of bismuth in tin; those between *a* and *c* contain the eutectic in addition to such a solid solution.

But we must here distinguish between the true or normal position of these boundaries and their apparent position.

We have seen in §§ 71 and 72, pp. 78 and 79, that for equilibrium, the question whether a binary alloy of two metals of limited reciprocal solubility, such as bismuth and tin, will be (1) simply a solid solution, or will be (2) eutectiferous, depends solely on whether the total quantity of the two metals

present in the whole mass is such that one of them is or is not theoretically capable of dissolving the whole of the other when solid. If yes, the alloy is non-eutectiferous; if no, it is eutectiferous. This, then, gives us the position of these boundaries, a and c , for equilibrium. a and c thus represent respectively tin saturated with bismuth and bismuth saturated with tin, a point to which we shall return in § 105, p. 121.

But equilibrium, as we have already seen, is by no means always reached, and the actual conditions may vary on either side of it. And through such variations, an alloy which in equilibrium would not be eutectiferous may actually contain a eutectic, and another which normally is eutectiferous may actually lack the eutectic.

This really follows from what has gone before; but it may be well to run through the two cases, still considering, to fix our ideas, the specific case of freezing bismuth-bearing tin.

We have seen that sudden freezing may apparently give rise to supersaturation. Now suppose that an alloy, a bismuth-bearing tin, of which the composition is very slightly to the right of a , so that normally it should contain a very small quantity of eutectic, is thus rapidly frozen, so that the tin becomes supersaturated with bismuth, and sufficiently supersaturated to retain in solid solution the whole of the bismuth present. The alloy then consists solely of a solid solution of bismuth in tin and is actually wholly free from eutectic, although it would have been eutectiferous had this supersaturation not existed.

Turning now to the opposite case, let us consider an alloy the composition of which is slightly at the left of a , so that for equilibrium it would contain no eutectic; and let us assume that the conditions of freezing have been such that the normal degree of selection has taken place, and in particular that there has been no supersaturation. Let us further suppose that, at the moment which we are considering, this alloy has just undergone this selective freezing, and is beginning to cool from the freezing-point downwards. In the frozen mass diffusion is at work, transferring to the earlier deposited layers, initially poor in bismuth, part of the excess of bismuth which the later deposited layers richer in bismuth contain, thus aiming to make the bismuth-content of the whole uniform. But suppose that this diffusion is so greatly restrained by rapid cooling from the freezing-point downwards that

but little of this transfer occurs, so that the initial heterogeneousness is far from being effaced. This leaves in the last deposited layers much more bismuth than the average of the whole; so that even though, as the present case assumed, there may not be in the mass as a whole enough bismuth to saturate the tin, yet there may be more than enough in these last deposited layers, which therefore are eutectiferous. Thus, in short, the eutectic may exist locally in parts of an alloy, the composition of which taken as a whole is outside the limits which the eutectiferous range would have if equilibrium existed.

Looking at the matter from another standpoint, we saw in § 64, p. 72, that if the layers freezing out, (as distinguished from the average of the already frozen continent), reach the saturation-point before the whole open sea has frozen, then some eutectic will form. The enrichment of these layers might well reach the saturation-point thus, even if the average composition of the whole mass was below the saturation-point. In this case diffusion tends to efface the eutectic; if diffusion is arrested by rapid cooling, this effacement may be incomplete; some of the eutectic may persist.

To sum this up, supersaturation may shift the apparent boundaries of the eutectiferous range towards each other, shortening or even effacing that range; incompleteness of diffusion may shift them away from each other, thus lengthening that range.

We have here been considering only the rate of cooling as influencing the degree of saturation and of diffusion. But in general, anything which leads to supersaturation should thereby tend to shorten the eutectiferous range, anything which restricts diffusion should thereby tend to lengthen it.

97. SOLUBILITY FALLS WITH THE TEMPERATURE. — For simplicity one point has hitherto been ignored, *viz.*, — that in accordance with the general rule that the solvent power of any given substance for any other usually increases with the temperature, we should temporarily assume that the solvent power of solid tin for solid bismuth decreases as the temperature falls. On this account during the saturation division ($B'C$, Fig. 31, p. 71), since the temperature is constantly falling and since the successive solid layers should be saturated with bismuth for the existing temperature, their percentage of bismuth should progressively de-

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

* 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.

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

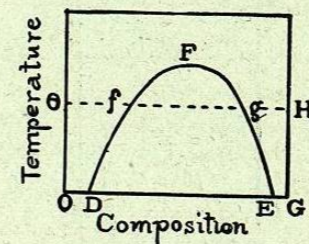


Fig. 43. Saturation-point Curve of Molten Binary Alloys.

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-

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