

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.

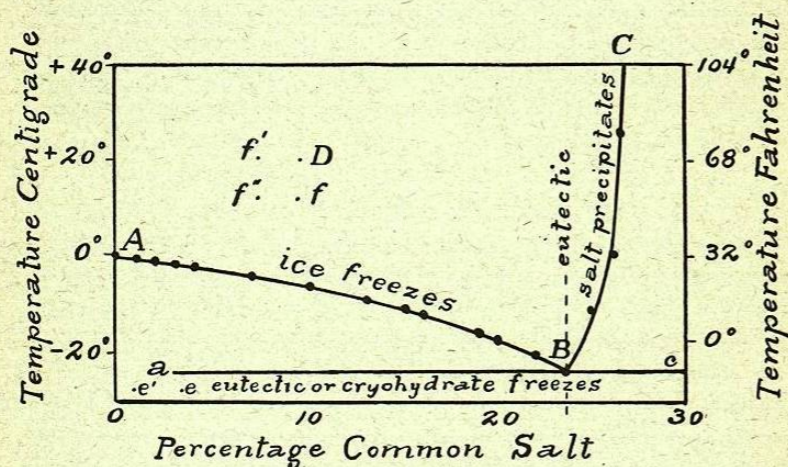


Fig. 27. Freezing-point Curve of Solution of Common Salt in Water.
Guthrie, *Phil. Mag.*, 5 Ser., I, p. 359, 1876.

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

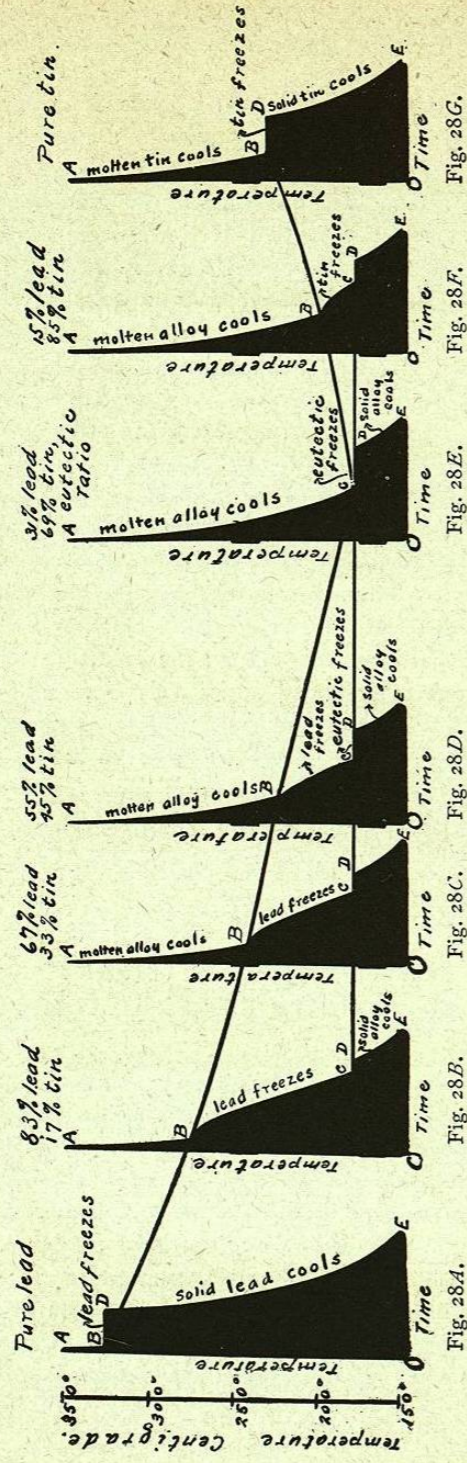
45. FREEZING-POINT CURVE OF SALT WATER. — If, now, proceeding as we did in §§ 41 and 42 with the freezing-points of the lead-tin alloys, we assemble as in Fig. 27 the freezing-points of all possible solutions of salt and water as shown in Figs. 7 to 11, p. 18, and plot them in a freezing-point curve, 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° 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,



Figs. 28A to 28H. Cooling and Freezing-point Curves of the Lead-tin Alloys, shown simultaneously.

Figs. 28A-G and Fig. 28H give two views of a lecture model made to show the relation between the cooling and freezing-point curves. The cooling-curve vanes are hinged along *AO*, and Figs. 28A-G give a front view with the vanes shut, i.e., flat against the back of the model. Fig. 28H shows the vanes opened, at right angles to the back of the model.

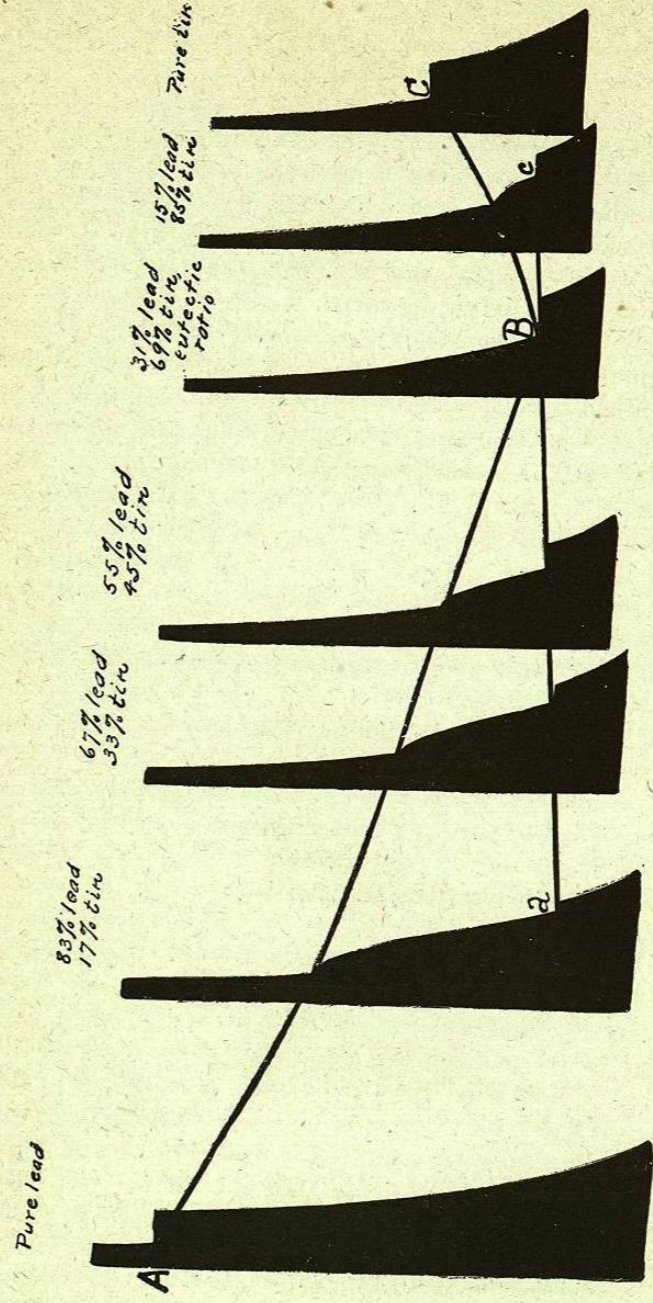


Fig. 28H.

while considerable, is limited. Each of these three assumptions refers to reciprocal solubility in the solid state.

In the last of these cases, if there is present a very large quantity of either metal with a very small quantity of the other, this small quantity dissolves in the larger one; but if the quantities of the two are more nearly equal, then there may be more of each than the other can dissolve.

48. IF TWO METALS ARE INSOLUBLE IN EACH OTHER WHEN SOLID, ALL THEIR ALLOYS SHOULD BE EUTECTIFEROUS. — The assumed complete insolubility of solid salt in solid ice, and of solid lead in solid tin, should cause all salt-ice, and all solid alloys of lead and tin, to be eutectiferous; in other words, if this insolubility were complete, then every salt-water solution and every lead-tin alloy when frozen would contain more or less of the eutectic, no matter how little salt the water initially contained, or how little lead the tin contained, or vice versa.

49. WHY SUCH A SERIES IS EUTECTIFEROUS THROUGHOUT. — The reason for this is first that the selection in freezing ought to be rigid; and second that rigid selection must eventually lead to the formation of a eutectic, no matter what the initial proportions of the two metals.

For our reason for the rigidity of the selection, let us return to the explanation offered in § 21, p. 26, of the selectiveness of the freezing of a salt-water solution, and apply it to the freezing of molten alloys of lead and tin. If we assume that these two metals are wholly insoluble in each other, and try to picture to ourselves that selection is not rigid, we find the idea unnatural, if not indeed untenable; so that rigid selection is what we naturally expect. For if in case, say of an alloy of much lead with little tin, selection were not rigid, so that a given minute layer in freezing out consisted not of lead alone but of lead with some tin, then the assumed complete insolubility of the two metals implies that the tin must be in distinct flakes, separate from the flakes of lead. But these flakes of tin certainly ought to redissolve and reënter the molten mother-metal, for the sufficient reason that the alloy which this reëntry would cause would be fusible, *i. e.*, could remain molten, at the existing temperature. And since the flakes of tin thus imaginarily deposited would in the very act of forming be exposed to the molten mother-metal, their opportunity to redissolve would be

most favorable, and all of them ought to redissolve completely, so that in effect only pure lead should permanently freeze, *i. e.*, the selection in freezing should be rigid.

The next following particles to freeze would for like reasons be pure tin-less lead, and this process of rigid selection and consequent extreme enrichment of the mother-metal in tin should continue. Should it continue indefinitely, eventually all the lead would have frozen out and only pure molten tin would be left, no matter how little tin were initially present. But as explained in § 29, p. 33, this selection ought of course to end when it has enriched the mother-metal up to the eutectic or most fusible ratio: once this ratio is reached no further selection in freezing should occur, for the sufficient reason that no selection can yield a mother-metal of lower freezing-point. Hence when the mother-metal is enriched up to the most fusible or eutectic composition, and simultaneously the temperature has fallen to the freezing-point of this eutectic and tends to descend below it, the mother-metal now freezes unselectively into the eutectic. Hence, the rigidity of the selection causes the enrichment of the mother-metal to reach the eutectic ratio, and this in turn causes the formation of a eutectic, no matter how little lead is initially present, and, by like reasoning, no matter how little tin is initially present, in short no matter what the initial composition, Q. E. D.

50. WHY THIS EUTECTIC IS COMPOSITE. — The eutectic should be composite for the same reason as in the case of salt water (§ 31, p. 38). The assumed insolubility of solid lead and solid tin in each other implies that each of these in the solid state must be free from the other, and hence that the particles which each forms must be distinct from those in which the other exists.

51. SERIES OF ALLOYS RARELY EUTECTIFEROUS THROUGHOUT. — Here let us note that those series of alloys which are apparently of the first type, that which is eutectiferous throughout, may on further examination prove to be of the third or partly eutectiferous type. For that a series should be eutectiferous throughout implies absolute reciprocal insolubility of its component metals. We may doubt whether this often occurs. It is probable that in most cases there is at least a slight reciprocal solubility, so that a short space at each end of the series is non-eutectiferous. The wholly eutectiferous type, then, is one which

is approached, but probably rarely reached. The salt-water and the tin-lead cases were assumed to be of this type, to help explain the general features of the constitution of alloys.*

52. IF TWO METALS ARE SOLUBLE IN EACH OTHER WHEN SOLID, SOME OR EVEN ALL OF THEIR ALLOYS SHOULD BE NON-EUTECTIFEROUS. — We have now seen that, if two metals when solid are absolutely insoluble in each other, all of their alloys should be composed (1) of the eutectic and (2) of the excess-metal, *i. e.*, of the metal present in excess over the eutectic ratio. But the case will be very different if the metals are soluble in each other when solid. Let us consider two cases, that of the silver-gold alloys, two metals which even when solid dissolve in each other in all proportions, and that of the bismuth-tin alloys, metals each of which can dissolve a limited but still a very considerable quantity of the other when solid.

53. SIX FEATURES OF THE GENESIS AND CONSTITUTION OF WHOLLY NON-EUTECTIFEROUS SERIES: SILVER-GOLD TYPE. — If two metals are soluble in each other in all proportions when solid,

(1) their freezing is indeed selective, but

(2) the selection is not rigid, *i. e.*, the layers which freeze out instead of being, as in the lead-tin case, the excess or solvent metal wholly free from the deficit or dissolved metal, are an alloy of the two metals, but richer in the excess-metal than the initial molten mass was: so that as freezing proceeds, though the mother-metal indeed becomes progressively enriched in the dissolved metal, yet that enrichment is not extreme, as it was in the lead-tin case,

* The quasi-alloys of iron with carbon indeed present two cases in which the insolubility appears to be complete. The first of these is the graphite or "kish," the excess-substance in cast iron containing more than 4.30 per cent of carbon. Its freedom from iron is certainly nearly and perhaps quite complete. (See Fig. 68. Compare also Percy, "Iron and Steel," p. 511. Dr. Percy indeed found evidences that this kish contained silicon, but his failure to record the presence of iron goes to show that none was present, to judge from his habits. See also "Principles of the Manufacture of Iron and Steel," Bell, p. 156.) The other case is that of the iron which separates out as ferrite from the austenite of slowly cooling steel, in passing through the critical range. This appears to be wholly free from carbon. (*Fifth Rept. Alloys Research Committee*, p. 50.) But more delicate observations are needed to establish firmly the completeness of insolubility even in these cases.

(3) as the mother-metal becomes progressively enriched in the deficit or dissolved metal, so the layers which freeze out from it are successively richer and richer in the dissolved metal,

(4) while one alloy of the series is strictly speaking a eutectic,

(5) it is not composite, and

(6) all the other alloys of the series are non-eutectiferous, in the sense of being free from a composite eutectic of the usual type.

Of these six facts, the fourth is a direct consequence of our definition of a eutectic, and the others are natural consequences of our conditions, as will shortly be explained.

Reasons for this Genesis and Constitution

54. FREEZING SELECTIVE, BUT THE SELECTION SHOULD NOT BE RIGID. — Taking up the first two of our six facts, let us consider the case of an alloy of 60 per cent of gold and 40 per cent of silver, premising that pure silver is apparently more fusible than any of its alloys with gold, and that the freezing-point descends continuously as the percentage of silver increases from 0 to 100. (Fig. 29, p. 67.)

First, if freezing is to be selective, in which direction should the selection be? Here we must look upon gold as the excess-metal, because there is more gold than that which corresponds to the eutectic ratio, which really is silver 100, gold 0. (See § 56, p. 66.) Hence if there is any selection, it should be that the layers freezing out are richer in gold, the excess-metal, than the initial mother-metal is.

Next, if we ask whether this selection should or should not occur, we see that we have the same reason as in our salt-water case (§ 21, p. 26) why it should, *viz.*, that if we conceive that it does not, but that the first deposited flake is of the 60:40 ratio, its silver should tend to redissolve and reënter the molten mother-metal, because the alloy which that reëntry would create would contain more than 40 per cent of silver, and would therefore be fusible and remain molten at the existing temperature, which by assumption is at the freezing-point of a 40:60 silver-gold alloy; because every increase of silver lowers the melting-

point of silver-gold alloys. In short the conception of unselective freezing is unnatural, so that selection is what we naturally expect.

But we should not expect selection to be rigid in the sense that the whole of the silver would remelt and reënter the mother-metal, so that in effect only pure gold should freeze, because that remelting and reëntry is opposed by the mild force which in any given frozen flake holds together the two metals, the solvent and the solute. Therefore it is natural that the struggle between the tendency of the silver to remelt and reënter the molten mother-metal, and the bond between the two metals in that flake holding them together and opposing the removal of the silver from the gold, should result in a compromise: we should expect part of the silver to remelt and part to remain frozen, so that, while freezing should be selective, the selection should not be rigid, which is what we set out to explain.

55. THESE REASONS CONTINUED: HETEROGENEOUSNESS OF SOLID SOLUTIONS.—To say that freezing is selective is to say that the mother-metal becomes progressively enriched in silver as freezing proceeds. That this progressive enrichment should be accompanied by a corresponding enrichment of the layers which freeze out so that each layer is richer in silver than the preceding, is so natural that no explanation is required.

But to assert this progressive enrichment of the successive layers is equivalent to saying that the solid solution as deposited is initially heterogeneous. Diffusion of course tends to efface this heterogeneousness. In § 86, p. 101, we will consider whether this effacement ought to be complete, or whether a remnant of this initial heterogeneousness ought to persist.

56. ONE MEMBER OF THE SERIES A EUTECTIC.—In any such series there must indeed be one alloy which is more fusible than any of the others; and this, following Guthrie's definition, is a eutectic. As silver appears to be more fusible than any of its alloys with gold, so in a sense it is the eutectic of the silver-gold series; and there is no break in the rise of the freezing-point as we pass through the series from pure silver to pure gold (Fig. 29). But in other series of alloys of two metals reciprocally soluble in all proportions at and even below their freezing-points, some one alloy might be more fusible not only than all the others but than either component metal, as in the

case of mercuric bromide and iodide, Fig. 44, p. 118. Such an alloy would be the eutectic of the series.

57. THAT EUTECTIC NOT COMPOSITE.—But this eutectic would be a solid solution, instead of consisting of interstratified plates of two distinct substances as in the salt-water and lead-tin cases. The reason is obvious. The reason why the salt-water and the lead-tin mother-metals froze on reaching the eutectic enrichment, was that they simultaneously reached the freezing-point of the eutectic, the lowest freezing-point of the series; freezing should not be deferred by further enrichment, because such enrichment would only raise the freezing-point. But the

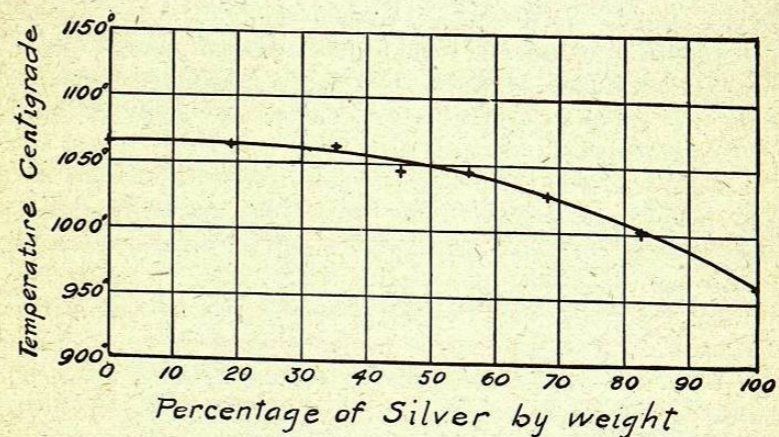


Fig. 29. Freezing-point Curve of Silver-gold Alloys.
Plotted from the data of Sir W. C. Roberts-Austen and T. K. Rose,
Proc. Royal Soc., Vol. LXXI, p. 162.

reason why the eutectic on freezing splits up into alternate plates of ice and salt, lead and tin, was a different one: it was that each substance when solid is insoluble in the other. Now this latter reason does not apply to our gold-silver type of alloys. As their metals are soluble in each other in all proportions, so no matter to what composition the eutectic corresponds, there is no reason why it should in freezing split up into different layers. So the absence of the composite structure from the quasi-eutectic alloy of the series is a natural consequence of the complete reciprocal solubility of the two metals.

58. THE OTHER ALLOYS OF THE SERIES NON-EUTECTIFEROUS. That no composite eutectic should form in any alloy of the series is in accordance with the reasoning in the last section.

But it appears that not even a non-composite eutectic forms, *i. e.*, that enrichment of the mother-metal does not proceed so rapidly as to bring any finite quantity of the mother-metal to the most fusible, *i. e.*, eutectic composition; so that no finite quantity of even the non-composite or quasi-eutectic forms. While further observations are needed to establish this as a general law, it would not be an unnatural one. Complete reciprocal insolubility of two metals forces selection to be rigid and the enrichment of the mother-metal to be extreme. But when two metals dissolve in each other without limit, it would not be unnatural that, as through the enrichment due to selective freezing the composition of the mother-metal approaches the eutectic ratio, the selection should become milder and milder, so that that approach should be asymptotic.

Further, however this may be, even if the enrichment of the later-frozen layers should bring them up to the eutectic ratio, diffusion into the poorer layers earlier deposited should tend to impoverish them below that ratio.

59. SHAPE OF THE COOLING CURVE. — The cooling curve for alloys of this class should be like that of Fig. 30. This resembles those of the eutectiferous alloys and of salt-water in having a rounded selective-freezing part *BC*, but it differs from them in lacking the eutectic-freezing part or jog *CD*.

60. IF THE RECIPROCAL SOLUBILITY OF TWO METALS WHEN SOLID IS LIMITED, THE SERIES OF THEIR ALLOYS SHOULD BE EUTECTIFEROUS IN THE MIDDLE BUT NOT AT ITS ENDS, AND THE EUTECTIC SHOULD BE COMPOSITE. — Tin when solid can dissolve a considerable proportion of bismuth, and conversely bismuth can thus dissolve tin.* Thus if there is present in the alloy as a whole a large proportion of tin and only a small proportion of bismuth, that bismuth can remain dissolved in the tin even after the whole has frozen. Conversely, if there is present in the alloy as a whole a large proportion of bismuth and only a small proportion of tin, that tin can remain dissolved in the

* A. W. Kapp, *Annalen der Physik*, 4th Ser., vol. VI, pp. 754-773, 1901.

bismuth even after the alloy has frozen. But there is the intermediate condition, in which there is more bismuth than the tin present can dissolve, yet not enough bismuth to act as the solvent and dissolve the whole of the tin. Under these conditions the alloy should be eutectiferous and its eutectic should be composite. The reasons for this have really been given already, but they may come out more clearly if we consider an individual case.

First we have the same reason as with the previous types (§§ 21, 49 and 54) why freezing should be selective, why as the freezing, *e. g.*, of an alloy of tin with a small quantity of bismuth, progresses, the mother-metal should become progressively enriched in bismuth, and the layers which successively freeze out should correspondingly become richer and richer in bismuth. Each layer should be richer in bismuth than the preceding layer, although each layer is poorer in bismuth than the then existing mother-metal. Now, should this enrichment of the mother-metal be so slight that even when its last particle freezes, it shall not contain more bismuth than the tin is able to retain dissolved when solid (say *N* per cent of bismuth), no composite eutectic should form; the enrichment should be continuous: there will be no reason why even the last frozen flake of the alloy should in freezing break up into a composite mass. Such is the state of affairs that we might expect if the initial quantity of bismuth dissolved in our tin is extremely small.

Suppose, however, that our initial molten tin contains a greater quantity of bismuth, so that a considerable quantity of unfrozen mother-metal shall still remain at the time when the composition of the layers in the act of freezing shall have reached this *N* per cent of bismuth. Up to this time each layer which has frozen has been richer in bismuth than the preceding one, simply because it has frozen out of a mother-metal richer in bismuth than that from which the preceding layer froze. In other words, the progressive enrichment in bismuth of the mother-metal has led to a progressive enrichment in bismuth of the successive layers; and this latter in turn has retarded the enrichment of the mother-metal, which has been gradual, instead of being extreme as in our salt-water and lead-tin types of assumed complete insolubility.

61. SUBSATURATION AND SATURATION DIVISIONS OF THE EXCESS-FREEZING PERIOD. — But at this point, when the tin which