

held molten at a temperature even below its own freezing-point of 231° .

20. FREEZING COVERS A CONSIDERABLE RANGE. — Next the freezing of our 15 per cent salt solution, instead of occurring at a fixed temperature, covers a considerable range, that from *B* to *C*. But this is clearly a consequence of what was described in § 18, p. 24. For as the water which first freezes in our flask to relatively pure ice, thereby rejects the salt which it had contained; and as this salt thereby concentrates progressively in the central region of still unfrozen water or "mother-liquor"; and finally as this consequently grows progressively richer in salt, it thereby acquires a progressively lower and lower freezing-point; or in other words as the enrichment of the mother-liquor in salt goes on, a lower and lower temperature is needed to induce the further freezing out even of relatively pure ice. Hence the considerable range of temperature covered by freezing: while that the curve is rounded, instead of being a straight line, represents the fact that this fall of the freezing-point is not strictly proportional to the time which it occupies, but becomes more and more rapid as the freezing progresses.

21. SELECTION NATURALLY TO BE EXPECTED. — Considering next the fact that the freezing of a salt-water solution is selective, let us ask whether this is what should naturally be expected; and to this end let us try to picture to ourselves what actually occurs in the freezing of a 15 per cent salt solution. These mental pictures, even if not strictly accurate, may be of great value in enabling us to frame the various facts into a consistent harmonious whole, instead of regarding them as simply arbitrary facts to be learned by rote, and quickly forgotten.

First let us conceive for an instant that the opposite is true, *i. e.*, that freezing is unselective, and see whether, in such a case as that of salt water, containing 15 per cent of salt, of a solvent and a solute which for simplicity we may assume form no chemical compound with each other, the conception is natural, or whether it is more natural to expect the freezing to be selective. To fix our ideas, let us suppose that a single most minute quantity of the liquor were to freeze unselectively, yielding a minute particle of salt ice of the same composition as the mother-liquor, 85 per cent of water and ice and 15 of salt. For simplicity let us assume that solid salt and solid ice are absolutely insoluble in each other.

(See § 51, p. 63.) On account of this reciprocal insolubility, what has first frozen must really be two distinct flakelets, one of pure ice and one of pure salt; and these two flakelets find themselves in contact with the liquid mother-liquor.

Reflection shows that our flakelet of salt ought to redissolve. First, while a 15 per cent salt solution cannot remain liquid at the existing temperature (which by assumption is at the freezing-point of such a mixture) a solution containing more than 15 per cent can, because as we have just seen any increase of salt in this range lowers the freezing-point. Hence if our salt flakelet were to redissolve and reënter the mother-liquor, the solution or new mother-liquor which its reëntry would form, would be fusible, *i. e.*, would remain liquid, at the existing temperature. But this is the general condition which determines whether a substance shall unite with and dissolve in any liquid to which it is exposed, *viz.*, that the product of their union is fusible, *i. e.*, can remain liquid, at the existing temperature. The salt flakelet should redissolve in the mother-liquor, simply because by doing so it would yield a mother-liquor fusible, *i. e.*, liquid, at the existing temperature.

But the flakelet of ice, *i. e.*, of frozen pure water, does not redissolve, simply because its reëntry into the mother-liquor would restore the 85:15 ratio, would make the mother-liquor infusible, *i. e.*, incapable of remaining liquid, at the existing temperature.

Hence in effect at this stage a single flakelet of pure ice has frozen out, because our salt which we conceived to have frozen would naturally redissolve. The freezing has thus far been rigidly selective. Clearly what has been true of the first flakelet should be true of succeeding ones.

Thus we see that selective freezing, instead of being a surprising phenomenon, is what we ought to expect; for, when we try to picture to ourselves unselective freezing we see that it ought to change itself spontaneously to selective freezing.

Attention is particularly directed to this reasoning, that whether a flake, assumed for argument to have frozen, will redissolve or remain frozen, should depend primarily on whether its remelting would or would not make the mother-mass fusible at the existing temperature; for from this point of view we readily see most simple explanations of several of our most important and indeed at first sight surprising phenomena.

22. SELECTIVE AND UNSELECTIVE FREEZING. — We have seen that freezing may be either of two types,

(1) the selective or concentrating type, like that of salt water, yielding an inclined or rounded freezing region in the cooling curve. In this type the substance which first freezes has not the exact composition of the molten or liquid mass from which it freezes, so that some component of that mass progressively concentrates in the still unfrozen mother-part, with consequent progressive change of the freezing-point of that mother-part, so that freezing covers a considerable range of temperature.

(2) The unselective type, in which the liquid or molten mass freezes without such selection or change. Here, because the composition of the part unfrozen remains constant throughout freezing, its freezing-point remains constant, and is represented by a horizontal jog theoretically with sharp corners, like *BD* in Fig. 7. (See § 15, p. 20.)

We have each of these types in the freezing of molten alloys as well as in that of aqueous solutions.

Of the selective type we have two classes,

(A), those yielding a homogeneous mass, as when that which freezes out is (1) a pure and definite substance (this has been for simplicity assumed to be true of the salt which freezes out of our salt water), or (2) a single metal wholly free from those with which it was united when molten, or (3) a definite chemical compound of two or more metals, or (4) *conceivably*, a solid solution, the successively deposited layers of which are of the same composition, *i. e.*, a homogeneous solid solution. As we shall see, the successive layers of a solid solution as they successively deposit, are not normally of like composition, *i. e.*, are not homogeneous in the act of solidifying, though diffusion tends to remove their initial heterogeneousness (§§ 54, 55, 60, and 114; pp. 65, 66, 68 and 135).

(B), those yielding a heterogeneous mass, as when that which freezes out is a heterogeneous solid solution.

23. THE JOG AND THE EUTECTIC. — In the cooling curve of salt water (Fig. 8, p. 18), besides the rounded part which we have been considering, there is a sharp-cornered horizontal jog *CD*. What is the meaning of this?

As already explained, as the freezing of the salt water progresses more and more ice freezes out, and the remaining still

liquid mother-liquor becomes progressively richer and richer in salt; and this goes on until, when the temperature has fallen to -22° C., the proportion of salt in the mother-liquor reaches 23.6 per cent, the "eutectic ratio," a term which will be explained shortly. But beyond this concentration in general it refuses to go, for a simple reason which we shall soon see. The progressive freezing of pure ice and the consequent enrichment of the mother-liquor in salt now cease, and, on further cooling, the mother-liquor gradually freezes without selection, *i. e.*, the ice which now forms has the same composition as the mother-liquor from which it forms, so that now the composition of both the nascent ice and the mother-liquor remains constant, and further so that the freezing-point of the mother-liquor therefore remains constant. Hence, finally, the horizontal jog *CD*. (See § 10, p. 17.)

But though the freezing of the mother-liquor from this point on is unselective, so that that which freezes out has the exact composition of the mother-liquor, this freezing is of special sort, in that the mother-liquor in freezing splits up into a conglomerate mass of distinct crystals of ice and distinct crystals of salt, interstratified in thin plates. But, as has just been said, this conglomerate which freezes during this period is uniform throughout; and the plates of salt form 23.6 per cent of it, and the plates of ice 76.4 of it; *i. e.*, the ratio of plates of the frozen water to those of frozen salt is throughout the eutectic the same as the ratio of liquid water to dissolved salt in the mother-liquor at the time when its further concentration was arrested, and when it froze unselectively to form this conglomerate eutectic.

24. FREEZING OF A 20 PER CENT SALT SOLUTION. — If, now, instead of starting with a solution of 15 per cent of salt we started with one of 20 per cent of salt (Fig. 9, p. 18), we should get a curve of the same family. The rounded part would begin at a lower temperature because, owing to the initial greater richness in salt, the freezing-point is lower, *i. e.*, a lower temperature is required to induce the first freezing out of ice. The rounded part would end at the same temperature as in the preceding case, because, no matter what the initial concentration of the salt is, the percentage of salt in the mother-liquor will reach this same eutectic ratio of 23.6 per cent at one and the same temperature, *viz.*, -22° C. But the jog will be longer in case of a 20 per cent than in the case of a 15 per cent solution of salt, simply because

in the former the quantity of mother-liquor remaining when the concentration has reached 23.6 per cent, will evidently be greater, and the time occupied in freezing it will be correspondingly greater.

Conversely, since the quantity of relatively saltless ice which will form before the mother-liquor has reached the eutectic ratio of 23.6 per cent will be less than in the 15 per cent solution case, not only will the length of the part *BC* be less, but the retardation caused by the freezing out of this relatively saltless ice will be correspondingly less, and hence the inflection which it causes between *B* and *C* will be less. Thus comparing the portion *BC* in Fig. 8 with that in Fig. 9 we note that the former is much more sharply inflected than the latter.

In short, dividing the freezing into two parts, the ice-freezing and the eutectic-freezing periods, *BC* and *CD*, as the proportion of salt approaches the eutectic ratio the lower will be the beginning of the ice-freezing part, and the shorter and less sharply inflected will it be; while the longer will the eutectic-freezing part *CD* be.

25. FREEZING OF A EUTECTIC SOLUTION. — If now, as in Fig. 10, the liquor initially contained exactly the eutectic proportion, 23.6 per cent of salt, then, as we progressively cool it, no freezing will take place until the temperature of -22° has been reached, when the whole will freeze unselectively, as a pure metal or pure water would, but splitting up as before into parallel plates of ice and of pure salt.

26. FREEZING OF A HYPER-EUTECTIC SOLUTION. — If, finally, instead of 23.6 per cent of salt there is 26 per cent of salt initially present, then our curve will be of the shape shown in Fig. 11, which is of the same family as those in Figs. 8 and 9. The freezing which is represented by the rounded part *BC* will, however, not be of water but of salt,* because the initial solution

* Or of a hydrate richer in salt than the eutectic. Guthrie, *Phil. Mag.*, 5th Ser., I, 1876, p. 355.

The precipitation of the excess of salt in this case is exactly that which occurs when any hot saturated solution, for instance that of cupric sulphate, is gradually cooled. And here we may note that the freezing and crystallizing of ice, the precipitation or crystallizing of a salt from a solution which through cooling becomes super-saturated, and the freezing of a metal, are really one and the same thing; they are a passage from the fluid to the solid state. Water in freezing looks different from salt precipitating out, and both of these occur at a temperature so very much lower

as a whole contains an excess of salt over the 23.6 per cent or eutectic ratio.

27. EUTECTIC AND CRYOHYDRATE. — Returning to our salt water solution, the fact that, no matter what the initial concentration of the solution is, the jog caused by the freezing of the eutectic occurs at the same temperature, and the mother-liquor which there freezes has the constant composition of 23.6 per cent of salt, shows that this percentage composition has some particular and important relation. This ratio of salt to water is the "eutectic" or "cryohydrate" ratio, the ratio which gives the lowest freezing-point, *i. e.*, the greatest fusibility. In case of aqueous liquids it is usually called the "cryohydrate"; in case of alloys it is called the "eutectic," which translated literally means the "well melting" alloy. Guthrie defined the eutectic in accordance with this meaning as the most fusible alloy. But as the cryohydrate and the eutectic are essentially one and the same thing, we may for our present purpose apply the name "eutectic" to both.

28. PROPERTIES OF THE EUTECTIC. — To recapitulate, the striking properties of the eutectic are:

(1) that its composition and hence its freezing-point are constant, no matter what the initial ratio between the solvent and the solute, *i. e.*, the composition of the solution or alloy,*

(2) that its composition is not, save occasionally and as it were by accident, in simple atomic proportions,†

than that at which metals commonly solidify, the circumstances are so different, that we usually do not appreciate that they are really one and the same thing. But this conception of the essential identity of the solidification of a metal, the freezing of water, and the precipitation of a salt is very important for the student of alloys.

* As will be explained in §§ 126 and 127, pp. 148 and 149, in case of the alloys of gold with aluminium, of antimony with copper, in short of alloys of those metals which form definite chemical compounds with each other, the eutectic which forms when one of those metals is in great excess, may differ from that formed when the other metal is in great excess. In other words, such a series of alloys may have one eutectic at one of its ends and another at the other end, and still others at different ranges; but each eutectic is of constant composition.

† Guthrie pointed out that "The statement therefore that alloys of minimum melting-points are got on mixing the metals in certain simple ratios of their atomic weights, is presumably to be put on one side." ("On Eutexia," *Phil. Mag.*, 5th Ser., XVII, 1884, p. 465.)

(3) that it consists of a conglomerate of distinct particles of the two components, mechanically mixed.

If the two components of the eutectic are soluble in each other (when solid) in all proportions, the eutectic is not a conglomerate but simply a solid solution. If the two components are soluble in each other but only to a limited degree, then the eutectic is a conglomerate of particles of the two components, the particles of each component being saturated with the other. In short, it is a conglomerate of saturated solid solutions of the two components. But

EUTECTIC STRUCTURE

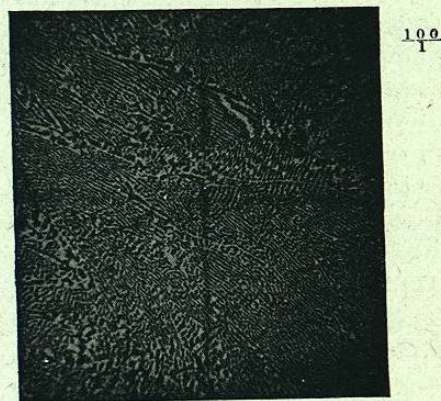


Fig. 13. Alloy of 58 per cent Bismuth, 42 per cent Tin.
Made by Wm. Campbell in the Author's Laboratory.

these facts we may for the moment leave out of sight. We will take them up and consider their explanations in §§ 57, 65 and 68; pp. 62, 73 and 74.

The most characteristic, and perhaps the most usual mode of occurrence is in alternate plates of each of the two components, interstratified, and not crossing each other. (Fig. 13.) But in a very considerable proportion of cases the two components of the eutectic, though clearly distinct from each other, have a cellular or spherulitic instead of a sheet-like structure. Fig. 17, p. 47, shows the banded or sheet-like and spherulitic structure of the eutectic occurring side by side in the same specimen.

The two components may, as in the case of alloys of lead and tin, be plates of one metal interstratified with plates of another metal; or as in the case of salt and water each may be a definite chemical compound, plates of ice being interstratified with those of sodium chloride; and the same may occur in the case of alloys. For instance in the case of alloys of copper and antimony (Fig. 51, p. 150) we have a eutectic which consists of layers of copper interstratified with layers of antimonide of copper. Again the quasi-eutectic or æolic (See § 148, p. 178) which forms in steel consists of plates of the definite carbide, cementite, Fe_3C , interstratified with plates of pure iron or ferrite (Fig. 63, p. 177). That which forms in oxide-bearing copper appears to consist of plates of cuprous oxide interstratified with plates of copper;* that in phosphoric iron appears to consist of plates of a definite iron phosphide Fe_3P interstratified with a saturated solution of that same phosphide in iron, *etc.*, *etc.*†

The alloys of three or of four metals may contain eutectics consisting of interstratified plates of the three or the four component metals.‡

29. REASONS FOR THE PROPERTIES OF THE EUTECTIC. —

There are extremely simple reasons why the eutectic formed in the freezing of salt water should have the properties which have just been enumerated, surprising as those properties at first seem. These reasons are readily seen on following the freezing of a solution of say 15 per cent of salt in 85 of water. To this end let us again follow the progress of freezing. It begins with the freezing out of a little pure ice; this enriches the residual mother-liquor in salt; and this in turn lowers the freezing-point of that mother-liquor, *i. e.*, the temperature to which we must cool it to induce further freezing of ice; and this joint freezing out of ice and lowering of the freezing-point go on progressively through the ice-freezing period, a residue of mother-liquor persisting unfrozen, because as fast as the temperature falls, so fast does the freezing-point of the mother-liquor fall thanks to its simultaneous enrich-

* Heyn, *Bulletin Société d'Encouragement pour l'Industrie Nationale*, CI, p. 276, 1901.

† Stead, *Journ. Iron and Steel Inst.*, II, 1900, p. 83.

‡ Guthrie, *Phil. Mag.*, 5th Ser., XVII, pp. 465-6; Charpy, *Bull. Soc. d'Encouragement*, 5th Ser., III, pp. 690-1, 1898; *The Metallographist*, II, p. 32, 1899.

ment in salt, so that at each instant the mother-liquor is at its freezing-point.

But there must be an end to this: there must be a limiting temperature at which no mixture of salt and water can (normally) remain liquid, and that limiting temperature is the freezing-point of the most fusible, *i. e.*, the most easily liquefiable mixture of salt and water, *viz.*, that with 23.6 per cent of salt, freezing at -22° C. On reaching this temperature and composition the mother-liquor itself should freeze. For, just as it was the progressive enrichment of the mother-liquor in salt that caused it to remain unfrozen in spite of the progressive cooling, simply because that enrichment gave to the mother-liquor a lower freezing-point; so when the enrichment in salt reaches and tends to pass 23.6 per cent it should fail to keep the mother-liquor from freezing, because further enrichment in salt, instead of lowering, would raise the freezing-point; instead of keeping the mother-metal from freezing it would make it freeze all the sooner. At every instant in the cooling until this 23.6 per cent is reached, the mother-liquor is at its then freezing-point, and is kept from actually freezing by the simultaneous fall in that freezing-point caused by the freezing out of water and consequent enrichment of the mother-liquor in salt. The mother-liquor at each instant is on the point of freezing, but in starting to freeze renders itself unfreezable at the existing temperature by thus as it were ejecting from itself a little water and so making itself richer in salt. But when it has reached 23.6 per cent of salt and simultaneously reached the freezing-point of that mixture, freezing cannot normally be deferred by further differentiation, because any change in composition would now raise the freezing-point; as the mother-liquor is now at its freezing-point, to raise its freezing-point without raising its temperature would freeze it. Hence, further selection offers no escape from freezing.

Hence we see why the composition and freezing-point of the eutectic are constant and independent of the initial proportions of salt and water. For, no matter what those proportions, since the condition which enables the mother-liquor to remain unfrozen through progressive cooling is that the change in its composition (which, through the freezing out of one component, accompanies that cooling), leads to a lower freezing-point; so this permissive condition ceases when the 23.6 per cent limit is reached simul-

taneously with the freezing-point for that limit, simply because no further change in composition can now yield a lower freezing-point, *i. e.*, no possible combination of salt and water can normally remain liquid at this temperature, a condition of affairs evidently wholly independent of the initial composition. Of course, the nearer the initial composition of the liquor is to this 23.6 ratio, the less will be the excess of water (or salt) to be frozen out before

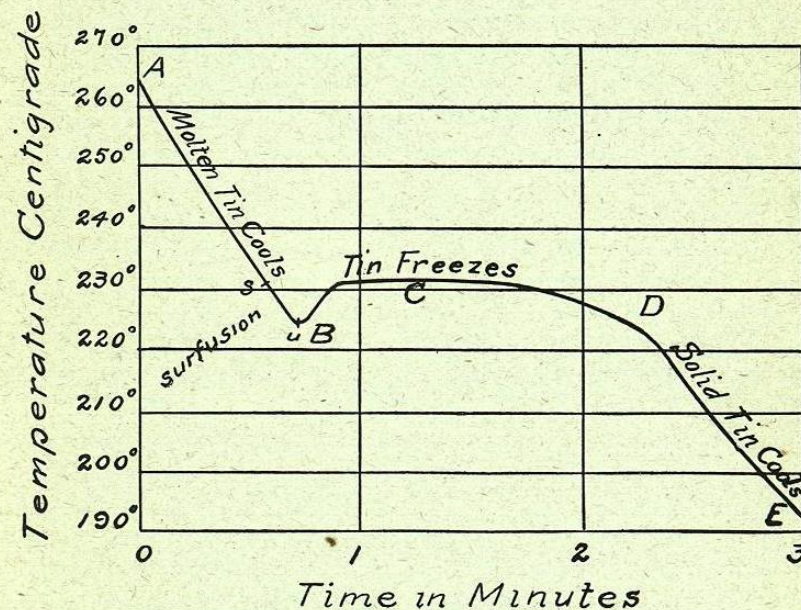


Fig. 14. Cooling Curve of Tin.

(Roberts-Austen, *Third Report Alloys Research Committee*, Fig. 7, Plate 39.)

The wording on this figure is the author's, not Professor Roberts-Austen's.

reaching this ratio, and the larger will be the quantity of the eutectic which will form; but the composition and freezing-point of the eutectic are clearly wholly independent of this.

30. SURFUSION. — These assertions represent the condition of equilibrium, the normal condition towards which our phenomena tend. But though our phenomena tend towards equilibrium they are often prevented from reaching it, for instance through surfusion, a matter which we will now consider.