It has long been known that water and other liquids, if kept perfectly still, may be cooled considerably below their true or normal freezing-point without actually freezing; but that if then agitated they at once freeze, and so rapidly that the latent heat of solidification raises the liquid quickly to its true freezing-point, 0° C. in case of water.

The same is true of molten metals. Thus, Fig. 14, p. 35, shows the cooling curve of molten tin, which passed about 5° below its normal freezing-point (231° C.) before it began freezing. The temperature then rose quickly to about 231°, and remained nearly stationary till the whole had frozen. This phenomenon of remaining molten below the true freezing-point is known as surfusion.

So in the familiar example of a solution of sodium sulphate. A solution of this substance saturated at its boiling-point can be cooled to the temperature of the room without crystallizing, although it thereby becomes very greatly supersaturated; *i. e.*, the water retains in solution very much more sodium sulphate than it is capable of absorbing at the room-temperature, and very much more than normally corresponds to its saturation-point at this temperature. But if a crystal of sodium sulphate is dipped into this supersaturated solution, the whole crystallizes, *i. e.*, solidifies or freezes very rapidly, the solidification or freezing radiating out from this crystal as a nucleus. The same effect is brought about by dipping a glass rod into the supersaturated solution; but if the rod is freed from dust, or heated and then cooled, it may not induce freezing.

In determining the freezing-point of alloys, surfusion may depress both freezing-points, *i. e.*, the temperature at which the excess-metal begins freezing, and that at which the eutectic begins freezing. The cooling curve in Fig. 15 shows an apparent case of surfusion of the eutectic in a tin-copper alloy,* containing about 96 per cent of tin and 4 per cent of copper. Had the freezing been normal, *i. e.*, had there been no surfusion, the eutectic should have begun to freeze when the temperature reached C, and the cooling curve should have been something like *ABCKDE*. The part *CK* has been dotted in here to show this normal course of freezing. But actually the freezing of the eutectic appears not

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* *Third Rept. Alloys Research Committee*, Plate 41. The wording on this figure is the author's, not Professor Stansfield's.

to have begun until the temperature fell to *J*. The heat liberated by its freezing then raised the temperature of the whole to *K*, and the rest of the eutectic froze at constant temperature, *KD*.

Another case of surfusion of a eutectiferous alloy is given in § 43, p. 54.

A means of preventing surfusion, like that used in the case of the supersaturation of sodium sulphate, is to drop a little solid alloy into the molten one, to act as a nucleus to start freezing. Agitation of the molten mass also arrests surfusion.

We are here reminded of the fact that water* can be raised far above its true boiling-point of 100° C., even to 180°, without actu-
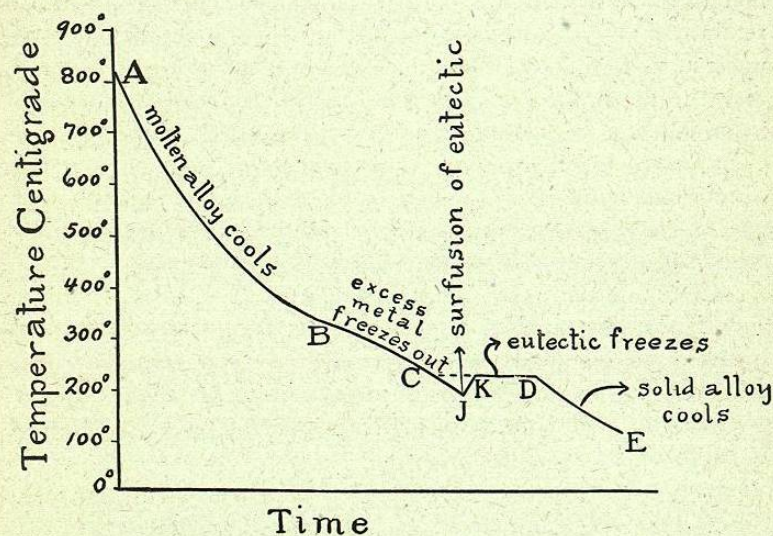

Fig. 15. Surfusion of a Eutectic in a Tin-copper Alloy Cooling Curve:
Tin 96 per cent, Copper 4 per cent.
(A. Stansfield, *Third Rept. Alloys Research Committee*, Appendix 2, Plate 41.)

ally boiling. If, however, a nucleus to start boiling is provided, *e. g.*, if bubbles of appreciable size of any gas once form within it, or are passed through it, boiling takes place rapidly or even violently. It is familiar that the bumping of solutions can often be prevented by offering a rough surface to induce boiling. These effects can be referred to surface-tension. The water evaporates within itself readily if there are bubbles into which it can evap-

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* At atmospheric pressure.

orate. The smaller the bubble the greater the resistance does its surface-tension offer to boiling, *i. e.*, to the entry of gas into it by evaporation from its sides. An infinitely small bubble, *i. e.*, a liquid free from bubbles, offers an infinite resistance to boiling. If the water initially contains dissolved air, or any other substance more volatile than itself, this volatilizes and creates bubbles into which steam can evaporate; hence the bumping tendency of liquids which, by long boiling, have been freed from volatile foreign matter.*

Thus, though there are definite temperatures which are the normal upper and lower bounds of the liquid state, within which bounds alone that state is normal, yet a liquid may be induced to retain its liquidity both above and below this range, may pass the upper bound without boiling and the lower one without freezing, in each case remaining in a state of unstable molecular equilibrium, liable to be upset by mechanical means, by inducing a nucleus from which freezing or boiling may start. Once this equilibrium is upset, the boiling or freezing, the change of state, goes on very rapidly, even violently, and the substance passes into the molecular state normal for the existing temperature.

The important point for us to recognize here is that surfusion may distort the cooling curves, so that those which have been sketched in this work are to be taken as types, in which this disturbing influence is for simplicity ignored. So in the explanations offered in this work of selective freezing, of the properties of the eutectic, *etc.*, the disturbing influence of surfusion is ignored.

31. Why the Eutectic is Composite. — That the eutectic formed on freezing salt-water solutions consists of alternate plates of salt and of ice simply represents the assumed fact that solid ice and solid salt are insoluble in each other, soluble as salt is in liquid water. (For brevity I purposely assume here that this insolubility is complete. See § 51, p. 63.)

That though liquid water dissolves salt, salt and solid water, *i. e.*, ice, are insoluble in each other, necessarily implies that when the eutectic freezes they must (normally) cease to remain dissolved in each other, *i. e.*, they must mutually expel each other,

* Compare "Theory of Heat," J. Clerk Maxwell, D. Appleton & Co., 1875, p. 289.

so that each isolates itself from the other. Hence their existence as distinct particles. That these distinct particles should in general have a sheet form would not, however, be so easily foreseen. Indeed, as we have seen (§ 28, p. 32) this form is by no means universal.

32. Why the Eutectic Is Not of Simple Atomic Proportions. — That the composition of the eutectic is not in simple atomic proportions is natural enough. Its composition is that of the solution (or molten alloy) of lowest freezing-point; and we see no reason why this lowest freezing-point should correspond to any simple atomic ratio. It is the freezing-point of a homogeneous liquid solution which we are considering, rather than the melting-point of a solid, which we know to be a conglomerate mass. The very indefiniteness and indeterminateness of composition of solutions, and their freedom from marked critical points, seem opposed to the idea that their lowest freezing-point, or indeed their maxima and minima in general, should correspond to simple atomic proportions.

33. Arrival at Eutectic Composition and Freezing-point are Simultaneous. — That the arrival at the eutectic composition and freezing-point must be simultaneous is simply a single instance of the general condition which we have traced during freezing; for we have seen (§ 29, p. 33) that at every instant during freezing the mother-metal is beginning to freeze, *i. e.*, is at its then freezing-point. That its freezing is not completed at that temperature is simply because the selective change of composition which accompanies the progress of freezing is to and through a series of compositions each corresponding to a lower freezing-point than the preceding.

34. Eutectic Plus Excess. — Now, looking at Figs. 8 to 11 collectively we may note that whatever be the initial percentage of salt in our salt-water solution, when it is frozen it will contain a eutectic of 23.6 per cent of salt. If there is initially present say 30 per cent of salt, or an excess of 6.4 per cent over this eutectic ratio of 23.6 per cent, then the mass when frozen will be a conglomerate consisting in the first place of the eutectic in its interstratified layers, and in the second place of this 6.4 per cent of salt in separate crystals, mechanically intermixed with the eutectic. If on the other hand there is say 15 per cent of salt initially present, so that there is 8.6 per cent excess of

water over the eutectic ratio, then the mass in freezing as a whole will form a conglomerate consisting of the eutectic as before, plus this 8.6 per cent excess of mechanically intermixed crystals of ice. In short, the frozen mass will in every case be a conglomerate, consisting of *a eutectic plus an excess-substance,* which will be either salt or ice, as the case may be. In the liquid state, if water is in excess over the eutectic ratio we say that we have salt dissolved in water; if salt is in excess we may say that we have water dissolved in salt. The excess-substance of the solid state is the solvent in the liquid state, in this view.

34 *A.* Precaution as to the Term " Excess-substance." —The student should here recognize clearly that the term " excess-substance " refers strictly to excess over the eutectic ratio, and does not at all refer to excess in absolute quantity. For instance in a salt water solution containing 30 per cent of salt and 70 per cent of water, the salt is the excess-substance simply because there is more salt than corresponds to the eutectic ratio of 23.6 per cent; and it is in this sense the excess-substance in spite of the fact that the absolute quantity of salt is less than half that of the water present. In some other cases the excess-substance may bear a still smaller ratio to the other or deficit-substance.

This fact that the excess-substance may be very much less in absolute quantity than the deficit-substance is certainly an objection to the term itself, because it may easily lead to confusion. On this account the expression "hyper-eutectic substance" has the great advantage of carrying its meaning, excess over the eutectic ratio, more clearly on its face. But the brevity and convenience of the expression " excess-substance " are so great that it will be used in this work, though not without some misgivings.

It is as if, assuming that a company of infantry should normally consist of one captain and one hundred privates, we were to find that in some individual company there happened to be ten captains and only ninety privates. We should here with perfect propriety say that there was an excess of captains, and every one would properly understand that we meant, not that there were absolutely more captains than privates, but that the captains were in excess over the normal ratio of 1 : 100.

35. The Excess-freezing and the Eutectic-freezing Periods. — From what has just been said, the division made at the

end of § 24, p. 30 into the ice-freezing and the eutectic-freezing periods, should be replaced by the more generic one of (1) the excess-freezing and (2) the eutectic-freezing periods (*BC* and *CD* in all the cooling curves in this work), a division which, as we shall see, applies to the freezing of our eutectiferous alloys, which are very numerous. (§§ 47 to 52, pp. 59 to 64.)

35*A.* Reasons for the Spherulitic Structure of Certain Eutectics. — My own observations lead me to believe that the banded sheet-like structure, with its zebra-like markings, is the normal structure, the structure with which the eutectic habitually comes into existence; and that the spherulitic structure is due to the drawing together or coalescing of the initially distinct particles of one of the two constituents of the eutectic. Indeed, the separate particles of each constituent may coalesce into larger but still distinct masses. Thus I found that in an alloy of 96.74 per cent copper with 3.30 per cent of silver by weight, when cooled very slowly, the eutectic at first sight seemed to be entirely lacking. There were little white lakes of silver in the great ground mass of copper; and towards the middle of these lakes were a very few small islands of copper. This was exactly what I had expected, although under the usual conditions of slow cooling this alloy contains a little distinct eutectic, together with much argentiferous copper.

The explanation is extremely simple. The eutectic itself doubtless consisted initially of sheetlets of argentiferous copper and other distinct sheetlets of cupriferous silver. But during the prolonged stay at a temperature very slightly below the freezing-point, the copper particles of the eutectic slowly migrated outwards, so as to coalesce with the continent of copper surrounding the pool of eutectic, and at the same time the silver particles coalesced so as to form a lake instead of a banded mass. The little islands of copper remaining were simply those which had not yet coalesced with the outer continent.

Again, on heating an alloy of 62.98 per cent silver and 37.00 per cent copper for seven hours to a temperature but slightly below the eutectic freezing-point, I obtained similar results. This alloy should normally consist of (1) copper as the excess-metal and (2) the eutectic, and under common conditions we should have large islands of copper in what we might call a marsh of eutectic. But in this alloy I found that the eutectic marsh in the neighbor-

hood of the islands of copper had converted itself into a free littoral region, *i. e.,* around the islands of copper there was a free littoral region of silver containing no bands of copper, from which I infer that the bands of copper initially present in this littoral region had coalesced with the islands of copper.

Further, the eutectic proper, while still distinctly recognizable, had lost to a great degree its banded structure, and the sheets of copper were in large part replaced by minute circular islands of copper, arranged in rows.

This coalescing and outward travel is like that of the bubbles floating on the surface of water in a tumbler. The bubbles initially near the edge of the tumbler quickly move outwards and attach themselves to the walls of the tumbler. Those initially nearer the centre, with less attraction towards the walls, and with the attraction of one wall partly offset by that of the opposite, move very slowly; but, given time enough, all will reach the sides of the tumbler.

In quite the same way, it seems to me, we can explain the spherulitic structure of certain eutectics. There has been, at a temperature high enough to give much mobility, a sojourn so long that the sheets of one component have drawn together into little spheres, like so much oil in water.

It has sometimes been said that in a eutectiferous alloy "structurally free" particles of the two constituents of the eutectic cannot coexist. This is wholly incorrect. It is true that there cannot be at the same time an excess of both constituents over the eutectic ratio. If, for instance, silver is in excess over the eutectic ratio, copper cannot simultaneously be in excess. But there is no reason why the particles of the eutectic should not so coalesce, each constituent by itself, that each forms masses of considerable size which, to the eye, are structurally free. Let us recognize that structural freedom may be an accident; as in the case described above, the metal in deficit may form structurally free masses. Hence, for precise thought, the expressions "excess-metal" and "deficit-metal" may be found better than "structurally free metal."

If I am right in this, then the banded structure of the eutectic may be looked upon simply as an accident, and we have to fall back upon its quality of being an alloy of lowest melting-point, and also that it is composed of distinct constituents, as its two

essential qualities. Of these the former evidently is the sole distinguishing quality.

35*B*. INFLUENCE OF THE STRUCTURE OF THE EUTECTIC. — I have often been puzzled by the very great degree of ductility which I have given to certain steels by extremely slow cooling. Now this change in the structure of the eutectic is certainly a possible cause, and one which should be investigated. Steel, as we shall see, is a eutectiferous alloy, and the two constituents of its quasi eutectic are sheets of glass-hard brittle cementite, Fe_3C, and other sheets of soft copper-like ferrite or free iron. It may well be that the prolonged sojourn at a high temperature which extreme slow cooling implies, may enable the sheets of cementite to depart somewhat from their initial sheet form and to change towards the spherical form. Further, it is but reasonable to suppose that rounded spheres of cementite should interfere less with the ductility of the whole mass than the same quantity of cementite in the form of sharp-edged sheets; and that even a fractional change from the sheet-like towards the spherical form should have an effect like in kind, though less in degree.

36. MANY ALLOYS PARALLEL WITH THE SALT-WATER SERIES. — Many of our alloys, for instance those of lead with tin, form a series similar to the salt-water series which we have been considering. Like it, lead and tin form a eutectic, a conglomerate of plates of lead interstratified with plates of tin. Its composition though not in atomic proportions is constant, *viz.,* lead 31 per cent, tin 69 per cent; hence its freezing-point is constant. Any given solid lead-tin alloy consists of the eutectic either alone or with an excess of lead or of tin, according to whether the alloy as a whole contains just 31 per cent of lead and 69 of tin, or an excess of lead or of tin over this ratio. The cooling curves of pure lead, pure tin, and of the 31-69 per cent alloy (Figs. 28 *A*, 28 *G*, and 28 *E*, p. 60) are comparable with those of pure water, pure salt, and the 23.6 per cent or eutectic salt solution (Figs. 7 and 10, p. 18), unselective, with their smoothness interrupted only by the jog (*BD* or *CD*). The cooling curves of the alloys which contain an excess of lead or of tin (say lead 67, tin 33 per cent, Fig. 28 *C*, and tin 85, lead 15 per cent, Fig. 28 *F*) are like those of salt water containing an excess of water or of salt above the eutectic ratio (Figs. 8, 9 and 11), with their selective or excess-freezing period *BC*, *i. e.,* the progressive freezing out of the excess-metal

and consequent enrichment of the still molten mother-metal in the deficit or dissolved metal (tin if lead is in excess, and lead if tin is in excess), beginning at a temperature below the freezing-point of the excess-metal (a temperature which is the lower the nearer the composition of the alloy as a whole is to the eutectic ratio), continuing through a considerable range of temperature with the rounded curve *BC,* and ending with the freezing of the eutectic at a constant temperature of 180°, represented by the jog *CD.*

37. STRATIFICATION ACCORDING TO DENSITY. — The fact that, in a partly frozen pond, the ice, the lighter substance, floats at the top and the water, the heavier, is beneath it, might well suggest to us that in frozen alloys we should find the different constituents stratified according to density. Indeed the general conditions might well suggest this. In fact such stratification is rarely marked, except in case of alloys which while molten break up into different parts which refuse to coalesce with each other. In this case, indeed, the stratification may be very decided. But in case of alloys which are homogeneous while molten but in freezing split up into different constituents, such as the eutectic and the excess-metal, we should hardly expect that stratification would be marked.

In the case of ice forming on a pond the conditions favor stratification; the cooling surface is the top; the coolest water, approaching the freezing-point, is the lightest and tends to rise (assuming that the whole of the water is below 8° C.); here ice forms; so that the lighter substance, the ice, here comes into existence at the top, and readily retains this natural position. But if we freeze water in a small iron crucible with roughened sides, and especially if we cover the upper surface of the water with sawdust to retard the removal of heat there and concentrate the cooling and freezing on the rough sides of the crucible, then the freezing will occur first along these rough sides, and the particles of ice as they form will tend to adhere to them rather than to rise to the top by gravity.

In the freezing of metallic masses we have a like effect. Freezing occurs most rapidly at the bottom and sides against the cool mould-walls, and more slowly at the top, to which the convection currents carry the hottest and lightest part of the molten metal. So the metal which first freezes forms a thin hollow cup along the sides and bottom of the mould, a cup which even if it

should be lighter than the molten metal would be restrained from rising by its adhesion to the mould-walls, and often by its very shape. The next layer to form attaches itself to this first, and so on.

Other reasons lead in the same direction. In case of a lead-tin-alloy, Fig. 28 *F,* because the freezing of the alloy is usually rapid, because the crystals of tin which freeze out from *B* to *C* are not only extremely minute but also very near in density to the mother-metal in which they form, and because the mother-metal itself during their formation is relatively viscous, at least when compared with an aqueous solution, the crystals of tin do not necessarily remove themselves bodily out of the mother-metal, as ice forms on the surface of a pond, but remain mechanically entangled in it or attached to the sides of the mould; and on examining under the microscope a polished section of the solid alloy, we find the little crystals of this excess of tin distributed through the mass with a uniformity of about the same order as that of the crystals of feldspar in a granite. It is no doubt for like reasons that, in our crystalline rocks, minerals varying considerably in density occur side by side, instead of being stratified according to their density.

If we were to cool our alloy so extremely slowly that its freezing occupied many hours, under favorable circumstances we might find a stratification according to gravity. This indeed is what happens in the peculiarly favorable case of the graphite of cast iron very slowly solidifying in the "mixers" of the great steel works. The graphite is so much lighter than the iron in which it forms, and the solidification is so extremely slow, that much graphite rises to the surface as "kish" and blows about the building. (§ 185, p. 210.) And in certain other alloys, the constituents of which differ much in density, stratification can be detected with a microscope. Indeed, in the case of the tin-antimony alloys, the microstructure of which is shown in Figs. 16 and 37, pp. 46 and 89, the cubes which form during freezing may, if the freezing is very slow, reach such a size and may be so free from attachments to the already solid walls of the freezing mass, that they swim to the top, and after the alloy has cooled can there be seen in a section properly prepared for this purpose. Fig. 16 shows how these little cubes have thus risen to the upper part of the molten mass.