as a whole contains 50 per cent of each metal and that as before each is theoretically capable of dissolving 25 per cent of the other.

73. IF THE TWO SOLUTIONS ARE SATURATED, THE SYSTEM IS IN EQUILIBRIUM. — For simplicity let us assume that we are dealing with an extremely minute quantity of our alloy, only 200 molecules, all told; that there are 100 molecules of metal A and 100 of metal B; and that these actually have grouped themselves in two masses, each a saturated solution of one metal in the other. Our constitution then would be

Grouping 1

	MASS 1	MASS 2
Per cent. of A	75	25
Per cent. of B	25	75
	100	100

In mass 1, A is the solvent and B the dissolved or solute metal; in mass 2, B is the solvent and A the dissolved metal.

Clearly no entry of the solvent or excess-metal from one mass into the other can occur, as we see on trying to suppose that it did occur. Suppose that from mass 1, 5 molecules of metal A transferred themselves to mass 2. This would leave in mass 1 $70 \times 100 \div (70 + 25) = 73.68$ per cent of A, and $25 \times 100 \div (70 + 25) = 26.32$ per cent of B; this condition is not of equilibrium, because it would supersaturate A with B, of which by assumption § 70, p. 77, 25 per cent suffices to saturate A. At the same time mass 2 would have been supersaturated with A, for it would contain $30 \times 100 \div (30 + 75) = 28.57$ per cent of A. This supersaturation is a second element of instability or a second case of lack of equilibrium. So neither mass would be in equilibrium.

Let us now suppose that instead of the solvent metal A, it is the dissolved or solute metal B, which changes from mass 1 to mass 2, and that 5 molecules of it thus transfer themselves. In this case the two masses will contain:

Grouping 2

	MASS 1	MASS 2
Per cent of A	$\dfrac{75 \times 100}{75 + 20} = 78.95$	$\dfrac{25 \times 100}{80 + 25} = 23.81$
Per cent of B	$\dfrac{20 \times 100}{75 + 20} = 21.05$	$\dfrac{60 \times 100}{80 + 25} = 76.19$
	100.00	100.00

In this case mass 1 consists of metal A unsaturated with metal B, and mass 2 consists of metal B unsaturated with metal A, because each contains less than 25 per cent, the saturation limit, of the dissolved metal. But this is not a condition of equilibrium, as we shall now see.

For if we had molten pure metal A and molten pure metal B in contact with each other, we should certainly expect each to diffuse into the other, and to continue diffusing until one or the other was saturated, or until diffusion and union were complete. Now for exactly this same reason, since each of these two masses in grouping 2 consists of a given metal unsaturated with the other, mass 1 containing more A than the B in it saturates or satisfies, and mass 2 containing more B than its A saturates, we should naturally expect the unsaturated or unsatisfied excess of A in 1 to diffuse across into 2, and the excess of B in 2 to diffuse across into 1. We should expect that this would go on until saturation was reached, which would clearly be when our original condition of grouping 1 was reached, that is, when mass 1 contained 75 per cent of A and 25 of B, and mass 2 contained 25 per cent of A and 75 of B.

In short, the ratio 75:25 in each mass is the only one to be expected, (1) because a lower ratio implies supersaturation, and (2) because a higher ratio ought to lead to diffusion of the excess or unsatisfied part of the solvent or 75 per cent metal of each mass into the other, until the 75:25 ratio was reached.

The change by diffusion from grouping 2 to grouping 1, so as to saturate each metal with the other, was easy to understand because each metal was assumed to be initially unsaturated, so that transfer in both directions could take place simultaneously. Suppose, however, that our 100 molecules of each metal grouped themselves initially in three separate masses as follows:

Grouping 3

	MASS 1		MASS 2		MASS 3	
	Molecules	Per cent	Molecules	Per cent	Molecules	Per cent
Metal *A*	90	75	10	25	0	0
Metal *B*	30	25	30	75	40	100
		100		100		100

But the grouping is evidently not that of equilibrium. Clearly the first thing which would happen would be that masses 2 and 3 would unite by diffusion, and our two masses then would be

Grouping 4

	MASS 1		MASS 2	
	Molecules	Per cent	Molecules	Per cent
Metal *A*	90	75	10	12.5
Metal *B*	30	25	30 + 40 = 70	87.5

This instability of masses 2 and 3 of grouping 3 in presence of each other clearly follows from the general law which we saw in § 71, p. 78, that a saturated and unsaturated solution of any metal *A* in another metal *B* cannot be in equilibrium.

When we come to study the phase rule, we shall further see that the instability of grouping 3 is simply an instance of the general law, that no system containing only two constituents (in this case two chemical elements) can be in equilibrium (except at a single temperature) if it has more than two " phases," *i. e.,* distinct kinds of masses or entities, in this case two distinct solutions and one free element.

Having thus seen that grouping 3 is not that of equilibrium, and tends to change over into grouping 4, let us next enquire whether this latter in turn is that of equilibrium or not.

Of the 70 molecules of *B* in mass 2, only 30 are saturated or satisfied by the 10 molecules of *A* in it; the remaining 40 molecules of *B* are unsaturated or unsatisfied. But the very fact that in this grouping 4 the solvent power of *B* remains unsatisfied, whereas in grouping 1 the solvent power of each metal is fully satisfied, shows

that 1 is the condition of greater stability, of equilibrium ; this is the condition which would naturally be reached, and that into which grouping 4 or indeed any other grouping would tend to resolve itself, by diffusion. In case of grouping 4, 15 molecules of metal *A* and 5 of metal *B* would tend to transfer themselves from mass 1 to mass 2, thus giving the equilibrium grouping 1.

Thus grouping 4 also is not that of equilibrium, and would tend to resolve itself into grouping 1.

We have thus seen that, whereas grouping 1, of complete reciprocal saturation, is that of equilibrium, these other groupings, 2, 3 and 4, are not ; and what has been thus found true of these would be found by like reasoning to be true of any grouping other than 1.

For the particular conditions which we have assumed, then, (1) the presence of 100 molecules of each metal, and (2) that each can dissolve 25 per cent of the other, we have found that reciprocal saturation of the two metals by each other is the condition of equilibrium. But what has thus been found true for these assumptions, made merely to fix our ideas, would by like reasoning be found true of any other set of assumptions, *mutatis mutandis.*

In short, 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 ; though in the molten state, because of greater molecular freedom, the condition of equilibrium would be more quickly reached.

Such a mechanical mixture of two alloys, especially of two molten alloys, tends naturally to become less and less intimate, as the particles of each alloy gradually coalesce into larger and larger masses ; and eventually they should separate from each other by gravity into two distinct layers, the lighter alloy floating upon the heavier. Be it understood that, when a mechanical mixture is spoken of as the normal condition, it is meant to include also this state of affairs in which the two alloys separate into two distinct layers, though it is admitted that " mixture " is rather an unfortunate term to apply to two distinct superposed layers. It is the end condition, to which the class name applies only by a stretch, such as we use when we say that a mathematical point is a circle of infinitesimal radius, and that a straight line is part of the arc of a circle of infinite radius.

74. The Constituents of the Eutectic Should Be Saturated with Each Other. — Let us now return to our study of the constitution of the eutectic which forms in the freezing of any bismuth-bearing tin, the bismuth-content of which is large enough to lead to the formation of a eutectic as explained in §§ 64 and 65, pp. 72 and 73:

We have already seen that this eutectic should be composed of sheets of tin saturated with bismuth, and other sheets of bismuth. The question now before us is whether those sheets of bismuth should in turn be saturated with tin. They should, for the reason that this eutectic falls into the class discussed in §§ 72 and 73, pp. 79 and 80, of alloys containing more of each metal than the other can dissolve. For we have seen that it contains as a whole more bismuth than the tin can dissolve, and we may admit that it also contains more tin as a whole than the bismuth in it could dissolve were it able to get at all that tin; for if not, there would have been no reason why, in freezing, it should split up at all. If the bismuth in the mother-metal at the time when it reached the eutectic composition and freezing-point were able to retain in solution after freezing the whole of the tin then in that mother-metal, it should so retain it, and the eutectic should remain as a single solution of tin in bismuth, instead of breaking up into a conglomerate.

Because, then, this eutectic contains more of each metal than the other can dissolve when solid, the flakes of each metal should be saturated with the other. In short, it should be a conglomerate of saturated solutions of the two metals in each other. This would be the state of equilibrium; and, owing to the conditions of the birth of the eutectic, we should expect the approximation to that state to be extremely close. For in the facts (1) that in the molten mother-metal at the time when it freezes into the eutectic the two component metals are presumably distributed with absolute uniformity, are in contact molecule with molecule, and (2) that in the passage from the molten to the solid state the high degree of fluidity should cause great ease and freedom of molecular motion, we seem to have just the conditions which should make these molecules group themselves in very close approximation to the stable condition of equilibrium, and break away from any other and unstable condition, should any such be momentarily entered into.

75. The Structure to be Expected from these Conditions in a Eutectiferous Alloy. — Still considering the case of bismuth-bearing tin to fix our ideas, let us for simplicity first assume that the successive layers which freeze out from the molten mass deposit themselves along the smooth walls of the enclosing vessel or mould, in perfectly smooth and parallel layers, like the successive peels of an onion, save that they are extremely thin, of a thinness approaching that of a molecule. Let us further neglect gravitation and the contraction due to cooling, and let us assume that the alloy is contained in a cubical mould, and that the rate at which the heat escapes from the surface of the mould is the same
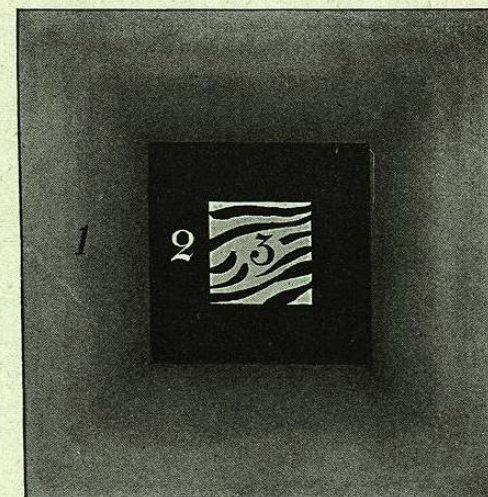

Fig. 34. The "Onion" Type of Freezing.

for all six sides of this cube, and hence that the rate of freezing and deposition of solid metal on all six sides is alike. Let us call this the onion type of freezing.

In this case the structure of the frozen ingot of our alloy should be that shown in Fig. 34. The outer part, marked 1, is the unsaturated bismuth-bearing tin, deposited during the subsaturation period of the selective freezing and corresponding to the part BB' of Fig. 31; part 2 is the saturated bismuth-bearing tin deposited during the saturation period of the selective freezing, and corresponding to part $B'C$ of Fig. 31; part 3 is the last frozen part, the conglomerate eutectic, corresponding to part CD of Fig. 31.

76. SEGREGATION.—This heterogeneousness of frozen alloys is recognized in metallurgical manufacture under the name of segregation. Fig. 35 shows how the carbon in a large ingot of gun-steel has thus segregated. In this case the segregation is found in the upper part of the axis of the ingot, because that is the last part of the mass to solidify. This in turn is due chiefly (1) to the fact that the bottom of the ingot is in contact with the cast iron
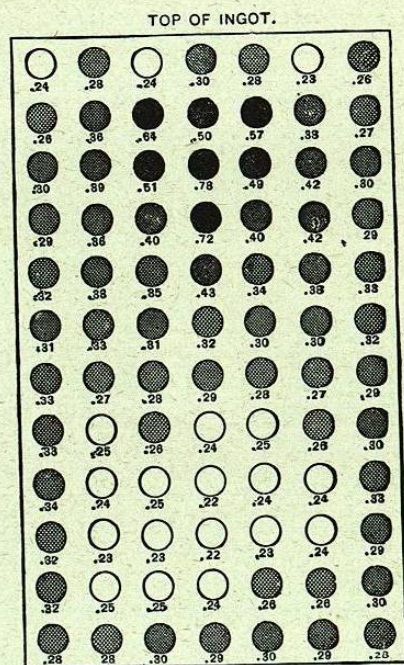
TOP OF INGOT.

Fig. 35. Percentage of Carbon at Different Points in the Vertical Section of a Large Ingot.

Maitland, "The Treatment of Gun-steel," Excerpt *Proc. Inst. Civ. Eng.*, LXXXIX., p. 12, 1887. The depth of shading of the spots is roughly proportional to the proportion of carbon.

bottom of the mould which is cold and hence absorbs heat greedily, while the upper surface of the ingot is exposed to the air into which heat escapes relatively slowly; and (2) to the fact that the hotter parts of the molten metal because lighter rise to the top, while the cooler ones, the temperature of which is sinking close to the freezing-point, sink to the bottom. Because the eutec-

tic is the most fusible and hence the last freezing part of the whole, so we expect to find it in the last frozen region wherever that may be. And for like reasons we expect that the saturated layers, No. 2 of Fig. 34, will surround this eutectic, whether this lies in the centre of the mass or not; and that outside of these saturated layers the unsaturated layers (1 of Fig. 34), will be disposed in general rough symmetry with the eutectic itself.

77. ABNORMAL SEGREGATION. — But, while it seems normal and natural that the segregate, *i. e.*, the mass expelled in the freezing of the earlier layers and found concentrated in the axis of the ingot, should be the most fusible of all the constituents which form in freezing, and that it should have a larger percentage of the dissolved or solute metal, or of the impurity if we may so call it, than the molten alloy as a whole did, yet this is not always the case. Thus in ingots of cupriferous silver the segregate, instead of being richer than the earlier frozen parts in copper, which is the dissolved or solute metal or the impurity, are actually richer in silver;[*] so that the segregate, which certainly appears from its position to be the last frozen part, is actually of a composition which should make it more infusible than the earlier frozen parts. Thus, in short, it here appears that the parts first to freeze are really more fusible than those last to freeze. And the same seems to be true of some other alloys.

The explanation of this phenomenon does not seem clear. Convection currents, and gravity stratification of the nascent solid constituents in the act of freezing, may contribute; but they do not seem at first sight to be in and by themselves a sufficient cause. Another explanation, somewhat more complex yet more cogent, is that, although in the act of freezing proper the first frozen parts were more infusible than the last frozen, or in short although the order of deposition in freezing was normal; yet in the slow cooling which followed freezing the silver migrated centreward, coalescing somewhat as drops of water suspended in oil tend to draw together and coalesce. That is to say, after the eutectic had frozen, there were present particles of saturated argentiferous copper and other particles of cupriferous silver. The isolated particles of each may have tended to migrate centreward

[*] W. Chandler Roberts (Roberts-Austen), *Proc. Roy. Soc.*, 23, p. 490, Figs. 1 and 3, 1875.

so as to coalesce with their kin, but both could not do this simul-
taneously; hence a competition between silver and copper; and in
this competition the silver may have conquered or outstripped the
copper.

For simplicity, and to follow out what seems to be the
normal type of segregation, we will, in the remainder of this
discussion, ignore this other and abnormal type.

78. MODIFICATIONS OF THIS STRUCTURE. — When we come
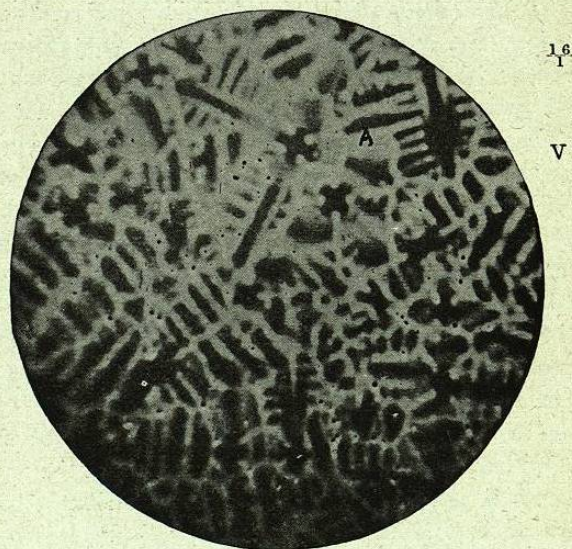to examine our alloys under the microscope we find a condition

Fig. 36. Alloy of 97.1 per cent Copper, 2.9 per cent Aluminium showing
Heterogeneousness of Solid Solution.

(Wm. Campbell, private communication.)

of affairs which, as shown in Figs. 17, 18, 19 and 36, differs
markedly from the type sketched in Fig. 34. Instead of a deposi-
tion of successive layers, of which each is the smooth surface
of a cube concentric with the mould, *i. e.,* with the outer surface of
the whole mass, we find indications rather of a growth like moss
or like miniature pine-trees, a growth along spines and shoots
instead of in smooth layers; a growth which, before freezing is
complete, must shut in and, to change the simile, landlock part

of the still molten mass, isolating it from the rest of the molten
metal. The shape of the individual pine-trees may vary greatly
with the composition of the mass, and perhaps with the attendant
conditions of freezing. The branches may be extended as indicated
in Fig. 42, p. 96, or rudimentary like those which start to branch out
horizontally from the lower part of the great crystal shown in
Fig. 5, p. 6. Again, the growth may take place through other forms,
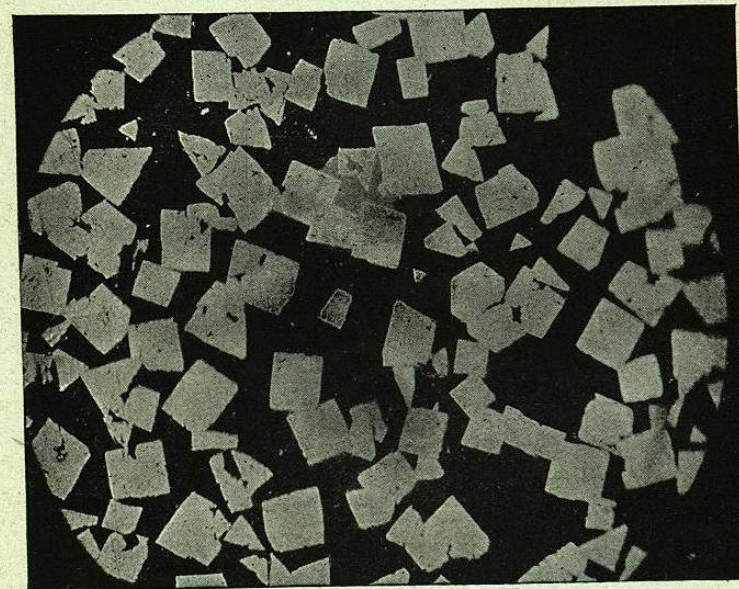such as the cubes (Fig. 37) in which antimonide of tin, SnSb,

Fig. 37. Alloy of 80 per cent Tin, 20 per cent Antimony.

Showing the Isolation of the Cubes of Tin-antimonide, SnSb; Horizontal
Section of the Ingot, 33 Diameters. Vertical illumination.

Prepared by William Campbell in the Author's Laboratory.

grows. In case the cooling is very slow, this growth may occur
around little nuclei which are either actual islands, *i. e.,* actually
wholly detached from the already frozen continent, or at least
are held to it by such a slight bond that their buoyancy suffices
to break this bond and thus to enable them to swim to the surface.
(Compare § 37, last paragraph, p. 45.) In either of these cases
the growth and final broadening of adjacent pine-trees until they