

to be monovariant, let us next examine the conditions of the case to see whether, judged from these, it really seems to be monovariant. Let us in short test the truth of the phase rule by an examination of several different systems.

For ease of reference, the elements, phases, components and degree of liberty of each of these cases are put together in condensed form in Table 14.

248. TIN IN THE ACT OF FREEZING, say at the stage represented by the point *C* in Fig. 14, p. 35. Here molten tin and solid tin are both present, and each of them is a distinct phase; so the equation becomes

Degree of Liberty = number of constituents + 1 — number of phases.

$$L = 2 + 1 - 2 = 1$$

so that the system is nonvariant.

Let us test this nonvariance. First, no change in composition is possible, since the chemical composition of the two phases is the same; the diffusion from one phase, the molten tin, into the other phase, solid tin, would leave the composition pure tin, *i. e.*, unaltered. Looking at it in another way, any change in composition would be a change from this system to another system; if the substance added dissolved in the tin, the system would be new, because a solid solution would be substituted for a pure metal; if it did not dissolve but remained apart, it would form an additional distinct and separate phase, and thus change the system from a di- to a tri-phase one.

The only change possible then is one in temperature. If we heat the system, some of the solid tin will melt, and the temperature will remain constant until the whole of the solid tin is melted; and during this constancy of temperature the system will remain unchanged, since a change in the proportions of the two different members of a system is not reckoned a change in the system; the phase rule is qualitative. But before we can actually raise the temperature above the melting-point, the whole of the solid tin must melt, *i. e.*, any actual elevation of temperature breaks up the system by completely removing one of its phases, solid tin, turning it from a di-phase into a mono-phase system.

In like manner if heat is abstracted, *e. g.*, by setting ice against the vessel which contains the freezing tin, the temperature

will remain constant until the molten part of the tin has all frozen, *i. e.*, no change in temperature will occur until the system breaks up by the complete removal of one of its phases, the molten tin, and so changes from a di-phase into a mono-phase system. In short, the system breaks up whenever the single variable condition, temperature, varies. It is therefore nonvariant; so that the phase rule proves to be true in this case.

249. WATER IN THE ACT OF FREEZING in like manner contains one constituent undecomposable under our conditions, in two phases, water and ice; so that  $L = 1 + 1 - 2 = 0$ , *i. e.*, the system is nonvariant, exactly as in the last case. No change in temperature can occur until either the whole of the ice or the whole of the water has been eliminated by changing into the other phase (all the ice melting and becoming water or all the water freezing and becoming ice), the system thereby changing from di-phase into mono-phase. The phase rule thus proves to be true in this case also.

250. SALT WATER ABOVE THE FREEZING-POINT. — There are two constituents, salt and water; there is one phase, a liquid solution;  $L = 2 + 1 - 1 = 2$ , the system is divariant. Now let us test this divariance.

Let us assume that the degree of concentration of the solution and the temperature are jointly represented by point *D*, Fig. 27, p. 58. Clearly the liquid solution will remain a liquid solution, *i. e.*, the system will remain mono-phase and unchanged if we lower the temperature arbitrarily to *f* without any change in composition, *e. g.*, by packing ice around the vessel which contains the solution; or if without changing the temperature we change the composition to *f'* by pouring in water; or if we simultaneously both dilute and cool the solution and bring its temperature and composition to *f''*. In short, the system remains mono-phase, *i. e.*, it is not broken up, even if both variable conditions, temperature and degree of concentration, are varied arbitrarily and each without reference to the simultaneous variation in the other. The system is therefore divariant.

251. SALT-ICE. — Assuming for simplicity as before that salt and frozen water are absolutely insoluble in each other, the salt ice say of composition and temperature *e* is a conglomerate of (1) the excess of pure ice above the eutectic ratio of 76.4 per cent water, 23.6 per cent salt and (2) the eutectic of interstratified

pure salt and pure ice. Here then are two constituents (salt and water), and two phases, (1) pure ice and (2) pure salt.  $L = 2 + 1 - 2 = 1$ , the system is monovariant. As before let us test this monovariance.

Here we need not enquire as to whether the system could survive a change in concentration simply because such change is unthinkable, on our present assumption that solid salt and ice are reciprocally absolutely insoluble. Hence the only variation to be considered is temperature. Clearly if the conglomerate of crystals of ice and other crystals of salt are heated (provided of course that the temperature does not reach the melting-point of the eutectic), no change will occur. The system is not split up on undergoing this variation, *i. e.*, it is monovariant.

What has been said of salt-water and salt-ice clearly applies to a molten and a solid lead-tin alloy.

252. LEAD-TIN ALLOY IN THE ACT OF SELECTIVE FREEZING. — To fix our ideas let us consider an alloy which, taken as a whole, contains 45 per cent of tin and 55 of lead; and let us suppose that, starting at  $350^\circ$  (point *G*, Fig. 24, p. 54), it has cooled to  $212^\circ$  (point *L'*), so that in cooling from *H* to *L'* selective freezing has been taking place.

In the freezing which has thus far occurred, crystals of the excess of lead have been born from the mother-metal, which has thereby been enriched in tin, until its composition at this instant is *M'*, or 56 per cent tin and 44 of lead, since at every instant during this selective freezing the composition of the mother-metal is normally that for which the existing temperature is the freezing-point.

Here are two constituents, lead and tin, two phases, solid lead and a molten solution containing 56 per cent of tin dissolved in 44 per cent of lead. The equation is  $L = 2 + 1 - 2 = 1$ . The system is monovariant. Let us test its monovariance.

The composition of the solid lead cannot vary, since we have for simplicity assumed that lead and tin are reciprocally completely insoluble; but the concentration of the molten solution of tin in lead can vary.

First let us see what happens if the temperature is lowered  $12^\circ$  to point *N'*. A little more lead will freeze out, the mother-metal will be enriched up to 60 per cent tin (point *Q*), but the phases will be the same as before, solid lead and a molten solution

of tin in lead; the system in short has not been broken up, for the change in concentration of a solution is not to be reckoned as a change in the system as such. In that the solution has this new degree of concentration it might indeed be called a new phase; but it is for our purpose the equivalent of the old one which it replaces.

But how about this same change in concentration; have not two conditions really varied, both temperature and composition, without breaking up the system; and is not the system therefore divariant in spite of the phase rule? Certainly not, for the change which has taken place in composition is simply that conformable with or corresponding to the change in temperature, and is not an arbitrary change. There has thus been but one arbitrary change.

Indeed it is this spontaneous shifting of concentration which has kept the system from breaking up and changing from (1) solid lead plus (2) molten solution of tin in lead, into the system (1) solid lead plus (2) solid tin, as we see on the slightest consideration. For, if by any device it could have been possible to prevent the change of concentration, so that when the temperature reached  $200^\circ$  the mother-metal still contained as it did at  $212^\circ$ , 56 per cent of tin and 44 of lead, that mother-metal would have frozen, since the temperature,  $200^\circ$ , is  $12^\circ$  below the freezing-point ( $212^\circ$ ) of such an alloy. A failure of the composition to shift conformably with the temperature would in effect be an arbitrary variation of the composition.

Thus far we have considered changes of temperature, and we have found the system monovariant, failing to break up if the temperature is changed, provided of course that the concentration shifts conformably, but breaking up if concentration does not so shift, *i. e.*, in effect shifts arbitrarily. Let us next take up the parallel case of changes in concentration.

Let us as before start with the system at  $212^\circ$ , consisting, therefore, of solid lead and a molten mother-metal of composition *M'*, with 56 per cent of tin and 44 of lead. Let us suppose that we shift the concentration of the molten mother-metal from *M'* to *S*, *e. g.*, by pouring into it enough of a molten alloy, also at  $212^\circ$ , and containing 70 per cent of tin and 30 of lead. If we simultaneously make the conformable change in temperature, *i. e.*, if we simultaneously lower the temperature from *S* to *Q*, from

212° to 200°, by external cooling, the system will remain unchanged; this is in fact what we did in the last case. But what will happen if we fail to change the temperature, and artificially change the concentration of the mother-metal by pouring it off and substituting another lot of molten metal at 212°?

Such molten metal at this temperature manifestly could not have more than the 44 per cent of lead contained in the mother-metal just poured off, because the existing temperature, 212°, is below the melting-point of any lead-tin alloy with more than 44 per cent of lead. So if any alloy with more than 44 per cent of lead were added, it would have to be solid, and being solid would consist of plates of lead interstratified with plates of tin; so that the system as a whole would be (1) solid lead, including that formed in the original cooling to 212° plus that in the alloy now added; plus (2) solid tin. This resultant system would be a wholly different one from what we are aiming to create, *viz.*, (1) solid lead plus (2) a molten solution of less than 56 per cent of tin in more than 44 per cent of lead.

As it is thus impossible to shift the concentration of the molten phase in the direction of greater richness in lead, let us try shifting it in the opposite direction of greater richness in tin; and let us suppose that we do this by pouring off our present 44 per cent mother-metal and substituting for it a new lot of molten alloy of composition *R*, 65 per cent tin. It is evident that our solid lead would immediately begin melting and entering this molten metal and would continue melting because, so long as the reëtrance of the lead into it did not reduce its percentage of tin below 56 per cent, the molten metal would remain molten. We have seen (§ 21, p. 26), that this is the general condition which determines whether a solid metal shall melt and enter into a molten metal with which it is in contact. If the alloy which its entrance into that molten metal would form would be so fusible that it would remain molten at the existing temperature, the solid metal would so melt and enter the molten one.

But suppose we now try again, and pour off this new molten metal, and add a third lot of molten alloy of 65 per cent of tin and 35 lead, like the last; this will in the same way dissolve more of our lead, and will keep dissolving it until the tin-content of the molten part shall have fallen to 56 per cent. So our steps to keep in contact with our solid lead at this temperature, a molten

metal with more than 56 per cent of tin, do not at first succeed; manifestly no matter how many times we replace the molten metal with new, its tin-content will always sink down to 56 per cent by taking up some of the originally solid lead, until the whole of the solid lead shall thus have been melted away; in short until our system shall have been broken up by the vanishing of one of its members, the solid lead.

Clearly the same result would follow if, instead of pouring off our mother-metal and replacing it by a new lot, we were to enrich it in tin, at constant temperature, by pouring into it a lot of molten alloy containing say 80 per cent tin and 20 per cent lead, initially at this same temperature 212°.

In short, the system cannot survive a shifting of the degree of concentration of the molten metal, unless it is accompanied by a conformable shifting of the temperature; for such shifting in the direction of greater richness in lead leads to a new di-phase system, solid lead plus solid tin, while in the direction of greater richness in tin it leads to a new and mono-phase system, molten solution of tin in lead. This result is wholly in accordance with the phase rule, since a shifting of concentration unaccompanied by the corresponding shifting of temperature is in effect an arbitrary shifting of both concentration and temperature, which, as the phase rule teaches, a monovariant system cannot survive.

Thus in every respect our system satisfies our tests of its monovariance.

253. THE SAME LEAD-TIN ALLOY (COMPOSITION *G*), AT THE FREEZING-POINT OF THE EUTECTIC, SAY AT *J*, FIG. 24. — Let us suppose that the whole of the excess of lead has frozen out, so that the mother-metal has been enriched to its eutectic ratio, *B*, of 69 per cent tin, 31 per cent lead; and that part of this eutectic mother-metal has frozen, while part still remains unfrozen.

The phases will be (1) solid lead, including (*A*) the excess over the eutectic ratio, frozen out between *H* and *J*, and (*B*) the plates of lead contained in the already frozen part of the eutectic; plus (2) solid tin, in the frozen part of the eutectic; plus (3) a molten solution of tin in lead, the still unfrozen part of the eutectic mother-metal. Three phases, and as before two constituents, lead and tin.

The equation becomes  $L = 2 + 1 - 3 = 0$ , *i. e.*, the system is nonvariant. Let us as before test this nonvariance.