PRESSURE-TEMPERATURE DIAGRAMS FOR BINARY SYSTEMS

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The first complete pressure-temperature diagram was given about a year ago by van't Hoff;¹ but he did not put in the curves for the partial pressures. The object of this paper is to fill this gap in our knowledge to a certain extent, qualitatively. We will first consider systems in which there can be only one liquid phase and in which the only solid phases possible are the two pure components. Two classes are then to be distinguished. In the first the vapor-pressure boundary curves for the less fusible component lie wholly below the corresponding set of curves for the more fusible substance; in the second, the vapor-pressure boundary curves for the less fusible substance lie wholly above the corresponding set of curves for the more fusible component. Intermediate systems with intersecting pressure curves are quite conceivable but do not need be considered in detail.

In Fig. 1 OB is the sublimation curve, OA is the vaporization curve and O the triple point for the more fusible component. O_1B_1 and O_1A_1 are the corresponding curves for the other component, O_1 being the triple point. If the eutectic temperature be that of the points H and H_1 , the partial pressure of the more fusible component, while it is solid phase, will be represented by OH provided we ignore any solvent action of the vapors. In the same way the partial pressure of the second component when present as solid phase will be O_1H_1 . The partial pressures of the substance which is not present as solid phase are given by D_1H_1 and DH, the curve D_1H_1 belonging with OH, while DH goes with O_1H_1 . By adding OH and D_1H_1 we get the curve OC, representing the boundary curve for solid, liquid and vapor

¹ Vorlesungen über theoretische Chemie, 35.

but this is not necessarily the case. It is conceivable that if the temperature and pressure of O differed but little from that of O_1 , and if the temperature of C were sufficiently low, the pressure corresponding to the point O might be higher than that of C. It seems probable that this will be the exceptional case, though it

Fig. 3

is the more probable state of things when there are intersecting vapor-pressure curves.

A very interesting case occurs when the less fusible component is more dense as solid than as liquid and when the other component is a gas at the temperature of O_1 . If we assume that the gas is practically insoluble in the liquid formed by melting the less fusible component, the pressure of the gas will be a more important factor than its solubility and we shall have a rise of freezing-point. This brings up the partial pressure of the solvent in the vapor phase. Ordinarily we say that the solid solvent is in equilibrium with solution and vapor when the partial pressure of the solvent in the system, solution and vapor, is equal to the vapor-pressure of the solvent in the system, solid and vapor. If we exclude a possible solvent action of the gas, this definition seems to be a sound one, and it follows therefore that the partial pressure of the solvent in the system, solid sol-

vent, solution and vapor, will be equal, at temperatures above the melting-point, to the vapor-pressure of the system, superheated solid and vapor. The details of such a system are shown in Fig. 4, with a complete disregard of scale. The apparent minimum in O_1A_1 is not to be taken seriously. It owes its existence to a desire not to crowd the curve O_1O_2 .

Fig. 4

O_1A_1 , O_1B_1 and O_1E_1 are the boundary curves for pure liquid and vapor, solid and vapor, solid and liquid respectively. O_1O_2 is the prolongation of B_1O_1 , the system being instable with respect to the liquid phase. The partial pressure of the gas is given by the curve DS . This, of course, continues to the next quadruple point; but we shall only consider the curves in the immediate neighborhood of the point O_1 so that it is quite immaterial whether the new phase appearing at the next quadruple point be pure solid, a compound or a second solution. The total vapor-pressure of the system is represented by O_1NC . If the gas were absolutely insoluble in the melt, this curve would coincide with O_1E_1 . As this can never be the case theoretically, the curve O_1NC will always lie above O_1E_1 . In the construction of Fig. 4 it has been assumed that with increasing pressure

the gas becomes more and more soluble in the melt until, at length, the lowering of the freezing-point due to the solubility overbalances the rise of freezing-point due to the increase of pressure. It has recently been pointed out by Tammann¹ that systems of this sort have been studied by Danien,² the components being air and naphthylamin, diphenylamin, paratoluidin or mononitronaphthalene. In Fig. 4 the temperature and pressure of the maximum freezing-point are represented by the point N. The point N_1 denotes the point on the curve O_1O_2 at which the temperature is that of the maximum freezing-point. As the total pressure of the system increases from O to N, the partial pressure of the less fusible component increases from O_1 to N_1 . As the total pressure of the system changes from N to C, the partial pressure of the solvent decreases from N_1 back to O_1 and is represented by the curve O_1B_1 as the system passes along the prolongation of O_1NC .

Since the field for solution and vapor is bounded by A_1O_1 and O_1NC , it is obvious that if we start at some point on O_1A_1 having a temperature lower than that of the point N and add the gas continuously at constant temperature keeping the volume of the system constant, the pressure will change until the solid phase appears at the pressure represented by the point on O_1N for that temperature. During this process the partial pressure of the solvent has increased from that of a point on O_1A_1 to a pressure represented by a point on O_1O_2 . From this we see that if we compress a liquid by means of a gas practically insoluble in it, we shall increase the partial pressure of the liquid quite apart from any solvent action of the gas. This phenomenon has been observed by Schiller³ and has been discussed at some length by Ostwald.⁴ From the diagram we see that, if the gas exerts no solvent action, the curve O_1O_2 represents the limiting partial pressures that can be reached in this way. In the same way in-

¹ Wied. Ann. **66**, 477 (1898).

² Comptes rendus, **112**, 785 (1891).

³ Wied. Ann. **60**, 755 (1897).

⁴ Lehrbuch, **2**, II, 361.

crease of pressure at temperatures below that of O_1 will cause an increase in the partial pressure of the less fusible component, the limiting values given by the prolongation of A_1O_1 .

Up to this point we have expressly excluded any solvent action in the vapor phase; but it is now desirable to determine what will be the effect of dropping this limitation. In Fig. 5 is

Fig. 5

given the diagram for a system in which such a solvent action takes place. To avoid cumbering the diagram with unnecessary curves, the assumption has been made that the vapor of the less fusible component exercises no perceptible solvent action on the other substance. The effect of this limitation will be pointed out in the discussion.

The essential feature of this system, in which it differs from that shown in Fig. 2, is the presence of the curve $O_1H_1B_2$. The partial pressure of the less fusible component when present as solid phase cannot be represented by the curve O_1B_1 ; as heretofore because that is the state of things when the solvent action of the vapor is excluded. The curve $O_1H_1B_2$ represents the partial pressures of the less fusible component when it is present as

solid phase in equilibrium with solution and vapor. It should be understood that no attempt has been made to draw any of these diagrams to scale. When some actual system coming under this head is studied, it will probably be found that $O_1H_1B_2$ passes through a maximum very near the point O_1 and that, for the rest of its course, it will coincide very nearly with O_1B_1 . In the same way it is more than probable that, in all cases in which the divergence of $O_1H_1B_2$ from O_1B_1 is marked, the curve DH will pass through a maximum just as in Fig. 2. These, however, are matters of detail varying from one system to another and have no effect on the general relations. If we were to take into account a solvent action due to the vapor of the less fusible component we should have a curve starting from O and lying just above OB. The point H would then be on this new curve and not on OB. If there were a point of maximum temperature on the curve O_1C we should also have to consider a curve starting from O_1 and lying above the prolongation of B_1O_1 .

From the last diagram it was clear that, when one component can dissolve in the vapor of the other, the partial pressures for the solvent in the system, solid solvent, solution and vapor, are given by a curve starting from the triple point and lying above the boundary curve for solid and vapor. The reverse state of things will be found in case the solid phase has a perceptible solvent action; in other words, in case a solid solution is formed. In Fig. 6 is given the diagram for a system in which two systems of solid solutions are possible.

OA is the vaporization curve and OB the sublimation curve for one of the pure components; O_1A_1 and O_1B_1 the corresponding curves for the other pure component. OHL gives the partial pressures of the more fusible component in one set of saturated solid solutions at different temperatures, while O_1H_1 gives the relation between the temperature and the partial pressure of the less fusible component when the solid phase is the other set of saturated solid solutions. If the temperature of the eutectic point be that of the points C, H and H_1 , the partial pressures of the solutes along the two boundary curves may be represented

by D_1H_1 and DH respectively. The boundary curves for the system are $OC = OH + D_1H_1$, $O_1C = O_1H_1 + DH$, and $CK = HL + H_1L_1$.

In cases where no solid solutions are possible the curve OC must lie above the curve OB because it is equal to the curve OB plus the curve for the partial pressures of the other component. When solid solutions occur, this is no longer necessary and in the present rather extreme case the curve OC lies completely below OB .

Fig. 6

If the two substances form one continuous series of solid solutions, the curves HL and H_1L_1 disappear and we have two continuous curves OHD and $O_1H_1D_1$. For the isomorphous mixtures studied by Küster¹ OHD and $O_1H_1D_1$ become the straight lines OD and O_1D_1 , and we have a state of things represented graphically in Fig. 7.

OD gives the partial pressures for the more fusible component in the system, solid solution, liquid solution and vapor, while O_1D_1 gives the corresponding values for the other. The sum of these two curves is OO_1 , which represents the total vapor-pressure along the boundary curve. Of course, it is very im-

¹ Zeit. phys. Chem. 8, 577 (1891).

probable that the curves OD and O_1D_1 are ever absolutely straight lines, but this diagram may be considered as the limiting case.

There is one other point that calls for discussion. At temperatures below that of the quadruple point, hydrated sodium

Fig. 7

sulfate can exist in stable equilibrium with solution and vapor, while the system, anhydrous sodium sulfate, solution and vapor, though realizable experimentally, is instable with respect to the hydrated salt. The metastable solution contains more sodium sulfate than the other and has a lower vapor-pressure. In one-component systems the phase that is in equilibrium with vapor at a higher pressure is instable with respect to the phase that is in equilibrium with vapor at a lower pressure. At first sight it would appear as though the solution saturated with respect to the anhydrous salt should be the more stable or, at any rate, that the difference of vapor-pressures would tend to change the equilibrium in one direction and that the difference of concentrations would tend to displace the equilibrium in the opposite direction, the latter tendency being the decisive one. As a matter of fact there is no such conflict of forces. Let the solution saturated with respect to the hydrated salt be called A and the solution saturated with respect to the anhydrous salt be called B. If these two solutions are brought in contact, salt will diffuse

from the place of higher concentration to that of lower concentration, in other words from B to A. The solution A being saturated, by definition, the salt that has diffused in will crystallize as decahydrate; in the meanwhile salt will dissolve in B to restore the original concentration and will then diffuse into A. The final result will be the disappearance of the anhydrous salt and of the difference between the solutions. The actual result, apart from the question of transference, will be that anhydrous salt goes into solution and that hydrated salt crystallizes.

Suppose, now, that the solutions be so arranged that they have a common vapor phase, diffusion however being impossible. This may be done by placing the solutions in two beakers under a bell-glass. Water will then distil from the place of higher pressure to the place of lower pressure, in other words from A to B. The solution in A will tend to become more concentrated and hydrated salt will therefore separate. The solution in B will tend to become more dilute and equilibrium will continually be restored by the anhydrous salt going into solution. The final equilibrium will depend on the relative masses of the phases. If the mass of solution in A be relatively small with reference to the mass of solution or to the mass of anhydrous salt in B, the final equilibrium will be hydrated crystals in A, solution and anhydrous salt in B. If the mass of solution be not relatively small with reference to either of the phases in B, the final equilibrium will be hydrated crystals and solution in A and a solution of the same composition in B. Whatever be the final combination of phases, the change taking place has been that anhydrous salt goes into solution and hydrated salt crystallizes. We see, therefore, that the anhydrous salt is the metastable form whether we consider the matter from the point of view of the vapor-pressures or of the concentrations.

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