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THE FREEZING-POINT—SOLUBILITY CURVES OF HYDRATES AND OTHER COMPOUNDS UNDER PRESSURE.

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ABSTRACT.

For the determination of equilibrium in systems under high pressure there are two principal modes of attack. We may either devise an experimental method for measuring directly the solubility at the various pressures, or determine indirectly the variation of concentration with pressure under conditions of equilibrium by measuring the compressibilities of the several phases and applying a simple thermodynamic relation. It has already been shown by previous studies at this Laboratory that for simple systems under pressures of several thousand bars (metric atmospheres) the indirect thermodynamic method is convenient and precise. Equilibrium curves for more complex cases, in which hydrates and other compounds appear, are now considered in detail and the various equations used in passing from volume-change measurements to points on the freezing-point—solubility curves are set forth. The method is illustrated by the determination of the solubility curve of a salt hydrate under pressure, and other representative types of equilibrium diagrams are discussed.

INTRODUCTION.

A study of the formation of rocks under the conditions that exist within the Earth resolves itself into detailed investigations of the influence of temperature and pressure on various combinations of minerals. In the Earth both temperature and pressure increase steadily from the surface downward. We recognize temperature as an essential factor in petrology because of well-known thermal effects, and we infer the importance of pressure because at a depth of only 30 kilometers, which is within what is commonly called the crust of the Earth, pressures of nearly 30,000 atmospheres must exist. It is evident that in experimental petrology it is necessary to take account of pressure as well as temperature, and to investigate melting phenomena of minerals and combinations of minerals subjected to pressures of considerable magnitude.

Although there has been more progress on the purely

thermal side, a beginning has been made in the study of melting-point and solubility curves for mixtures under high pressure. The recent development of the necessary technique will doubtless lead to much further work in this important field of experimentation. Two classes of methods, direct and indirect, have been used in determining equilibrium in systems under pressure. By the first type of method we measure directly the change of solubility, for example, or some property associated with this change. On the other hand, by the second kind of method we take advantage of a simple and useful thermodynamic principle and measure merely the compressibilities of the various solutions and other phases occurring in the system, and from these measurements of volume-change calculate various points on the freezing-point or solubility curve. For application to systems under pressures of several thousands of atmospheres the indirect, or thermodynamic, method seems more convenient as well as more accurate.[1] The thermodynamic principle utilized in this indirect method is that equilibrium in a physical-chemical system is dependent on the chemical potential of the separate phases and that the chemical potential at various pressures is related very simply to the change of volume under pressure.

THE THERMODYNAMIC METHOD.

Simple Cases.

The principle involved may be summarized by the two equations,

$$\mu'_1 = \mu''_1 \tag{1}$$

$$\frac{d\mu'_1}{dP} = \bar{v}'_1 \tag{2}$$

According to the first equation the necessary and sufficient condition for equilibrium may be expressed in terms of the chemical potential (μ) of any component. The equilibrium with respect to component (1), for example, in the two phases indicated by the superscripts prime and double prime is determined by the equality of the corresponding μ's. The meaning of the second equation is that as the pressure varies, the tem-

[1] Adams, L. H.: J. Am. Chem. Soc., 53, 3769-3813, 1931.

perature and composition remaining constant, the change in the μ of component (1) is determined by the product of the pressure-change and the quantity $\bar{v}_1$, which is called the fictive volume of the component and is evaluated from measurements of the densities (ρ) of the solutions, or of their reciprocals, the specific volumes (v), by means of the expression

$$\bar{v}_1 = v + x_2 \left(\frac{\partial v}{\partial x_1}\right)_{P,\,T} \qquad (3)$$

In a binary solution at any given constant pressure and temperature this equation is applicable to any value of x_1, the weight-fraction of the component under consideration (x_2 being the weight-fraction of the other component and therefore equivalent to $1 - x_1$). By the interchange of subscripts, equations (1), (2) and (3) become applicable to the other component of the binary system. It should be noted that the thermodynamic method is not restricted to binary systems but applies equally well to a system containing any number of components.

The experimental methods for measuring the volume-changes required for the determination of the freezing-point or solubility curve have already been described in full detail.[2, 3] It is sufficient at this time merely to recall that the densities at atmospheric pressure and the compressions of the various solid phases and of solutions at several concentrations are measured with as much precision as possible; the effective specific volumes, in solution, of each component (i.e. the fictive volumes) are then computed by means of equation (3) or a modification of it. Next, by the use of the relation expressed in equation (2), the chemical potential (μ) of each component in solution is calculated for a suitable range of pressures and concentrations, and finally, the pressure at which, for each concentration, the respective μ's of a given component in the two phases become equal is determined. This establishes a series of points on the equilibrium curve in the system under consideration. We find for example[4] that μ_2, the potential of NH_4NO_3 in an aqueous solution containing 29.7 per cent (by weight) becomes equal at 10,000 bars to μ_s, the potential of solid NH_4NO_3 at the same pressure and at the same temperature, namely 25°. Therefore, the solubility of NH_4NO_3,

[2] Ref. 1, pp. 3773-3780.
[3] Gibson, R. E.: J. Am. Chem. Soc., 53, 1522, 1937.
[4] Adams, L. H., and Gibson, R. E.: J. Am. Chem. Soc., 54, 4520-4537, 1932.

which at atmospheric pressure is 67.6 per cent, is decreased to 29.7 per cent by subjecting the system to a pressure of 10,000 bars.

In order to facilitate the calculation, we deal with the *differences* between the μ's in the various solutions and the μ's in some reference state. Accordingly we write equation (1) in the form

$$\mu_s - \mu_l = \mu_1 - \mu_l \tag{4}$$

from which by equation (2) we have

$$\int_{P_f}^{P} (v_s - v_l)\,dP = (\mu_1 - \mu_l)_0 + \int_0^P (\bar{v}_1 - v_l)\,dP \tag{5A}$$

as the condition of equilibrium in convenient form for calculating the freezing-point curve, under varying pressure, of a component that is liquid at atmospheric pressure. Here P_f refers to the freezing-pressure of the pure component (1), and the subscripts s and l refer respectively to the pure liquid (1) and to the pure solid (1). Zero, when used as a subscript or as one of the limits of integration, refers to atmospheric pressure. The determination of points on the freezing-point curve is carried out by first plotting as ordinates the values of the left-hand member of equation (5A) at various pressures, and then for a number of concentrations (e.g. various x_2's) plotting a series of curves each expressing the numerical value of the right-hand member of equation (5A) as a function of pressure at the given constant x_2. It is convenient to use either graphical or tabular integration. The intersections of the first curve with the curves for the various x_2's obviously give pairs of values of P and x_2 for which there is equilibrium between solid and liquid, and thus yield a series of points on the P—x, or freezing-pressure, curve.

This particular method, which involves the plotting of a series of μ—P curves at constant x, will be called Procedure A. An alternative method is based on the following equation, which is obtained by rearrangement of equation (5A),

$$(\mu_1 - \mu_l)_0 = -\int_0^{P_f} (\bar{v}_1 - v_l)\,dP - \int_{P_f}^{P} (\bar{v}_1 - v_s)\,dP \tag{5B}$$

Because the left-hand member of this equation is a function of x_2, we may determine the freezing-pressure of solutions

of various concentrations by first plotting $(\mu_1 - \mu_l)_0$ as ordinate with x_2 as abscissa, and then finding the intersections of this curve with the separate curves obtained by plotting as ordinates

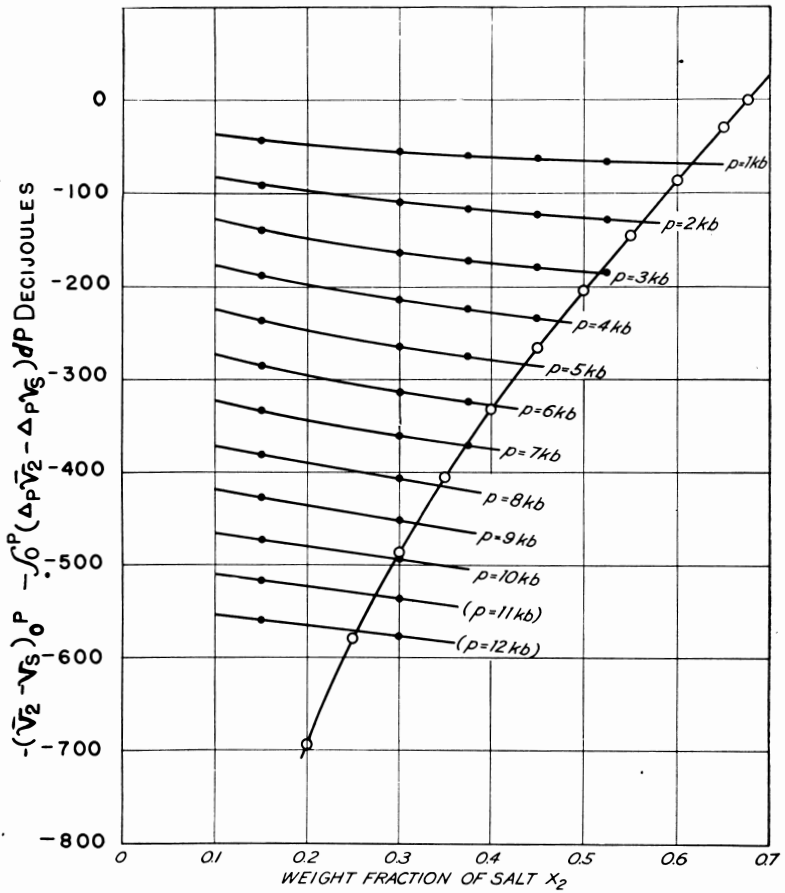

Fig. 1 (after Adams and Gibson). Illustration of method for determining points on a solubility curve by noting the intersections of curves for chemical potential.

the values of the right-hand member of equation (5B) at constant pressure and varying concentration. According to Procedure B, therefore, we determine equilibrium by means of a series of μ—x curves at constant P.

If the equilibrium curve pertains to a phase that is solid at atmospheric pressure (and at the temperature under consideration), the working equation for use by Procedure A takes the form

$$\int_0^P (v_s - \bar{v}'_2)\,dP = (\mu_2 - \mu'_2)_0 + \int_0^P (\bar{v}_2 - \bar{v}'_2)\,dP \qquad (6A)$$

In this instance we are dealing with component (2), and the superscript prime here refers to concentration at which the

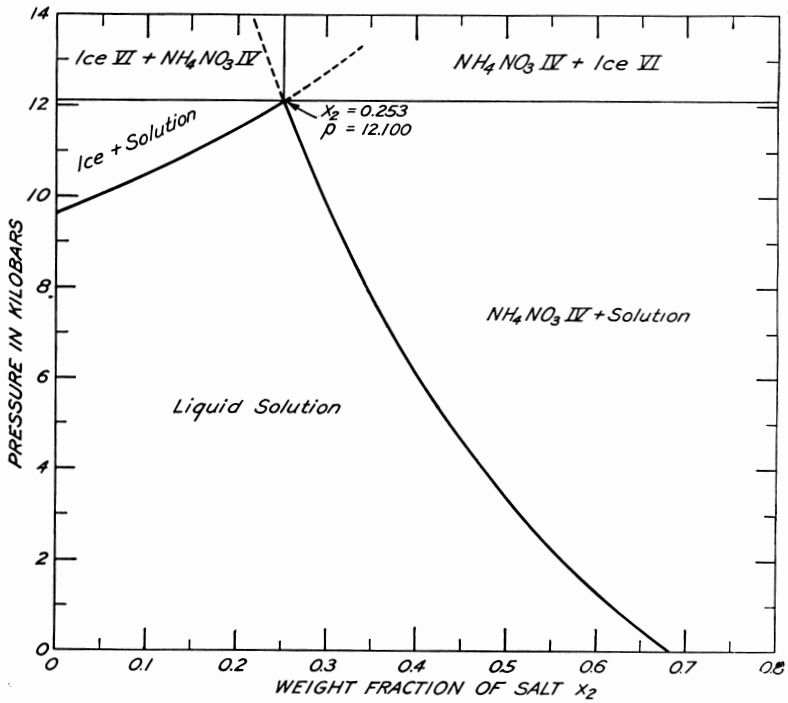

Fig. 2 (after Adams and Gibson). Equilibrium diagram for the system, NH_4NO_3—H_2O, at 25°. The solubility curve shown on the right was determined graphically as shown in Fig. 1.

solution is saturated (at one atmosphere) and in equilibrium with solid component (2). As before, points on the equilibrium curve are determined by plotting the left-hand member of the equation with P as abscissa and finding the intersections of this curve with the family of curves obtained by plotting

the right-hand member of equation (6A) with variable P and constant x_2. The alternative form of the equation—obtained by a slight rearrangement—is

$$(\mu_2 - \mu'_2)_0 = -\int_0^P (\bar{v}_2 - v_s)\,dP \qquad (6B)$$

Because it is convenient in the course of the computation to deal with the *volume-changes* ($\Delta_p v$) under pressure rather than the volumes at the various pressures, more useful forms of (6A) and (6B) are obtained by putting $v_s = (v_s)_0 + \Delta_p v_s$ and $\bar{v}_2 = (\bar{v}_2)_0 + \Delta_p \bar{v}_2$, and noting that the integral of $(v_s)_0\,dP$ is $(v_s)_0 P$, whereupon we have

$$(v_s - \bar{v}'_2)_0 P + \int_0^P (\Delta_p v_s - \Delta_p \bar{v}'_2)\,dP$$
$$= (\mu_2 - \mu'_2)_0 + (v_2 - v'_2)_0 P + \int_0^P (\Delta_p \bar{v}_2 - \Delta_p \bar{v}'_2)\,dP \qquad (7A)$$

and

$$(\mu_2 - \mu'_2)_0 = -(\bar{v}_2 - v_s)_0 P - \int_0^P (\Delta_p \bar{v}_2 - \Delta_p v_s)\,dP \qquad (7B)$$

Probably the most generally useful in actual practice are equation (5A) for determining the freezing-point curve of an originally liquid component, and equation (7B) for the solubility curve of an originally solid component. An example of the application of the latter equation is shown in Figs. 1 and 2, which are taken from the paper by Adams and Gibson[4] on the system, NH_4NO_3—H_2O. The intersections of the curve for μ_2—μ'_2, in Fig. 1, with the family of curves representing the right-hand member of equation (7B) (as well as 6B) yield the points on the part of the diagram in Fig. 2 that pertain to the solubility of NH_4NO_3 under pressure.

Hydrates and other Compounds.

Having summarized the necessary steps in determining equilibrium curves by the thermodynamic method for simple cases, we proceed now to consider equilibrium curves involving hydrates and other compounds. Compared with the procedure for the simple cases discussed above, the principal difference is due to necessity for choosing new components and for interrelating their properties. It is well known that the thermodynamic treatment of physical-chemical systems is facilitated by a proper choice of components and that it is allowable to

choose as the components in a system any compounds or mixtures in terms of which the compositions of the several phases may be expressed. For some purposes it is necessary to include among the chosen components a composition equivalent to that of any solid phase under consideration, if that phase is invariant in composition. For example, in dealing with the system, NaCl—H_2O, under circumstances in which the hydrate, $NaCl.2H_2O$, makes its appearance, we must select $NaCl.2H_2O$ as one component of the aqueous solution, the other component then being any convenient quantity such as for example excess or deficiency of water.

It is important to note the transformation equations for the various components that may be selected. From elementary principles it follows that

$$\bar{v}_3 = (1 - x_0)\,\bar{v}_1 + x_0\bar{v}_2 \tag{8}$$

$$(\mu_3 - \mu'_3) = (1 - x_0)(\mu_1 - \mu'_1) + x_0(\mu_2 - \mu'_2) \tag{9}$$

in which the subscript, 3, refers to the component whose composition is that of the hydrate or other compound, and x_0 denotes the weight-fraction of anhydrous salt in the hydrate itself. Subscripts 1 and 2, as before, refer respectively to pure solvent and anhydrous salt. Because in many instances the properties of the solutions expressed in terms of components 1 and 2 are already available, it usually is unnecessary to compute $\bar{v}_3$ and μ_3 directly from the original measurements.

By analogy with equation (6A) or (6B) we have

$$\int_0^P (v_c - \bar{v}'_3)\,dP = (\mu_3 - \mu'_3)_0 + \int_0^P (\bar{v}_3 - \bar{v}'_3)\,dP \tag{10A}$$

or

$$(\mu_3 - \mu'_3)_0 = -\int_0^P (\bar{v}_3 - v_c)\,dP \tag{10B}$$

in which v_c denotes the specific volume of the solid compound. From (8) and (9) it follows that

$$\int_0^P (v_c/x_0 - \bar{v}'_2 - \bar{v}'_1/r_0)\,dP = (\mu_2 - \mu'_2)_0 + (\mu_1 - \mu'_1)_0/r_0 + \int_0^P [(v_2 - v'_2) + (\bar{v}_1 - \bar{v}'_1)/r_0]\,dP \tag{11A}$$

$$(\mu_2 - \mu'_2)_0 + (\mu_1 - \mu'_1)_0/r_0 = -\int_0^P (\bar{v}_2 + \bar{v}_1/r_0 - v_c/x_0)\,dP \tag{11B}$$

r_o being the equivalent of $x_o/(1-x_o)$. These equations are in form for calculating the solubility curves for hydrates by Procedures A and B described above and are directly applicable to hydrates stable at atmospheric pressure. Probably (11B) is the more generally useful form.

In actual practice it will usually be preferable to make the same change in equations (11A) and (11B) as was made in

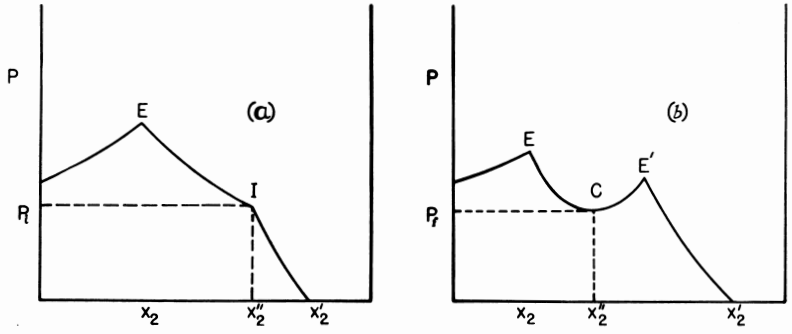

Fig. 3. Schematic diagram showing equilibrium curves under pressure on a system involving a hydrate or other compound that (a) melts incongruently and (b) melts congruently.

transforming equations (6A) and (6B) to (7A) and (7B), namely to replace $\bar{v}_1$ by $(\bar{v}_1)_o + \Delta_p\bar{v}_1$, and similarly for $\bar{v}_2$ and v_c.

If at a temperature that is higher than the temperature T for which the $P-x$ diagram is being constructed a salt hydrate melts incongruently to a mixture of anhydrous salt and solution, and if the transformation temperature is lowered by pressure so that at the temperature T and at or above a pressure P_i the anhydrous salt rather than the hydrate becomes the phase that is stable in contact with solution, then the equilibrium diagram may take a form similar to that shown in Fig. 3a. The complete solubility curve for the salt consists of two branches, one pertaining to the hydrate and the other to the anhydrous salt. The first of these, which is readily evaluated by equation (11), begins at atmospheric pressure (substantially zero on the scale of this diagram) and extends to the transformation point I where it intersects the solubility curve of the anhydrous salt. Evaluation of the latter curve is carried by means of the expression obtained by suitable change of the

limits of integration in equations (6) or (7). We thus obtain, for example,

$$\int_{P_i}^{P}(v_s - \bar{v}''_2)\,dP = (\mu_2 - \mu''_2)_o + \int_o^P (\bar{v}_2 - \bar{v}''_2)\,dP \qquad (12A)$$

$$(\mu_2 - \mu''_2)_o = -\int_o^{P_i}(\bar{v}_2 - \bar{v}''_2)\,dP - \int_{P_i}^{P}(\bar{v}_2 - v_s)\,dP \qquad (12B)$$

For this purpose we may also use equation (6B) or (7B) without alteration other than changing μ'_2 to μ'''_2, the μ of the solution (metastably) saturated with respect to the anhydrous salt (at $P = 0$), thus beginning our calculation at atmospheric pressure and with the initial, metastable, portion of the solubility curve.

If on the other hand the incongruent melting-temperature is initially lower than T and is raised by pressure, then at a pressure P_i the hydrate enters the $P - x$ diagram. For this case the low-pressure branch of the solubility curve pertains to anhydrous salt, and the high-pressure branch, extending from I to E in Fig. 3a, pertains to the hydrate. The first branch may of course be determined by equation (6) or (7). For the hydrate curve a slight modification of (11) is required in order to take into account the changed limits of integration. Convenient forms of equations for a hydrate curve beginning at pressure P_i and concentration x''_2 are

$$\int_{P_i}^{P}(v_c/x_o - \bar{v}''_2 - \bar{v}''_1/r_o)\,dP =$$

$$(\mu_2 - \mu''_2)_o + (\mu_1 - \mu''_1)_o/r_o + \int_o^P [\bar{v}_2 - \bar{v}''_2 + (\bar{v}_1 - \bar{v}''_1)/r_o]\,dP \qquad (13A)$$

$$(\mu_2 - \mu''_2)_o + (\mu_1 - \mu''_1)_o/r_o = -\int_o^{P_i}[\bar{v}_2 - \bar{v}''_2 + (\bar{v}_1 - \bar{v}''_1)/r_o]\,dP$$

$$-\int_{P_i}^{P}(\bar{v}_2 + \bar{v}_1/r_o - v_c/x_o)\,dP \qquad (13B)$$

Just as with previous equations, it is often preferable to deal with volume-changes rather than with volumes. We therefore may substitute, in equations (13A) or (13B), $(\bar{v}_1)_o + \Delta_p\bar{v}_1$, for example, in place of $\bar{v}_1$, in order to obtain the final working equation.

In the event that the hydrate under consideration melts con-

gruently the equilibrium diagram may resemble that shown in Fig. 3b. The curve for hydrate-solution equilibrium has a minimum at C, the point at which the concentration x_2 of (anhydrous) salt in the solution equals x_0 the weight-fraction of anhydrous salt in the solid hydrate. At E and E' the hydrate curve intersects equilibrium curves of other solids. These intersections thus mark the compositions and freezing-pressures of eutectics analogous to those encountered in $T - x$ diagrams. It is easily shown that an appropriate and convenient equation for determining the equilibrium curve of a compound that melts congruently is obtained from equation (13B) by merely replacing P_i in that equation by P_f, the freezing-pressure (at temperature T) of the pure compound, and noting that x''_2 is now equal to x_0. A separate measurement of P_f is obviously required.

It is important to note that the shape of the equilibrium curve is a consequence of the theorem enunciated by Gibbs[5] to the effect that when a compound has been chosen as one of the components in a system, the other component being a part of this compound, then μ_3, the chemical potential of the compound, has its greatest value when the solution has the composition of the compound. That is, μ_3 (or $\mu_3 - \mu''_3$, or $\mu_2 - \mu''_2 + (\mu_1 - \mu''_1)/r_0$), when plotted as a function of x_2, will have a maximum at $x_2 = x_0$. Therefore, a curve representing the right-hand member of (13B) may, for certain values of P, intersect the curve of $\mu_3 - \mu''_3$ at two points and thus yield two points on the desired solubility, or freezing-point, curve. A further consequence is that $P - x$ as well as $T - x$ curves must have a maximum or minimum at the composition of the compound.

A more general case of two hydrates may also be represented diagrammatically by Fig. 3a, if we suppose the low-pressure branch of the solubility curve to refer to one hydrate and the high-pressure branch to a second hydrate, P_i being the pressure at which the incongruent melting or freezing takes place. In this instance, also, equation (13B) gives us the condition of equilibrium along the curve for either hydrate. Under these circumstances x_0 is the weight-fraction of anhydrous salt in the particular hydrate under consideration, v_c is its specific volume, and x''_2 is the composition of the solution at the low-pressure end of the equilibrium curve for the compound.

[5] Gibbs, J. W.: Scientific Papers, New York, Vol. I, pp. 93, 99, 135, 1906.

Indeed, equation (13B) is a general one from which the equations pertaining to all the types of curves previously discussed may be obtained. For example, by putting $P_i = 0$, $x_o = 1$, $v_c = v_s$, and $x''_2 = x'_2$, we obtain equation (6B) for a simple solubility curve beginning at atmospheric pressure. The appropriate equation (12B), for an anhydrous salt stable only at high pressures, may be obtained from (13B) by putting $x_o = 1$ and $v_c = v_s$. It should be noted that equation (12B) applies also to a solid that inverts at P_i from one form to another without change of composition. To obtain the equation (11B), for a hydrate curve beginning at atmospheric pressure we put $P_i = 0$ and $x''_2 = x'_2$. Finally, the equation (5B), for determining the freezing-pressure curve of the solvent, may be derived from (13B) by substituting P_f for P_i, and putting $v_c = v_s$, $x_o = 1$, and x''_2 (which now becomes x''_1) $= 1$, that is, $\bar{v}''_2 = \bar{v}_1$ and $\mu''_2 = \mu_1$.

EXAMPLE OF EQUILIBRIUM CURVE FOR A HYDRATE UNDER PRESSURE.

A portion of the $P - x$ diagram for the system, Na_2SO_4—H_2O, at 25° will serve as an illustration of the determination of a hydrate equilibrium curve by the thermodynamic method. At 25° the stable solid phase in contact with solution is $Na_2SO_4.10H_2O$ and the saturated solution contains 21.8 per cent by weight of Na_2SO_4. Anhydrous Na_2SO_4 at atmospheric pressure becomes stable only above the incongruent melting-point, 31.38 per cent. Some unpublished measurements by Dr. R. E. Gibson and the author on the compression of Na_2SO_4 solutions readily yield values of $\bar{v}_1$ and $\bar{v}_2$ at various pressures and concentrations. The chemical potentials, μ_1 and μ_2, of H_2O and Na_2SO_4 in the solutions at atmospheric pressure may be derived from published data on the vapor pressure and freezing-points of Na_2SO_4 solutions and on the emf.'s of cells involving Na_2SO_4. Although the compression of anhydrous Na_2SO_4 has been measured,[6] that of $Na_2SO_4.10H_2O$ has not yet been determined. Even though this datum is lacking, it is possible to construct an equilibrium diagram of moderate accuracy, because it happens that at low pressures the compression of the decahydrate is not an important factor in the calculation and that the decahydrate at 25° is stable only at moderate pressures. Based upon our knowledge of the compressions of

[6] Adams, L. H., and Gibson, R. E.: J. Wash. Acad. Sci., 21, 381-390, 1931.

various solids the assumption will be made that the compression of $Na_2SO_4.10H_2O$ is 4 x 10^{-6} reciprocal bars. It is not likely that the true compression differs sufficiently from this amount to introduce a serious error into our computations.

The necessary data being on hand, equation (11B) was used to determine the solubility curve of the decahydrate at 25°. In Fig. 4 is shown a plot of $(\mu_2 - \mu'_2) + (\mu_1 - \mu'_1)/r_o$, the

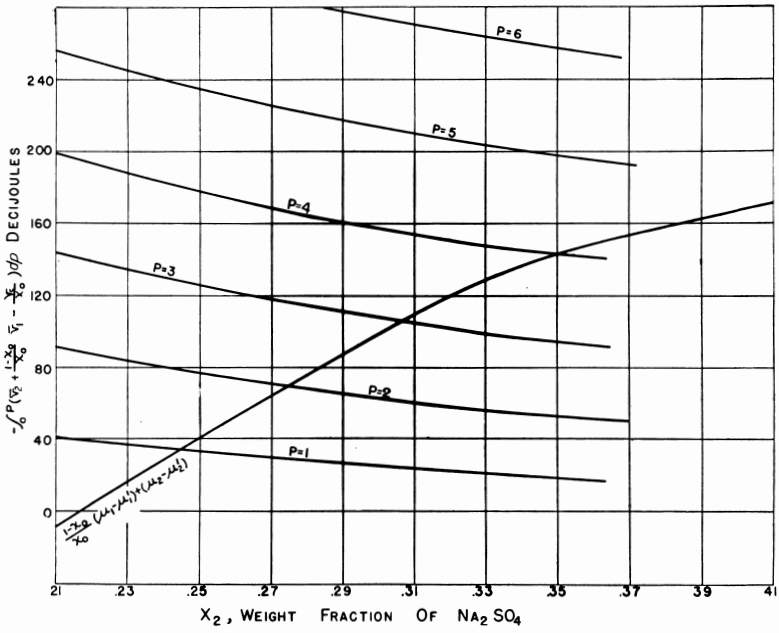

Fig. 4. Chemical potential curves for $Na_2SO_4.10H_2O$ under pressure, used for the graphical solution of equation (11B).

left-hand member of (11B), as a function of x_2. As before, r_o is the equivalent of $x_o/(1 - x_o)$. In the same figure the right-hand member of (11B) for a series of constant pressures, viz. 1, 2, 3, 4, 5 and 6 kilobars respectively, is also plotted as a function of x_2. As explained above, the intersections shown in this diagram yield points on the solubility curve of the decahydrate. At 1000, 2000, 3000 and 4000 bars the values of x_2 are found by this procedure to be 0.246, 0.275, 0.307 and 0.350 respectively. From the circumstance that the curve for $\mu_2 - \mu'_2 + (\mu_1 - \mu'_1)/r_o$ is concave downward (having a maximum at $x = 0.441$) and that the other curves in Fig. 4

are concave upward, it becomes probable that the curve for $P = 5$ kilobars does not intersect the μ-curve and that the decahydrate, therefore, is not stable at pressures as high as 5000 bars (at 25°). This supposition is confirmed by Fig. 5 in which there are plotted the points obtained for the solubility curve of the decahydrate as well as a curve for the solubility of the anhydrous salt under pressure. This curve was obtained

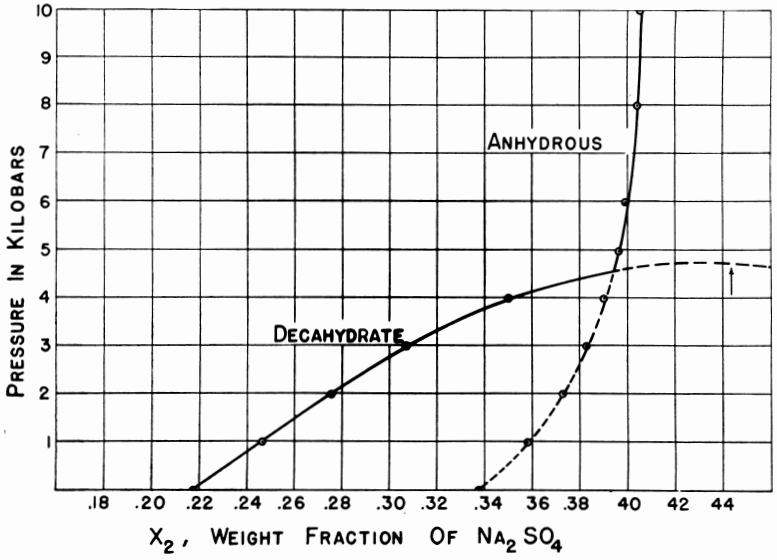

Fig. 5. A portion of the equilibrium diagram for the system, Na_2SO_4—H_2O, at 25°. The solubility of the decahydrate was obtained from the intersections of the curves drawn in Fig. 4.

by the application of equation (7B) to the data mentioned above. It begins at low pressure as a metastable portion of the solubility curve and appears to have a flat maximum of x_2 at about 10,000 bars. The intersection with the hydrate curve determines the transition-pressure, which is thus found to be 4600 bars at 25°—in substantial agreement with unpublished direct measurements (by Dr. Gibson and the author) of the pressure at which incongruent melting takes place.

By inspection of Fig. 5 it will be seen that the solubility curve of the hydrate, like the curve for μ, is concave towards the x_2-axis, which is in accord with the circumstance that the curve must have a horizontal tangent at the point corresponding

to x_0, that is, at the point, $x_2 = 0.441$, indicated by the arrow. The significant fact is that whereas for anhydrous salts dx_2/dP, the rate of increase of solubility with pressure, even when positive, becomes less at the high pressures, the solubility of the hydrate, on the contrary, may increase at a rate that becomes greater as the pressure increases. The result is that in the present instance the two curves for decahydrate and anhydrous salt, respectively, intersect at a relatively low pressure, thus causing the hydrate to be stable only within a limited pressure range.

REPRESENTATIVE TYPES OF FREEZING-POINT DIAGRAMS.

A consideration of the factors involved in the various equations previously set forth for calculating equilibrium relations under pressure by the thermodynamic method gives us important information concerning the various possible types of freezing-point curves in binary systems. Some conclusions as to the merely qualitative aspects of various types of diagrams are illustrated in Fig. 6. The shaded portions of the various fields represent the conditions under which the mixtures are entirely liquid. The first group (*a*) pertains to simple systems that do not involve compounds. Nos. 1 to 6 of this group show in succession diagrams for two components both of which are solid at atmospheric pressure; for one component solid and the other liquid at atmospheric pressure; for both components liquid; for a component whose solubility at first increases and then decreases under pressure; for one component having an enantiotropic inversion; and for both components having such inversions.

The diagram (*b*1) illustrates the case of a hydrate the incongruent melting-temperature of which is lowered by pressure so that at constant temperature there is an incongruent melting at a certain pressure. The solubility curve on the right-hand side of the diagram at the lower pressures pertains to hydrate and at the higher pressures to the anhydrous salt or another hydrate. Diagram (*b*2) shows the appearance of a $P - x$ diagram for the same system but at a higher constant temperature, namely one that is above the incongruent melting-temperature. The solubility curve on the right is for the anhydrous salt, and under the conditions specified the hydrate does not come into the diagram. In diagram (*b*3) we have the same conditions as in (*b*1) except that the solubility of the

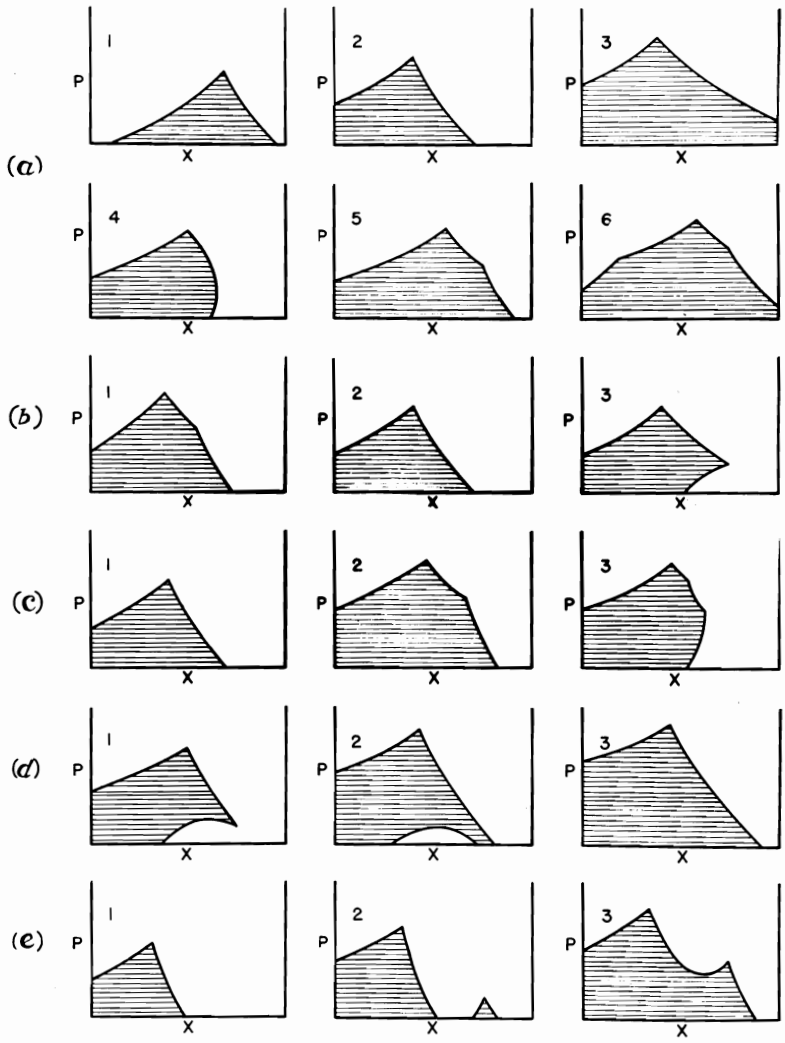

Fig. 6. Representative types of equilibrium diagrams for binary systems under pressure.

hydrate is increased rather than decreased by pressure. In this respect the diagram resembles the one for the system, Na_2SO_4—H_2O.

For systems in which there is encountered an incongruent

melting-point that is raised by pressure we may have diagrams similar to those in group (*c*). The first of these, (*c*1), pertains to a temperature below the transformation temperature, and is similar to (*b*2) except that here the right-hand equilibrium curve is that of the hydrate rather than that of the anhydrous salt. If the constant temperature under consideration is above the transformation, equilibrium curves as in (*c*2) will usually be obtained. The case of an incongruent melting-temperature that is first raised by pressure and then lowered (the melting-point thus showing a maximum) is illustrated by (*c*3). This diagram closely resembles the one for the system,[7] NaCl—H_2O, at 25°, which is below the maximum temperature on the $P - T$ curve for the hydrate. In this case increasing pressure causes the hydrate to appear and then to disappear at a somewhat higher pressure.

If the hydrate, or other compound, melts congruently and if the melting-temperature is depressed by pressure, the series of diagrams (*d*) are obtained. The first is at a temperature below the melting-temperature of the compound and below also the eutectic (on the $T - x$ diagram) between the compound under consideration and the adjacent solid. Diagrams (*d*2) and (*d*3) refer, respectively, to temperatures that are above the eutectic-temperature but below the melting-temperature, and to temperatures above both the melting-temperature and the eutectic-temperature. It is of course unusual for the melting-temperature of a substance to be lowered by pressure, but it is not unlikely that among hydrates some examples of this will be found. It is worthy of note that the general relations shown in (*d*1) or (*d*2) are approached though not attained in the sodium sulphate system.

For the more usual case of a compound the melting-temperature of which is raised by pressure we have the diagrams (*e*1), (*e*2) and (*e*3). In the first the temperature is below both the melting-temperature of the compound and an adjacent eutectic-temperature; in the second the temperature is still below the melting-temperature but is above the eutectic-temperature, and in the third the temperature is above both transformation-temperatures.

The equilibrium curves shown in Fig. 6 do not cover all the possible types of equilibrium diagrams for systems under pressure, but they represent the ones that will most commonly be

[7] Adams, L. H., and Gibson, R. E.: J. Am. Chem. Soc., 52, 4252-4264, 1930.

encountered and they serve to illustrate the correspondence between $T - x$ and $P - x$ diagrams.

CONCLUDING REMARKS.

In the foregoing discussion of equilibrium diagrams nothing has been said concerning solid solutions. Melting-point curves for systems in which this effect occurs may be determined by the same methods as have been described for systems involving solids of constant composition. By a slight extension of the equations that have been presented they become applicable to equilibria between solid solutions and other phases, as well as to systems containing any number of constituents.

It is interesting to compare the methods used in high-pressure and in high-temperature investigations of systems containing two or more components. Indirect methods may be employed in either field of research, but for the determination of equilibrium relations at high pressures the indirect thermodynamic method has peculiar advantages. This is because equilibrium under pressure depends upon volume, which can be measured with unusual precision. On the other hand, direct observation of phenomena taking place within a container sufficiently strong to withstand a pressure of several thousand atmospheres involves great experimental difficulties, which hinder the attainment of satisfactory accuracy. The indirect method will doubtless find increasing use in studies of the melting behavior of mixtures under high pressures, and when applied to silicate solutions will serve as an important tool in the solving of petrologic problems.