Application of the Gibbs-Konovalow Equations to Binary Phase Equilibria

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The Gibbs-Konovalow relations are shown to provide a unified approach to the description of binary two-phase equilibria. The relations are applied to a consideration of high order transitions* (7) and are shown to easily lead to well-known, but generally uncorrelated, behavior of slopes of lines separating two single-phase regions in binary systems. In particular, the conditions under which the slope of the temperature-composition line is zero, constant, or undefined in the neighborhood of congruent* and peritectic* processes are derived.

Chemists, physicists, and metallurgists share an interest in the nature of heterogeneous equilibria. A knowledge of the thermodynamic restrictions on phase boundaries is useful in processes such as the preparation from their various melts of pure solid compounds, of solid compounds with semiconductor impurity levels, of ultrapure metals and of alloys with given compositions. The phase boundaries in binary equilibrium systems have been described analytically by Wilson (*18*) and more recently by Rastogi (*13*). The equations necessary for a general description of binary phase diagrams first derived by Gibbs (*8*) and independently by Konovalow provide a unified thermodynamic treatment of binary heterogeneous equilibria and, in particular, of the various solid-liquid equilibria.

Although known for over a century, the Gibbs-Konovalow (G-K) relations are not frequently used in the discussion of binary phase diagrams (*11*). The derivation of the G-K relations and the application of the relations to solution phenomena are discussed in texts by Epstein (*6*), by Prigogine and Defay (*12*), and by Kirkwood and Oppenheim (*9*). The relations were independently developed by Stout (*15*) in a consideration of higher order transitions in mixtures of ^{3}He and ^{4}He.

It is the particular purpose of this article to further discuss the application of the G-K relations to higher order transitions, and to illustrate how they apply to melting phenomena; specifically how they apply to the solution of pure component in a two-component melt, to the melting of solid solutions, to the congruent melting of a compound which decomposes in the melt, and to binary equilibria in the neighborhood of peritectic decomposition. For completeness, a derivation of the G-K relations and some of their general implications are discussed briefly.

STATEMENT OF THE G-K THEOREM

The implications of the G-K relations can be stated in two equivalent ways: (1) *A first-order transformation between phases of the same composition occurs at a local upper or lower bound of the temperature-composition and pressure-composition curves.* The limiting values of the slopes of these curves, as the overall composition approaches the composition of the congruent process, is frequently zero, but may be nonzero or undefined in certain cases discussed later. (2) *If an equilibrium transition (that is, a congruent transformation by reference 7) between two binary phases occurs at a state at which the slopes of the temperature-composition and pressure-composition curves are defined and nonzero then the transition is higher order than first, that is, the entropy and volume changes are zero.*

One important implication of the second statement is that if two solid phases with the same components are of different types of structure but are not separated by a two-phase region, then the two phases are separated by a higher order transition (ΔS and ΔV equal zero) or, perhaps, by no transition at all. Examples are the face centered tetragonal to face centered cubic transition in the thalium-indium system, the continuous change from *h* (hexagonal closest packed) to *hc* (lanthanum type) structure type observed in the neodymium-scandium system (*2*) and the β-β′ order disorder transition in the copper-zinc system. Some workers in the field of condensed phase relations have postulated the existence of two-phase regions between, for example, disordered phases and ordered superstructures of different types of structures (see Figure 1). Such two-phase regions do not necessarily exist.

We note at this point that the concept of order of an incongruent transformation is distinct from that of order of a congruent transition. The phases coexisting in equilibrium in the former case have differences in molar entropies given by

$$\Delta\bar{\bar{S}} = \bar{\bar{S}}^{\alpha} - \bar{\bar{S}}^{\beta} = \Sigma X_i^{\alpha}\bar{S}_i^{\alpha} - \Sigma X_i^{\beta}\bar{S}_i^{\beta}$$

and differences in molal volumes given by

$$\Delta\bar{\bar{V}} = \bar{\bar{V}}^{\alpha} - \bar{\bar{V}}^{\beta} = \Sigma X_i^{\alpha}\bar{V}_i^{\alpha} - \Sigma X_i^{\beta}\bar{V}_i^{\beta}$$

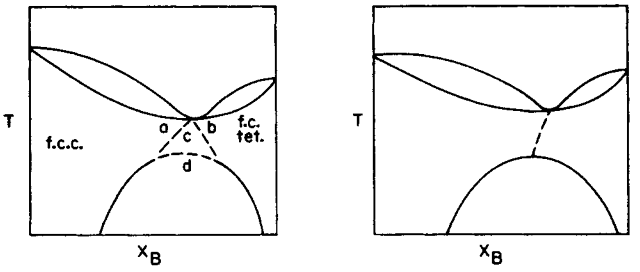

Fig. 1. If data are obtained at all points except that region surrounded by the dotted lines in I and labeled C, there has been a tendency to extrapolate the miscibility gap upward as indicated by lines *a* and *b*, rather than across, as indicated by line *d*. The G-K relations indicate that there is no reason that the diagram could not be drawn as in II with the dotted line indicating a higher order transition.

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* The meanings of these terms will be amplified in the text.

which in general are nonzero, although they could be fortuitously and independently zero at a finite number of states. Thus the order of an incongruent transformation is not appropriately defined by the criteria applicable to congruent transitions.

DERIVATION OF THE RELATIONS

Let α and β be two phases, each containing the same two components, A and B, in which $\mu_A{}^\alpha = \mu_A{}^\beta$ and $\mu_B{}^\alpha = \mu_B{}^\beta$ in some region of T, P, $X_B{}^\alpha$, X_B space. In this region

$$d\mu_i{}^\alpha = d\mu_i{}^\beta \qquad (1)$$

Combination of this equation with the difference between the Gibbs-Duhem equations for the two phases yields

$$\Delta\bar{\bar{S}}dT - \Delta\bar{\bar{V}}dP + \Delta X_B\,(d\mu_B - d\mu_A) = 0 \qquad (2)$$

where $\Delta\bar{\bar{S}}$ and $\Delta\bar{\bar{V}}$ are the differences between the molar entropies and volumes, respectively, of α and β. With $\mu_i{}^\alpha$ as a function of T, P, and X_B, the total differential of $\mu_i{}^\alpha$ is

$$d\mu_i{}^\alpha = (\partial\mu_i{}^\alpha/\partial T)_{P,X_i}\,dT + (\partial\mu_i{}^\alpha/\partial P)_{T,X_i}\,dP + (\partial\mu_i{}^\alpha/\partial X_B{}^\alpha)_{T,P}\,dX_B{}^\alpha \qquad (3)$$

and thus

$$d\mu_B{}^\alpha - d\mu_A{}^\alpha = (\bar{S}_A{}^\alpha - \bar{S}_B{}^\alpha)\,dT - (\bar{V}_A{}^\alpha - \bar{V}_B{}^\alpha)\,dP - \{(\partial\mu_A{}^\alpha/\partial X_B{}^\alpha)_{T,P} - (\partial\mu_B{}^\alpha/\partial X_B{}^\alpha)_{T,P}\}\,dX_B{}^\alpha \qquad (4)$$

where $\bar{S}_i{}^\alpha$ and $\bar{V}_i{}^\alpha$ are the partial molar entropy and volume, respectively, of the i^{th} component in phase α. Substitution of (4) into the combined Gibbs-Duhem equation, with $\left.\frac{\partial\mu_A{}^\alpha}{\partial X_B{}^\alpha}\right)_{T,P} = -\left.\frac{\partial\mu_A{}^\alpha}{\partial X_A{}^\alpha}\right)_{T,P}$, yields

$$\{\Delta\bar{\bar{S}} + (\bar{S}_A{}^\alpha - \bar{S}_B{}^\alpha)\,\Delta X_B\}\,dT - \{\Delta\bar{\bar{V}} + (\bar{V}_A{}^\alpha - \bar{V}_B{}^\alpha)\,\Delta X_B\}\,dP + \left\{\left.\frac{\partial\mu_A{}^\alpha}{\partial X_A{}^\alpha}\right)_{T,P} + \left.\frac{\partial\mu_B{}^\alpha}{\partial X_B{}^\alpha}\right)_{T,P}\right\}\Delta X_B dX_B{}^\alpha = 0 \qquad (5)$$

There are two independent intensive variables in a two-component, two-phase system; hence we may write

$$\left.\frac{\partial P}{\partial X_B{}^\alpha}\right)_P = \frac{-\left\{\left.\frac{\partial\mu_A{}^\alpha}{\partial X_A{}^\alpha}\right)_{T,P} + \left.\frac{\partial\mu_B{}^\alpha}{\partial X_B{}^\alpha}\right)_{T,P}\right\}\Delta X_B}{\Delta\bar{\bar{S}} + (\bar{S}_A{}^\alpha - \bar{S}_B{}^\alpha)\,\Delta X_B} \qquad (6)$$

and

$$\left.\frac{\partial P}{\partial X_B{}^\alpha}\right)_T = \frac{\left\{\left.\frac{\partial\mu_A{}^\alpha}{\partial X_A{}^\alpha}\right)_{T,P} + \left.\frac{\partial\mu_B{}^\alpha}{\partial X_B{}^\alpha}\right)_{T,P}\right\}\Delta X_B}{\Delta\bar{\bar{V}} + (\bar{V}_A{}^\alpha - \bar{V}_B{}^\alpha)\,\Delta X_B} \qquad (6)$$

the G-K relations. The denominator can be simplified and the numerator can be expressed in a more symmetric form in the following manner. The Gibbs-Duhem equation yields

$$X_A{}^\alpha\left.\frac{\partial\mu_A{}^\alpha}{\partial X_B{}^\alpha}\right)_{T,P} + X_B{}^\alpha\left.\frac{\partial\mu_B{}^\alpha}{\partial X_B{}^\alpha}\right)_{T,P} = 0 \qquad (8)$$

which, together with Equations (6) and (7) and other standard thermodynamic relations yield

$$\left.\frac{\partial T}{\partial X_B{}^\alpha}\right)_P = -\frac{(X_B{}^\alpha - X_B{}^\beta)\left.\frac{\partial\mu_B{}^\alpha}{\partial X_B{}^\alpha}\right)_{T,P}}{X_A{}^\alpha\{X_A{}^\beta(\bar{S}_A{}^\beta - \bar{S}_A{}^\beta) + X_B{}^\beta(\bar{S}_B{}^\alpha - \bar{S}_B{}^\beta)\}} \qquad (9)$$

and

$$\left.\frac{\partial P}{\partial X_B{}^\alpha}\right)_T = \frac{(X_B{}^\alpha - X_B{}^\beta)\left.\frac{\partial\mu_B{}^\alpha}{\partial X_B{}^\alpha}\right)_{T,P}}{X_A{}^\alpha\{X_A{}^\beta(\bar{V}_A{}^\alpha - \bar{V}_A{}^\beta) + X_B{}^\beta(\bar{V}_B{}^\alpha - \bar{V}_B{}^\beta)\}} \qquad (10)$$

AN APPLICATION OF G-K RELATIONS

I. General Remarks and Discussion of Cases in Which $\partial\mu_B/\partial X_B{}^\alpha)_{T,P}$ Approaches Infinity

Equations (6) and (7) and (9) and (10) are of general validity for two-phase equilibria in binary systems. The relations are the differential equations of the curves which are the loci of the state points of two phase equilibria in T-X or P-X space, that is, the curves which appear on binary phase diagrams. An illustration of the application of Equations (6) and (9) to equilibrium between liquid and a congruently melting compound with a range of composition is given in Figure 2. The remainder of this article deals with the application of these equations to special cases (II to VI).

The second statement of the theorem follows immediately from Equation (6) and (7). If a transition occurs with changing composition then

$$(\partial T/\partial X_B{}^\alpha)_P \neq 0 \qquad (11)$$

and

$$(\partial P/\partial X_B{}^\alpha)_T \neq 0 \qquad (12)$$

and if there is no two-phase region,

$$X_B{}^\alpha - X_B{}^\beta = \Delta X_B = 0 \qquad (13)$$

Equations (9) to (13) are compatible only if $\Delta\bar{\bar{S}}$ and $\Delta\bar{\bar{V}}$ are zero, which is the criterion for higher order transitions. Stout's treatment of this subject (*15*) differs from the above both in approach and in conclusions drawn in that he assumes a higher order transformation and shows, from the vanishing of the coefficients of dT, dP, and $dX_B{}^\alpha$ [see Equation (5)], that the transformation must be congruent. Our approach is to note that a higher order transformation must be congruent to be meaningfully defined. We then use the G-K relations to show that the nonvanishing of the slope of a congruent transformation line implies a higher order transition.

The remainder of this discussion presents applications of the G-K relations more extensive than those extant in modern works (*12*), and demonstrates that the features of phase diagrams discussed elsewhere (*11*, *12*, *13*, and *18*) result from consideration of the G-K relations. The discussion which follows is primarily concerned with ap-

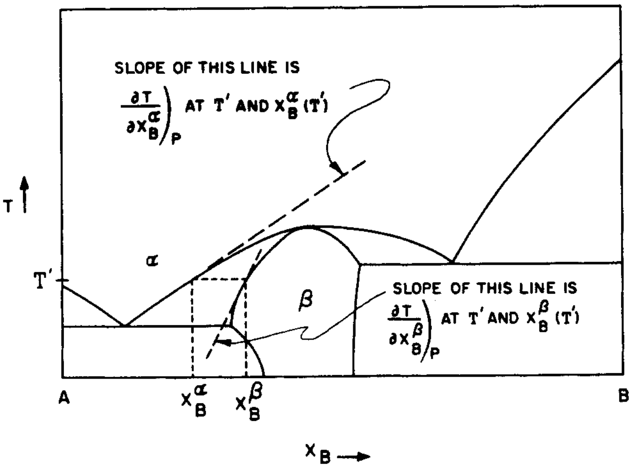

Fig. 2. A geometrical representation of the slopes of phase boundaries on a general binary phase diagram.

plication of the G-K relations to the nature of the upper bounds to the T-X curves in the various cases in which solid and liquid are in equilibrium.

The treatment is readily generalized to other condensed phase-condensed phase equilibria. The vaporization of a condensed phase will not be discussed at length. In the one simple case of the vaporization of a condensed phase in which the components obey Raoult's and Henry's laws, the G-K relations [Equations (7) or (10)] yield the mole fraction derivative of the pressure obtained directly from Raoult's and Henry's laws.

The first statement of the theorem follows immediately from Equation (9) if $(\partial\mu_B/\partial X_B{}^\alpha)_{T,P}$ is finite when $X_B{}^\alpha$ equals $X_B{}^\beta$; in this case the T-X and P-X curves are at extremums at this point. There are, however, three common cases in which $(\partial\mu_B/\partial X_B{}^\alpha)_{T,P}$ approaches infinity or is, for all practical purposes, infinite.

The first of these to be considered is the case of a solution in the limit of pure component A, in which A is an element, where

$$\lim_{X_B{}^\alpha\to 0} (\partial\mu_B/\partial X_B{}^\alpha)_{T,P} = \lim_{X_B\to 0} RT/X_B{}^\alpha = \infty \qquad (14)$$

The second case is that of a solution in the limit as the solution composition approaches the composition of a compound which is, for practical purposes, undissociated in the melt (for example, benzene but not brass). This may be seen as follows: let A and B be the components and AB_y (y not necessarily rational) the compound in a binary system. Let X_A and X_B be the *component* mole fractions of components A and B, and let N_A, N_B, and N_{AB_y} be the species mole fractions of species A, B, and AB_y, respectively. If AB_y is undissociated in the sense that N_{AB_y} is essentially unity when $X_B/X_A = y$ (for example, as with water at 0°C. in the hydrogen-oxygen system), then as the composition of the compound is approached from the B rich side

$$\lim_{X_B/X_A\to y} (\partial\mu_B/\partial X_B)_{T,P} = \lim_{N_B\to 0} (\partial\mu_B/\partial X_B)_{T,P}$$

and thus

$$\lim_{X_B/X_A\to y} \left.\frac{\partial\mu_B}{\partial X_B}\right)_{T,P} = \lim_{N_B\to 0} \left.\frac{\partial\mu_B}{\partial N_B}\right)_{T,P} \left.\frac{\partial N_B}{\partial X_B}\right)_{T,P} \qquad (15)$$

and the limit of $(\partial\mu_B/\partial N_B)_{T,P}$ is the product of the limits of the two terms on the right side of Equation (15). We evaluate each term on the right-hand side of Equation (15) independently. In the limit of Henry's law behavior of B in AB_y

$$\lim_{N_B\to 0} (\partial\mu_B/\partial N_B)_{T,P} = \lim_{N_B\to 0} RT/N_B = \infty \qquad (16)$$

hence $(\partial\mu_B/\partial X_B)_{T,P}$ becomes infinite unless $(\partial N_B/\partial X_B)_{T,P}$ goes to zero. To evaluate $(\partial N_B/\partial X_B)_{T,P}$ consider a solution of B in AB_y. By a mole balance

$$X_B = \frac{N_B + yN_{AB_y}}{1 + yN_{AB_y}} \qquad (17)$$

and hence

$$\left.\frac{\partial N_B}{\partial X_B}\right)_{T,P} = (1 + yN_{AB_y}) \qquad (18)$$

and

$$\lim_{N_B\to 0} (\partial N_B/\partial X_B)_{T,P} = (1 + y) \neq 0 \qquad (19)$$

Therefore

$$\lim_{X_B/X_A\to y} (\partial\mu_B/\partial X_B)_{T,P} = \infty \qquad (20)$$

Melting (or solution) in the above two cases can be treated similarly since, without loss of generality, the compound can be chosen as a component of a two component system. These cases are thus covered by the treatments of sections III and IV, which deal with equilibria between solid and liquid when the only species in the liquid are the components.

The third case in which $(\partial\mu/\partial X)_{T,P}$ is infinite is that of a pure compound which exhibits no solid solution, that is, a line compound. In this case the solidus line is vertical; hence $(\partial T/\partial X)_P$ of the solidus is infinite. Now, in general, a liquid which coexists in equilibrium with such a solid is of different composition than the solid, and the numerators of Equations (6) and (7) and, therefore, Equations (9) and (10) may be simply shown to be nonzero. Therefore, $(\partial\mu/\partial X)_{T,P}$ is infinite by Equation (9). An interesting point is that it then follows from the numerator of Equation (9) that if a line compound melts congruently, that is, at point P in Figure 3, the slope of the solidus is undefined. The liquidus in the case in which a line compound melts without and with dissociation is discussed in sections III and V, respectively.

II. Equilibrium Between Liquid and Solid Solution in the Region 0 $< X_B <$ 1

For a solution in which no compound is formed by the components, and in which μ_B is an analytic function of X_B, $(\partial\mu_B/\partial X_B)_{T,P}$ can be shown to remain finite at all compositions except at the compositions of pure components. Equation (9) then directly yields the result that in the case of solid solution–liquid solution equilibrium, the liquidus and solidus curves touch if, and only if, both have zero slope at all points of contact (*6, 10*). This statement applies also to solid solution–solid solution, solid solution–vapor, and liquid solution–vapor equilibria. In other words, subject to the restriction mentioned above, one directly obtains the well-known result that azeotropic boiling and congruent melting of solutions are extremum phenomena.

An example of melting behavior of this type is provided by the melting of scandium-yttrium alloys (*1*).

III. Pure Solid Component in Equilibrium with Liquid Solution in Which Solvent Obeys Raoult's Law

The equation of the liquidus is given in this case by the well-known expression for freezing point depression. The liquidus curve for a thorium-niobium solution in equilibrium with solid thorium appears to be one example of this type of common behavior (*4*).

The freezing point expression is shown to result from the consideration of the limiting behavior of Equation (9) as follows. Let α be a liquid solution of A and B in equilibrium with phase β, which is composed of pure solid A. If A obeys Raoult's law in α, then the denominator of Equation (9) can be evaluated by

$$X_A{}^\beta(\bar{S}_A{}^\alpha - \bar{S}_A{}^\beta) + X_B{}^\beta(\bar{S}_B{}^\alpha - \bar{S}_B{}^\beta) = (\bar{S}_A{}^\alpha - \bar{S}_A{}^\beta) \qquad (21)$$

and, the utilization of

$$\bar{S}_A{}^\alpha = \bar{\bar{S}}{}^A{}_{\text{liq}} - R \ln X_A{}^\alpha \qquad (22)$$

and

$$\bar{S}_A{}^\beta = \bar{\bar{S}}{}^A{}_{\text{solid}} \qquad (23)$$

yields

$$\bar{S}_A{}^\alpha - \bar{\bar{S}}_A{}^\beta = \bar{\bar{S}}{}^A{}_{\text{liq}} - \bar{\bar{S}}{}^A{}_{\text{solid}} - R \ln X_A{}^\alpha \qquad (24)$$

which, upon substitution into (9), yields

$$\left.\frac{\partial T}{\partial X_B{}^\alpha}\right)_P = -\frac{RT}{X_A{}^\alpha(\Delta H_f{}^A/T_f{}^A - R \ln X_A{}^\alpha)} \qquad (25)$$

where the usual assumption of the temperature independence of the heat of fusion (ΔH_f^A) has been made. Integration of Equation (25) and rearrangement yield

$$R \ln X_A^\alpha = \Delta H_f(1/T_f - 1/T) \qquad (26)$$

the usual freezing point depression expression.

IV. Equilibrium Between Solid Solution of Components and Liquid Solution of Components (No Decomposition of Components in the Melt)

In this section the freezing and melting behavior of liquid solid solutions will be considered. If solid solution occurs, the freezing point may be raised or lowered. An example of a system which behaves in this fashion is the germanium-silicon system (*14*) in which both the solid and liquid solutions are nearly ideal (*16*).

The application of the G-K relation [Equation (9)] to the case of regular solid solution–regular liquid solution equilibrium provides the equations for the curves such as obtained in this case. For a binary regular solution of A and B the chemical potential of B is given by

$$\mu_B = \mu_B^o + RT \ln X_B + X_A^2 w \qquad (27)$$

where $w\, X_A^2$ is the excess chemical potential. When Equation (27) is combined with (9) and standard thermodynamic relations, the equation

$$\left.\frac{\partial T}{\partial X_B^\alpha}\right)_P = - \frac{(X_B^\alpha - X_B^\beta)\ \left\{\dfrac{RT}{X_B^\alpha} - 2X_A^\alpha w\right\}}{X_A^\alpha \left\{ X_B^\beta \dfrac{\Delta H_f^B}{T_f^A} + X_A^\beta \dfrac{\Delta H_f^A}{T_f^A} - R \ln \left(\dfrac{X_A^\alpha}{X_A^\beta}\right)^{X_A^\beta} \left(\dfrac{X_B^\alpha}{X_B^\beta}\right)^{X_B^\beta} \right\}} \qquad (28)$$

results for the liquidus line. In obtaining Equation (28) the heats of fusion were assumed to be temperature independent. If X_A^β is unity and w is zero, then (28) reduces to (25).

Equation (28) relates the mole fraction of the components in the liquid and solid to the slope of the liquidus and the thermodynamic parameters, that is, it is possible, using (28), to determine the solidus from the liquidus if the heats and temperatures of fusion and w are known.

If the equilibrium constant K for the reaction

$$B(\text{in } \alpha) = B(\text{in } \beta)$$

is introduced into (28) and the equation is considered in the limit as X_B^α and X_B^β approach zero, that is, infinitely dilute solution of B in A, then

$$\lim_{X_B^\alpha, X_B^\beta \to 0} \left.\frac{\partial T}{\partial X_B^\alpha}\right)_P = \frac{R(T_f^A)^2}{\Delta H_f^A} \lim_{X_B^\alpha, X_B^\beta \to 0} (K - 1) \quad (29)$$

results. From Equation (29) it follows that if $K < 1$, then the melting and freezing points are depressed, and if $K > 1$, then the melting and freezing points are elevated.

In the ideal case Equation (28) reduces to

$$\left.\frac{\partial T}{\partial X_B^\alpha}\right)_P = \frac{RT^2(X_B^\beta/X_B^\alpha - X_A^\beta/X_A^\alpha)}{X_A^\beta\, \Delta H_f^A + X_B^\beta\, \Delta H_f^B} \qquad (30)$$

V. Pure Solid Component in Equilibrium with Liquid Solution in Which Dissociation Occurs

Previously a discussion was presented which covered the case of a line compound melting into a solution which contains molten compound plus some other component. In reality all compounds dissociate to some extent. This dissociation is in some cases (for example, water, benzene, carbon tetrachloride, etc.) negligible for experimental purposes at the melting point of the compound or below, and in these cases the treatment of section III applies. In some cases the dissociation is not negligible. An exceptionally clear case of melting behavior of this type is the melting of Ga(I) [Ga(III)I$_4$] (5). In general, compounds which melt with dissociation in the melt exhibit the type of behavior shown by compound C in Figure 3.

The equation of the liquidus in the neighborhood of the melting point is given by Equation (9). As before, consider the melting of AB_y and let X_A and X_B be the component mole fractions and N_A, N_B, and N_{AB_y} be the species mole fractions. As X_B/X_A approaches y, the composition of phase α approaches the composition of phase β; hence, the slope of the T-X curve approaches zero, again unless $(\partial\mu_B^\alpha/\partial X_B^\alpha)_{T,P}$ approaches infinity. By calculus

$$(\partial\mu_B^\alpha/\partial X_B^\alpha)_{T,P} = (\partial\mu_B^\alpha/\partial N_B^\alpha)_{T,P}\ (\partial N_B^\alpha/\partial X_B^\alpha)_{T,P} \quad (31)$$

In a solution in which B obeys Henry's law

$$(\partial\mu_B^\alpha/\partial N_B^\alpha)_{T,P} = RT/N_B^\alpha \qquad (32)$$

The terms of Equation (31) can be evaluated by a consideration of the equilibrium constant for the solution reaction

$$AB_y(\text{solid}) = AB_y(\text{solution})$$

Again by assuming Henry's law

$$K = N^\alpha{}_{AB_y} \qquad (33)$$

A mole balance and Equation (33) yield

$$X_B^\alpha = \frac{N_B^\alpha + yK}{1 + yK} \qquad (34)$$

which upon differentiation gives

$$(\partial N_B^\alpha/\partial X_B^\alpha)_{T,P} = 1 + yK \qquad (35)$$

If K at the congruent melting temperature is not unity, that is, if the compound is dissociated in the melt, then the species mole fraction of B is not zero and, by (32), $(\partial\mu_B^\alpha/\partial N_B^\alpha)$ remains finite, and, according to Equations (35) and (31), $(\partial\mu_B^\alpha/\partial X_B^\alpha)_{T,P}$ remains finite. Thus there is, in the case of congruent melting with dissociation in the melt, a maximum in the liquidus at the melting point of the compound.

On the other hand, if K is unity, then the results of section III apply and the limiting slope at the congruent melting point is constant on the B side of the compound and constant, with different value and different sign, on the A side of the compound. The slope at X_B/X_A equal to

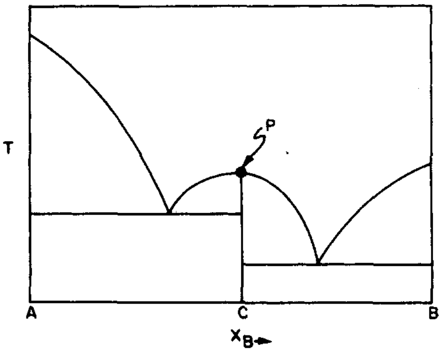

Fig. 3. Condition for maximum at point *P* is that the equilibrium constant for dissociation of compound C be nonzero.

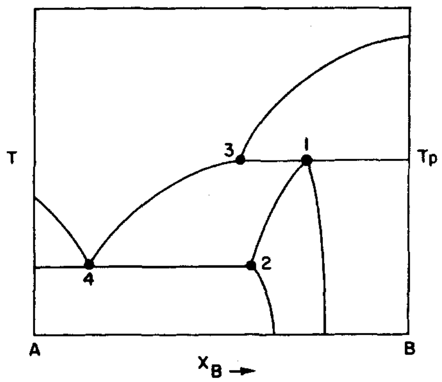

Fig. 4. Solidus at point 1 must have nonzero slope. Solidus at point 2 and liquidus at point 3 must have discontinuous slopes.

y is then undefined and the upper bound to the T-X curve is a singular point.

The nature of the T-X curve in the neighborhood of a congruent melting compound can be examined by means of the second derivative of the T-X curve. In the hypothetical case of a compound which melts without dissociation in the melt the second derivative is zero in the limit as compound composition is approached from either side. In the case of a compound which melts with finite dissociation, the second derivative is nonzero and negative.

VI. Behavior of Equilibrium Lines in the Neighborhood of Peritectic Processes

Peritectic decomposition, an example of which is a compound melting to form a liquid and a solid of different compositions, involves the equilibrium coexistence of three phases and is thus not properly described by the G-K relations. The values of the slopes of the peritectic solidus lines *in the neighborhood* of the decomposition temperature, however, involve two-phase equilibria. These values may therefore be obtained by a discussion of the limiting behavior as the temperature and composition approach the peritectic values. Similarly, the liquidus lines are subject to the constraints of binary equilibria and are thus appropriately discussed by means of the G-K relations.

We discuss peritectic behavior with reference to Figure 4. The solidus (phase) lines in the neighborhood of point 1 may be simply shown to have nonzero slope in the following manner: the equation of the solidus lines is again given by Equation (6). In the neighborhood of point 1, $\Delta X \neq 0$, $\mu_B{}^\alpha$ is a monotune increasing function of $X_B{}^\alpha$ *(17)*, and $\Delta\bar{\bar{S}} \neq \infty$. Therefore $(\partial T/\partial X_B{}^\alpha)_p \neq 0$. The behavior of the liquidus in the neighborhood of point 3 may be similarly discussed. For $T > T_p$, the slope is governed by the equilibrium is between liquid and pure component B. For $T < T_p$ the slope of the liquidus is determined by the equilibrium between liquid and peritectically melting compound. Since clearly all terms in Equation (6) are discontinuously different for $T > T_p$ and $T < T_p$, the slope of the liquidus must generally suffer a discontinuity at $T = T_p$. A similar comment applies at point 2, and to the liquidus lines in the neighborhood of the eutectic at point 4.

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NOTATION

A,B = components
$\Delta H_f{}^A$ = enthalpy of fusion of pure A
K = equilibrium constant
N_i = mole fraction of i^{th} species
P = pressure
R = gas constant
$\Delta\bar{\bar{S}}$ = difference between molar entropies of two phases
$\bar{\bar{S}}^\alpha$ = molar entropy of phase α
$\bar{S}_i{}^\alpha$ = partial molar entropy of i^{th} component in phase α
T = absolute temperature
$T_f{}^A$ = melting point of pure A
$\Delta\bar{\bar{V}}$ = difference between molar volumes of two phases
$\bar{\bar{V}}^\alpha$ = molar volume of phase α
$X_i{}^\alpha$ = mole fraction of i^{th} component in phase α
X_B = overall mole fraction of B
y = stoichiometry number
$\mu_i{}^\alpha$ = chemical potential of i^{th} component in phase α
ω = interaction parameter in regular solution theory

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