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The Calculation of the Compositions of Phases in Equilibrium

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The Gibbs method¹ of calculation of the compositions of two phases of a two-component system which are in equilibrium is to plot at constant pressure and temperature the Gibbs free energy ($E - TS + PV$) per unit quantity of the system against the fraction of one component in the system for each of the phases, with the same standard states for each phase. A common tangent indicates equilibrium, and the compositions of the two phases are given by the points of tangency. This method is excellent for illustrative purposes, but it has the disadvantage for quantitative calculations that it is difficult to determine the points of tangency accurately, especially if the fraction of either component is small, because the slope of the curves is infinite for zero fraction of either component.

The method of Seltz² is to plot first the activity of each component against the mole fraction with the same standard state for each phase. If the composition of one phase is plotted against the composition of the other phase for which the activity of the first component is the same, and is also plotted against the composition of the other phase for which the activity of the second component is the same, the two curves will intersect at the equilibrium compositions. Seltz increases the accuracy of the method by plotting the difference in compositions of the two phases, instead of the composition of the first phase itself, against the composition of the second phase. The accuracy of this method is limited only by the accuracy with which the activities are known, or, if these are given analytically, by the patience of the computer. However, the determination of each point on the final curve requires the reading of a point on each of two other curves, so that the attainment of high accuracy becomes tedious.

The following method is as accurate as that of Seltz, and considerably simpler and more direct.³

(1) J. Willard Gibbs, "Collected Works," Longmans, Green & Co., New York, N. Y., 1906, p. 118.

(2) H. Seltz, THIS JOURNAL, **56**, 307 (1934); **57**, 391 (1935). For the application of these two methods, see G. Scatchard and W. J. Hamer, *ibid.*, **57**, 1805, 1809 (1935).

(3) This method was developed by analogy to Slater's method of plotting free energy *versus* pressure for two phases of a one-component system, and determining equilibrium by the intersection of the two stable branches (J. C. Slater, "Introduction to Chemical Physics," McGraw-Hill Book Company, Inc., New York, N. Y., 1939, pp. 187-188).

It is to plot for each phase at constant temperature and pressure the chemical potential, or the activity, of one component against the same property of the other component, with the same standard states for each phase. An intersection locates an equilibrium point since the potential, or activity, of each component is the same in the two phases. If the thermodynamic functions are plotted against the composition for the region near this intersection, the two activities, or chemical potentials, give two check determinations of the equilibrium composition. For the survey of the whole range, the activity has the advantage that its change is only from a number of the order of unity to zero, whereas the chemical potential goes to minus infinity. For the exact location of an intersection it sometimes saves computation to use the common logarithm of the activity, which is the chemical potential divided by $2.3RT$.

If the standard states are the two components in the same state of aggregation as the mixture, the activity-activity plot for an ideal solution is a straight line, $a_1 + a_2 = 1$. Negative deviations from Raoult's law lead to curves nearer the origin and positive deviations lead to curves further from the origin. If the components are not completely miscible, there are two intersecting stable branches and an unstable branch connecting two cusps, just as in the free energy-pressure plot for a one component system. The limit of absolute immiscibility is represented by the two straight lines $a_1 = 1$ and $a_2 = 1$, with the unstable branch entirely at infinity.

Figure 1 shows a_1 *versus* a_2 , and Fig. 2 shows a_1 and a_2 *versus* x for a series of mixtures for which

$$\log a_1 = \log x + B[1 - x/(2 - x)]^2 \quad (1)$$

$$\log a_2 = \log (1 - x) + 2B[x/(2 - x)]^2 \quad (2)$$

Reading any set of curves from top to bottom, B is $2/3$, $1/2$, 0 , $-2/3$. These curves correspond to the simple theory of non-polar mixtures⁴ with the molal volume of the second component twice that of the first. For these equations, critical mixing occurs when $B = 0.565$, $x = 0.732$, $a_1 = 0.924$ and $a_2 = 0.638$.

If there is a second phase in a different state of

(4) G. Scatchard, *Chem. Rev.*, **8**, 321 (1931).

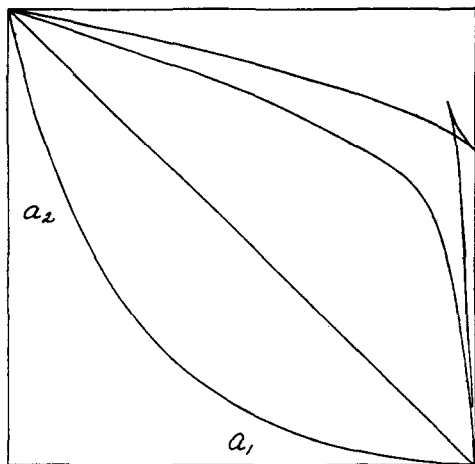


Fig. 1.—Activity-activity curves for a single state of aggregation.

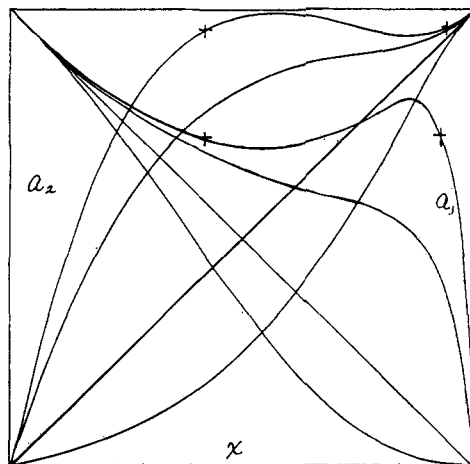


Fig. 2.—Activity-mole fraction curves for a single state of aggregation.

aggregation, the activity of a pure component will be unity in this second state only at the transition temperature. We will designate the state of higher energy, which is stable at higher temperatures, with primes and let the activity of each pure component in that state be unity at each temperature. We will let the unprimed symbols refer to the phase of lower energy, and designate the activity of a pure component in that state with a superscript zero. Then

$$\log a_1^0 = \int_{\theta=T_1}^T (\Delta H_1/2.3R\theta^2)d\theta \quad (3)$$

in which T is the temperature at which a_1^0 is determined, T_1 is the temperature of transition, and ΔH_1 is the enthalpy change for the transition of one mole. If this enthalpy is independent of the temperature

$$\log a_1^0 = (\Delta H_1/2.3RT) (1/T_1 - 1/T) \quad (4)$$

In what follows we will speak of the state of lower energy as the solid, that of higher energy as the liquid, and the transition as melting, for this is the combination which is most often encountered. The whole discussion may be made more general, however, merely by using the more general language of this paragraph.

If the solid is the first component pure, the corresponding curve will be $a_1 = a_1^0$, a straight line parallel to the a_2 axis. There are some who claim that this limit of a pure phase can never be reached in equilibrium with a mixture, but that the second component is always soluble to a finite extent. If there is a slight solubility, the lines will not be exactly parallel to the axis, but a_1 will decrease slightly as a_2 increases. The ques-

tion of practical importance is whether the difference between a_1 and a_1^0 is greater than the error of determining either. If the difference between a_1 and a_1^0 can be ignored, there results the familiar freezing point curve, which can more conveniently be calculated directly.

If the solid is a compound of ν_1 molecules of the first component with ν_2 molecules of the second,

$$a_1^{\nu_1} a_2^{\nu_2} = K_c = K_c^0 \exp \int_{\theta=T_c}^T (\Delta H_c/R\theta^2)d\theta \quad (4)$$

in which T_c is the melting point of the compound and ΔH_c is its enthalpy of melting per mole. $K_c^0 = (a_1^{\nu_1} a_2^{\nu_2})$ at T_c and $x = \nu_1/(\nu_1 + \nu_2)$. If the components are slightly soluble in the compound, there will be very little change in the activity-activity curve, but the activity-composition curves for the compound will be altered from perpendicular lines at $x = \nu_1/(\nu_1 + \nu_2)$ to very steep lines near this abscissa, always obeying approximately the relation $a_1^{\nu_1} a_2^{\nu_2}$ is equal to $K_c x/x_c$ or to $K_c(1-x)/(1-x_c)$, whichever is smaller than K_c . The limit of zero solubility of a component in a compound has the same status as that of zero solubility of one component in the other, which is discussed above, and the important practical question is whether the difference between $a_1^{\nu_1} a_2^{\nu_2}$ and K_c is greater than the error of determining either.

Figure 3 gives the curve corresponding to equations (1) and (2) with $B = -2/3$ as a full line, and those corresponding to a_1 equal to 0.5, 0.45 and 0.4 and for $a_1 a_2$ equal to 0.90, 0.81 and 0.72 as broken lines. Although it is very probable that the parameter B decreases with increasing tem-

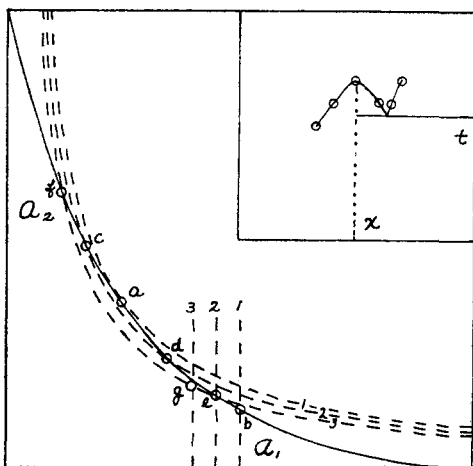


Fig. 3.—Activity-activity curves showing compound and pure component in one state.

perature, the change need not be great, and this diagram may be taken as three diagrams condensed in one to represent the equilibrium at three temperatures between a liquid and two solid phases, the first component pure and the equimolar compound. The full line belongs to each of these diagrams, but a broken line belongs only to the diagram corresponding to its number. In the first group the compound curve is just tangent to the liquid curve at *a*, which corresponds to the maximum in the equilibrium diagram; the liquid curve intersects the solid component line at *b* so that this temperature is well below the melting point of the first component; if the diagram is complete, all the temperatures illustrated are above the melting point of the second component. The second group of curves shows equilibrium of the liquid with the compound at *c* and at *d*, and with the first component at *e*; the fact that the third compound curve intersects the second solid component curve near *e* has no significance for they belong to different diagrams. The third group shows equilibrium between the liquid and the compound at *f*, and between the compound and the solid component at *g*. It is obvious that there is a eutectic at a temperature about midway between those represented by groups two and three. The insets in this figure and the two which follow show the derived temperature-composition equilibrium diagrams. The circles are the points determined by the intersections, also marked by circles, in the corresponding activity-activity diagrams.

In Fig. 4 the full curve represents equations (1) and (2) with $B = \frac{2}{3}$ and the broken lines rep-

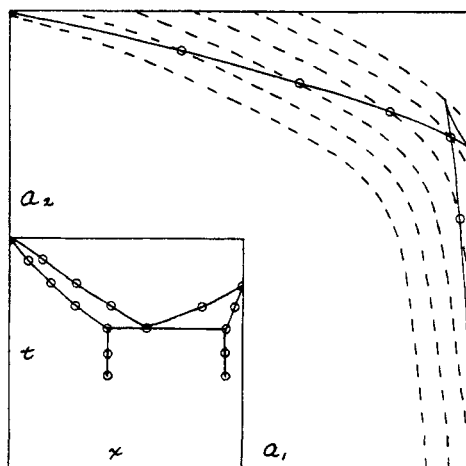


Fig. 4.—Activity-activity curves showing eutectic.

resent these equations with $B = \frac{1}{2}$ and with $a_1^0 = 0.9 a_2^0$ and a_2^0 equal to 1.00, 1.05, 1.10, 1.15, 1.20 and 1.25, successively. If we take as unity the activities of the pure components in the solid rather than in the liquid, this diagram corresponds to the solid line for the solid state and the broken lines for the liquid state, each at a different temperature, except that the B 's are again regarded as independent of the temperature. The first curve is at the melting point of the second component and, as the temperature decreases, the activity of the second component in the equilibrium solutions decreases. The first three broken lines represent temperatures above the melting point of the first component. The fourth curve shows two pairs of solutions in equilibrium, and the fifth shows a eutectic in which one liquid is in equilibrium with two solid phases. The sixth curve shows two solid phases in equilibrium, but no stable liquid phase.

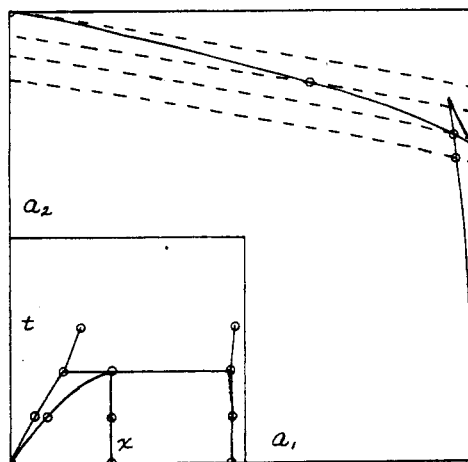


Fig. 5.—Activity-activity curves showing peritectic.

Figure 5 shows the same full curve and the same value B for the broken curve as in Fig. 4. Here, however, $a_1^0 = 0.5 a_2^0$ and a_2^0 is 1.00, 0.95, 0.90 and 0.85. The first is again at the melting point of the pure second component, and the other broken curves represent higher temperatures, but all below the melting point of the first component. The second shows equilibrium between the liquid and the solid phase richer in the second component, the fourth shows equilibrium between the liquid and the solid phase poorer in the second component, while the third shows one liquid in equilibrium with both solid phases at a peritectic point.

From Figs. 4 and 5 we may see that on the temperature-composition diagram the lines of two-phase equilibrium will start downward from the melting point of the second component if the negative of the slope of the a_2 versus a_1 curve— $-da_2/da_1$ is greater for the liquid than for the solid, and that the equilibrium lines will start upward if $-da_2/da_1$ is less for the liquid than for the solid. Since the solutions obey both Raoult's law and Henry's law at the limit of the pure second component, the limit of $-da_2/da_1$ is $1/k_1 a_1^0$ and that of da_2'/da_1' is $1/k_1'$, if k_1 and k_1' are the Henry's law constants in the solid and in the liquid and $a_1^{0'}$ is again taken as unity. So the equilibrium curves will start downward if $k_1 a_1^0$ is greater than k_1' . This will occur even when a_1^0 is less than unity, that is, below the melting point of the first component, if k_1 is enough greater than k_1' , that is if the deviations from Raoult's law are enough more positive in the solid than in the liquid. Such a behavior leads to a minimum in the equilibrium diagram which may be a eutectic. If a_1^0 is greater than unity, but the deviations in the solid are enough more negative than in the liquid to make $k_1 a_1^0/k_1'$ less than unity, there will be a maximum in the equilibrium diagram.

Similarly at the triple point, if $-da_2/da_1$ for the liquid lies between those for the two solid phases, there will be a peritectic, if it does not there will be a eutectic, but it is not so simple to relate this condition to the deviations from Raoult's law. The change from peritectic to eutectic must come when the composition of the liquid is

the same as that of one of the solid phases. Although the component present in greater quantity may possibly have deviations from Raoult's law greater in a phase where there is complete miscibility than in a phase of the same composition in a state of aggregation in which miscibility is incomplete, such a relation is certainly highly improbable. The usual change would then occur when the activity of the pure component is greater than unity in the pure liquid, that is, at a temperature below the melting point of the pure component, and there should be a range of peritectic temperatures, probably both below and above the melting point, for systems which also have a minimum equilibrium temperature.

Even with systems which follow simple equations like (1) and (2), the possible variety of behavior is very great. If the volumes, the melting points and the heats of melting are known for the pure components and for any compounds, however, this variety is greatly reduced, as only one parameter for each phase is left undetermined. One of the great advantages of the use of analytical expressions for the chemical potentials or the activities is to determine which equilibrium curves correspond to simple behavior, and they are often not the ones which are themselves simplest geometrically. It is hoped that the present method is simple and easy enough to apply so that equilibrium curves corresponding to simple equations for the chemical potentials will be used much more often as a check upon experimental measurements.

Summary

The compositions of two phases of a binary system which are in equilibrium may be conveniently determined by plotting for each phase the activity, or the chemical potential, of one component against the same property of the other component, with the same standard for each state of aggregation. At equilibrium the two curves intersect. The corresponding compositions may be determined from an auxiliary plot of either activity, or chemical potential, against composition. The application of this method to several typical systems is illustrated.