

9

Nonideal Solutions

If you're not part of the solution, you're part of the precipitate.

Harry J. Tillman

Nonideal solutions are described by activity coefficients referred to either the ideal solution or the ideally dilute solution. Activity coefficients may be determined from partial pressures and distribution coefficients. Often, the activity coefficient of the solvent is determined from a colligative property, and that of the solute by integrating the Gibbs–Duhem equation, most conveniently by using the osmotic coefficient. Liquid–vapor-phase diagrams of nonideal systems can show maximum or minimum boiling-point azeotropes. Liquids may be partially miscible. Solids can form solid solutions and compounds, which may melt congruently or incongruently. Ternary systems can be described by triangular phase diagrams.

9.1 Activity Coefficients

Unlike the model of the ideal gas, which is an accurate representation of the behavior of real gases under usual laboratory conditions, both the ideal solution

and ideally dilute solution models have limited practical applicability. The ideal solution model provides sufficient accuracy to describe real solutions only in very special cases. These are solutions in which the components are very similar in size, shape, and interaction with one another. The ideally dilute solution model, on the other hand, although applicable to all solutions, has practical use only at very low concentrations, where solutes only interact with surrounding solvent molecules. In fact, for the case of ions in solution, interactions between charged particles extend to such a large separation that the ideally dilute solution is not useful under almost all conditions. Both the ideal and ideally dilute solution models, however, provide particularly simple forms for the variation of the thermodynamic properties of solutions with concentration. In our discussion of real solutions, we will maintain this simple form for these variations.

Because all thermodynamic functions can be obtained from the chemical potential, we will concentrate on maintaining the form of μ . In Eq. (47) of Chapter 6, the chemical potential was expressed in terms of activity as

$$\mu = \mu^0 + RT \ln a \quad (1)$$

In both the ideal and the ideally dilute solution models, the activity can be set equal to the mole fraction, $a = x$, for all components. In order to maintain the form of Eq. (1) for real solutions, we define an *activity coefficient*, γ , so that

$$a = \gamma x \quad (2)$$

$$\mu = \mu^0 + RT \ln \gamma x \quad (3)$$

holds for all components of a solution. The value of γ depends on that for μ^0 , the chemical potential in the standard state. The two references used for comparison with the properties of real solutions are the ideal solution and the ideally dilute solution.

When the ideal solution is used as the reference for real solutions, thermodynamic properties are designated by (RL) for *Raoult's law reference*. This reference is often used in solutions in which all solutes are liquids at the temperature of interest, especially when the compositions of components are varied over a considerable range. In this case, for every component, we write Eq. (3) as

$$\mu_i(\text{RL}) = \mu_i^* + RT \ln \gamma_i x_i \quad (4)$$

(i.e., the chemical potential in the standard state is that of the pure component). Because the solution approaches pure i as $x_i \rightarrow 1$,

$$\gamma_i(\text{RL}) \rightarrow 1 \quad \text{as } x_i \rightarrow 1 \quad (5)$$

At other concentrations, deviations of $\gamma_i(\text{RL})$ from unity measure deviations of the solutions from ideal behavior.

When the ideally dilute solution is used as the reference for real solutions, thermodynamic properties are designated by (HL) for *Henry's law reference*. This reference is always used when some components are not liquids at the temperatures employed and may also be used if they are all liquids, but only very dilute solutions are being considered. For this reference, we treat the solvent in the same manner as for the (RL) reference:

$$\mu_A(\text{HL}) = \mu_A^* + RT \ln \gamma_A x_A \quad (6)$$

with

$$\gamma_A \rightarrow 1 \quad \text{as } x_A \rightarrow 1 \quad (7)$$

For the solutes in the (HL) reference, we compare behaviors with that in the infinitely dilute solution ($x_i \rightarrow 0$, $x_A \rightarrow 1$):

$$\mu_i(\text{HL}) = \mu_i^0 + RT \ln \gamma_i x_i \quad (8)$$

with

$$\gamma_i \rightarrow 1 \quad \text{as } x_i \rightarrow 0 \quad (9)$$

The standard state for solutes in the (HL) reference is therefore the hypothetical state of pure solute ($x_i = 1$), but with solute molecules interacting only with solvent molecules ($\gamma_i = 1$). Practically, chemical potentials in the standard state are obtained by making measurements at very low concentrations and extrapolating them to $x_i = 1$, assuming that Henry's law continues to hold to this concentration. At nonzero concentration of solutes, activity coefficients in the (HL) reference measure deviations of the solution from ideally dilute behavior.

Activities in the (HL) reference are more usually expressed in terms of molality:

$$a_i = \gamma_{m,i} m_i \quad (10)$$

$$\mu_i(\text{HL}) = \mu_{m,i}^0 + RT \ln \gamma_{m,i} m_i \quad (11)$$

with

$$\gamma_{m,i} \rightarrow 1 \quad \text{as } m_i \rightarrow 0 \quad (12)$$

Alternatively, molarity can be used:

$$a_i = \gamma_{c,i} c_i \quad (13)$$

$$\mu_i(\text{HL}) = \mu_{c,i}^0 + RT \ln \gamma_{c,i} c_i \quad (14)$$

with

$$\gamma_{c,i} \rightarrow 1 \quad \text{as } c_i \rightarrow 0 \quad (15)$$

The standard states for the solute in these expressions are the hypothetical state of 1.0 *m* or 1.0 *M*, respectively, but with solute molecules interacting only with

solvent molecules at these concentrations. In both Eqs. (11) and (14), it is the numerical value of the molality or molarity of the solution that is used, because it is not permissible to take the logarithm of quantities with units. At higher concentrations, the activity coefficients in Eqs. (11) and (14) contain a contribution from the nonproportionality of molality and molarity to mole fraction [see Eqs. (4) and (5) of [Chapter 8](#), as well as that due to the system not following the ideally dilute law [Eq. (43) of Chapter 8].

9.2 Excess Thermodynamic Functions

An alternative way of expressing the deviation from ideal solution behavior is by means of excess thermodynamic functions. These are defined as the difference between a thermodynamic property of a solution and the thermodynamic property it would have if it were an ideal solution:

$$X^E = X - X^{\text{id}} \quad (16)$$

Adding and subtracting the thermodynamic property for the unmixed components,

$$X^E = (X - \sum_i n_i X_{m,i}) - (X^{\text{id}} - \sum_i n_i X_{m,i}) = \Delta_{\text{mix}} X - \Delta_{\text{mix}} X^{\text{id}} \quad (17)$$

Thus, an excess thermodynamic property is also the difference between the thermodynamic property for mixing the real and ideal solutions. For the Gibbs free energy, this becomes, using Eq. (3) and Eq. (35) of Chapter 8,

$$G^E = RT \sum_i n_i \ln \gamma_i x_i - RT \sum_i n_i \ln x_i = RT \sum_i n_i \ln \gamma_i = H^E - TS^E \quad (18)$$

where the (RL) reference is used. Because $\Delta_{\text{mix}} H^{\text{id}} = \Delta_{\text{mix}} V^{\text{id}} = 0$,

$$H^E = \Delta_{\text{mix}} H \quad (19)$$

$$V^E = \Delta_{\text{mix}} V \quad (20)$$

In the usual manner, we can show that

$$H^E = \left(\frac{\partial(T^{-1} G^E)}{\partial T^{-1}} \right)_{P,x} \quad (21)$$

$$S^E = - \left(\frac{\partial G^E}{\partial T} \right)_{P,x} \quad (22)$$

$$V^E = \left(\frac{\partial G^E}{\partial P} \right)_{T,x} \quad (23)$$

9.3 Determining Activity Coefficients

9.3.1 Activity Coefficients from Partial Pressures of Vapors

Because activities, activity coefficients, chemical potentials, and partial pressures are all measures of escaping tendency, one of the most straightforward ways of measuring activity coefficients is by measuring partial pressures of vapors in equilibrium with solutions. We will assume that the vapors may be treated as ideal gases, because deviations from ideal behavior are generally much smaller in gases than in solutions. Equating the chemical potential of a component of the vapor in equilibrium with a solution with that of the component in the solution, we have for the (RL) reference state

$$\mu_i(\text{RL}) = \mu_{i,l}^* + RT \ln \gamma_i x_i = \mu_{i,g} = \mu_{i,g}^0 + RT \ln(P_i/P^0) \quad (24)$$

Doing the same for the pure component,

$$\mu_{i,l}^* = \mu_{i,g}^0 + RT \ln(P_i^*/P^0) \quad (25)$$

Combining these two equations gives

$$RT \ln \gamma_i x_i = RT [\ln(P_i/P^0) - \ln(P_i^*/P^0)] \quad (26)$$

or

$$\gamma_i = \frac{P_i}{x_i P_i^*} \quad (27)$$

In other words, the activity coefficient is just the ratio of the partial pressure of the component to the partial pressure expected if the solution were ideal.

In Fig. 1, the partial pressures of two different nonideal solutions are contrasted with ideal behavior ($P_i = x_i P_i^*$), shown as the central straight line. In the upper curve, the partial pressure is greater than an ideal solution. This is called *positive deviation* from ideal behavior and gives an activity coefficient greater than unity, and, from Eq. (1), an activity greater than the mole fraction. This behavior gives a positive contribution to the excess Gibbs free energy. Positive deviation for a component results when it feels less attraction to molecules of other components of the solution than it does to molecules of itself. In the lower curve, representing *negative deviation* from ideal behavior, the escaping tendency of the component is lower than in the ideal solution, and this is indicated by $P_i < x_i P_i^*$, $\gamma_i < 1$, $a_i < x_i$, and a negative contribution to the excess Gibbs free energy. It is noteworthy that as $x_i \rightarrow 1$, both the lower and upper curves become tangent to the line representing ideal solution behavior, because in

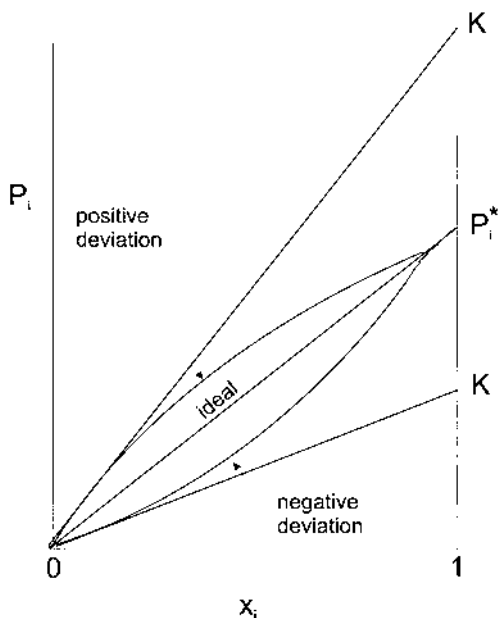


Figure 1 Positive and negative deviations for ideal behavior.

a practically pure liquid, molecules interact predominantly with similar molecules.

Example 1. Partial pressures of chloroform and acetone solutions (in torr at 35.2°C) above a solution of these components are given below. Calculate the Raoult's law reference activity coefficients for each component at each composition.

x_{chl}	0	0.060	0.184	0.263	0.361	0.424	0.508	0.581
P_{chl}	0	9	32	50	73	89	115	140
P_{Ac}	345	323	276	241	200	174	138	109
x_{chl}	0.662	0.802	0.918	1.00				
P_{chl}	170	224	266	293				
P_{Ac}	79	38	13	0				

(Data from JH Hildebrand, RL Scott. Solubilities of Nonelectrolytes. New York: Reinhold, (1950, p 181.) These original data are plotted in [Fig. 2](#).

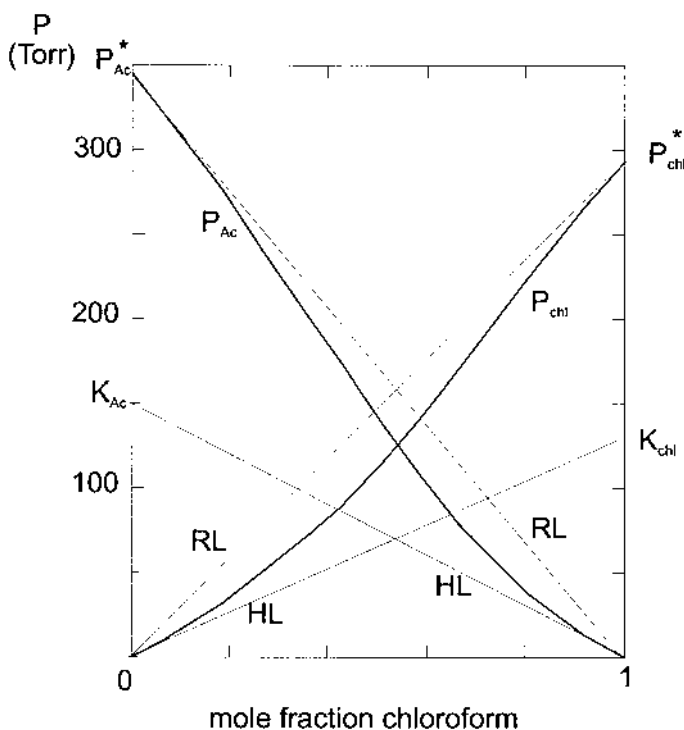


Figure 2 Acetone–chloroform solution partial pressures.

Solution: We use Eq. (27) for both components. A sample calculation is

$$x_{chl} = 0.424, \quad x_{Ac} = 1 - 0.42 = 0.576$$

$$\gamma_{chl}(\text{RL}) = \frac{89}{0.424(293)} = 0.72$$

$$\gamma_{Ac}(\text{RL}) = \frac{174}{0.576(345)} = 0.87$$

The results are plotted in Fig. 3. As can be seen, with the Raoult's law reference, the acetone–chloroform system shows negative deviation from ideal behavior. This is unusual and is due to there being some tendency to form hydrogen bonds between acetone and chloroform. Note that as the system approaches either of the pure components, the vapor-pressure curve of that component becomes tangent to its Raoult's law line.

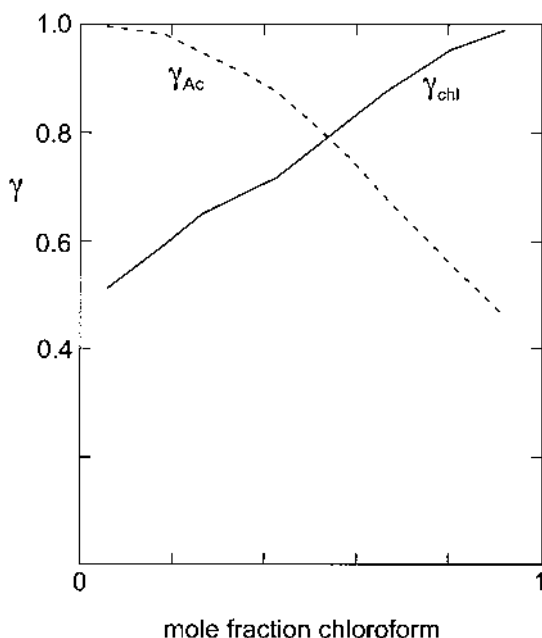


Figure 3 Acetone–chloroform solution Raoult's law activity coefficients: solid curve: γ_{chl} ; dashed curve: γ_{Ac} .

For the (HL) reference state, the chemical potential of the solvent is the same as in the (RL) reference state, so that Eq. (27) holds for the solvent. For solutes, with the (HL) reference state, we have

$$\mu_i(\text{HL}) = \mu_{i,l}^0 + RT \ln \gamma_i x_i = \mu_{i,g} = \mu_{i,g}^0 + RT \ln(P_i/P^0) \quad (28)$$

or

$$\exp\left(\frac{\mu_{i,l}^0 - \mu_{i,g}^0}{RT}\right) = \frac{P}{P^0 \gamma_i x_i} \quad (29)$$

Using Eq. (49) of [Chapter 8](#),

$$\gamma_i = \frac{P}{K_i x_i} \quad (30)$$

In other words, the activity coefficient is just the ratio of the partial pressure of the component to the partial pressure expected if Henry's law held to the concentration of interest. In order to use Eq. (30), the Henry's law constant for the particular solute–solvent combination is needed. This can be obtained from vapor

pressure measurements on solutions dilute enough so that γ_i can be taken as unity.

Example 2. Using Fig. 2, what is the Henry's law constant treating acetone as the solute and what is the Henry's law constant treating chloroform as the solute? Calculate Henry's law reference activity coefficients for both of these cases.

Solution: The Henry's law constants are found by drawing the tangent lines to the vapor-pressure curves and measuring their slopes. Because these lines begin at the origins ($x_i = 0$ and $P_i = 0$), the slopes are just the intercept with the $x_i = 1$ axis, or from Fig. 2, $K_{Ac} = 150$ torr and $K_{chl} = 140$ torr. The accuracy of this procedure is limited by how well the initial slopes can be determined from limited data. (See Problem 6.)

A sample calculation of the Henry's law reference activity coefficients is

$$x_{chl} = 0.424, \quad x_{Ac} = 1 - 0.42 = 0.576$$

$$\gamma_{chl}(\text{RL}) = \frac{89}{0.424(140)} = 1.50$$

$$\gamma_{Ac}(\text{RL}) = \frac{174}{0.576(150)} = 2.01$$

The Henry's law reference activity coefficients are plotted in Fig. 4. Note that this system shows positive deviation with respect to the ideally dilute behavior of Henry's law.

9.3.2 Activity Coefficients from Distribution Coefficients

When a solute is distributed at equilibrium between two solvents, its vapor pressure, which is a measure of its escaping tendency, must be equal above the two solvents:

$$P_i = \gamma_1 K_1 x_1 = \gamma_2 K_2 x_2 \quad (31)$$

The distribution coefficient is then

$$K_{12} \equiv \frac{x_1}{x_2} = \frac{\gamma_2 K_2}{\gamma_1 K_1} \quad (32)$$

This result holds even if the partial pressure of the solute above the solvents is immeasurably small.

Example 3. K_{12} of I_2 between glycerine and CCl_4 (x_{gly}/x_{CCl_4}) is 0.50 at $x_{gly} = 0.0001$ and is 0.40 at $x_{gly} = 0.002$. Assuming that both solutions are ideally dilute at the lower concentration and that the

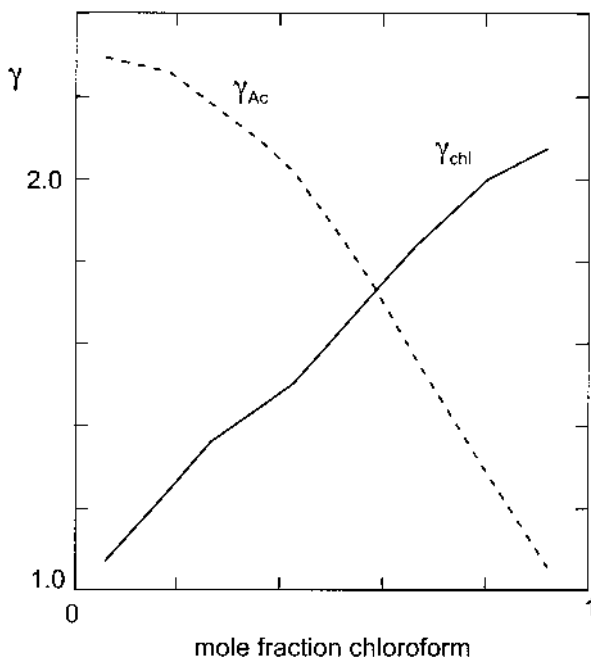


Figure 4 Acetone–chloroform solution Henry’s law activity coefficients: solid curve for chloroform with acetone as the solvent, dashed curve for acetone with chloroform as the solvent.

CCl_4 solution is also ideally dilute at the higher concentration, find γ_{gly} at $x_{\text{gly}} = 0.002$.

Solution: At $x_{\text{gly}} = 0.0001$, both solutions are ideal so $K_{\text{CCl}_4}/K_{\text{gly}} = 0.50$. At $x_{\text{gly}} = 0.002$, $0.40 = (1/\gamma_{\text{gly}})0.50$, where $\gamma_{\text{gly}} = 0.50/0.40 = 1.25$.

Note that if there is some mutual solubility of the two solvents, activity coefficients measured by this method are actually for solvents which are the dilute solutions of one of the solvents in the other.

9.3.3 Activity Coefficients from Colligative Properties

The phenomena of freezing-point depression, boiling-point elevation, and osmotic pressure all result from the reduction in the escaping tendency of solvent in a solution due to the addition of solute. They can all be used to determine the activity of the solvent. For example, as long as pure solvent freezes out of the

solution, Eq. (55) of [Chapter 8](#) for the freezing point of a solution holds and can be rearranged to

$$\gamma_A = \frac{1}{x_A} \exp \left[\frac{\Delta_{\text{fus}} H^*}{R} \left(\frac{1}{T_f^*} - \frac{1}{T_f} \right) \right] = \frac{1}{x_A} \exp \left(- \frac{\Delta_{\text{fus}} H^* \theta_f}{R(T_f^*)^2} \right) \quad (33)$$

Likewise, if only the solvent in the solution is volatile, Eq. (56) of Chapter 8 for the boiling point of a solution holds and can be rearranged to

$$\gamma_A = \frac{1}{x_A} \exp \left[\frac{\Delta H_{\text{vap}}^*}{R} \left(\frac{1}{T_b} - \frac{1}{T_b^*} \right) \right] = \frac{1}{x_A} \exp \left(- \frac{\Delta H_{\text{vap}}^* \theta_b}{R(T_b^*)^2} \right) \quad (34)$$

Finally, if only the solvent passes through a semipermeable membrane, Eq. (58) of Chapter 8 holds and can be rearranged to

$$\gamma_A = \frac{1}{x_A} \exp \left(- \frac{\Pi V_m^*}{RT} \right) \quad (35)$$

Example 4. The freezing point of a 20% by weight aqueous solution of ethanol is 10.92°C. What is the activity coefficient of water in this solution?

Solution:

$$x_A = 80 \text{ g} \frac{\text{mol}}{18 \text{ g}} \left(80 \text{ g} \frac{\text{mol}}{18 \text{ g}} + 20 \text{ g} \frac{\text{mol}}{46 \text{ g}} \right)^{-1} = 0.911$$

From Eq. (64) of Chapter 8 and [Table 1](#) of Chapter 8, we have, for water,

$$\frac{R(T_f^*)^2}{\Delta_{\text{fus}} H^*} = \frac{1.86 \text{ K kg}}{\text{mol}} \frac{\text{mol}}{0.018 \text{ kg}} = 103 \text{ K}$$

From Eq. (33),

$$\gamma_A = \frac{1}{0.911} \exp \left(- \frac{10.92 \text{ K}}{103 \text{ K}} \right) = 0.987$$

9.3.4 Activity Coefficient of the Solute from That of the Solvent

Quite often, the solute in a solution is not volatile and, thus, its escaping tendency cannot be directly measured. However, in a *binary* solution, changes in the escaping tendency of the solute and solvent are related by the Gibbs–Duhem

equation [Eq. (15) of [Chapter 8](#)], which, when written for partial molar Gibbs free energies (chemical potentials), becomes (at constant temperature)

$$n_A d\mu_A + n_B d\mu_B = n_A RT d \ln a_A + n_B RT d \ln a_B = 0 \quad (36)$$

or

$$n_A \left(d \ln \gamma_A + \frac{dx_A}{x_A} \right) + n_B \left(d \ln \gamma_B + \frac{dx_B}{x_B} \right) = 0 \quad (37)$$

Because $x_A + x_B = 1$ and $dx_A + dx_B = 0$ in a binary solution, we have

$$d \ln \gamma_B = -\frac{x_A}{x_B} d \ln \gamma_A \quad (38)$$

A relation such as Eq. (38) between the activity coefficient of the solvent and solute of a two-component solution is expected, because such a solution can only have a single degree of freedom at fixed T and P . The negative sign in this equation indicates that the activity coefficients of the solvent and solute change in the opposite direction and that the deviation from ideal behavior must both be positive or both be negative for the two components of the solution. The magnitude of the change is larger for the component present in a lower concentration. This is illustrated in [Fig. 3](#) for the acetone–chloroform system.

Substituting $x_B = 1 - x_A$ and integrating for a Raoult's law reference where $x_A = 0$, $x_B = 1$, and $\gamma_B = 1$,

$$\ln \gamma_B = - \int_{x_A=0}^{x_A} \frac{x_A}{1 - x_A} d \ln \gamma_A \quad (39)$$

Example 5. Use the Raoult's law reference activity coefficients calculated for chloroform in Example 1 to calculate the activity coefficient of acetone at $x_{\text{chl}} = 0.508$ in a chloroform–acetone solution.

Solution: The calculation is shown in the following table. The integral in Eq. (36) of [Chapter 6](#) is evaluated stepwise, using the trapezoidal rule. A is chloroform.

x_A	0	0.060	0.184	0.263	0.361	0.424	0.508
$\frac{x_A}{1 - x_A}$	0	0.064	0.225	0.357	0.565	0.736	1.032
γ_A	0.50	0.512	0.594	0.649	0.690	0.716	0.772
Area		0.00077	0.0214	0.0259	0.0281	0.0241	0.0663

$$\text{Total area} = 0.167 \quad \ln \gamma_B = -0.167 \quad \gamma_B = 0.846$$

This compares with $\gamma_{Ac} = 0.813$ calculated directly from the partial pressure of acetone at this mole fraction. The difference is probably primarily due to the large intervals used in evaluating the integral.

If the solute is a solid, we will usually want to use a molality-based Henry's law reference, with $a_B = \gamma_B m$. Equation (15) of [Chapter 8](#) then becomes

$$d \ln a_B = d \ln \gamma_B + d \ln m = -\frac{n_A}{n_B} d \ln a_A \quad (40)$$

To avoid singularities in the integrand when integrating Eq. (40), it is advantageous to define a quantity ϕ , called the *osmotic coefficient*, as

$$\phi \equiv -\frac{n_A}{n_B} \ln a_A \quad (41)$$

ϕ can be determined by any of the methods that we have discussed for measuring activity coefficients of the solvent. From Eq. (41), we have

$$d \ln a_A = -\frac{n_B}{n_A} d\phi - \phi d\left(\frac{n_B}{n_A}\right) \quad (42)$$

Substituting into Eq. (40) gives

$$d \ln \gamma_B = d\phi + \phi d\left(\frac{n_B}{n_A}\right) \left(\frac{n_B}{n_A}\right)^{-1} - \frac{dm}{m} \quad (43)$$

Because n_B/n_A is proportional to m , Eq. (43) can be written

$$d \ln \gamma_B = d\phi + \frac{(\phi - 1)}{m} dm \quad (44)$$

Integrating with a lower limit of the infinitely dilute solution (where $\gamma_B = 1$, $\ln \gamma_B = 0$, $a_A = x_A = 1$, $\phi = 1$),¹

$$\ln \gamma_B = (\phi - 1) + \int_0^m \frac{(\phi - 1)}{m'} dm' \quad (45)$$

(A prime has been used to distinguish the integration variable from the molality of the solution.)

9.4 Equilibrium Constants

Equation (2) can be combined with Eq. (36) of [Chapter 7](#) to give

$$\Delta_{rxn} G^\circ = -RT \ln K_a = -RT \ln \prod_i a_i^{\nu_i} = -RT \ln \prod_i \gamma_i^{\nu_i} x_i^{\nu_i} \quad (46)$$

Performing the products over activity coefficients and mole fractions separately,

$$\Delta_{rxn}G^\circ = -RT \ln \left(\prod_i \gamma_i^{v_i} \prod_i x_i^{v_i} \right) = -RT \ln K_\gamma K_x \quad (47)$$

Because K_γ depends on concentrations and the product $K_\gamma K_x$ is concentration independent, K_x must also depend on concentration. This shows that the simple equilibrium calculations usually carried out in first courses in chemistry are approximations. Actually such calculations are often rather poor approximations when applied to solutions of ionic species, where deviations from ideality are quite large. We shall see that calculations using Eq. (47) can present some computational difficulties. Concentrations are needed in order to obtain activity coefficients, but activity coefficients are needed before an equilibrium constant for calculating concentrations can be obtained. Such problems are usually handled by the method of successive approximations, whereby concentrations are initially calculated assuming ideal behavior and these concentrations are used for a first estimate of activity coefficients, which are then used for a better estimate of concentrations, and so forth. $\Delta_{rxn}G^\circ$ is calculated with the standard state used to define the activity. If molality-based activity coefficients are used, the relevant equation is

$$\Delta_{rxn}G^\circ = -RT \ln K_\gamma K_m \quad (48)$$

whereas if molarity-based activity coefficients are used,

$$\Delta_{rxn}G^\circ = -RT \ln K_\gamma K_c \quad (49)$$

is employed.

9.5 Phase Diagrams of Binary Nonideal Systems

9.5.1 Liquid–Vapor-Phase Diagrams

Positive deviation from ideal behavior is the usual occurrence for solutions of volatile components, and it results either when solute–solute and solvent–solvent interactions are stronger than solute–solvent interactions or when the addition of the solute breaks up “structure” (usually due to hydrogen-bonding) in the solvent. A case of mildly positive deviation is illustrated by the diethyl ether–ethanol system shown in Fig. 5. Here, the resulting total vapor pressure of the solution increases continuously as the concentration of the more volatile component (diethyl ether) is increased.

A more extreme case of positive deviation is illustrated by the ethanol–benzene system shown in Fig. 6, where the addition of benzene breaks up the hydrogen-bond interactions in ethanol. The total pressure in this system shows a

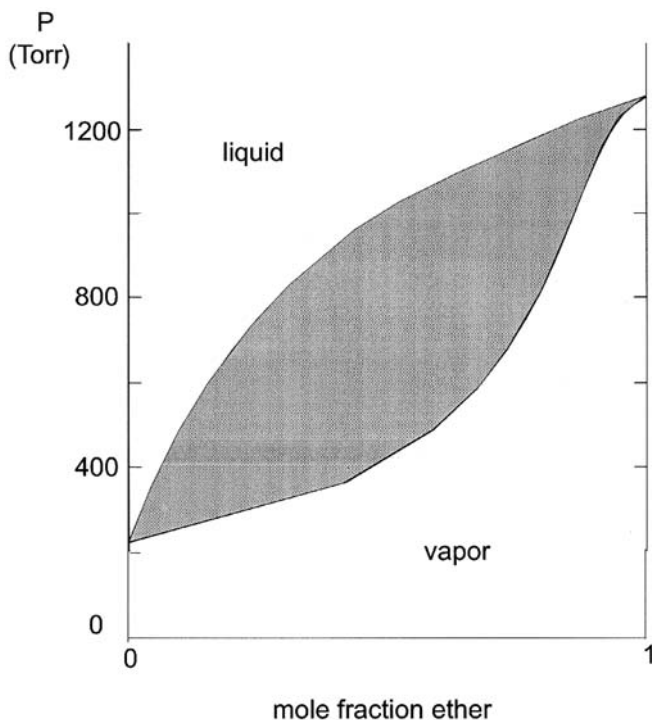


Figure 5 Ethyl ether–ethyl alcohol vapor-pressure diagram at 50°C. (Data from J Timmermans. *Physiochemical Constants of Binary Systems in Concentrated Solutions*. Volume 2. New York: Interscience, 1960, p 401.)

maximum as a function of concentration. This maximum is called an *azeotrope* and the concentration at the maximum is known as the azeotropic concentration.

The boiling-point diagrams, corresponding to [Fig. 6](#) is shown in [Fig. 7](#). Corresponding to the maximum vapor pressure of the azeotrope is its minimum boiling point, which may not occur at exactly the same concentration, depending on the pressure for which the diagram is drawn. Another example of a minimum-boiling-point azeotrope is the water–ethanol system, which forms an azeotrope with 4% water (by mass).

In systems with negative deviation from ideal behavior, maximum-boiling-point azeotropes can occur. This is illustrated in [Fig. 8](#) for the chloroform–acetone system, treated in Example 1. This system shows negative deviation from ideal behavior due to the possibility of hydrogen bonds between chloroform and acetone, which cannot occur with the pure components.

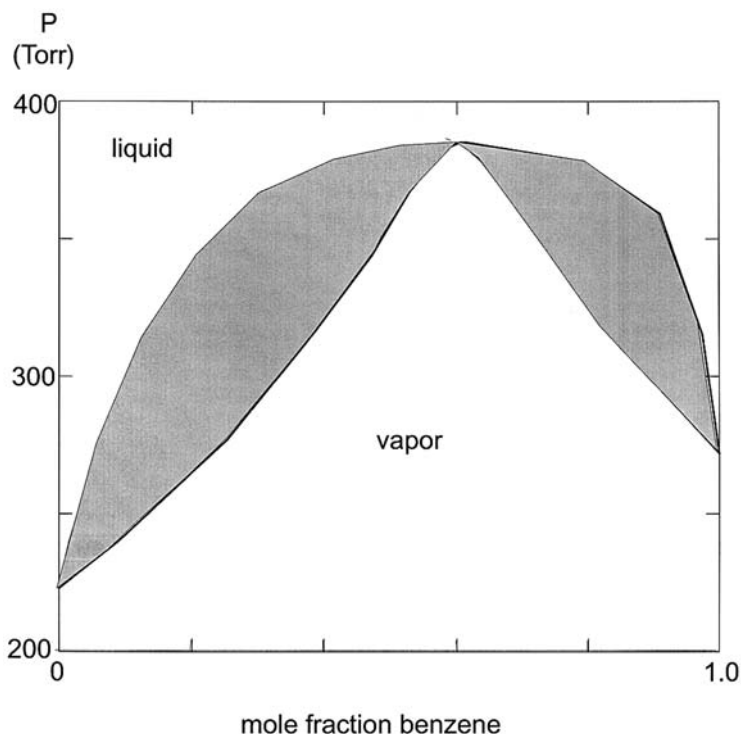


Figure 6 Benzene–ethyl alcohol vapor pressure diagram at 50°C. (Data from J Timmermans. *Physiochemical Constants of Binary Systems in Concentrated Solutions*. Volume 2. New York: Interscience, 1960, p 60.)

For both minimum- and maximum-boiling-point azeotropes, fractional distillation can only separate a solution into a pure component and the azeotrope, not into the two pure components. It is not possible to distill past an azeotropic concentration. “Absolute alcohol” cannot be prepared by simply distilling aqueous solutions obtained by fermenting grains.

9.5.2 Liquid–Liquid-Phase Diagrams

If positive deviation from ideal behavior becomes great enough, a solution may separate into two liquid phases. We say that the components of this system are *partially miscible*. An example of this behavior is the water–ethyl ether system, which separates into water-rich and ether-rich phases at room temperature. By contrast, water and ethanol are *completely miscible* and do not separate. A phase

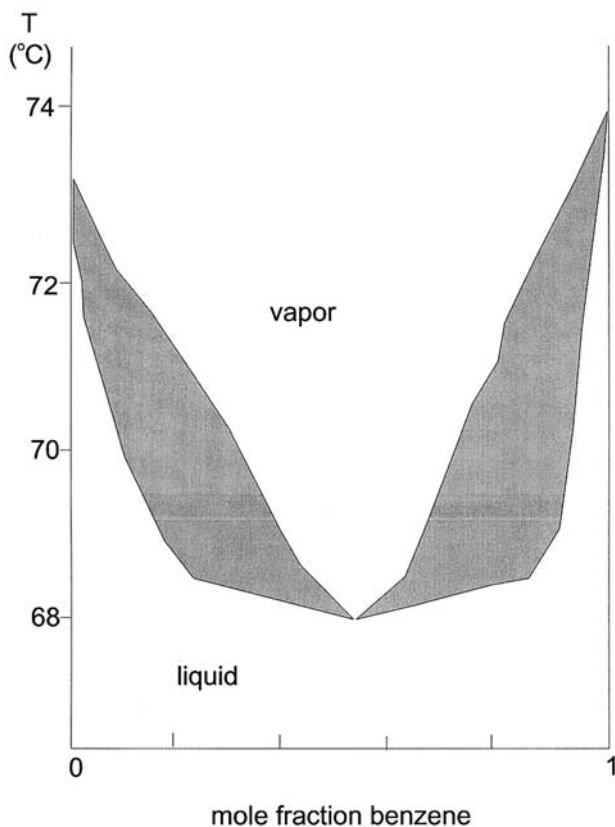


Figure 7 Benzene–ethyl alcohol boiling-point diagram at 1.0 atm. Data from same source as Fig. 6.

diagram for the liquid portion of the water–phenol system, indicating the two-phase region where separation occurs, is shown in Fig. 9.

In Fig. 9, the curve on the left-hand side of the two-phase region gives the solubility of phenol in water as a function of temperature, whereas that on the right-hand side of the region gives the solubility of water in phenol. Because dissolving one component in another increases entropy and $\Delta G = \Delta H - T\Delta S$, we can generally expect solubility to increase with temperature. The two solubility curves move toward each other and finally meet at T_c , the *critical solution temperature*, which is 65.8°C for water–phenol. This is a critical temperature in the same sense as the critical temperature of a single-component gas–liquid system. Above this temperature, no liquid-phase separation is

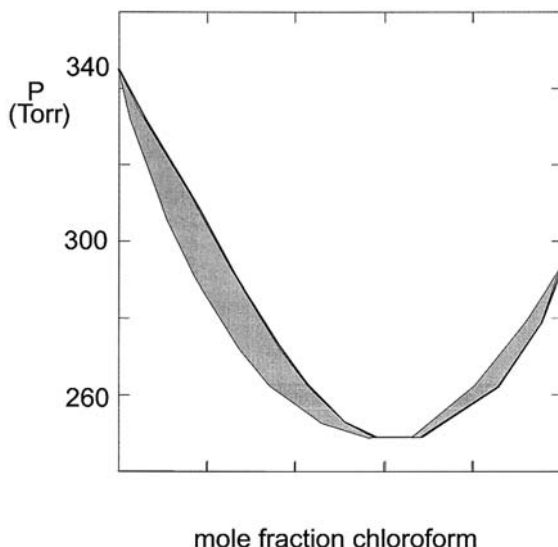


Figure 8 Acetone–chloroform vapor pressure diagram at 35.2°C. (Data from Example 1.)

observed. Cases are also known in which the solubility of two liquids increases as temperature is lowered. This is due to an enthalpic effect, such as the formation of hydrogen bonds between solute and solvent. An example of this behavior occurs with water and triethylamine. In this case, T_c is at the bottom of the two-phase region on the phase diagram. Some systems are known in which liquid-phase separation occurs, but with solubility increasing as temperature both increases and decreases, giving both upper and lower critical solution temperatures.

9.5.3 Solid–Liquid Phase Diagrams

In [Chapter 8](#), the simple case of totally immiscible solids, exhibiting a minimum melting eutectic, was discussed. There are a variety of other behaviors that can be demonstrated in solid–liquid equilibria. For example, a solid solution may be formed. In a solid solution, the arrangement of atoms shows some degree of randomness on the molecular level. This occurs in a *substitutional solid solution*, where the components are very similar and can substitute for each other in the solid lattice. Although the lattice is regular, which atoms in the lattice are substituted is random. (If the substitution were periodic, the system would be a *compound*.) Copper and nickel illustrate this behavior and form a substitutional solid solution at all concentrations. Another type of solid solution is an *interstitial*

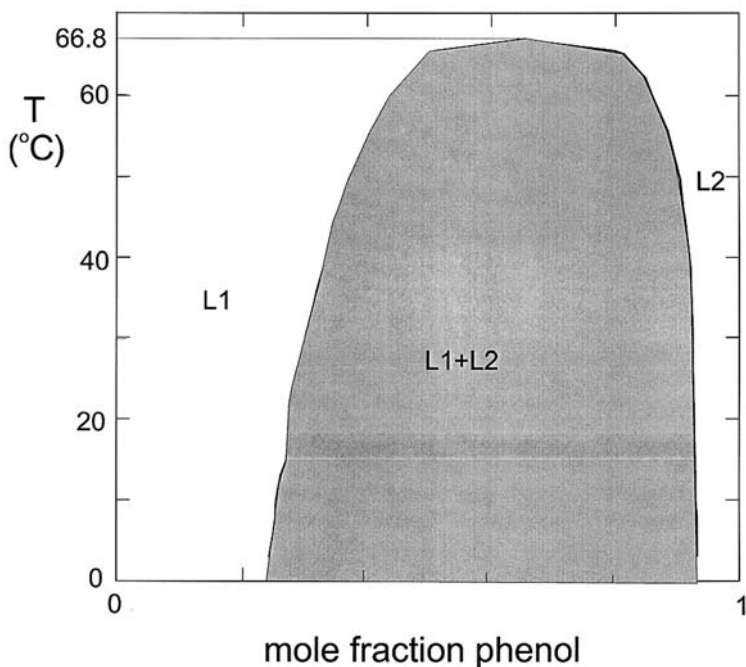


Figure 9 Water-phenol liquid-phase diagram. (Data from J Timmermans. *Physiochemical Constants of Binary Systems in Concentrated Solutions*. Volume 4. New York: Interscience, 1960, p 324.)

solid solution, which occurs when the atoms of one component are small enough to fit into the interstitial holes in the lattice of the other component. Although the lattice is regular, just which holes are filled is random. (If all the holes were filled, the system would be a compound.) Many types of steel are at least partially composed of a solid solution of up to 4% carbon in iron.

If in both the solid and liquid phases, the components are completely miscible, the resulting phase diagram will look much like one of those already discussed for the equilibrium of gases with liquid solutions. For example, if both the liquid and solid solutions approach ideal behavior, the phase diagram will look like [Fig. 8 of Chapter 8](#). Positive and negative deviations from ideal behavior can occur in both phases and combine to give a maximum or minimum in the melting point, similar to the gas-liquid diagrams shown in [Figs. 7 and 8](#). Phase diagrams, however, only present properties at equilibrium and give no information about how rapidly equilibrium is attained. Because the atoms in a solid are largely fixed in their positions,² convection in a solid is negligible, diffusion is extremely slow, and the equilibrium arrangement may not be approached for

many thousands or millions of years. As a result, the properties of solids are as much determined by their thermal history (their rates of heating and cooling) as by their equilibrium properties.

A very common occurrence is that, in the liquid phase, the components are completely miscible, whereas in the solid phase, the components are only partially miscible, usually in small ranges around the pure components. This is illustrated in Fig. 10. Except for the single-phase solid solution regions in the vicinity of the pure solid components, this diagram is similar to Fig. 10 of Chapter 8. It shows a eutectic, which freezes to a mixture of fine crystals of the two solid solutions. These three coexisting phases are represented by a horizontal line on the phase diagram.

A number of binary systems form solid compounds of fixed stoichiometry. The phase diagram for an A–B system, which forms a compound A_2B , is shown in Fig. 11. Although there are three possible components: A, B, and A_2B , in this system, they are connected by a chemical equilibrium relationship, and so there are only two independent components. The phase diagram looks like two separate

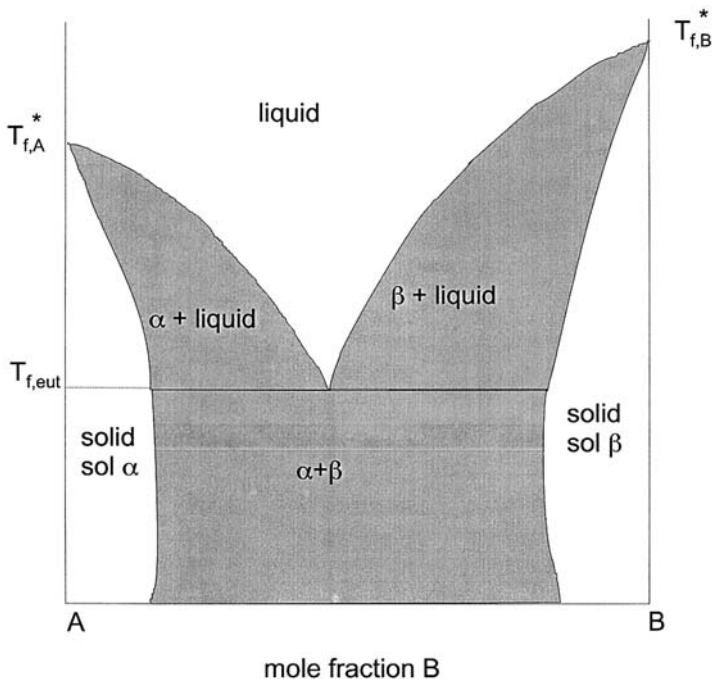


Figure 10 Solid–liquid-phase diagram with solid solution formation.

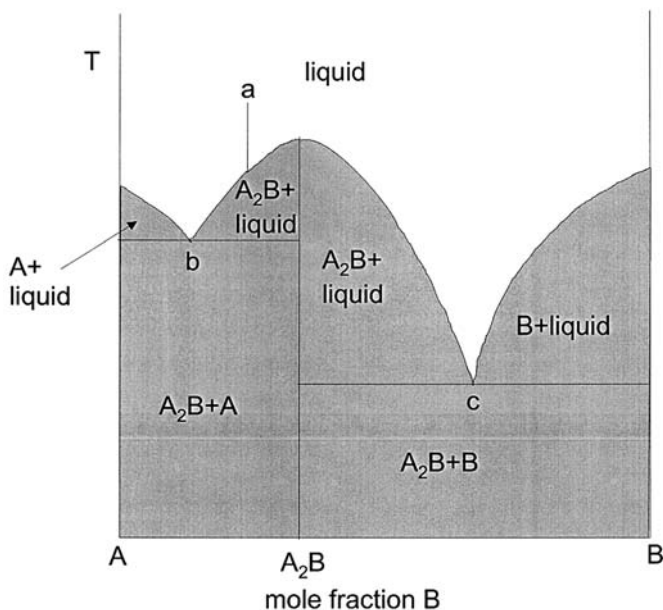


Figure 11 Solid-liquid-phase diagram with compound formation.

diagrams, one for $A-A_2B$ and the other for $B-A_2B$, side by side. For example, when cooling a solution of composition a , A_2B begins to precipitate out. Further cooling precipitates more A_2B and moves the liquid concentration toward the left-hand eutectic at point b . At the eutectic temperature, there is a halt in the cooling while the remainder of the liquid converts into a very fine mixture of A and A_2B crystals. Note that a second eutectic at point c exists in this system, but it is never accessed starting with solutions containing mole fractions of B less than 0.33.

A_2B melts to a liquid of the same composition as the compound. We say that it *melts congruently*. Some compounds *melts incongruently*, (i.e., to liquids of a different composition). This behavior is illustrated by the compound $\text{NaOH} \cdot 2\text{H}_2\text{O}$ in the NaOH -water phase diagram shown in Fig. 12.³

When solid $\text{NaOH} \cdot 2\text{H}_2\text{O}$ is heated to 10°C , it converts to a mixture of $\text{NaOH} \cdot \text{H}_2\text{O}$ and solution of composition a . During melting, this solution exists at equilibrium with the two solid phases, $p = 3$, and the system is invariant (at the pressure of the diagram). This is similar to the behavior of a eutectic solution, but because the solution of composition a is of lower concentration than both of the solids, it is known as a *peritectic solution*, with a corresponding peritectic temperature and peritectic composition.

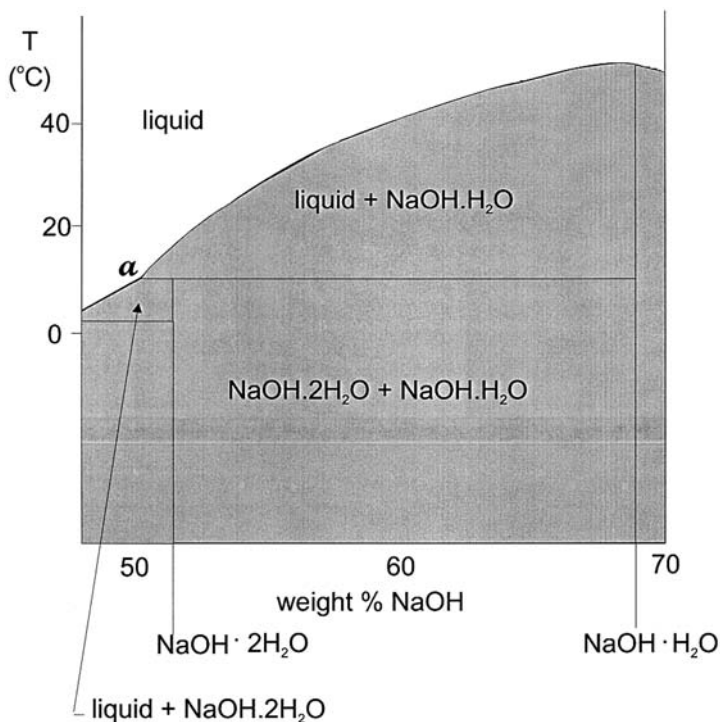


Figure 12 Solid–liquid-phase diagram, showing incongruent melting.

9.6 Phase Diagrams of Ternary Systems

Ternary systems have three components. We will only briefly discuss the use of phase diagrams to describe such systems. If a single phase is present, a three-component system has $f = 3 - 1 + 2 = 4$ degrees of freedom. Because the maximum number of variables that can be represented in a plane is two, two intensive variables must be held constant. These are usually taken as temperature and pressure. The three concentration variables are related and are usually plotted on a triangular diagram. The equilateral triangle is particularly useful for this purpose because of its symmetry. A triangular diagram for the A–B–C system is shown in Fig. 13. The apexes of the triangle represent the pure components, and the perpendicular distance from an apex to the opposite side represents 100 units (mol% or wt%) of that component. The sum of the perpendicular distances to the three sides from any interior point of the triangle equals 100 units. Because there are no phase boundaries in Fig. 13, it represents a completely soluble (or

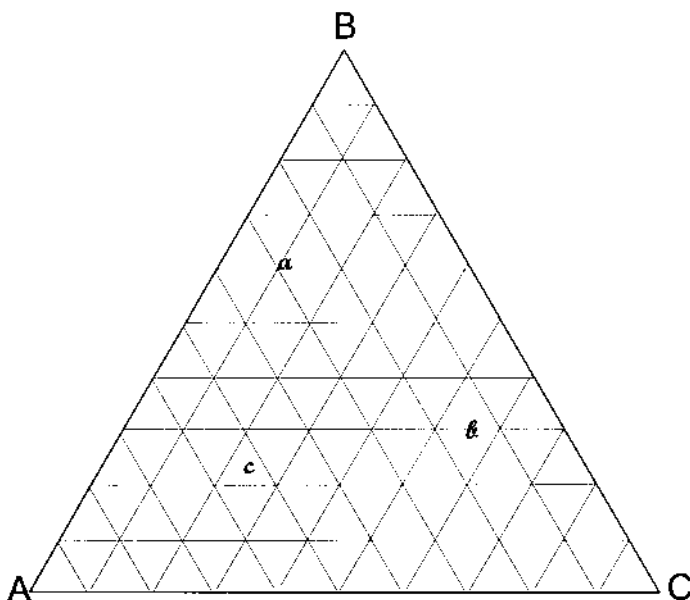


Figure 13 Equilateral-triangle ternary-phase diagram.

insoluble) system. The coordinates lines shown in Fig. 13 are usually omitted for more complicated systems in order to avoid cluttering the diagram.

Example 6. Give the percent concentrations of A, B, and C corresponding to points *a*, *b*, and *c* in Fig. 13 and show that they sum to 100 for each of the points.

Solution:

$$\textbf{a: } A = 30, B = 60, C = 10; A + B + C = 100$$

$$\textbf{b: } A = 15, B = 30, C = 55; A + B + C = 100$$

$$\textbf{c: } A = 53, B = 23, C = 24; A + B + C = 100$$

In Fig. 14, the phase diagram for the three-component $\text{NaNO}_3\text{--KNO}_3\text{--H}_2\text{O}$ system at 36°C is shown. An aqueous solution of two electrolytes has only three components if the electrolytes have an ion in common. Point C on this diagram represents the solubility of KNO_3 in water. To the right of point C on the bottom line of the triangle, the system consists of a saturated solution of KNO_3 and solid KNO_3 . As NaNO_3 is added to these solutions, the solubility of KNO_3 decreases, but the solution is not yet saturated with NaNO_3 . When the overall concentration of the system lies in the region C–B– KNO_3 (e.g., point *a*), the

relative amount of the solution and solid KNO_3 can be determined from the lever rule on the tie line. At point B, the solution is saturated both with NaNO_3 and KNO_3 . Region B– NaNO_3 – KNO_3 is a three-phase region, with the saturated solution existing with both solid NaNO_3 and solid KNO_3 . Figure 14 thus contains one-phase, two-phase, and three-phase regions. In inspecting ternary diagrams, these usually can be easily distinguished because the one-phase and two-phase regions have at least one side that is curved, whereas all of the sides of the three-phase region are straight lines. (Unfortunately, curve A–B in this diagram looks very much like a straight line.)

The phase diagram of the N_2H_4 – NaOH – H_2O system shown in Fig. 15 includes a two-phase region, A–P–B, in which the system separates into two liquid solutions. Because there are no isotherms or isobars to connect coexisting phases on a ternary-phase diagram (temperature and pressure are constant for the entire diagram), the tie lines for coexisting solutions are determined experimentally. Several of these tie lines are drawn in the two-phase region. In this diagram,

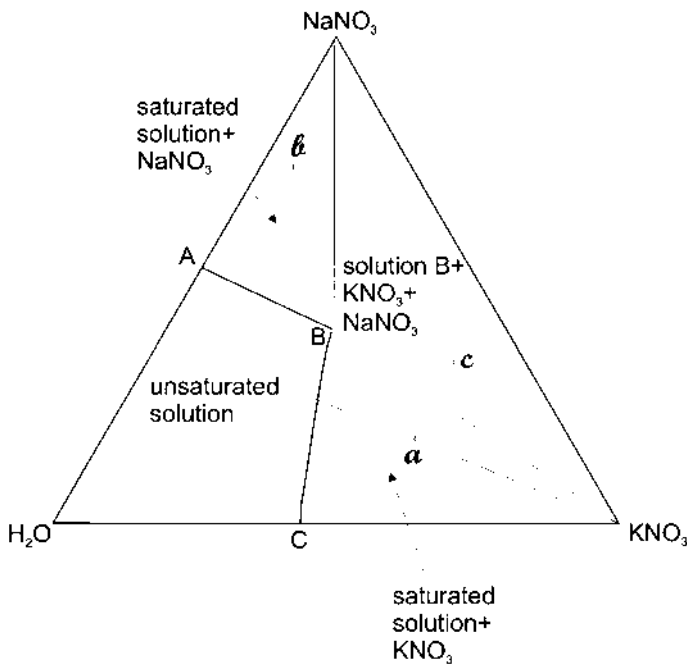


Figure 14 Phase diagram for NaNO_3 – KNO_3 – H_2O , system at 50°C . (Adapted from FF Purdon, VW Slater. *Aqueous Solutions and the Phase Diagram*. London: Edward Arnold, 1946, p 32.)

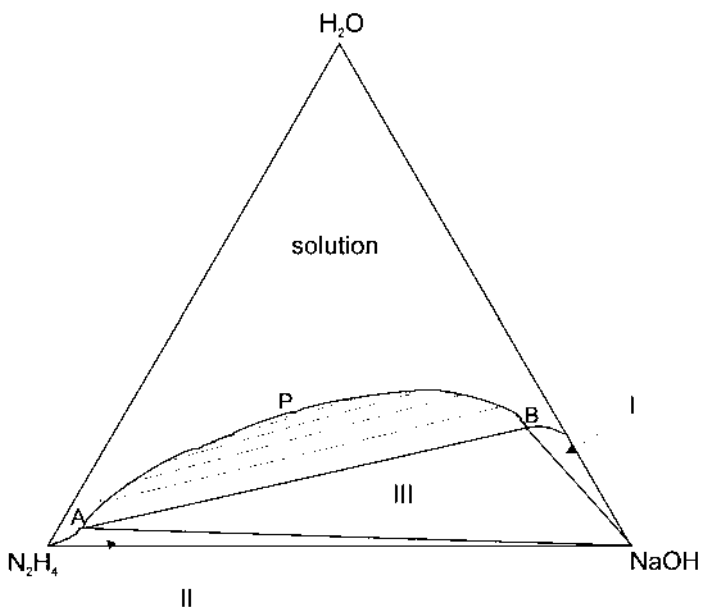


Figure 15 Phase diagram of the N_2H_4 – NaOH – H_2O system at 100°C . (Adapted from RA Penneman, and LF Audrieth. J Am Chem Soc 71: 1644, 1949.)

region III is a three-phase region, where solutions A and B coexist with solid NaOH .

The ternary-phase diagrams presented here illustrate only a small sample of the variety of equilibrium behaviors observed in solid–liquid equilibria in three-component systems. This subject, along with kinetic considerations make up much of the subject matter of a variety of fields, including metallurgy and geology.

Questions

1. Why would a Raoult's law reference be inappropriate for aqueous sugar solutions, no matter how concentrated?
2. Indicate whether each of the following is true or false (A is solvent, i is a solute)
 - (a) $\gamma_A(\text{RL}) \rightarrow 1$ as $x_A \rightarrow 1$
 - (b) $\gamma_A(\text{HL}) \rightarrow 1$ as $x_A \rightarrow 1$
 - (c) $\gamma_i(\text{HL}) \rightarrow 1$ as $x_i \rightarrow 1$
 - (d) $\gamma_i(\text{HL}) \rightarrow 0$ as $x_i \rightarrow 1$
 - (e) $\gamma_i(\text{HL}) \rightarrow 1$ as $x_i \rightarrow 0$

3. Why do we not choose the state of infinite dilution as the standard state of the solute in a solution?
4. Benzene and toluene form an ideal solution, which follows Raoult's law, and has the activity coefficient on the mole fraction scale equal to 1 at all concentrations. If we described this solution by a molality-based Henry's law, would the activity coefficient be equal to 1 at all concentrations. If not, why?
5. Sketch the partial pressures above a solution in which both solute and solvent show positive deviation from ideal solution behavior. Using Raoult's law reference for both solute and solvent, sketch the activity coefficients for this solution.
6. Indicate whether each of the following is always greater than zero (GT), always equal to zero (EQ), always less than zero (LT), or none of the above (NA):
 - (a) The boiling point of a solution that shows positive deviation from ideal behavior minus the boiling point of the same solution, if it were ideal
 - (b) The excess enthalpy of a solution that shows positive deviation from ideal behavior
 - (c) The mole fraction of the more volatile component of a maximum-boiling-point azeotrope minus the mole fraction of the vapor in equilibrium with the azeotrope
 - (d) The entropy of a solid solution of two elements minus the entropy of a compound of the same two elements with approximately the same composition as the solution
7. List five ways of determining the activity coefficient of a nonionized solute.
8. Use Fig. 5 to estimate the purity of ethanol that is obtained from three distillations of an equimolar ethanol–diethyl ether mixture. Assume that, in each stage of the distillation, half the solution is evaporated and condensed.
9. Why are the concentrations of the azeotropes in Figs. 6 and 7 not exactly the same?
10. Draw the liquid portion of a phase diagram for a binary system that shows both an upper and a lower critical solution temperature.
11. Describe the $\text{NaNO}_3\text{--KNO}_3\text{--H}_2\text{O}$ system at the concentrations given by points *b* and *c* in Fig. 14.
12. For the $\text{N}_2\text{H}_4\text{--NaOH--H}_2\text{O}$ system described by Fig. 15, what phases exist when the system concentration lies in region I? In region II?

Problems

1. Prove that $G^E = H^E - TS^E$.
- 2.* L'Hospital rule states that if two functions, $f(x)$ and $g(x)$, both approach zero as x approaches zero, the ratio $f(x)/g(x)$ can be evaluated as the ratio of the slopes of the curves

as they approach zero,

$$\lim_{x \rightarrow 0} \frac{f(x)}{g(x)} = \lim_{x \rightarrow 0} \left[\left(\frac{df}{dx} \right) \left(\frac{dg}{dx} \right)^{-1} \right]$$

Show that L'Hospital rule gives for the limit of the osmotic coefficient.

$$\lim_{m \rightarrow 0} \phi = - \lim_{m \rightarrow 0} \left[(\ln a_A) \left(\frac{n_i}{n_A} \right)^{-1} \right] = 1.$$

3. At 30°C the vapor pressure of CS₂ is 430 mm Hg. A solution of CS₂ in acetone with $x_{\text{CS}_2} = 0.040$ at this temperature is in equilibrium with a partial pressure of CS₂ of 80 mm Hg. This solution can be considered ideally dilute. The partial pressure of CS₂ over an equimolar solution of CS₂ and acetone is 330 torr. Calculate γ_{CS_2} for the equimolar solution, using both the Raoult's law and Henry's law reference states.

4. At 30°C, the density of carbon tetrachloride is 1.57478 g/mL and the density of cyclohexane is 0.76918 g/mL. The density of a carbon tetrachloride–cyclohexane solution with $x_{\text{CCl}_4} = 0.6506$ is 1.27034 g/mL. What is V^E for 1 mol of a solution of this concentration?

5. A benzene–methanol solution with $x_{\text{CH}_3\text{OH}} = 0.5191$ and $y_{\text{CH}_3\text{OH}} = 0.5571$ has a total vapor pressure of 292.5 torr. The vapor pressure of methanol is 150 torr and that of benzene is 210 torr at the temperature of the solution. Calculate the Raoult's law reference activity coefficients for benzene and methanol in this solution.

6. It is difficult to draw tangent lines to partial pressure curves for estimating Henry's law constant with accuracy. Show that an alternative way of obtaining the Henry's law constant is as $K_i = \lim_{x_i \rightarrow 0} \gamma_i(\text{RL})P_i^*$. From the data for the acetone–chloroform system given in Example 1, evaluate K_{Ac} and K_{chl} , and compare the values obtained with those determined by drawing tangent lines.

7. The vapor pressure at 25°C over a solution of nonvolatile solute *B* dissolved in solvent *A* are given as follows:

x_B :	0	0.01	0.02	0.03
P (torr):	420	406.2	392.7	379.3

(a) Calculate γ_A for each of the four solutions.

(b) The density of pure *A* is 0.90 g/cm³ and its molecular weight is 60 g/mol. What is the osmotic pressure at 25°C of the solution with $x_B = 0.03$ in contact with pure *A* through a membrane that only allows passage of *A*.

8. Calculate G^E for 1 mol of a chloroform–acetone solution for each of the concentrations given in Example 1. Sketch how G^E depends on the concentration of the solution.

9. Calculate $\Delta_{\text{mix}}G$ for preparing 1 mol of a chloroform–acetone solution with $x_{\text{chl}} = 0.424$ from its components. Compare your result to what would have been obtained if the solution were ideal.

10. The freezing-point depression of a 32% by weight aqueous solution of ethylene glycol is 16.23°C. What is the activity coefficient of water in this solution?
11. Derive a relationship between the vapor pressure of the solvent above a solution and the osmotic pressure of the solution.
12. Show that the Gibbs–Duhem equation requires that in a binary solution, both solvent and solute must show positive deviation from ideal behavior or must both show negative deviation from ideal behavior.
13. Using the results of Example 1, calculate the osmotic coefficient for a chloroform–acetone solution with $x_{\text{chl}} = 0.424$, treating acetone as the solvent.

Notes

1. ϕ approaches the indeterminate form 0/0 as $x_i \rightarrow 0$. It can, however, be shown to be unity by L'Hospital rule. See Problem 2.
2. It is the vibration of the atoms around these fixed positions that allows diffusion to occur.
3. Only part of this phase diagram is shown because the full diagram is quite complicated. See FF Purdo, VW Slater. Aqueous Solution and the Phase Diagram. London: Arnold, 1946, p 18.