

9 Ideal and Real Solutions

Problem numbers in italics indicate that the solution is included in the *Student Solutions Manual*.

Conceptual Problems

Q9.1 Why is the magnitude of the boiling point elevation less than that of the freezing point depression?

The boiling point elevation is less than the freezing point depression because the chemical potential of the vapor is a much more steeply decreasing function of temperature than the solid, as seen in Figure 9.11a. This is due to the relation $d\mu = -S_m dT$ at constant P and the fact that the molar entropy of a vapor is much larger than that of a solid. When the μ_{liquid} curve is displaced down by the addition of the solute, (see Fig. 9.11a), the intersection of the μ_{liquid} curve with the μ_{solid} curve and the μ_{gas} curve determines the shift in the freezing and boiling temperatures. Because the magnitude of the slope of the μ_{gas} curve is greater than that of the μ_{solid} curve, T_b moves up less than the T_m moves down.

Q9.2 Fractional distillation of a particular binary liquid mixture leaves behind a liquid consisting of both components in which the composition does not change as the liquid is boiled off. Is this behavior characteristic of a maximum or a minimum boiling point azeotrope?

This behavior is characteristic of a maximum-boiling azeotrope. After initially giving off the more volatile component, the liquid remaining tends to the composition of the maximum boiling point at intermediate composition. After the more volatile component has boiled away, the azeotrope evaporates at constant composition.

Q9.3 In the description of Figure 9.24b, the following sentence appears: "At the point when the L_2 phase disappears, the temperature increases beyond 94°C and the vapor composition changes along the $i-j$ curve." Why does the vapor composition change along the $i-j$ curve?

At the point when the L_2 phase disappears, we are left with a dilute solution of butanol in water. The composition of the vapor is given by point i , and the composition of the solution is given by point g . As more vapor is produced, $Z_{butanol}$ decreases and the boiling temperature increases. The composition of the liquid and the vapor is given by the ends of a tie line crossing the $L_1 + V$ region. We see that the liquid follows the composition on the curve $g-k-0$, and the vapor follows the composition along the curve $i-j-0$.

Q9.4 Explain why chemists doing quantitative work using liquid solutions prefer to express concentration in terms of molality rather than molarity.

The molality of a solution is the preferred unit because it is independent of P and T . A kilogram of a substance is a conserved quantity, independent of temperature and pressure. The volume, however, changes as T or P are varied because the thermal expansion coefficient and the isothermal compressibility are not zero. Moles per kilogram is thus a more useful concentration unit than moles per liter, which changes with the thermodynamic state.

Q9.5 Explain the usefulness of a tie line on a $P-Z$ phase diagram such as that of Figure 9.4.

The tie line allows the compositions of the liquid and vapor phases to be determined geometrically for a given total composition and pressure. Specifically, the ratio of moles in liquid and vapor phase is inversely proportional to the ratio of tie line distances.

- P9.2** At a given temperature, a nonideal solution of the volatile components A and B has a vapor pressure of 795 Torr. For this solution, $y_A = 0.375$. In addition, $x_A = 0.310$, $P_A^* = 610$ Torr, and $P_B^* = 495$ Torr. Calculate the activity and activity coefficient of A and B.

$$P_A = y_A P_{total} = 0.375 \times 795 \text{ Torr} = 298 \text{ Torr}$$

$$P_B = 795 \text{ Torr} - 298 \text{ Torr} = 497 \text{ Torr}$$

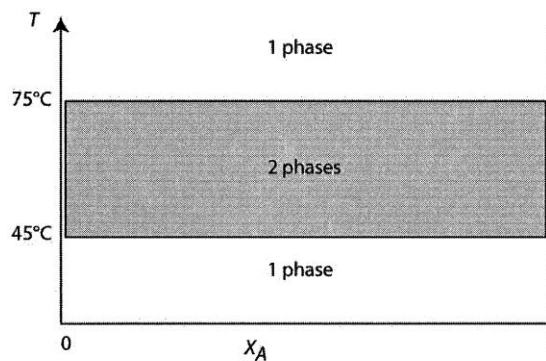
$$a_A = \frac{P_A}{P_A^*} = \frac{298 \text{ Torr}}{610 \text{ Torr}} = 0.489$$

$$\gamma_A = \frac{a_A}{x_A} = \frac{0.488}{0.310} = 1.58$$

$$a_B = \frac{P_B}{P_B^*} = \frac{497 \text{ Torr}}{495 \text{ Torr}} = 1.00$$

$$\gamma_B = \frac{a_B}{x_B} = \frac{1.00}{0.690} = 1.45$$

- P9.3** Two liquids, A and B, are immiscible for $T < 75.0^\circ\text{C}$ and for $T > 45.0^\circ\text{C}$ and are completely miscible outside of this temperature range. Sketch the phase diagram, showing as much information as you can from these observations.



The figure is drawn with a very narrow single phase region near $x_A = 0$ and $x_A = 1$. Although the problem states that the two liquids are immiscible, no two liquids are ever completely immiscible; just as for the reaction $A \rightleftharpoons B$, the equilibrium constant can approach 0 or ∞ , but is never exactly equal to these values because of the driving force of the entropy of mixing.

- P9.4** At 350. K, pure toluene and hexane have vapor pressures of 3.57×10^4 Pa and 1.30×10^5 Pa, respectively.
- Calculate the mole fraction of hexane in the liquid mixture that boils at 350. K at a pressure of 1 atm.
 - Calculate the mole fraction of hexane in the vapor that is in equilibrium with the liquid of part (a).

(a) $P_{total} = x_{hex} P_{hex}^* + (1 - x_{hex}) P_{tol}^*$
 $1.01325 \times 10^5 \text{ Pa} = 1.30 \times 10^5 \text{ Pa } x_{hex} + 3.57 \times 10^4 \text{ Pa } (1 - x_{hex})$
 $x_{hex} = 0.697$

(b) $y_B = \frac{x_{hex} P_{hex}^*}{P_{tol}^* + (P_{hex}^* - P_{tol}^*) x_{hex}}$
 $= \frac{0.697 \times 1.30 \times 10^5 \text{ Pa}}{3.57 \times 10^4 \text{ Pa} + 0.697 \times (1.30 \times 10^5 \text{ Pa} - 3.57 \times 10^4 \text{ Pa})}$
 $= 0.893$

- P9.5** The partial molar volumes of water and ethanol in a solution with $x_{H_2O} = 0.45$ at 25°C are 17.0 and 57.5 cm³ mol⁻¹, respectively. Calculate the volume change upon mixing sufficient ethanol with 3.75 mol of water to give this concentration. The densities of water and ethanol are 0.997 and 0.7893 g cm⁻³, respectively, at this temperature.

$$V = n_{H_2O}\bar{V}_{H_2O} + n_{Et}\bar{V}_{Et}$$

$$\bar{V}_{H_2O} = 17.0 \text{ cm}^3 \text{ mol}^{-1} \text{ and } \bar{V}_{Et} = 57.5 \text{ cm}^3 \text{ mol}^{-1}$$

$$n_{H_2O} = 3.75 \text{ and } x_{H_2O} = \frac{n_{H_2O}}{n_{H_2O} + n_{Et}} = 0.450$$

$$\frac{3.75 \text{ mol}}{3.75 \text{ mol} + n_{Et}} = 0.450; \quad n_{Et} = 4.58$$

The total mixed volume is given by

$$V = n_{H_2O}\bar{V}_{H_2O} + n_{Et}\bar{V}_{Et}$$

$$= 3.75 \text{ mol} \times 17.0 \text{ cm}^3 \text{ mol}^{-1} + 4.58 \text{ mol} \times 57.5 \text{ cm}^3 \text{ mol}^{-1}$$

$$= 327 \text{ cm}^3$$

$$V_{unmixed} = n_{H_2O} \frac{M_{H_2O}}{\rho_{H_2O}} + n_{Et} \frac{M_{Et}}{\rho_{Et}}$$

$$= 3.75 \text{ mol} \times 18.02 \text{ g mol}^{-1} \times \frac{1 \text{ cm}^3}{0.997 \text{ g}}$$

$$+ 4.58 \text{ mol} \times 46.07 \text{ g mol}^{-1} \times \frac{1 \text{ cm}^3}{0.7893 \text{ g}}$$

$$= 335 \text{ cm}^3$$

$$\Delta V = V - V_{unmixed} = 327 \text{ cm}^3 - 335 \text{ cm}^3 = -8 \text{ cm}^3$$

- P9.6** A solution is made up of 222.9 g of ethanol and 130.8 g of H₂O. If the volume of the solution is 403.4 cm³ and the partial molar volume of H₂O is 17.0 cm³ mol⁻¹, what is the partial molar volume of ethanol under these conditions?

$$V = n_{H_2O}\bar{V}_{H_2O} + n_{ethanol}\bar{V}_{ethanol}$$

$$\bar{V}_{ethanol} = \frac{V - n_{H_2O}\bar{V}_{H_2O}}{n_{ethanol}} = \frac{403.4 \text{ cm}^3 - \frac{130.8 \text{ g}}{18.02 \text{ g mol}^{-1}} \times 17.0 \text{ cm}^3 \text{ mol}^{-1}}{\frac{222.9 \text{ g}}{46.04 \text{ g mol}^{-1}}} = 57.9 \text{ cm}^3 \text{ mol}^{-1}$$

- P9.7** The osmotic pressure of an unknown substance is measured at 298 K. Determine the molecular weight if the concentration of this substance is 31.2 kg m⁻³ and the osmotic pressure is 5.30 × 10⁴ Pa. The density of the solution is 997 kg m⁻³.

$$\pi = \frac{n_{solute}RT}{V} = \frac{c_{solute}RT}{M_{solute}}; \quad M_{solute} = \frac{c_{solute}RT}{\pi}$$

$$M_{solute} = \frac{31.2 \text{ kg m}^{-3} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}}{5.34 \times 10^4 \text{ Pa}} = 1.45 \times 10^3 \text{ g mol}^{-1}$$

- P9.8** At 303 K, the vapor pressure of benzene is 120. Torr and that of hexane is 189 Torr. Calculate the vapor pressure of a solution for which $x_{benzene} = 0.28$ assuming ideal behavior.

$$P_{total} = x_{benzene}P_{benzene}^* + x_{hexane}P_{hexane}^*$$

$$= 0.28 \times 120. \text{ Torr} + (1 - 0.28) \times 189 \text{ Torr} = 1.7 \times 10^2 \text{ Torr}$$

- P9.9** The volatile liquids A and B, for which $P_A^* = 165$ Torr and $P_B^* = 85.1$ Torr are confined to a piston and cylinder assembly. Initially, only the liquid phase is present. As the pressure is reduced, the first vapor is observed at a total pressure of 110. Torr. Calculate x_A .

The first vapor is observed at a pressure of

$$P_{total} = x_A P_A^* + (1 - x_A) P_B^*$$

$$x_A = \frac{P_{total} - P_B^*}{P_A^* - P_B^*} = \frac{110. \text{ Torr} - 85.1 \text{ Torr}}{165 \text{ Torr} - 85.1 \text{ Torr}} = 0.312$$

- P9.10** At high altitudes, mountain climbers are unable to absorb a sufficient amount of O_2 into their bloodstreams to maintain a high activity level. At a pressure of 1 bar, blood is typically 95% saturated with O_2 , but near 18,000 feet where the pressure is 0.50 bar, the corresponding degree of saturation is 71%. Assuming that the Henry's law constant for blood is the same as for water, calculate the amount of O_2 dissolved in 1.00 L of blood for pressures of 1 bar and 0.500 bar. Air contains 20.99% O_2 by volume. Assume that the density of blood is 998 kg m^{-3} .

By Dalton's law, $P_{O_2} = 0.2099P$. At sea level,

$$n_{O_2} = n_{H_2O} x_{O_2} = n_{H_2O} \frac{P_{O_2}}{k_H^{O_2}} = \frac{\rho_{H_2O} V P_{O_2} f_{sat}}{k_H^{O_2} M_{H_2O}}$$

$$n_{O_2} = \frac{998 \text{ kg m}^{-3} \times 10^{-3} \text{ m}^3 \times 0.2099 \text{ bar} \times 0.95}{4.95 \times 10^4 \text{ bar} \times 18.02 \times 10^{-3} \text{ kg mol}^{-1}} = 2.23 \times 10^{-4} \text{ mol}$$

$$\text{mass} = n_{O_2} M = 2.23 \times 10^{-4} \text{ mol} \times 32.0 \text{ g mol}^{-1} = 7.14 \times 10^{-3} \text{ g}$$

At 18,000 feet,

$$n_{O_2} = n_{H_2O} x_{O_2} = n_{H_2O} \frac{P_{O_2}}{k_H^{O_2}} = \frac{\rho_{H_2O} V P_{O_2} f_{sat}}{k_H^{O_2} M_{H_2O}}$$

$$n_{O_2} = \frac{998 \text{ kg m}^{-3} \times 10^{-3} \text{ m}^3 \times 0.2099 \times 0.500 \text{ bar} \times 0.71}{4.95 \text{ bar} \times 18.02 \times 10^{-3} \text{ kg mol}^{-1}} = 8.34 \times 10^{-5} \text{ mol}$$

$$\text{mass} = n_{O_2} M = 8.34 \times 10^{-5} \text{ mol} \times 32.0 \text{ g mol}^{-1} = 2.67 \times 10^{-3} \text{ g}$$

- P9.11** At -47°C , the vapor pressure of ethyl bromide is 10.0 Torr and that of ethyl chloride is 40.0 Torr. Assume that the solution is ideal. Assume there is only a trace of liquid present and the mole fraction of ethyl chloride in the vapor is 0.80 and answer these questions:

- What is the total pressure and the mole fraction of ethyl chloride in the liquid?
- If there are 5.00 mol of liquid and 3.00 mol of vapor present at the same pressure as in part (a), what is the overall composition of the system?

$$(a) \quad P_{total} = \frac{P_{EB}^* \times P_{EC}^*}{P_{EC}^* + (P_{EB}^* - P_{EC}^*) y_{EC}}$$

$$= \frac{10.0 \text{ Torr} \times 40.0 \text{ Torr}}{40.0 \text{ Torr} + (10.0 \text{ Torr} - 40.0 \text{ Torr}) \times 0.80}$$

$$= 25 \text{ Torr}$$

$$P_{total} = x_{EC} P_{EC}^* + (1 - x_{EC}) P_{EB}^*$$

$$x_{EC} = \frac{P_{total} - P_{EB}^*}{P_{EC}^* - P_{EB}^*} = \frac{25 \text{ Torr} - 10.0 \text{ Torr}}{40.0 \text{ Torr} - 10.0 \text{ Torr}}$$

$$= 0.50$$

- (b) We use the lever rule.

$$\begin{aligned}n_{liq}^{tot}(Z_{EB} - x_{EB}) &= n_{vap}^{tot}(y_{EB} - Z_{EB}) \\Z_{EB} - x_{EB} &= (1 - Z_{EC}) - (1 - x_{EC}) = x_{EC} - Z_{EC} \\y_{EB} - Z_{EB} &= (1 - y_{EC}) - (1 - Z_{EC}) = Z_{EC} - y_{EC}\end{aligned}$$

Therefore

$$\frac{n_{liq}^{tot}}{n_{vap}^{tot}} = \frac{y_{EC} - Z_{EC}}{Z_{EC} - x_{EC}} = \frac{5.00}{3.00}$$

We solve for Z_{EC} .

$$\begin{aligned}Z_{EC} &= \frac{n_{liq}^{tot}x_{EC} + n_{vap}^{tot}y_{EC}}{n_{liq}^{tot} + n_{vap}^{tot}} = \frac{5.00 \text{ mol} \times 0.50 + 3.00 \text{ mol} \times 0.80}{8.00 \text{ mol}} = 0.61 \\Z_{EB} &= 1 - Z_{EC} = 0.39\end{aligned}$$

- P9.12**
- A and B form an ideal solution at 298 K, with
- $x_A = 0.320$
- ,
- $P_A^* = 84.3$
- Torr, and
- $P_B^* = 41.2$
- Torr.

- a. Calculate the partial pressures of A and B in the gas phase.
 b. A portion of the gas phase is removed and condensed in a separate container. Calculate the partial pressures of A and B in equilibrium with this liquid sample at 298 K.

$$\begin{aligned}\text{(a)} \quad P_A &= x_A P_A^* = 0.320 \times 84.3 \text{ Torr} = 27.0 \text{ Torr} \\P_B &= (1 - x_A) P_B^* = 0.680 \times 41.2 \text{ Torr} = 28.0 \text{ Torr}\end{aligned}$$

- (b) The composition of the initial gas is given by

$$y_A = \frac{P_A}{P_A + P_B} = \frac{27.0 \text{ Torr}}{27.0 \text{ Torr} + 28.0 \text{ Torr}} = 0.491; \quad y_B = 0.509$$

For the portion removed, the new x_A and x_B values are the previous y_A and y_B values.

$$\begin{aligned}P_A &= x_A P_A^* = 0.491 \times 84.3 \text{ Torr} = 41.4 \text{ Torr} \\P_B &= (1 - x_A) P_B^* = 0.509 \times 41.2 \text{ Torr} = 21.0 \text{ Torr}\end{aligned}$$

- P9.13**
- Describe what you would observe if you heated the liquid mixture at the composition corresponding to point
- i
- in Figure 9.24b from a temperature below
- T_a
- to 118°C.

The mixture of two liquids will increase in temperature without a change in composition until $T = 94^\circ\text{C}$. It will begin to boil at that temperature without a change from its initial composition. Boiling will continue until no liquid is left and then the temperature will increase to 118°C.

- P9.14**
- The heat of fusion of water is
- $6.008 \times 10^3 \text{ J mol}^{-1}$
- at its normal melting point of 273.15 K. Calculate the freezing point depression constant
- K_f
- .

$$\begin{aligned}K_f &= \frac{RM_{\text{solvent}} T_{\text{fusion}}^2}{\Delta H_{\text{fusion},m}} = \frac{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 18.02 \times 10^{-3} \text{ kg mol}^{-1} \times (273.15 \text{ K})^2}{6.008 \times 10^3 \text{ J mol}^{-1}} \\K_f &= 1.861 \text{ K kg mol}^{-1}\end{aligned}$$

- P9.15**
- At 39.9°C, a solution of ethanol (
- $x_1 = 0.9006$
- ,
- $P_1^* = 130.4$
- Torr) and isooctane (
- $P_2^* = 43.9$
- Torr) forms a vapor phase with
- $y_1 = 0.6667$
- at a total pressure of 185.9 Torr.

- a. Calculate the activity and activity coefficient of each component.
 b. Calculate the total pressure that the solution would have if it were ideal.

- (a) The activity and activity coefficient for ethanol are given by

$$a_1 = \frac{y_1 P_{total}}{P_1^*} = \frac{0.6667 \times 185.9 \text{ Torr}}{130.4 \text{ Torr}} = 0.9504$$

$$\gamma_1 = \frac{a_1}{x_1} = \frac{0.9504}{0.9006} = 1.055$$

Similarly, the activity and activity coefficient for isooctane are given by

$$a_2 = \frac{(1 - y_1) P_{total}}{P_2^*} = \frac{0.3333 \times 185.9 \text{ Torr}}{43.9 \text{ Torr}} = 1.411$$

$$\gamma_2 = \frac{a_2}{x_2} = \frac{1.411}{1 - 0.9006} = 14.2$$

- (b) If the solution were ideal, Raoult's law would apply.

$$P_{Total} = x_1 P_1^* + x_2 P_2^*$$

$$= 0.9006 \times 130.4 \text{ Torr} + (1 - 0.9006) \times 43.9 \text{ Torr}$$

$$= 121.8 \text{ Torr}$$

- P9.16**
- Calculate the solubility of H
- ₂
- S in 1 L of water if its pressure above the solution is 2.75 Pa. The density of water at this temperature is 997 kg m
- ⁻³
- .

$$x_{H_2S} = \frac{n_{H_2S}}{n_{H_2S} + n_{H_2O}} \approx \frac{n_{H_2S}}{n_{H_2O}} = \frac{P_{H_2S}}{k_{H_2S}^H} = \frac{2.75 \times 10^5 \text{ bar}}{568 \text{ bar}} = 4.84 \times 10^{-8}$$

$$n_{H_2O} = \frac{\rho_{H_2O} V}{M_{H_2O}} = \frac{10^{-3} \text{ m}^3 \times 997 \text{ kg m}^{-3}}{18.02 \times 10^{-3} \text{ kg mol}^{-1}} = 55.3$$

$$n_{H_2S} = x_{H_2S} n_{H_2O} = 4.84 \times 10^{-8} \times 55.3 = 2.68 \times 10^{-6} \text{ mol}$$

- P9.17**
- The binding of NADH to human liver mitochondrial isozyme was studied [
- Biochemistry*
- 28 (1989): 5367] and it was determined that only a single binding site is present with
- $K = 2.0 \times 10^7 \text{ M}^{-1}$
- . What concentration of NADH is required to occupy 10% of the binding sites?

Beginning with the expression for the fraction of occupied sites:

$$\bar{v} = \frac{Kc_{NADH}}{1 + Kc_{NADH}}$$

This expression can be rearranged to express the concentration of ligand (NADH) versus \bar{v} and K :

$$\bar{v} = \frac{Kc_{NADH}}{1 + Kc_{NADH}}$$

$$\bar{v}(1 + Kc_{NADH}) = Kc_{NADH}$$

$$\bar{v} = (1 - \bar{v})Kc_{NADH}$$

$$\frac{\bar{v}}{(1 - \bar{v})K} = c_{NADH} = \frac{0.1}{(1 - 0.1) \times 2.0 \times 10^7 \text{ M}^{-1}}$$

$$c_{NADH} = 5.6 \times 10^{-9} \text{ M}$$

- P9.18**
- Given the vapor pressures of the pure liquids and the overall composition of the system, what are the upper and lower limits of pressure between which liquid and vapor coexist in an ideal solution?

Referring to Figure 9.4, it is seen that the maximum pressure results if $Z_A = x_A$.

$$P_{max} = Z_A P_A^* + (1 - Z_A) P_B^*$$

The minimum pressure results if $Z_A = y_A$. Using Equation (9.12),

$$P_{\min} = \frac{P_A^* P_B^*}{P_A^* + (P_B^* - P_A^*) Z_A}$$

P9.19 A and B form an ideal solution. At a total pressure of 0.720 bar, $y_A = 0.510$ and $x_A = 0.420$. Using this information, calculate the vapor pressure of pure A and of pure B.

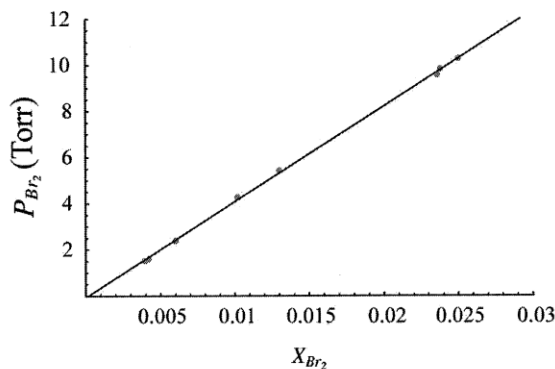
$$P_{\text{total}} = x_A P_A^* + y_B P_{\text{total}}$$

$$P_A^* = \frac{P_{\text{total}} - y_B P_{\text{total}}}{x_A} = \frac{0.720 \text{ bar} \times (1 - 0.510)}{0.420} = 0.840 \text{ bar}$$

$$P_B^* = \frac{P_{\text{total}} - P_A^* x_A}{1 - x_A} = \frac{0.874 \text{ bar} \times (0.420 \times 0.510 - 0.420)}{(0.420 - 1) \times 0.510} = 0.608 \text{ bar}$$

P9.20 The partial pressures of Br_2 above a solution containing CCl_4 as the solvent at 25°C are found to have the values listed in the following table as a function of the mole fraction of Br_2 in the solution [Lewis G. N., and Storch, H. *J. American Chemical Society* 39 (1917): 2544]. Use these data and a graphical method to determine the Henry's law constant for Br_2 in CCl_4 at 25°C .

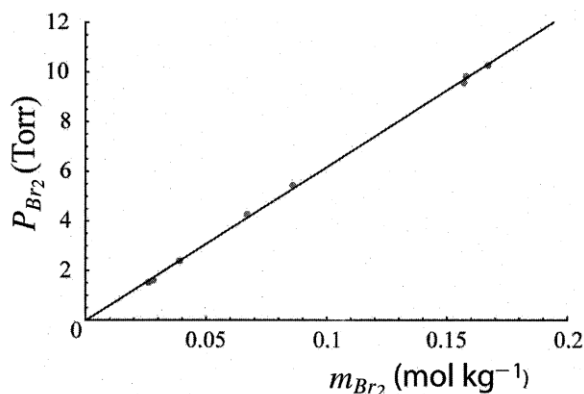
	P (Torr)		P (Torr)	
0.00394	1.52	0.0130	5.43	
0.00420	1.60	0.0236	9.57	
0.00599	2.39	0.0238	9.83	
0.0102	4.27	0.0250	10.27	



The best fit line in the plot is $P_{\text{Br}_2} (\text{Torr}) = 413 x_{\text{Br}_2} - 0.063$. Therefore, the Henry's law constant in terms of mole fraction is 413 Torr.

P9.21 The data from Problem P9.20 can be expressed in terms of the molality rather than the mole fraction of Br_2 . Use the data from the following table and a graphical method to determine the Henry's law constant for Br_2 in CCl_4 at 25°C in terms of molality.

m_{Br_2} (mol kg ⁻¹)	P_{Br_2} (Torr)	m_{Br_2} (mol kg ⁻¹)	P_{Br_2} (Torr)
0.026	1.52	0.086	5.43
0.028	1.60	0.157	9.57
0.039	2.39	0.158	9.83
0.067	4.27	0.167	10.27

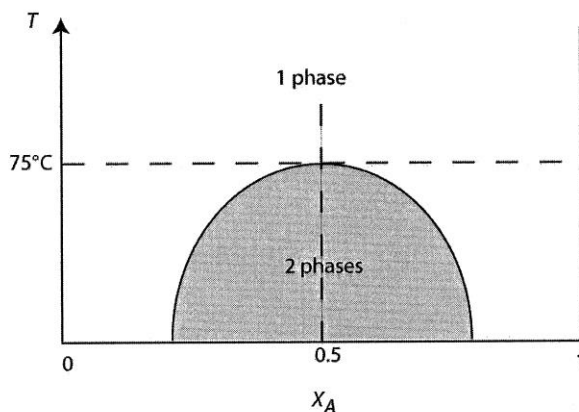


The best fit line in the plot is $P_{Br_2}(\text{Torr}) = 61.9 m_{Br_2} - 0.0243$. Therefore, the Henry's law constant in terms of molality is $61.9 \text{ Torr (mol kg}^{-1}\text{)}^{-1}$.

- P9.22** The densities of pure water and ethanol are 997 and 789 kg m^{-3} , respectively. For $x_{\text{ethanol}} = 0.35$, the partial molar volumes of ethanol and water are 55.2 and $17.8 \times 10^{-3} \text{ L mol}^{-1}$, respectively. Calculate the change in volume relative to the pure components when 2.50 L of a solution with $x_{\text{ethanol}} = 0.35$ is prepared.

$$\begin{aligned}
 V &= n_{H_2O} \bar{V}_{H_2O} + n_{\text{ethanol}} \bar{V}_{\text{ethanol}} \\
 \frac{V}{n_{\text{total}}} &= x_{H_2O} \bar{V}_{H_2O} + x_{\text{ethanol}} \bar{V}_{\text{ethanol}} = 0.65 \times 17.8 \times 10^{-3} \text{ L mol}^{-1} + 0.35 \times 55.2 \times 10^{-3} \text{ L mol}^{-1} \\
 \frac{V}{n_{\text{total}}} &= 0.0309 \text{ L mol}^{-1} \\
 n_{\text{total}} &= \frac{2.50 \text{ L}}{0.0309 \text{ L mol}^{-1}} = 80.9 \text{ mol} = n_{H_2O} + n_{\text{ethanol}} \\
 \frac{x_{\text{ethanol}}}{x_{H_2O}} &= \frac{n_{\text{ethanol}}}{n_{H_2O}} = \frac{0.350}{0.650}; \quad n_{H_2O} = 52.6 \text{ mol} \quad n_{\text{ethanol}} = 28.3 \text{ mol} \\
 V_{\text{ideal}} &= n_{\text{ethanol}} \frac{M_{\text{ethanol}}}{\rho_{\text{ethanol}}} + n_{H_2O} \frac{M_{H_2O}}{\rho_{H_2O}} \\
 &= 28.3 \text{ mol} \times \frac{46.07 \times 10^{-3} \text{ kg mol}^{-1}}{789 \text{ kg m}^{-3}} + 52.6 \text{ mol} \times \frac{18.02 \times 10^{-3} \text{ kg mol}^{-1}}{998 \text{ kg m}^{-3}} = 2.60 \text{ L} \\
 \Delta V &= V - V_{\text{ideal}} = -0.10 \text{ L}
 \end{aligned}$$

- P9.23** Two liquids, A and B, are immiscible for $x_A = x_B = 0.5$, for $T < 75.0^\circ\text{C}$ and completely miscible for $T > 75.0^\circ\text{C}$. Sketch the phase diagram, showing as much information as you can from these observations.



The shape of the 2 phases region cannot be determined from the information given. It may exist over a smaller or larger range of concentration, and it need not be symmetric about 0.5.

- P9.24** An ideal solution is formed by mixing liquids A and B at 298 K. The vapor pressure of pure A is 151 Torr and that of pure B is 84.3 Torr. If the mole fraction of A in the vapor is 0.610, what is the mole fraction of A in the solution?

$$\text{Using Equation (9.11), } x_A = \frac{y_A P_B^*}{P_A^* + (P_B^* - P_A^*)y_A} = \frac{0.610 \times 84.3 \text{ Torr}}{151 \text{ Torr} + (84.3 \text{ Torr} - 151 \text{ Torr}) \times 0.610} = 0.466$$

- P9.25** A solution is prepared by dissolving 45.2 g of a nonvolatile solute in 119 g of water. The vapor pressure above the solution is 22.51 Torr and the vapor pressure of pure water is 23.76 Torr at this temperature. What is the molecular weight of the solute?

$$x_{\text{H}_2\text{O}} = \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2\text{O}}^*} = \frac{22.51 \text{ Torr}}{23.76 \text{ Torr}} = 0.947$$

$$x_{\text{solute}} = 0.0526 = \frac{n_{\text{solute}}}{n_{\text{solute}} + n_{\text{H}_2\text{O}}};$$

$$n_{\text{solute}} = \frac{x_{\text{solute}} \frac{m_{\text{H}_2\text{O}}}{M_{\text{H}_2\text{O}}}}{x_{\text{H}_2\text{O}}} = \frac{0.0526 \times \frac{119 \text{ g}}{18.02 \text{ g mol}^{-1}}}{0.947} = 0.367 \text{ mol}$$

$$M = \frac{45.2 \text{ g}}{0.367 \text{ mol}} = 123 \text{ g mol}^{-1}$$

- P9.26** A sample of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) of mass 13.2 g is placed in a test tube of radius 1.25 cm. The bottom of the test tube is a membrane that is semipermeable to water. The tube is partially immersed in a beaker of water at 298 K so that the bottom of the test tube is only slightly below the level of the water in the beaker. The density of water at this temperature is 997 kg m^{-3} . After equilibrium is reached, how high is the level of the water in the tube above that in the beaker? What is the value of the osmotic pressure? You may find the approximation $\ln(1/(1+x)) \approx -x$ useful.

Using Equation (9.39) and expressing the number of moles of solvent in terms of the density and height of the column of water,

$$\pi V_m^* + RT \ln x_{\text{solvent}} = \pi V_m^* + RT \ln \frac{n_{\text{solvent}}}{n_{\text{solvent}} + n_{\text{sucrose}}} = 0$$

$$\rho g h V_m^* + RT \ln \frac{\frac{\rho A h}{M}}{\frac{\rho A h}{M} + n_{\text{sucrose}}} = \rho g h V_m^* + RT \ln \frac{1}{1 + \frac{n_{\text{sucrose}} M}{\rho A h}} = 0$$

Expanding the argument of the logarithmic term in a Taylor series, $\ln \frac{1}{1+x} \approx -x$,

$$\rho g h V_m^* - RT \frac{n_{\text{sucrose}} M}{\rho A h} = 0$$

$$h = \sqrt{\frac{RT n_{\text{sucrose}} M}{\rho^2 A g V_m^*}} = \sqrt{\frac{RT n_{\text{sucrose}}}{\rho A g}}$$

$$= \sqrt{\frac{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K} \times \frac{13.2 \times 10^{-3} \text{ kg}}{0.18016 \text{ kg mol}^{-1}}}{997 \text{ kg m}^{-3} \times 3.14 \times (1.25 \times 10^{-2} \text{ m})^2 \times 9.81 \text{ m s}^{-2}}} = 6.15 \text{ m}$$

$$\pi = \rho g h = 997 \text{ kg m}^{-3} \times 9.81 \text{ m s}^{-2} \times 6.15 \text{ m} = 6.01 \times 10^4 \text{ Pa}$$

P9.27 A volume of 5.50 L of air is bubbled through liquid toluene at 298 K, thus reducing the mass of toluene in the beaker by 2.38 g. Assuming that the air emerging from the beaker is saturated with toluene, determine the vapor pressure of toluene at this temperature.

$$P = \frac{nRT}{V} = \frac{2.38 \text{ g} \times \frac{1 \text{ mol}}{92.14 \text{ g mol}^{-1}} \times 0.08314 \text{ L bar K}^{-1} \times 298 \text{ K}}{5.50 \text{ L}} = 0.116 \text{ bar}$$

P9.28 The vapor pressures of 1-bromobutane and 1-chlorobutane can be expressed in the form

$$\ln \frac{P_{\text{bromo}}}{\text{Pa}} = 17.076 - \frac{1584.8}{T - 111.88 \text{ K}}$$

and

$$\ln \frac{P_{\text{chloro}}}{\text{Pa}} = 20.612 - \frac{2688.1}{T - 55.725 \text{ K}}$$

Assuming ideal solution behavior, calculate x_{bromo} and y_{bromo} at 305 K and a total pressure of 9750 Pa.

At 305 K, $P_{\text{bromo}}^\circ = 7113 \text{ Pa}$ and $P_{\text{chloro}}^\circ = 18552 \text{ Pa}$.

$$P_{\text{total}} = x_{\text{bromo}} P_{\text{bromo}}^\circ + (1 - x_{\text{bromo}}) P_{\text{chloro}}^\circ$$

$$x_{\text{bromo}} = \frac{P_{\text{total}} - P_{\text{chloro}}^\circ}{P_{\text{bromo}}^\circ - P_{\text{chloro}}^\circ} = \frac{9750 \text{ Pa} - 18552 \text{ Pa}}{7113 \text{ Pa} - 18552 \text{ Pa}} = 0.769$$

$$y_{\text{bromo}} = \frac{x_{\text{bromo}} P_{\text{bromo}}^\circ}{P_{\text{total}}} = \frac{0.769 \times 7113 \text{ Pa}}{9750 \text{ Pa}} = 0.561$$

- P9.29** In an ideal solution of A and B, 3.00 mol are in the liquid phase and 5.00 mol are in the gaseous phase. The overall composition of the system is $Z_A = 0.375$ and $x_A = 0.250$. Calculate y_A .

$$n_{liq}^{tot}(Z_B - x_B) = n_{vapor}^{tot}(y_B - Z_B)$$

$$y_B = \frac{n_{liq}^{tot}(Z_B - x_B) + n_{vapor}^{tot}Z_B}{n_{vapor}^{tot}} = \frac{3.00 \text{ mol} \times (0.625 - 0.750) + 5.00 \text{ mol} \times 0.625}{5.00 \text{ mol}}$$

$$= 0.550$$

$$y_A = 1 - 0.550 = 0.450$$

- P9.30** Assume that 1-bromobutane and 1-chlorobutane form an ideal solution. At 273 K, $P_{chloro}^* = 3790$ Pa and $P_{bromo}^* = 1394$ Pa. When only a trace of liquid is present at 273 K, $y_{chloro} = 0.750$.

- Calculate the total pressure above the solution.
- Calculate the mole fraction of 1-chlorobutane in the solution.
- What value would Z_{chloro} have in order for there to be 4.86 mol of liquid and 3.21 mol of gas at a total pressure equal to that in part (a)? [Note: This composition is different from that of part (a).]

$$(a) \quad y_{chloro} = \frac{P_{chloro}^* P_{total} - P_{chloro}^* P_{bromo}^*}{P_{total}(P_{chloro}^* - P_{bromo}^*)}$$

$$0.750 = \frac{3790 \text{ Pa} \times P_{total} - 3790 \text{ Pa} \times 1394 \text{ Pa}}{P_{total} \times (3790 \text{ Pa} - 1394 \text{ Pa})}$$

$$P_{total} = \frac{3790 \text{ Pa} \times 1394 \text{ Pa}}{3790 \text{ Pa} - 0.750 \times (3790 \text{ Pa} - 1394 \text{ Pa})} = 2.65 \times 10^3 \text{ Pa}$$

$$(b) \quad P_{total} = x_{chloro} P_{chloro}^* + (1 - x_{chloro}) P_{bromo}^*$$

$$x_{chloro} = \frac{P_{total} - P_{bromo}^*}{P_{chloro}^* - P_{bromo}^*} = \frac{2650 \text{ Pa} - 1394 \text{ Pa}}{3790 \text{ Pa} - 1394 \text{ Pa}} = 0.524$$

$$(c) \quad n_{liq}^{tot}(Z_{chloro} - x_{chloro}) = n_{vapor}^{tot}(y_{chloro} - Z_{chloro})$$

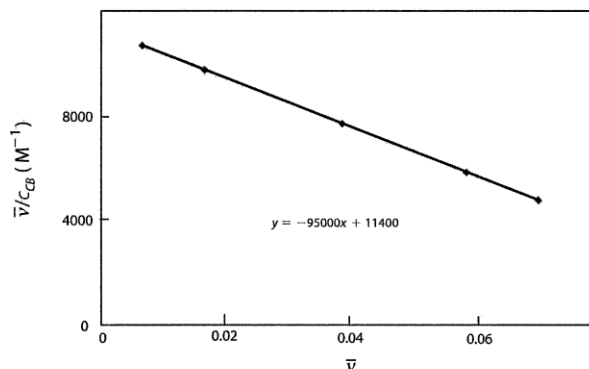
$$Z_{chloro} = \frac{n_{vapor}^{tot} y_{chloro} + n_{liq}^{tot} x_{chloro}}{n_{vapor}^{tot} + n_{liq}^{tot}} = \frac{3.21 \text{ mol} \times 0.750 + 4.86 \text{ mol} \times 0.524}{3.21 \text{ mol} + 4.86 \text{ mol}} = 0.614$$

- P9.31** DNA is capable of forming complex helical structures. An unusual triple-helix structure of poly(dA).2poly(dT) DNA was studied by P. V. Scaria and R. H. Shafer [*Journal of Biological Chemistry* 266 (1991): 5417] where the intercalation of ethidium bromide was studied using UV absorption and circular dichroism spectroscopy. The following representative data were obtained using the results of this study:

$c_{Eth}(\mu\text{M})$	0.63	1.7	5.0	10.0	14.7
\bar{v}	0.007	0.017	0.039	0.059	0.070

Using the data, determine K and N for the binding of ethidium bromide to the DNA triple-helical structure.

The Scatchard plot of the data is:



Best fit to the data by a straight line results in a slope of -95000 M^{-1} such that $K = 95000 \text{ M}^{-1}$. The y intercept is 11400 M^{-1} , which is equal to the product of K and N ; therefore, $N = 0.12$ corresponding to 2.8 base triplets per binding site.

- P9.32** Calculate the activity and activity coefficient for CS_2 at $x_{\text{CS}_2} = 0.722$ using the data in Table 9.3 for both a Raoult's law and a Henry's law standard state.

The Henry's law constant for CS_2 is 1750 Torr as discussed in Section 9.10

$$a_{\text{CS}_2}^R = \frac{P_{\text{CS}_2}}{P_{\text{CS}_2}^*} = \frac{446.9 \text{ Torr}}{512.3 \text{ Torr}} = 0.872$$

$$\gamma_{\text{CS}_2}^R = \frac{a_{\text{CS}_2}^R}{x_{\text{CS}_2}} = \frac{0.872}{0.722} = 1.21$$

$$a_{\text{CS}_2}^H = \frac{P_{\text{CS}_2}}{k_{H,\text{CS}_2}} = \frac{446.9 \text{ Torr}}{1750 \text{ Torr}} = 0.255$$

$$\gamma_{\text{CS}_2}^H = \frac{a_{\text{CS}_2}^H}{x_{\text{CS}_2}} = \frac{0.255}{0.722} = 0.354$$

- P9.33** The dissolution of 7.75 g of a substance in 825 g of benzene at 298 K raises the boiling point by 0.575°C . Note that $K_f = 5.12 \text{ K kg mol}^{-1}$, $K_b = 2.53 \text{ K kg mol}^{-1}$, and the density of benzene is 876.6 kg m^{-3} . Calculate the freezing point depression, the ratio of the vapor pressure above the solution to that of the pure solvent, the osmotic pressure, and the molecular weight of the solute. $P_{\text{benzene}}^* = 103 \text{ Torr}$ at 298 K.

$$\Delta T_b = K_b m_{\text{solute}}; \quad m_{\text{solute}} = \frac{\Delta T_b}{K_b} = \frac{0.575 \text{ K}}{2.53 \text{ K kg mol}^{-1}} = 0.227 \text{ mol kg}^{-1}$$

$$M = \frac{7.75 \text{ g}}{0.227 \text{ mol kg}^{-1} \times 0.825 \text{ kg}} = 41.3 \text{ g mol}^{-1}$$

$$\Delta T_f = -K_f m_{\text{solute}} = -5.12 \text{ K kg mol}^{-1} \times 0.227 \text{ mol kg}^{-1} = -1.16 \text{ K}$$

$$\begin{aligned} \frac{P_{\text{benzene}}}{P_{\text{benzene}}^*} = x_{\text{benzene}} &= \frac{n_{\text{benzene}}}{n_{\text{benzene}} + n_{\text{solute}}} \\ &= \frac{825 \text{ g}}{78.11 \text{ g mol}^{-1} + \frac{7.75 \text{ g}}{41.3 \text{ g mol}^{-1}}} = 0.983 \\ \pi = \frac{n_{\text{solute}}RT}{V} &= \frac{7.75 \times 10^{-3} \text{ kg}}{41.3 \times 10^{-3} \text{ kg mol}^{-1}} \times \frac{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}}{\frac{825 \times 10^{-3} \text{ kg}}{876.6 \text{ kg m}^{-3}}} = 4.93 \times 10^5 \text{ Pa} \end{aligned}$$

- P9.34** Describe what you would observe if you heated the solid at the composition 40. atomic percent Si in Figure 9.26 from 300.°C to 1300.°C.

The transition follows a path along a vertical line beginning at 40% Si composition and 300.°C. There would be no change in the solid until 363°C, at which it would melt to give a liquid at the eutectic composition and solid Si. As the temperature increases beyond 363°C, the liquid becomes enriched in Si, following the liquid – liquid + solid curve extending from the eutectic point to the 100% Si axis. At about 820°C, all the Si melts and there is no further change in composition of the solution as it is heated to 1300°C.

- P9.35** An ideal dilute solution is formed by dissolving the solute A in the solvent B. Write expressions equivalent to Equations (9.9) through (9.13) for this case.

We obtain the equations by replacing P_A^* by k_A^H .

$$\begin{aligned} P_{\text{tot}} &= P_A + P_B = x_A k_H^A + (1 - x_A) P_B^* \\ y_A &= \frac{P_A}{P_{\text{tot}}} = \frac{x_A k_H^A}{P_B^* + (k_H^A - P_B^*) x_A} \\ x_A &= \frac{y_A P_B^*}{k_H^A + (P_B^* - k_H^A) y_A} \\ P_{\text{tot}} &= \frac{k_H^A P_B^*}{k_H^A + (P_B^* - k_H^A) y_A} \\ y_A &= (k_H^A P_{\text{tot}} - k_H^A P_B^*) / [P_{\text{tot}} (k_H^A - P_B^*)] \end{aligned}$$

- P9.36** Describe the changes you would observe as the temperature of a mixture of phenol and water at point a in Figure 9.21 is increased until the system is at point a' . How does the relative amount of separate phases of phenol and water change along this path?

As T increases, the number of moles in separate phases decreases until the system consists of a single phase at point a' . The number of moles of each of the two immiscible solutions can be determined at any temperature by applying the lever rule to the appropriate tie line. For example, at point a , $\text{mols } L_1 \times (x_2 - x_1) = \text{mols } L_2 \times (x_3 - x_2)$.

- P9.37** Describe the changes you would observe as the temperature of a mixture of triethylamine and water at point a in Figure 9.22 is increased until the system is at point a'' . How does the relative amount of separate phases of triethylamine and water change along this path?

At point a , the two components are completely miscible, and phase separation does not occur until point a' is reached. As the temperature increases further, the amount of material in separate phases increases continuously. The relative amounts of L_1 and L_2 can be determined at each temperature using the lever rule and the appropriate tie line. For example, at point b which lies between a' and a'' , $\text{mols } L_1 \times (x_{b_1} - x_{L_1}) = \text{mols } L_2 \times (x_{L_2} - x_b)$.

- P9.38** Describe the changes in a beaker containing water and butanol that you would observe along the path $a \rightarrow b \rightarrow c$ in Figure 19.24b. How would you calculate the relative amounts of different phases present along the path?

Initially, the temperature of L_2 is increased with some change in its composition as indicated by the left boundary of the L_2 area. At T_b , boiling begins. If the vapor is collected, it has the composition of point b . If this vapor is cooled, it separates into L_1 and L_2 phases at 94°C . The mole fraction of butanol in these phases can be determined from the Z values corresponding to points g and h , respectively. As the mixture is cooled further to point c , liquid L_1 becomes more concentrated in water and L_2 becomes more concentrated in butanol. The relative amounts of L_1 and L_2 can be determined at each temperature using the lever rule and the appropriate tie line. For example, at point c , $\text{mols } L_1 \times (x_c - x_d) = \text{mols } L_2 \times (x_e - x_c)$.

- P9.39** Describe the changes in a beaker containing water and butanol that you would observe along the path $f \rightarrow j \rightarrow k$ in Figure 19.24b. How would you calculate the relative amounts of different phases present along the path?

As the temperature is increased from point f , liquid L_1 becomes less concentrated in water and L_2 becomes less concentrated in butanol. At 94°C , the two liquids present having the composition given by h and g coexist with the vapor phase, which has the composition i . As T increases further, there is a single liquid phase L_1 whose composition varies along the $g-k$ curve in equilibrium with the vapor phase whose composition varies along the $i-j$ curve as the temperature increases. At point j , nearly the whole system is in the vapor phase, with a trace of liquid having the composition k . At point l , the entire system is in the vapor phase at the initial composition. The relative amounts of L_1 and L_2 can be determined at each temperature using the lever rule and the appropriate tie line. For example, at point f , $\text{mols } L_1 \times (x_f - x_d) = \text{mols } L_2 \times (x_e - x_f)$.

- P9.40** Describe the changes in a beaker containing water and butanol that you would observe along the path $f \rightarrow j \rightarrow k$ in Figure 19.24b. How would you calculate the relative amounts of different phases present along the path?

As the temperature is increased from point f , liquid L_1 becomes less concentrated in water and L_2 becomes less concentrated in butanol. At 94°C , the two liquids present having the composition given by h and g coexist with the vapor phase, which has the composition i . As T increases further to point j , the composition of liquid phase L_1 changes from x_g to x_k , and the vapor phase composition changes from y_i to y_j . At point j , the vapor is removed and cooled to produce a liquid of composition x_k . The relative amounts of L_1 and L_2 can be determined at each temperature using the lever rule and the appropriate tie line. For example, at point f , $\text{mols } L_1 \times (x_f - x_d) = \text{mols } L_2 \times (x_e - x_f)$.

- P9.41** Describe the system at points a and c in Figure 19.25b. How would you calculate the relative amounts of different phases present at these points?

Point a corresponds to essentially pure solid B in equilibrium with a solution whose composition is given by point b . Point c corresponds to essentially pure solid A in equilibrium with a solution whose composition is given by point c . The relative amounts of pure A and B and the liquid can be determined at each temperature using the lever rule and the appropriate tie line. For example, at point c , $\text{mols } A \times (x_c - 0) = \text{mols } \text{Liquid} \times (x_d - x_c)$.