

Use Equations 16.17 and 16.18 with  $T_c = 561.75$  K and  $P_c = 48.7575$  bar to calculate the van der Waals parameters and the Redlich-Kwong parameters.

$T/\text{K}$	$P/\text{bar}$	$\rho^g/\text{mol}\cdot\text{L}^{-1}$
290.0	0.0860	0.00359
300.0	0.1381	0.00558
310.0	0.2139	0.00839
320.0	0.3205	0.01223
330.0	0.4666	0.01734
340.0	0.6615	0.02399
350.0	0.9161	0.03248

We can do this in the same way as the previous problem after finding  $a$ ,  $b$ ,  $A$ , and  $B$  using Equations 16.17 and 16.18:

$$a = \frac{27(RT_c)^2}{64P_c} = \frac{27[(0.083145 \text{ dm}^3\cdot\text{bar}\cdot\text{mol}^{-1})(561.75)]^2}{64(48.7575 \text{ bar})} = 18.876 \text{ dm}^6\cdot\text{bar}\cdot\text{mol}^{-2}$$

$$b = \frac{RT_c}{8P_c} = \frac{(0.083145 \text{ dm}^3\cdot\text{bar}\cdot\text{mol}^{-1})(561.75)}{8(48.7575 \text{ bar})} = 0.11974 \text{ dm}^3\cdot\text{mol}^{-1}$$

$$A = 0.42748 \frac{R^2 T_c^{5/2}}{P_c} = 0.42748 \frac{(0.083145 \text{ dm}^3\cdot\text{bar}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})^2 (561.75 \text{ K})^{5/2}}{48.7575 \text{ bar}} \\ = 453.21 \text{ dm}^6\cdot\text{bar}\cdot\text{mol}^{-1}\cdot\text{K}^{1/2}$$

$$B = 0.086640 \frac{RT_c}{P_c} = 0.086640 \frac{(0.083145 \text{ dm}^3\cdot\text{bar}\cdot\text{mol}^{-1})(561.75)}{48.7575 \text{ bar}} = 0.082996 \text{ dm}^3\cdot\text{mol}^{-1}$$

Now substitute into the appropriate equations to find the vapor pressure  $P$  for each temperature and density:

$T/\text{K}$	$P(\text{van der Waals})/\text{bar}$	$P(\text{Redlich-Kwong})/\text{bar}$
290	0.00842	0.00757
300	0.13869	0.13843
310	0.21514	0.21459
320	0.32305	0.32194
330	0.47109	0.46897
340	0.66927	0.66541
350	0.92897	0.92225

## Solutions I Liquid-Liquid Solutions

### PROBLEMS AND SOLUTIONS

24-1. In the text, we went from Equation 24.5 to 24.6 using a physical argument involving varying the size of the system while keeping  $T$  and  $P$  fixed. We could also have used a mathematical process called *Euler's theorem*. Before we can learn about Euler's theorem, we must first define a *homogeneous function*. A function  $f(z_1, z_2, \dots, z_N)$  is said to be homogeneous if

$$f(\lambda z_1, \lambda z_2, \dots, \lambda z_N) = \lambda f(z_1, z_2, \dots, z_N)$$

Argue that extensive thermodynamic quantities are homogeneous functions of their extensive variables.

If we change extensive variables by a factor of  $\lambda$ , then we change an extensive function of these variables by a factor of  $\lambda$ .

24-2. Euler's theorem says that if  $f(z_1, z_2, \dots, z_N)$  is homogeneous, then

$$f(z_1, z_2, \dots, z_N) = z_1 \frac{\partial f}{\partial z_1} + z_2 \frac{\partial f}{\partial z_2} + \dots + z_N \frac{\partial f}{\partial z_N}$$

Prove Euler's theorem by differentiating the equation in Problem 24-1 with respect to  $\lambda$  and then setting  $\lambda = 1$ .

Apply Euler's theorem to  $G = G(n_1, n_2, T, P)$  to derive Equation 24.6. (*Hint*: Because  $T$  and  $P$  are intensive variables, they are simply irrelevant variables in this case.)

Start with

$$\lambda f(z_1, z_2, \dots, z_N) = f(\lambda z_1, \lambda z_2, \dots, \lambda z_N)$$

differentiate with respect to  $\lambda$  to obtain

$$f(z_1, z_2, \dots, z_N) = \frac{\partial f(\lambda z_1, \lambda z_2, \dots, \lambda z_N)}{\partial \lambda z_1} \frac{\partial \lambda z_1}{\partial \lambda} + \dots + \frac{\partial f(\lambda z_1, \lambda z_2, \dots, \lambda z_N)}{\partial \lambda z_N} \frac{\partial \lambda z_N}{\partial \lambda} \\ = z_1 \frac{\partial f(\lambda z_1, \lambda z_2, \dots, \lambda z_N)}{\partial \lambda z_1} + \dots + z_N \frac{\partial f(\lambda z_1, \lambda z_2, \dots, \lambda z_N)}{\partial \lambda z_N}$$

Now set  $\lambda = 1$

$$f(z_1, z_2, \dots, z_N) = z_1 \frac{\partial f}{\partial z_1} + \dots + z_N \frac{\partial f}{\partial z_N}$$

To apply this result to  $G = G(n_1, n_2, T, P)$ , we let  $f = G$ ,  $z_1 = n_1$ , and  $z_2 = n_2$  to write

$$\begin{aligned} G(n_1, n_2, T, P) &= n_1 \left( \frac{\partial G}{\partial n_1} \right)_{T, P, n_2} + n_2 \left( \frac{\partial G}{\partial n_2} \right)_{T, P, n_1} \\ &= n_1 \mu_1 + n_2 \mu_2 \end{aligned}$$

24-3. Use Euler's theorem (Problem 24-2) to prove that

$$Y(n_1, n_2, \dots, T, P) = \sum n_j \bar{Y}_j$$

for any extensive quantity  $Y$ .

Simply let  $Y = f$  and  $n_j = z_j$  in Problem 24-2 to write

$$\begin{aligned} Y(n_1, n_2, \dots, T, P) &= n_1 \left( \frac{\partial Y}{\partial n_1} \right)_{T, P, n_{k \neq 1}} + n_2 \left( \frac{\partial Y}{\partial n_2} \right)_{T, P, n_{k \neq 2}} + \dots \\ &= n_1 \bar{Y}_1 + n_2 \bar{Y}_2 + \dots \end{aligned}$$

24-4. Apply Euler's theorem to  $U = U(S, V, n)$ . Do you recognize the resulting equation?

All three variables,  $S$ ,  $V$  and  $n$ , are extensive. Using Euler's theorem (Problem 24-2) gives

$$\begin{aligned} U &= S \left( \frac{\partial U}{\partial S} \right)_{V, n} + V \left( \frac{\partial U}{\partial V} \right)_{S, n} + n \left( \frac{\partial U}{\partial n} \right)_{S, V} \\ &= S(T) + V(-P) + n(\mu) \\ &= TS - PV + \mu n \end{aligned}$$

or

$$G = \mu n = U - TS + PV = H - TS = A + PV$$

This is the defining equation for the Gibbs energy.

24-5. Apply Euler's theorem to  $A = A(T, V, n)$ . Do you recognize the resulting equation?

The extensive variables are  $V$  and  $n$ . Using Euler's theorem (Problem 24-2) gives

$$\begin{aligned} A &= V \left( \frac{\partial A}{\partial V} \right)_{T, n} + n \left( \frac{\partial A}{\partial n} \right)_{T, V} \\ &= V(-P) + n(\mu) \end{aligned}$$

or

$$G = A + PV$$

This is the defining equation for the Gibbs energy.

24-6. Apply Euler's theorem to  $V = V(T, P, n_1, n_2)$  to derive Equation 24.7.

Use the result of Problem 24-3 with  $V = Y$ .

24-7. The properties of many solutions are given as a function of the mass percent of the components. If we let the mass percent of component-2 be  $A_2$ , then derive a relation between  $A_2$  and the mole fractions,  $x_1$  and  $x_2$ .

$$A_2 = \frac{m_2}{m_1 + m_2} \times 100 = \frac{M_2 n_2}{M_1 n_1 + M_2 n_2} \times 100 \quad (1)$$

where the number of moles of component  $j$  is  $n_j = m_j/M_j$  where  $M_j$  is its molar mass. Now divide numerator and denominator of Equation 1 by  $n_1 + n_2$  to write

$$A_2 = \frac{M_2 x_2}{M_1 x_1 + M_2 x_2} \times 100$$

24-8. The *CRC Handbook of Chemistry and Physics* gives the densities of many aqueous solutions as a function of the mass percentage of solute. If we denote the density by  $\rho$  and the mass percentage of component-2 by  $A_2$ , the *Handbook* gives  $\rho = \rho(A_2)$  (in  $\text{g} \cdot \text{mL}^{-1}$ ). Show that the quantity  $V = (n_1 M_1 + n_2 M_2)/\rho(A_2)$  is the volume of the solution containing  $n_1$  moles of component 1 and  $n_2$  moles of component-2. Now show that

$$\bar{V}_1 = \frac{M_1}{\rho(A_2)} \left[ 1 + \frac{A_2}{\rho(A_2)} \frac{d\rho(A_2)}{dA_2} \right]$$

and

$$\bar{V}_2 = \frac{M_2}{\rho(A_2)} \left[ 1 + \frac{(A_2 - 100)}{\rho(A_2)} \frac{d\rho(A_2)}{dA_2} \right]$$

Show that

$$V = n_1 \bar{V}_1 + n_2 \bar{V}_2$$

in agreement with Equation 24.7.

The mass of component  $j$  in the solution is  $m_j = n_j M_j$ , so the total mass is  $n_1 M_1 + n_2 M_2$ . Therefore, the volume is the mass divided by the density, or  $V = (n_1 M_1 + n_2 M_2)/\rho(A_2)$ . Now

$$\bar{V}_1 = \left( \frac{\partial V}{\partial n_1} \right)_{n_2} = \frac{M_1}{\rho(A_2)} - \frac{n_1 M_1 + n_2 M_2}{\rho^2(A_2)} \left[ \frac{\partial \rho(A_2)}{\partial n_1} \right]_{n_2}$$

But, using Equation 1 of Problem 24-7,

$$\begin{aligned} \left[ \frac{\partial \rho(A_2)}{\partial n_1} \right]_{n_2} &= \left[ \frac{d\rho(A_2)}{dA_2} \right] \left( \frac{\partial A_2}{\partial n_1} \right)_{n_2} = \left[ \frac{d\rho(A_2)}{dA_2} \right] \left[ -\frac{M_2 n_2 M_1}{(n_1 M_1 + n_2 M_2)^2} \times 100 \right] \\ &= \left[ \frac{d\rho(A_2)}{dA_2} \right] \left( -\frac{A_2 M_1}{n_1 M_1 + n_2 M_2} \right) \end{aligned}$$

Substitute this into  $\bar{V}_1$  above to get

$$\bar{V}_1 = \frac{M_1}{\rho(A_2)} + \frac{A_2 M_1}{\rho^2(A_2)} \frac{d\rho(A_2)}{dA_2} = \frac{M_1}{\rho(A_2)} \left[ 1 + \frac{A_2}{\rho(A_2)} \frac{d\rho(A_2)}{dA_2} \right]$$

Similarly

$$\bar{V}_2 = \left( \frac{\partial V}{\partial n_2} \right)_{n_1} = \frac{M_2}{\rho(A_2)} - \frac{n_1 M_1 + n_2 M_2}{\rho^2(A_2)} \left[ \frac{\partial \rho(A_2)}{\partial n_2} \right]_{n_1}$$

But

$$\begin{aligned} \left[ \frac{\partial \rho(A_2)}{\partial n_2} \right]_{n_1} &= \left[ \frac{d\rho(A_2)}{dA_2} \right] \left( \frac{\partial A_2}{\partial n_2} \right)_{n_1} \\ &= \left[ \frac{d\rho(A_2)}{dA_2} \right] \left[ \frac{100 M_2}{n_1 M_1 + n_2 M_2} - \frac{100 n_2 M_2^2}{(n_1 M_1 + n_2 M_2)^2} \right] \\ &= \left[ \frac{d\rho(A_2)}{dA_2} \right] \left[ \frac{100 M_2 n_1 M_1}{(n_1 M_1 + n_2 M_2)^2} \right] \end{aligned}$$

Substituting this into  $\bar{V}_2$  gives

$$\bar{V}_2 = \frac{M_2}{\rho(A_2)} \left[ 1 - \frac{A_1}{\rho(A_2)} \frac{d\rho(A_2)}{dA_2} \right] = \frac{M_2}{\rho(A_2)} \left[ 1 + \frac{(A_2 - 100)}{\rho(A_2)} \frac{d\rho(A_2)}{dA_2} \right]$$

because  $A_1 + A_2 = 100$ . Finally,

$$n_1 \bar{V}_1 + n_2 \bar{V}_2 = \frac{n_1 M_1 + n_2 M_2}{\rho(A_2)} + \frac{(n_1 M_1 A_2 - n_2 M_2 A_1)}{\rho^2(A_2)} \frac{d\rho(A_2)}{dA_2}$$

But

$$n_1 M_1 A_2 - n_2 M_2 A_1 = \frac{n_1 M_1 M_2 n_2 - n_2 M_2 M_1 n_1}{n_1 M_1 + n_2 M_2} \times 100 = 0$$

so

$$n_1 \bar{V}_1 + n_2 \bar{V}_2 = \frac{n_1 M_1 + n_2 M_2}{\rho(A_2)} = V$$

24-9. The density (in  $\text{g} \cdot \text{mol}^{-1}$ ) of a 1-propanol-water solution at 20°C as a function of  $A_2$ , the mass percentage of 1-propanol, can be expressed as

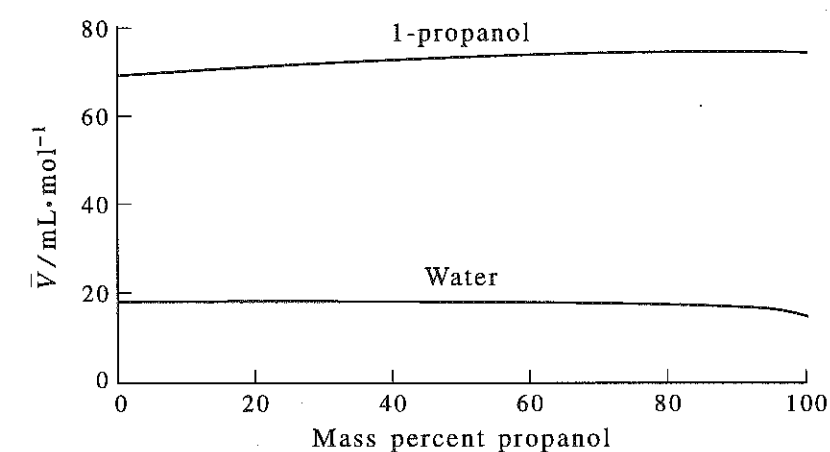
$$\rho(A_2) = \sum_{j=0}^7 \alpha_j A_2^j$$

where

$$\begin{aligned} \alpha_0 &= 0.99823 & \alpha_4 &= 1.5312 \times 10^{-7} \\ \alpha_1 &= -0.0020577 & \alpha_5 &= -2.0365 \times 10^{-9} \\ \alpha_2 &= 1.0021 \times 10^{-4} & \alpha_6 &= 1.3741 \times 10^{-11} \\ \alpha_3 &= -5.9518 \times 10^{-6} & \alpha_7 &= -3.7278 \times 10^{-14} \end{aligned}$$

Use this expression to plot  $\bar{V}_{\text{H}_2\text{O}}$  and  $\bar{V}_{1\text{-propanol}}$  versus  $A_2$  and compare your values with those in Figure 24.1.

Substitute  $\rho(A_2)$  into  $\bar{V}_1 = \bar{V}_{1\text{-propanol}}$  in Problem 24-8 and into  $\bar{V}_2 = \bar{V}_{\text{H}_2\text{O}}$  to obtain



24-10. Given the density of a binary solution as a function of the mole fraction of component 2 [ $\rho = \rho(x_2)$ ], show that the volume of the solution containing  $n_1$  moles of component 1 and  $n_2$  moles of component 2 is given by  $V = (n_1 M_1 + n_2 M_2) / \rho(x_2)$ . Now show that

$$\bar{V}_1 = \frac{M_1}{\rho(x_2)} \left[ 1 + \left( \frac{x_2(M_2 - M_1) + M_1}{M_1} \right) \frac{x_2}{\rho(x_2)} \frac{d\rho(x_2)}{dx_2} \right]$$

and

$$\bar{V}_2 = \frac{M_2}{\rho(x_2)} \left[ 1 - \left( \frac{x_2(M_2 - M_1) + M_1}{M_2} \right) \frac{1 - x_2}{\rho(x_2)} \frac{d\rho(x_2)}{dx_2} \right]$$

Show that

$$V = n_1 \bar{V}_1 + n_2 \bar{V}_2$$

in agreement with Equation 24.7.

The total mass of the solution is  $n_1 M_1 + n_2 M_2$ , so its volume (mass/density) is  $V = (n_1 M_1 + n_2 M_2) / \rho(x_2)$ .

$$\bar{V}_1 = \left( \frac{\partial V}{\partial n_1} \right)_{n_2} = \frac{M_1}{\rho(x_2)} - \frac{n_1 M_1 + n_2 M_2}{\rho^2(x_2)} \left[ \frac{\partial \rho(x_2)}{\partial n_1} \right]_{n_2}$$

But,

$$\begin{aligned} \left[ \frac{\partial \rho(x_2)}{\partial n_1} \right]_{n_2} &= \left[ \frac{d\rho(x_2)}{dx_2} \right] \left( \frac{\partial x_2}{\partial n_1} \right)_{n_2} = \left[ \frac{d\rho(x_2)}{dx_2} \right] \left[ -\frac{n_2}{(n_1 + n_2)^2} \right] \\ &= - \left[ \frac{d\rho(x_2)}{dx_2} \right] \left( \frac{x_2}{n_1 + n_2} \right) \end{aligned}$$

Substitute this result into  $\bar{V}_1$  to get

$$\begin{aligned}\bar{V}_1 &= \frac{M_1}{\rho(x_2)} + \frac{(n_1 M_1 + n_2 M_2) x_2}{(n_1 + n_2) \rho^2(x_2)} \frac{d\rho(x_2)}{dx_2} = \frac{M_1}{\rho(x_2)} + \frac{(x_1 M_1 + x_2 M_2) x_2}{\rho^2(x_2)} \frac{d\rho(x_2)}{dx_2} \\ &= \frac{M_1}{\rho(x_2)} \left[ 1 + \frac{x_1 M_1 + x_2 M_2}{M_1} \frac{x_2}{\rho(x_2)} \frac{d\rho(x_2)}{dx_2} \right] \\ &= \frac{M_1}{\rho(x_2)} \left[ 1 + \frac{M_1 + x_2(M_2 - M_1)}{M_1} \frac{x_2}{\rho(x_2)} \frac{d\rho(x_2)}{dx_2} \right]\end{aligned}$$

Similarly

$$\bar{V}_2 = \left( \frac{\partial V}{\partial n_2} \right)_{n_1} = \frac{M_2}{\rho(x_2)} - \frac{n_1 M_1 + n_2 M_2}{\rho^2(x_2)} \left[ \frac{\partial \rho(x_2)}{\partial n_2} \right]_{n_1}$$

But

$$\begin{aligned}\left[ \frac{\partial \rho(x_2)}{\partial n_2} \right]_{n_1} &= \frac{d\rho(x_2)}{dx_2} \left[ \frac{\partial x_2}{\partial n_2} \right]_{n_1} = \frac{d\rho(x_2)}{dx_2} \left[ \frac{1}{n_1 + n_2} - \frac{n_2}{(n_1 + n_2)^2} \right] \\ &= \frac{d\rho(x_2)}{dx_2} \left[ \frac{n_1}{(n_1 + n_2)^2} \right] = \frac{d\rho(x_2)}{dx_2} \frac{x_1}{n_1 + n_2}\end{aligned}$$

Substitute this result into  $\bar{V}_2$  to get

$$\begin{aligned}\bar{V}_2 &= \frac{M_2}{\rho(A_2)} - \frac{(x_1 M_1 + x_2 M_2) x_1}{\rho^2(x_2)} \frac{d\rho(x_2)}{dx_2} \\ &= \frac{M_2}{\rho(A_2)} \left\{ 1 - \left[ \frac{M_1 + x_2(M_2 - M_1)}{M_2} \right] \frac{1 - x_2}{\rho(x_2)} \frac{d\rho(x_2)}{dx_2} \right\}\end{aligned}$$

Finally,

$$n_1 \bar{V}_1 + n_2 \bar{V}_2 = \frac{n_1 M_1 + n_2 M_2}{\rho(x_2)} + \frac{M_1 + x_2(M_2 - M_1)}{\rho^2(A_2)} \frac{d\rho(A_2)}{dA_2} (n_1 x_2 - n_2 x_1)$$

But

$$n_1 x_2 - n_2 x_1 = \frac{n_1 n_2}{n_1 + n_2} - \frac{n_2 n_1}{n_1 + n_2} = 0$$

so

$$n_1 \bar{V}_1 + n_2 \bar{V}_2 = \frac{n_1 M_1 + n_2 M_2}{\rho(x_2)} = V$$

**24-11.** The density (in  $\text{g} \cdot \text{mol}^{-1}$ ) of a 1-propanol/water solution at  $20^\circ\text{C}$  as a function of  $x_2$ , the mole fraction of 1-propanol, can be expressed as

$$\rho(x_2) = \sum_{j=0}^4 \alpha_j x_2^j$$

where

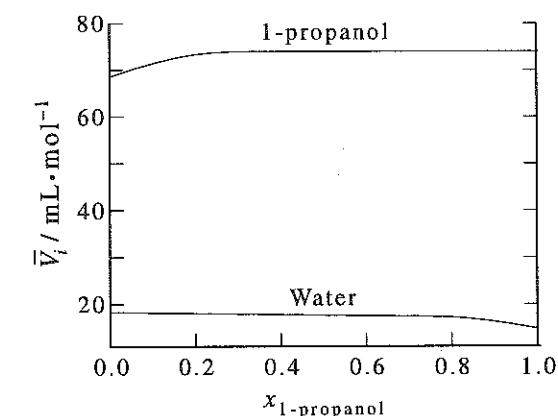
$$\alpha_0 = 0.99823 \quad \alpha_3 = -0.17163$$

$$\alpha_1 = -0.48503 \quad \alpha_4 = -0.01387$$

$$\alpha_2 = 0.47518$$

Use this expression to calculate the values of  $\bar{V}_{\text{H}_2\text{O}}$  and  $\bar{V}_{1\text{-propanol}}$  as a function of  $x_2$  according to the equation in Problem 24-10.

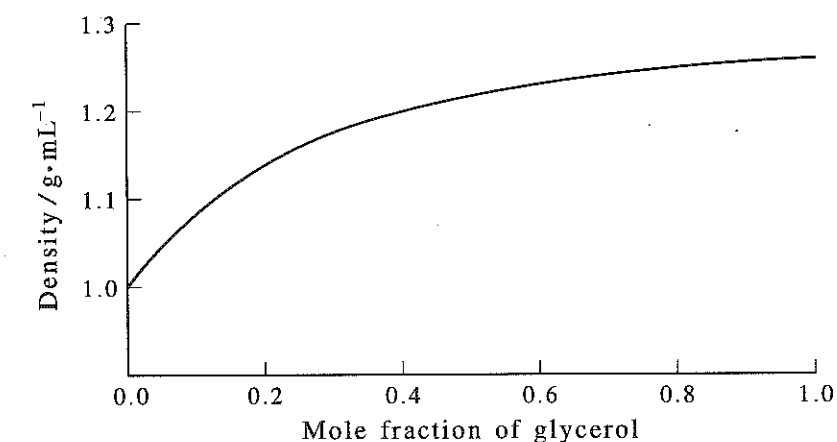
Substitute  $\rho(x_2)$  into  $\bar{V}_1 = \bar{V}_{1\text{-propanol}}$  and  $\bar{V}_2 = \bar{V}_{\text{H}_2\text{O}}$  in Problem 24-10 to obtain



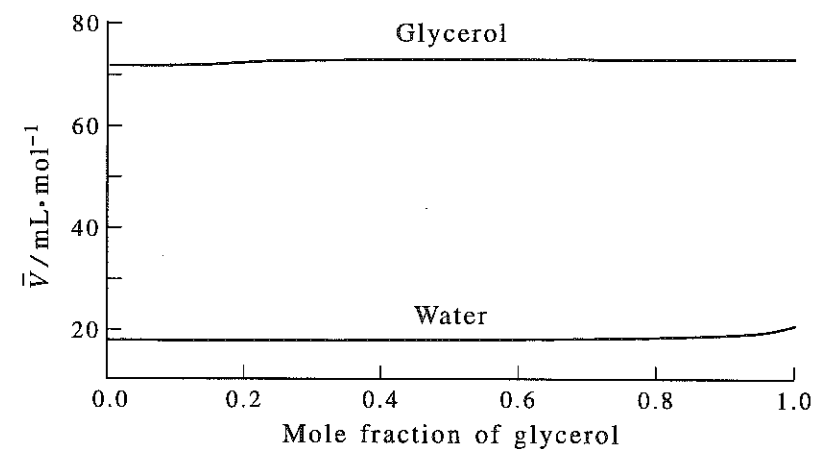
**24-12.** Use the data in the *CRC Handbook of Chemistry and Physics* to curve fit the density of a water/glycerol solution to a fifth-order polynomial in the mole fraction of glycerol, and then determine the partial molar volumes of water and glycerol as a function of mole fraction. Plot your result.

The curve fit of the density-mole fraction data gives (see the accompanying figure)

$$\begin{aligned}\rho(x_2) &= 0.99849 + 1.1328x_2 - 2.7605x_2^2 + 4.1281x_2^3 \\ &\quad - 3.2887x_2^4 + 1.0512x_2^5\end{aligned}$$



Substitute this result into the equations for  $\bar{V}_1$  and  $\bar{V}_2$  given in Problem 24-10 with  $M_1 = 18.02$  and  $M_2 = 92.09$  to get the following result:



**24-13.** Just before Example 24-2, we showed that if one component of a binary solution obeys Raoult's law over the entire composition range, the other component does also. Now show that if  $\mu_2 = \mu'_2 + RT \ln x_2$  for  $x_{2,\min} \leq x_2 \leq 1$ , then  $\mu_1 = \mu'_1 + RT \ln x_1$  for  $0 < x_1 < 1 - x_{2,\min}$ . Notice that for the range over which  $\mu_2$  obeys the simple form given,  $\mu_1$  obeys a similarly simple form. If we let  $x_{2,\min} = 0$ , we obtain  $\mu_1 = \mu'_1 + RT \ln x_1$  ( $0 \leq x_1 \leq 1$ ).

Start with the Gibbs-Duhem equation

$$x_1 d\mu_1 + x_2 d\mu_2 = 0$$

Solve for  $d\mu_1$

$$\begin{aligned} d\mu_1 &= -\frac{x_2}{x_1} d\mu_2 = -\frac{x_2}{x_1} \frac{RT}{x_2} dx_2 & x_{2,\min} \leq x_2 \leq 1 \\ &= \frac{RT}{x_1} dx_1 & 0 \leq x_1 \leq 1 - x_{2,\min} \end{aligned}$$

Integrate to obtain

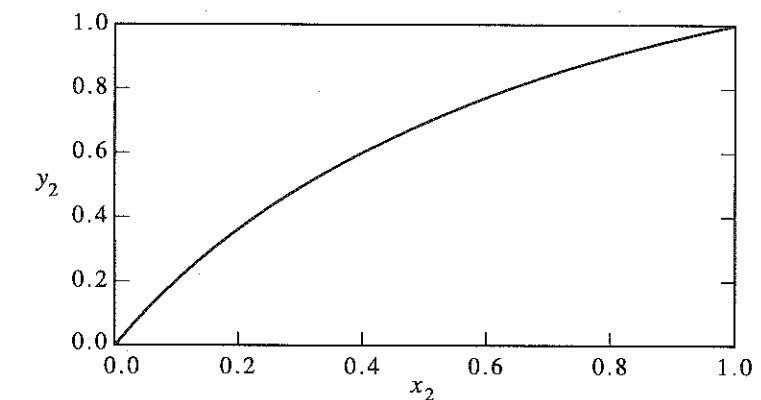
$$\mu_1 = \mu'_1 + RT \ln x_1 \quad 0 \leq x_1 \leq 1 - x_{2,\min}$$

**24-14.** Continue the calculations in Example 24-3 to obtain  $y_2$  as a function of  $x_2$  by varying  $x_2$  from 0 to 1. Plot your result.

We use the equation

$$y_2 = \frac{P_2}{P_{\text{total}}} = \frac{x_2 P_2^*}{x_1 P_1^* + x_2 P_2^*} = \frac{x_2 (45.2 \text{ torr})}{(1 - x_2)(20.9 \text{ torr}) + x_2 (45.2 \text{ torr})}$$

A plot of  $y_2$  against  $x_2$  is



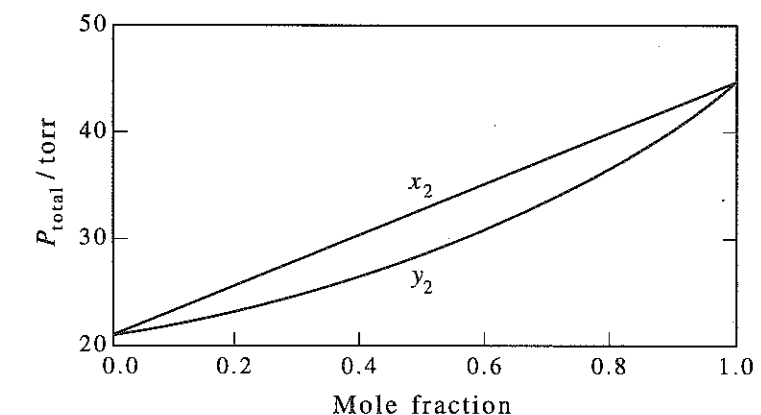
**24-15.** Use your results from Problem 24-14 to construct the pressure-composition diagram in Figure 24.4.

$$P_{\text{total}} = (1 - x_2)(20.9 \text{ torr}) + x_2(45.2 \text{ torr})$$

Solve the equation given in Problem 24-14 for  $x_2$  in terms of  $y_2$

$$x_2 = \frac{(20.9 \text{ torr}) y_2}{45.2 \text{ torr} + (20.9 \text{ torr} - 45.2 \text{ torr}) y_2}$$

Let  $x_2$  vary from 0 to 1 in the first equation to calculate  $P_{\text{total}}$  as a function of  $x_2$ . Now let  $y_2$  vary from 0 to 1 to calculate  $x_2$  and then  $P_{\text{total}}$  to give  $P_{\text{total}}$  as a function of  $y_2$ . A plot of  $P_{\text{total}}$  against  $x_2$  and  $y_2$  is



**24-16.** Calculate the relative amounts of liquid and vapor phases at an overall composition of 0.50 for one of the pair of values,  $x_2 = 0.38$  and  $y_2 = 0.57$ , that you obtained in Problem 24-14.



We use Equation 24.19

$$\frac{n^l}{n^{\text{vap}}} = \frac{y_2 - x_a}{x_a - x_2} = \frac{0.57 - 0.50}{0.50 - 0.38} = 0.58$$

**24-17.** In this problem, we will derive analytic expressions for the pressure-composition curves in Figure 24.4. The liquid (upper) curve is just

$$P_{\text{total}} = x_1 P_1^* + x_2 P_2^* = (1 - x_2) P_1^* + x_2 P_2^* = P_1^* + x_2 (P_2^* - P_1^*) \quad (1)$$

which is a straight line, as seen in Figure 24.4. Solve the equation

$$y_2 = \frac{x_2 P_2^*}{P_{\text{total}}} = \frac{x_2 P_2^*}{P_1^* + x_2 (P_2^* - P_1^*)} \quad (2)$$

for  $x_2$  in terms of  $y_2$  and substitute into Equation (1) to obtain

$$P_{\text{total}} = \frac{P_1^* P_2^*}{P_2^* - y_2 (P_2^* - P_1^*)}$$

Plot this result versus  $y_2$  and show that it gives the vapor (lower) curve in Figure 24.4.

We solve Equation 2 for  $x_2$  to obtain

$$x_2 = \frac{y_2 P_1^*}{P_2^* - y_2 (P_2^* - P_1^*)}$$

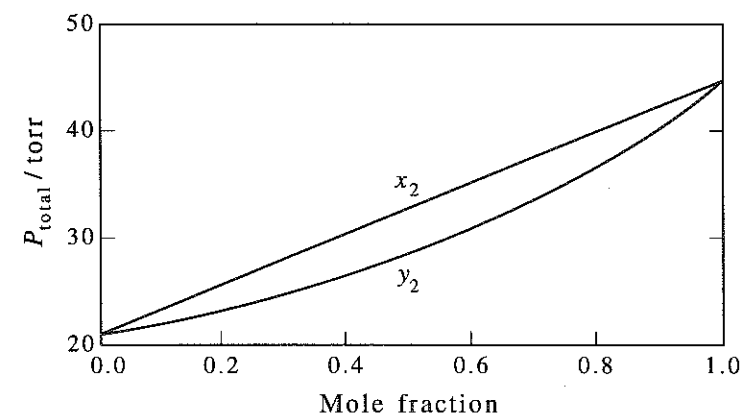
Substitute this result into

$$P_{\text{total}} = P_1^* + x_2 (P_2^* - P_1^*)$$

to get

$$P_{\text{total}} = \frac{P_1^* P_2^*}{P_2^* - y_2 (P_2^* - P_1^*)}$$

The plots of  $P_{\text{total}}$  against  $x_2$  and  $y_2$  for  $P_1^* = 20.9$  torr and  $P_2^* = 45.2$  torr are



**24-18.** Prove that  $y_2 > x_2$  if  $P_2^* > P_1^*$  and that  $y_2 < x_2$  if  $P_2^* < P_1^*$ . Interpret this result physically.

Start with

$$y_2 = \frac{x_2 P_2^*}{P_1^* + x_2 (P_2^* - P_1^*)}$$

Divide both sides by  $x_2$  and the numerator and denominator of the right side by  $P_1^*$  to obtain

$$\frac{y_2}{x_2} = \frac{P_2^*/P_1^*}{1 + x_2 (P_2^*/P_1^* - 1)} = \frac{R}{1 + x_2 (R - 1)}$$

where  $R = P_2^*/P_1^*$ . Now subtract 1 from both sides

$$\frac{y_2}{x_2} - 1 = \frac{R - 1 - x_2 (R - 1)}{1 + x_2 (R - 1)} = \frac{x_1 (R - 1)}{1 + x_2 (R - 1)}$$

If  $R > 1$  ( $P_2^* > P_1^*$ ), then the right side is always positive because  $0 \leq x_1 \leq 1$  and  $0 \leq x_2 \leq 1$  and so  $y_2 > x_2$ . If  $R < 1$  ( $P_2^* < P_1^*$ ), then the right side is always negative.

This result simply says that the mole fraction of a given component in the vapor phase will be greater than that of the other component if it is more volatile.

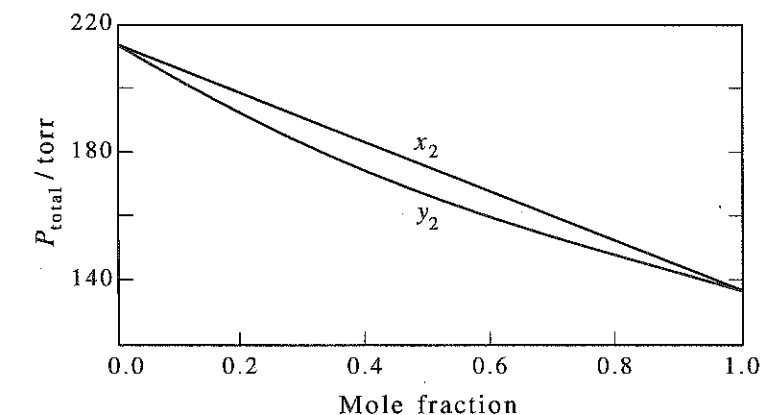
**24-19.** Tetrachloromethane and trichloroethylene form essentially an ideal solution at 40°C at all concentrations. Given that the vapor pressure of tetrachloromethane and trichloroethylene at 40°C are 214 torr and 138 torr, respectively, plot the pressure-composition diagram for this system (see Problem 24-17).

Plot

$$P_{\text{total}} = P_1^* + x_2 (P_2^* - P_1^*) = 214 \text{ torr} - x_2 (76 \text{ torr})$$

and

$$P_{\text{total}} = \frac{P_1^* P_2^*}{P_2^* - y_2 (P_2^* - P_1^*)} = \frac{(214 \text{ torr})(138 \text{ torr})}{138 \text{ torr} + y_2 (76 \text{ torr})}$$



**24-20.** The vapor pressures of tetrachloromethane (1) and trichloroethylene (2) between 76.8°C and 87.2°C can be expressed empirically by the formulas

$$\ln(P_1^*/\text{torr}) = 15.8401 - \frac{2790.78}{t + 226.4}$$

and

$$\ln(P_2^*/\text{torr}) = 15.0124 - \frac{2345.4}{t + 192.7}$$

where  $t$  is the Celsius temperature. Assuming that tetrachloromethane and trichloroethylene form an ideal solution between 76.8°C and 87.2°C at all compositions, calculate the values of  $x_1$  and  $y_1$  at 82.0°C (at an ambient pressure of 760 torr).

Let 1 denote tetrachloromethane and 2 denote trichloroethylene.

$$\ln(P_1^*/\text{torr}) = 15.8401 - \frac{2790.78}{82.0 + 226.4} = 6.7919$$

or  $P_1^* = 890$  torr. Similarly,  $P_2^* = 648$  torr. Therefore, (see Example 24-5)

$$x_1 = \frac{P_2^* - 760 \text{ torr}}{P_2^* - P_1^*} = \frac{648 \text{ torr} - 760 \text{ torr}}{648 \text{ torr} - 890 \text{ torr}} = 0.463$$

$$y_1 = \frac{P_1}{760 \text{ torr}} = \frac{x_1 P_1^*}{760 \text{ torr}} = \frac{(0.463)(890 \text{ torr})}{760 \text{ torr}} = 0.542$$

**24-21.** Use the data in Problem 24-20 to construct the entire temperature-composition diagram of a tetrachloromethane/trichloroethylene solution.

The vapor pressures of tetrachloromethane (1) and trichloroethylene (2) between 76.8°C and 87.2°C are given by

$$\ln(P_1^*/\text{torr}) = 15.8401 - \frac{2790.84}{t + 226.4}$$

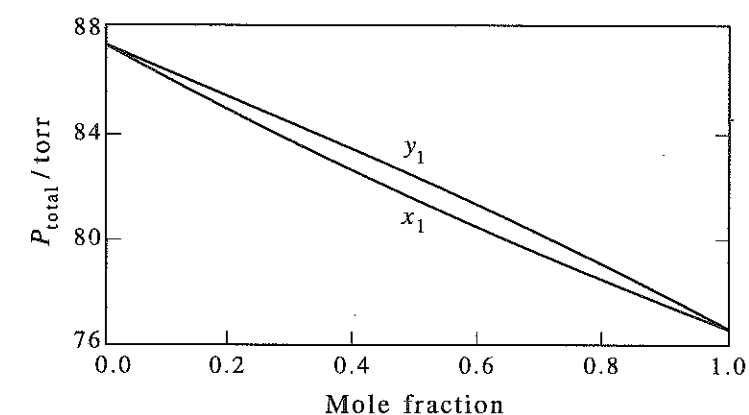
$$\ln(P_2^*/\text{torr}) = 15.0124 - \frac{2345.4}{t + 192.7}$$

where  $t$  is the Celsius temperature. The mole fractions of tetrachloromethane (1) in the liquid and vapor phases at temperature  $t$  are given by

$$x_1 = \frac{P_2^* - 760 \text{ torr}}{P_2^* - P_1^*} \quad \text{and} \quad y_1 = \frac{x_1 P_1^*}{760 \text{ torr}}$$

Some data and the plot are given below.

$t/^\circ\text{C}$	$P_1^*/\text{torr}$	$P_2^*/\text{torr}$	$x_1$	$y_1$
76.8	761.7	549.8	0.992	0.994
77.6	780.3	564.2	0.906	0.930
78.4	799.3	578.8	0.822	0.864
79.2	818.7	593.7	0.739	0.796
80.0	838.5	608.9	0.658	0.726
80.8	858.6	624.5	0.579	0.654
81.6	879.1	640.3	0.501	0.580
82.4	900.0	656.4	0.425	0.504
83.2	921.3	672.8	0.360	0.435
84.0	942.9	706.6	0.207	0.262
85.6	987.4	724.0	0.137	0.178
86.4	1010	741.7	0.068	0.091
87.2	1033	759.7	0.001	0.001



**24-22.** The vapor pressures of benzene and toluene between 80°C and 110°C as a function of the Kelvin temperature are given by the empirical formulas

$$\ln(P_{\text{benz}}^*/\text{torr}) = -\frac{3856.6 \text{ K}}{T} + 17.551$$

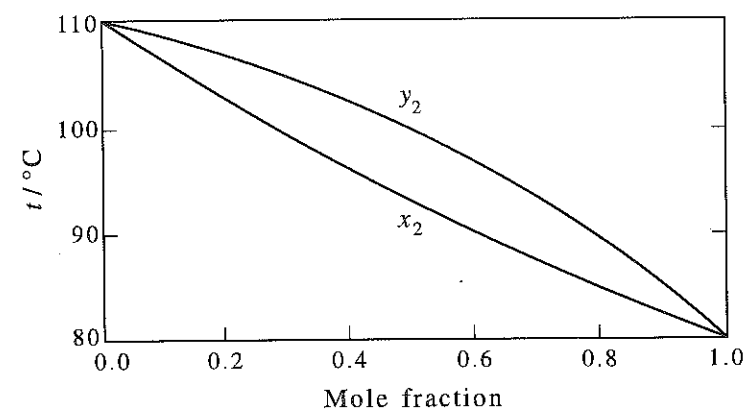
and

$$\ln(P_{\text{tol}}^*/\text{torr}) = -\frac{4514.6 \text{ K}}{T} + 18.397$$

Assuming that benzene and toluene form an ideal solution, use these formulas to construct a temperature-composition diagram of this system at an ambient pressure of 760 torr.

This problem is very similar to Problems 24–20 and 24–21. Some data and the plot are given below

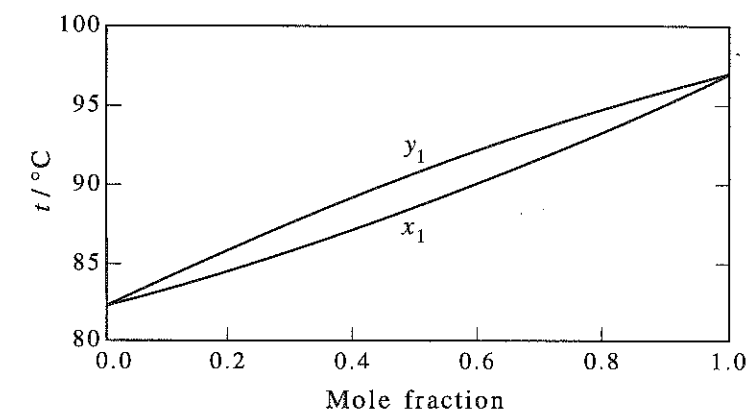
$T/K$	$t/^\circ\text{C}$	$P_1^*/\text{torr}$	$P_2^*/\text{torr}$	$x_1$	$y_1$
353.0	79.85	754.3	272.5	1.000	1.000
355.0	81.85	802.2	292.9	0.917	0.968
357.0	83.85	852.5	314.5	0.828	0.929
359.0	85.85	905.4	337.5	0.744	0.886
361.0	87.85	960.9	361.8	0.665	0.840
363.0	89.85	1019.2	387.6	0.590	0.791
365.0	91.85	1080.3	415.0	0.519	0.737
367.0	93.85	1144.3	443.9	0.451	0.680
369.0	95.85	1211.4	474.5	0.387	0.618
371.0	97.85	1281.6	506.9	0.327	0.551
373.0	99.85	1355.0	541.1	0.269	0.480
375.0	101.8	1431.9	577.1	0.214	0.403
377.0	103.8	1512.2	615.2	0.161	0.321
379.0	105.8	1596.0	655.3	0.111	0.234
381.0	107.8	1683.6	697.6	0.063	0.140
383.0	109.8	1775.0	742.1	0.017	0.040



**24–23.** Construct the temperature-composition diagram for 1-propanol and 2-propanol in Figure 24.5 by varying  $t$  from  $82.3^\circ\text{C}$  (the boiling point of 2-propanol) to  $97.2^\circ\text{C}$  (the boiling point of 1-propanol), calculating (1)  $P_1^*$  and  $P_2^*$  at each temperature (see Example 24–5), (2)  $x_1$  according to  $x_1 = (P_2^* - 760)/(P_2^* - P_1^*)$ , and (3)  $y_1$  according to  $y_1 = x_1 P_1^*/760$ . Now plot  $t$  versus  $x_1$  and  $y_1$  on the same graph to obtain the temperature-composition diagram.

This problem is very similar to Problem 24–21. Some data and the plot are

$t/^\circ\text{C}$	$P_1^*/\text{torr}$	$P_2^*/\text{torr}$	$x_1$	$y_1$
82.3	419.6	760.9	0.003	0.001
84.3	456.0	823.7	0.173	0.104
85.3	475.2	856.7	0.254	0.159
86.3	495.1	890.8	0.331	0.215
87.3	515.6	926.1	0.405	0.274
88.3	536.8	962.4	0.476	0.336
89.3	558.8	1000.0	0.544	0.400
90.3	581.5	1038.7	0.610	0.466
91.3	605.0	1078.7	0.673	0.536
92.3	629.2	1120.0	0.733	0.607
93.3	654.2	1162.5	0.792	0.682
94.3	680.1	1206.4	0.848	0.759
95.3	706.8	1251.7	0.902	0.839
96.3	734.3	1298.3	0.955	0.922
97.2	759.9	1341.5	1.000	1.000



**24–24.** Prove that  $\bar{V}_j = \bar{V}_j^*$  for an ideal solution, where  $\bar{V}_j^*$  is the molar volume of pure component  $j$ .

The chemical potentials of compounds 1 and 2 of an ideal solution are given by

$$\mu_j = \mu_j^* + RT \ln x_j \quad j = 1 \text{ and } 2$$

The Gibbs energy is given by

$$G = n_1 \mu_1 + n_2 \mu_2 = n_1 \mu_1^* + n_2 \mu_2^* + n_1 RT \ln x_1 + n_2 RT \ln x_2$$

The volume is given by

$$\begin{aligned} V &= \left( \frac{\partial G}{\partial P} \right)_{T, n_1, n_2} = n_1 \left( \frac{\partial \mu_1^*}{\partial P} \right)_T + n_2 \left( \frac{\partial \mu_2^*}{\partial P} \right)_T \\ &= n_1 \bar{V}_1^* + n_2 \bar{V}_2^* \end{aligned}$$



By comparing this result to Equation 24.7, we see that  $\bar{V}_j^* = \bar{V}_j$ .

- 24-25. The volume of mixing of miscible liquids is defined as the volume of the solution minus the volume of the individual pure components. Show that

$$\Delta_{\text{mix}} \bar{V} = \sum x_i (\bar{V}_i - \bar{V}_i^*)$$

at constant  $P$  and  $T$ , where  $\bar{V}_i^*$  is the molar volume of pure component  $i$ . Show that  $\Delta_{\text{mix}} \bar{V} = 0$  for an ideal solution (see Problem 24-24).

Problem 24-24 shows that  $\bar{V}_j^* = \bar{V}_j$  for an ideal solution, so  $\Delta_{\text{mix}} \bar{V} = 0$ .

- 24-26. Suppose the vapor pressures of the two components of a binary solution are given by

$$P_1 = x_1 P_1^* e^{x_2^2/2}$$

and

$$P_2 = x_2 P_2^* e^{x_1^2/2}$$

Given that  $P_1^* = 75.0$  torr and  $P_2^* = 160$  torr, calculate the total vapor pressure and the composition of the vapor phase at  $x_1 = 0.40$ .

$$\begin{aligned} P_{\text{total}} &= P_1 + P_2 = x_1 P_1^* e^{x_2^2/2} + x_2 P_2^* e^{x_1^2/2} \\ &= (0.40)(75.0 \text{ torr})e^{(0.60)^2/2} + (0.60)(160 \text{ torr})e^{(0.40)^2/2} \\ &= 35.9 \text{ torr} + 104 \text{ torr} = 140 \text{ torr} \end{aligned}$$

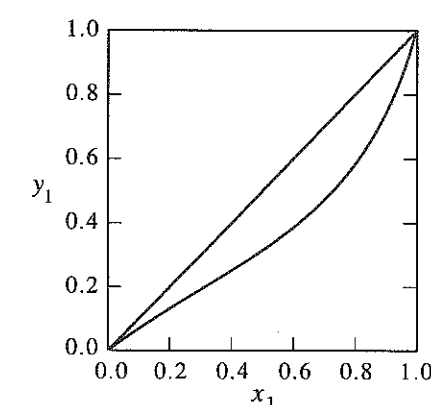
$$y_1 = \frac{P_1}{P_{\text{total}}} = \frac{35.9 \text{ torr}}{140 \text{ torr}} = 0.26$$

- 24-27. Plot  $y_1$  versus  $x_1$  for the system described in the previous problem. Why does the curve lie below the straight line connecting the origin with the point  $x_1 = 1, y_1 = 1$ ? Describe a system for which the curve would lie above the diagonal line.

We simply use

$$\begin{aligned} y_1 &= \frac{P_1}{P_{\text{total}}} = \frac{x_1 P_1^* e^{x_2^2/2}}{x_1 P_1^* e^{x_2^2/2} + x_2 P_2^* e^{x_1^2/2}} \\ &= \frac{x_1 (75.0 \text{ torr}) e^{(1-x_1)^2/2}}{x_1 (75.0 \text{ torr}) e^{(1-x_1)^2/2} + (1-x_1)(160 \text{ torr}) e^{x_1^2/2}} \end{aligned}$$

A plot of  $y_1$  against  $x_1$  is the curved line shown below.



The straight line connecting the origin with the point  $x_1 = y_1 = 1$  is given by  $y_1 = x_1$ . Therefore, component 1 is less volatile than component 2, so the vapor is richer in component 2;  $y_1 < x_1$  because  $P_1^* < P_2^*$ .

- 24-28. Use the expressions for  $P_1$  and  $P_2$  given in Problem 24-26 to construct a pressure-composition diagram.

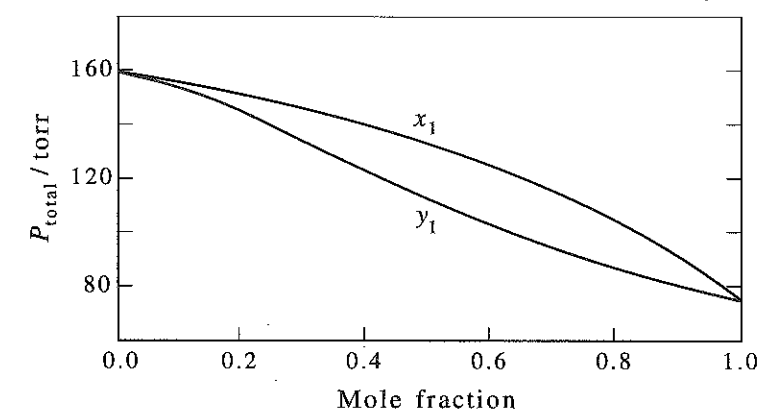
Start with

$$\begin{aligned} P_{\text{total}} &= P_1 + P_2 = x_1 P_1^* e^{x_2^2/2} + x_2 P_2^* e^{x_1^2/2} \\ &= x_1 (75.0 \text{ torr}) e^{(1-x_1)^2/2} + (1-x_1)(160 \text{ torr}) e^{x_1^2/2} \end{aligned}$$

and

$$\begin{aligned} y_1 &= \frac{P_1}{P_{\text{total}}} = \frac{x_1 P_1^* e^{x_2^2/2}}{x_1 P_1^* e^{x_2^2/2} + x_2 P_2^* e^{x_1^2/2}} \\ &= \frac{x_1 (75.0 \text{ torr}) e^{(1-x_1)^2/2}}{x_1 (75.0 \text{ torr}) e^{(1-x_1)^2/2} + (1-x_1)(160 \text{ torr}) e^{x_1^2/2}} \end{aligned}$$

Now calculate  $P_{\text{total}}$  and  $y_1$  as a function of  $x_1$  and then plot  $P_{\text{total}}$  against  $x_1$  and  $y_1$ .



24-29. The vapor pressure (in torr) of the two components in a binary solution are given by

$$P_1 = 120x_1e^{0.20x_2^2+0.10x_2^3}$$

and

$$P_2 = 140x_2e^{0.35x_1^2-0.10x_1^3}$$

Determine the values of  $P_1^*$ ,  $P_2^*$ ,  $k_{H,1}$ , and  $k_{H,2}$ .

Use the fact that  $P_j \rightarrow x_j P_j^*$  as  $x_j \rightarrow 1$  to obtain

$$P_1 \rightarrow 120x_1 \quad \text{as } x_1 \rightarrow 1 \quad \text{and} \quad P_2 \rightarrow 140x_2 \quad \text{as } x_2 \rightarrow 1$$

or  $P_1^* = 120$  torr and  $P_2^* = 140$  torr. Now use the fact that  $P_j \rightarrow k_{H,j}x_j$  as  $x_j \rightarrow 0$  to obtain

$$P_1 \rightarrow 120x_1e^{0.30} = 162 \text{ torr} = k_{H,1}$$

and

$$P_2 \rightarrow 140x_1e^{0.25} = 180 \text{ torr} = k_{H,2}$$

24-30. Suppose the vapor pressure of the two components of a binary solution are given by

$$P_1 = x_1 P_1^* e^{\alpha x_2^2 + \beta x_2^3}$$

and

$$P_2 = x_2 P_2^* e^{(\alpha+3\beta/2)x_1^2 - \beta x_1^3}$$

Show that  $k_{H,1} = P_1^* e^{\alpha+\beta}$  and  $k_{H,2} = P_2^* e^{\alpha+\beta/2}$ .

Use the fact that  $P_j \rightarrow k_{H,j}x_j$  as  $x_j \rightarrow 0$  to obtain

$$P_1 \rightarrow x_1 P_1^* e^{\alpha+\beta} \quad \text{and} \quad P_2 \rightarrow x_2 P_2^* e^{\alpha+\beta/2}$$

or

$$k_{H,1} = P_1^* e^{\alpha+\beta} \quad \text{and} \quad k_{H,2} = P_2^* e^{\alpha+\beta/2}$$

24-31. The empirical expression for the vapor pressure that we used in Examples 24-6 and 24-7, for example,

$$P_1 = x_1 P_1^* e^{\alpha x_2^2 + \beta x_2^3 + \dots}$$

is sometimes called the *Margules equation*. Use Equation 24.29 to prove that there can be no linear term in the exponential factor in  $P_1$ , for otherwise  $P_2$  will not satisfy Henry's law as  $x_2 \rightarrow 0$ .

Assume that there is a linear term in the exponent of  $P_1$ .

$$P_1 = x_1 P_1^* e^{\alpha x_2}$$

Then

$$\frac{\partial \ln P_1}{\partial x_1} = \frac{1}{x_1} - \alpha$$

According to Equation 24.29,

$$\begin{aligned} \frac{\partial \ln P_2}{\partial x_2} &= \frac{x_1}{x_2} \frac{\partial \ln P_1}{\partial x_1} \\ &= \frac{1}{x_2} - \alpha \frac{x_1}{x_2} = \frac{1}{x_2} - \alpha \frac{1-x_2}{x_2} \\ &= \frac{1-\alpha}{x_2} + \alpha \end{aligned}$$

Integration with respect to  $x_2$  gives

$$\ln P_2 = (1-\alpha) \ln x_2 + \alpha x_2 + \ln A$$

where  $\ln A$  is an integration constant. Then

$$P_2 = Ax_2^{1-\alpha} e^{\alpha x_2}$$

As  $x_2 \rightarrow 0$ ,  $P_2 \rightarrow Ax_2^{1-\alpha}$ . But according to Henry's law,  $P_2 \rightarrow k_{H,2}x_2$  as  $x_2 \rightarrow 0$ , so  $\alpha$  must equal zero.

24-32. In the text, we showed that the Henry's law behavior of component-2 as  $x_2 \rightarrow 0$  is a direct consequence of the Raoult's law behavior of component 1 as  $x_1 \rightarrow 1$ . In this problem, we will prove the converse: the Raoult's law behavior of component 1 as  $x_1 \rightarrow 1$  is a direct consequence of the Henry's law behavior of component-2 as  $x_2 \rightarrow 0$ . Show that the chemical potential of component-2 as  $x_2 \rightarrow 0$  is

$$\mu_2(T, P) = \mu_2^\circ(T) + RT \ln k_{H,2} + RT \ln x_2 \quad x_2 \rightarrow 0$$

Differentiate  $\mu_2$  with respect to  $x_2$  and substitute the result into the Gibbs-Duhem equation to obtain

$$d\mu_1 = RT \frac{dx_1}{x_1} \quad x_2 \rightarrow 0$$

Integrate this expression from  $x_1 = 1$  to  $x_1 \approx 1$  and use the fact that  $\mu_1(x_1 = 1) = \mu_1^*$  to obtain

$$\mu_1(T, P) = \mu_1^*(T) + RT \ln x_1 \quad x_1 \rightarrow 1$$

which is the Raoult's law expression for chemical potential. Show that this result follows directly from Equation 24.29.

Start with

$$\mu_2 = \mu_2^* + RT \ln \frac{P_2}{P_2^*} = \mu_2^* - RT \ln P_2^* + RT \ln P_2$$

As  $x_2 \rightarrow 0$ ,  $P_2 \rightarrow k_{H,2}x_2$ , so

$$\begin{aligned} \mu_2 &= \mu_2^* - RT \ln P_2^* + RT \ln k_{H,2} + RT \ln x_2 \quad (x_2 \rightarrow 0) \\ &= \mu^\circ(T) + RT \ln k_{H,2} + RT \ln x_2 \quad (x_2 \rightarrow 0) \end{aligned}$$

Now

$$\frac{d\mu_2}{dx_2} = \frac{RT}{x_2}$$

and so according to the Gibbs-Duhem equation

$$d\mu_1 = -\frac{x_2}{x_1}d\mu_2 = -\frac{x_2}{x_1}\frac{RT}{x_2}dx_2 = RT\frac{dx_1}{x_1} \quad (x_2 \rightarrow 0)$$

Now integrate this expression from  $x_1 = 1$  to  $x_1 \approx 1$  (because the expression is valid only for  $x_2 \approx 0$ , or  $x_1 \approx 1$ ) to obtain

$$\mu_1 = \mu_1^* + RT \ln x_1 \quad (x_1 \rightarrow 1)$$

24-33. In Example 24-7, we saw that if

$$P_1 = x_1 P_1^* e^{\alpha x_2^2 + \beta x_2^3}$$

then

$$P_2 = x_2 P_2^* e^{(\alpha + 3\beta/2)x_1^2 - \beta x_1^3} \quad (x_2 \rightarrow 0)$$

Show that this result follows directly from Equation 24.29.

Start with

$$\ln P_1 = \ln x_1 + \ln P_1^* + \alpha(1 - x_1)^2 + \beta(1 - x_1)^3$$

and differentiate with respect to  $x_1$  to obtain

$$\frac{\partial \ln P_1}{\partial x_1} = \frac{1}{x_1} - 2\alpha(1 - x_1) - 3\beta(1 - x_1)^2$$

According to Equation 24.29

$$\begin{aligned} \frac{\partial \ln P_2}{\partial x_2} &= \frac{x_1}{x_2} \frac{\partial \ln P_1}{\partial x_1} = \frac{1}{x_2} - 2\alpha x_1 - 3\beta x_1 x_2 \\ &= \frac{1}{x_2} - 2\alpha + 2\alpha x_2 - 3\beta x_2 + 3\beta x_2^2 \end{aligned}$$

Now integrate with respect to  $x_2$  to obtain

$$\ln P_2 = \ln x_2 - 2\alpha x_2 + (2\alpha - 3\beta)\frac{x_2^2}{2} + \beta x_2^3 + A$$

where  $A$  is an integration constant. Substituting  $x_2 = 1 - x_1$  in the last three terms gives

$$\begin{aligned} \ln P_2 &= \ln x_2 - 2\alpha(1 - x_1) + \left(\frac{2\alpha - 3\beta}{2}\right)(1 - x_1)^2 + \beta(1 - x_1)^3 + A \\ &= \ln x_2 - 2\alpha + 2\alpha x_1 + \alpha - 2\alpha x_1 + \alpha x_1^2 - \frac{3}{2}\beta + 3\beta x_1 - \frac{3}{2}\beta x_1^2 \\ &\quad + \beta - 3\beta x_1 + 3\beta x_1^2 - \beta x_1^3 + A \\ &= \ln x_2 + \alpha x_1^2 + \frac{3}{2}\beta x_1^2 - \beta x_1^3 + \left(A - \alpha - \frac{\beta}{2}\right) \end{aligned}$$

Rewrite this expression as

$$P_2 = x_2 B e^{\alpha x_1^2 + \frac{3}{2}\beta x_1^2 - \beta x_1^3}$$

where  $B = A - \alpha - \beta/2$ . Note that  $B = P_2^*$  because  $P_2 \rightarrow x_2 P_2^*$  as  $x_2 \rightarrow 1$ .

24-34. Suppose we express the vapor pressures of the components of a binary solution by

$$P_1 = x_1 P_1^* e^{\alpha x_2^2}$$

and

$$P_2 = x_2 P_2^* e^{\beta x_1^2}$$

Use the Gibbs-Duhem equation or Equation 24.29 to prove that  $\alpha$  must equal  $\beta$ .

Start with

$$\ln P_1 = \ln x_1 + \ln P_1^* + \alpha x_2^2$$

Differentiate with respect to  $x_1$  to obtain

$$\frac{\partial \ln P_1}{\partial x_1} = \frac{1}{x_1} - 2\alpha(1 - x_1)$$

Use Equation 24.29 to get

$$\frac{\partial \ln P_2}{\partial x_2} = \frac{x_1}{x_2} \frac{\partial \ln P_1}{\partial x_1} = \frac{1}{x_2} - 2\alpha x_1 = \frac{1}{x_2} - 2\alpha + 2\alpha x_2$$

Integrate with respect to  $x_2$  to get

$$\begin{aligned} \ln P_2 &= \ln x_2 - 2\alpha x_2 + \alpha x_2^2 + A \\ &= \ln x_2 - 2\alpha + 2\alpha x_1 + \alpha - 2\alpha x_1 + \alpha x_1^2 + A \\ &= \ln x_2 + \alpha x_1^2 + (A - \alpha) \end{aligned}$$

where  $A$  is an integration constant. Therefore,

$$P_2 = B x_2 e^{\alpha x_1^2}$$

where  $B = A - \alpha$ . Clearly  $B = P_2^*$  because  $P_2 \rightarrow P_2^* x_2$  as  $x_2 \rightarrow 1$ .

24-35. Use Equation 24.29 to show that if one component of a binary solution obeys Raoult's law for all concentrations, then the other component also obeys Raoult's law for all concentrations.

According to Raoult's law

$$P_1 = x_1 P_1^*$$

Therefore,

$$\frac{\partial \ln P_1}{\partial x_1} = \frac{1}{x_1}$$

and Equation 24.29 gives

$$\frac{\partial \ln P_2}{\partial x_2} = \frac{1}{x_2}$$

which upon integration gives

$$\ln P_2 = \ln x_2 + A$$

$$P_2 = Ax_2 = P_2^* x_2$$

where  $A$  is an integration constant.

**24–36.** Use Equation 24.29 to show that if one component of a binary solution has positive deviations from Raoult's law, then the other component must also.

Equation 24.29 says that

$$x_1 \left( \frac{\partial \ln P_1}{\partial x_1} \right) = x_2 \left( \frac{\partial \ln P_2}{\partial x_2} \right)$$

or

$$\frac{\partial \ln P_1}{\partial \ln x_1} = \frac{\partial \ln P_2}{\partial \ln x_2}$$

For an ideal solution,  $P_j^{\text{id}} = x_j P_j^*$  and so

$$\frac{\partial \ln P_1^{\text{id}}}{\partial \ln x_1} = \frac{\partial \ln P_2^{\text{id}}}{\partial \ln x_2} = 1$$

If  $P_1 > P_1^{\text{id}} = x_1 P_1^*$  (positive deviation from ideality), then

$$\frac{\partial \ln P_1}{\partial \ln x_1} > 1$$

and so

$$\frac{\partial \ln P_2}{\partial \ln x_2} > 1$$

Conversely, if one component has negative deviations from ideality ( $\partial \ln P_1 / \partial \ln x_1 < 1$ ), then the other must also.

**24–37.** If the vapor pressures of the two components in a binary solution are given by

$$P_1 = x_1 P_1^* e^{ux_2^2/RT} \quad \text{and} \quad P_2 = x_2 P_2^* e^{ux_1^2/RT}$$

show that

$$\Delta_{\text{mix}} \bar{G}/u = \Delta_{\text{mix}} G/(n_1 + n_2)u = \frac{RT}{u}(x_1 \ln x_1 + x_2 \ln x_2) + x_1 x_2$$

$$\Delta_{\text{mix}} \bar{S}/R = \Delta_{\text{mix}} S/(n_1 + n_2)R = -(x_1 \ln x_1 + x_2 \ln x_2)$$

and

$$\Delta_{\text{mix}} \bar{H}/u = \Delta_{\text{mix}} H/(n_1 + n_2)u = x_1 x_2$$

A solution that satisfies these equations is called a *regular solution*. A statistical thermodynamic model of binary solutions shows that  $u$  is proportional to  $2\varepsilon_{12} - \varepsilon_{11} - \varepsilon_{22}$ , where  $\varepsilon_{ij}$  is the interaction energy between molecules of components  $i$  and  $j$ . Note that  $u = 0$  if  $\varepsilon_{12} = (\varepsilon_{11} + \varepsilon_{22})/2$ , which means that energetically, molecules of components 1 and 2 “like” the opposite molecules as well as their own.

Use the equations

$$G^{\text{sln}} = n_1 \mu_1 + n_2 \mu_2$$

and

$$\mu_j = \mu_j^* + RT \ln \frac{P_j}{P_j^*}$$

to write

$$G^{\text{sln}} = n_1 \mu_1^* + n_2 \mu_2^* + n_1 RT \ln(x_1 e^{ux_2^2/RT}) + n_2 RT \ln(x_2 e^{ux_1^2/RT})$$

But  $n_1 \mu_1^* + n_2 \mu_2^*$  is the Gibbs energy of the two pure liquid components, so

$$\Delta_{\text{mix}} G = G^{\text{sln}} - n_1 \mu_1^* - n_2 \mu_2^* = n_1 RT \ln x_1 + n_2 RT \ln x_2 + u(n_1 x_2^2 + n_2 x_1^2)$$

Divide by the total number of moles,  $n_1 + n_2$ , to get

$$\Delta_{\text{mix}} \bar{G} = RT(x_1 \ln x_1 + x_2 \ln x_2) + ux_1 x_2(x_2 + x_1)$$

Now divide by  $u$  and use the fact that  $x_1 + x_2 = 1$  to get

$$\Delta_{\text{mix}} \bar{G}/u = \frac{RT}{u}(x_1 \ln x_1 + x_2 \ln x_2) + x_1 x_2$$

Use the equation  $\Delta_{\text{mix}} \bar{S} = -(\partial \Delta_{\text{mix}} \bar{G} / \partial T)$  to obtain

$$\Delta_{\text{mix}} \bar{S} = -R(x_1 \ln x_1 + x_2 \ln x_2)$$

Now use  $\Delta_{\text{mix}} \bar{G} = \Delta_{\text{mix}} \bar{H} - T \Delta_{\text{mix}} \bar{S}$  to get

$$\Delta_{\text{mix}} \bar{H}/u = x_1 x_2$$

**24–38.** Prove that  $\Delta_{\text{mix}} \bar{G}$ ,  $\Delta_{\text{mix}} \bar{S}$ , and  $\Delta_{\text{mix}} \bar{H}$  in the previous problem are symmetric about the point  $x_1 = x_2 = 1/2$ .

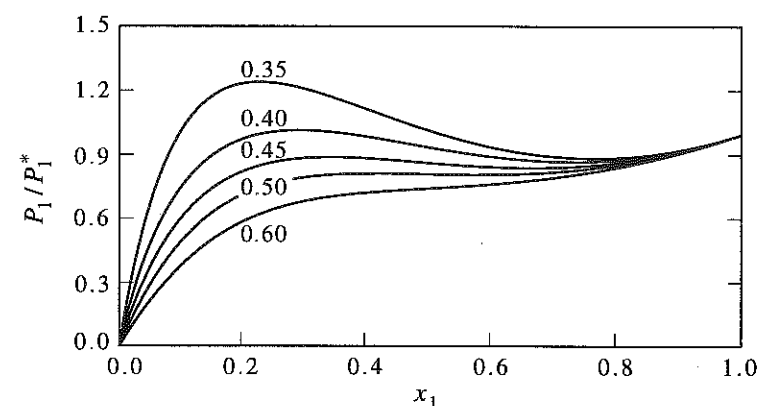
Each expression is symmetric in  $x_1$  and  $x_2$ . Therefore, they must be symmetric about  $x_1 = x_2 = 1/2$ .

**24–39.** Plot  $P_1/P_1^* = x_1 e^{ux_2^2/RT}$  versus  $x_1$  for  $RT/u = 0.60, 0.50, 0.45, 0.40$ , and  $0.35$ . Note that some of the curves have regions where the slope is negative. The following problem has you show that this behavior occurs when  $RT/u < 0.50$ . These regions are similar to the loops of the van der Waals equation or the Redlich-Kwong equation when  $T < T_c$  (Figure 16.8), and in this case correspond



to regions in which the two liquids are not miscible. The critical value  $RT/u = 0.50$  corresponds to a solution critical temperature of  $0.50u/R$ .

See plot



- 24-40. Differentiate  $P_1 = x_1 P_1^* e^{u(1-x_1)^2/RT}$  with respect to  $x_1$  to prove that  $P_1$  has a maximum or a minimum at the points  $x_1 = \frac{1}{2} \pm \frac{1}{2} \left(1 - \frac{2RT}{u}\right)^{1/2}$ . Show that  $RT/u < 0.50$  for either a maximum or a minimum to occur. Do the positions of these extremes when  $RT/u = 0.35$  correspond to the plot you obtained in the previous problem?

$$\frac{dP_1}{dx_1} = 0 = P_1^* e^{u(1-x_1)^2/RT} - \frac{2u}{RT} x_1 (1-x_1) P_1^* e^{u(1-x_1)^2/RT} = 0$$

Cancelling several factors and rearranging gives

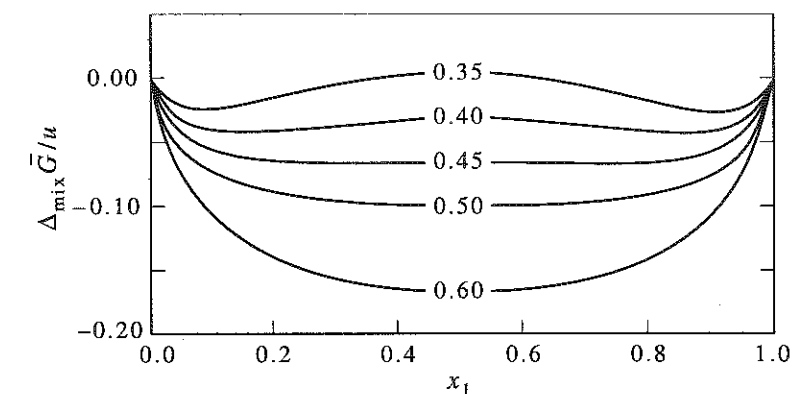
$$x_1^2 - x_1 + \frac{RT}{2u} = 0$$

or

$$x_1 = \frac{1}{2} \pm \frac{1}{2} \left(1 - \frac{2RT}{u}\right)^{1/2}$$

The values of  $x_1$  will not be real unless  $2RT/u < 1$ , or unless  $RT/u < 0.50$ . When  $RT/u = 0.35$ ,  $x_1 = 0.226$  (a maximum) and  $0.774$  (a minimum).

- 24-41. Plot  $\Delta_{\text{mix}} \bar{G}/u$  in Problem 24-37 versus  $x_1$  for  $RT/u = 0.60, 0.50, 0.45, 0.40$ , and  $0.35$ . Note that some of the curves have regions where  $\partial^2 \Delta_{\text{mix}} \bar{G} / \partial x_1^2 < 0$ . These regions correspond to regions in which the two liquids are not miscible. Show that  $RT/u = 0.50$  is a critical value, in the sense that unstable regions occur only when  $RT/u < 0.50$ . (See the previous problem.)



Differentiate  $\Delta_{\text{mix}} \bar{G}$  with respect to  $x_1$  to obtain

$$\frac{\partial \Delta_{\text{mix}} \bar{G}}{\partial x_1} = \frac{RT}{u} [\ln x_1 + 1 - \ln(1-x_1) - 1] + 1 - 2x_1 = 0$$

or

$$\frac{RT}{u} \ln \frac{x_1}{1-x_1} = 2x_1 - 1$$

Note that both sides of this equation equal zero when  $x_1 = 1/2$ . The unstable regions occur when  $\partial^2 \Delta_{\text{mix}} \bar{G} / \partial x_1^2 < 0$ :

$$\begin{aligned} \frac{\partial^2 \Delta_{\text{mix}} \bar{G}}{\partial x_1^2} &= \frac{RT}{u} \left( \frac{1}{x_1} + \frac{1}{1-x_1} \right) - 2 \\ &= \frac{RT}{u} \left[ \frac{1}{x_1(1-x_1)} \right] - 2 \end{aligned}$$

The unstable regions are centered at  $x_1 = x_2 = 1/2$ , so substituting  $x_1 = x_2 = 1/2$  into  $\partial^2 \Delta_{\text{mix}} \bar{G} / \partial x_1^2$  gives the inequality

$$\frac{4RT}{u} - 2 < 0$$

or

$$\frac{RT}{u} < \frac{1}{2}$$

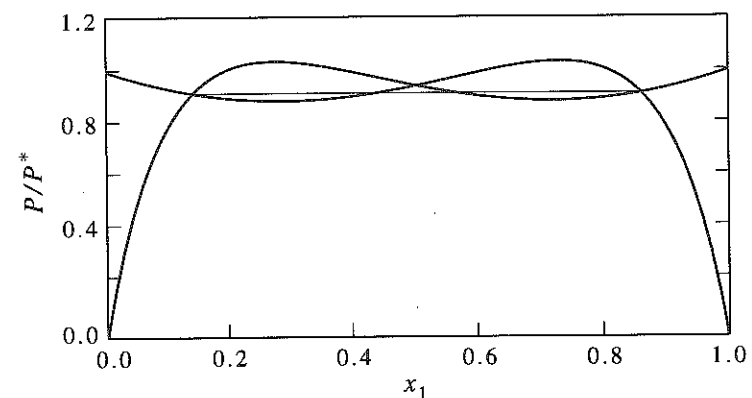
- 24-42. Plot both  $P_1/P_1^* = x_1 e^{ux_1^2/RT}$  and  $P_2/P_2^* = x_2 e^{ux_2^2/RT}$  for  $RT/u = 0.60, 0.50, 0.45, 0.40$ , and  $0.35$ . Prove that the loops occur for values of  $RT/u < 0.50$ .

See Problem 24-40 for proof that unstable regions occur only for  $RT/u < 0.50$ .

- 24-43. Plot both  $P_1/P_1^* = x_1 e^{ux_1^2/RT}$  and  $P_2/P_2^* = x_2 e^{ux_2^2/RT}$  against  $x_1$  for  $RT/u = 0.40$ . The loops indicate regions in which the two liquids are not miscible, as explained in Problem 24-39. Draw a horizontal line connecting the left-side and the right-side intersections of the two curves. This line, which connects states in which the vapor pressure (or chemical potential) of each component is the same in the two solutions of different composition, corresponds to one of the horizontal lines in Figure 24.12. Now set  $P_1/P_1^* = x_1 e^{ux_1^2/RT}$  equal to  $P_2/P_2^* = x_2 e^{ux_2^2/RT}$  and solve for  $RT/u$  in terms of  $x_1$ . Plot  $RT/u$  against  $x_1$  and obtain a coexistence curve like the one in Figure 24.13.



The plot of  $P_1/P_1^*$  and  $P_2/P_2^*$  against  $x_1$  for  $RT/u = 0.40$  is shown below.



Write

$$x_1 e^{ux_2^2/RT} = x_2 e^{ux_1^2/RT}$$

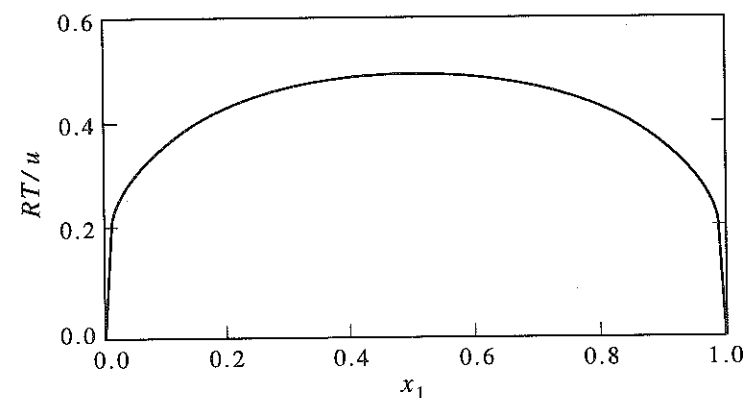
as

$$e^{u(x_2^2 - x_1^2)/RT} = \frac{x_2}{x_1}$$

and take logarithms to get

$$\frac{RT}{u} = \frac{x_2^2 - x_1^2}{\ln(x_2/x_1)} = \frac{1 - 2x_1}{\ln[(1 - x_1)/x_1]}$$

A plot of  $RT/u$  against  $x_1$  follows.

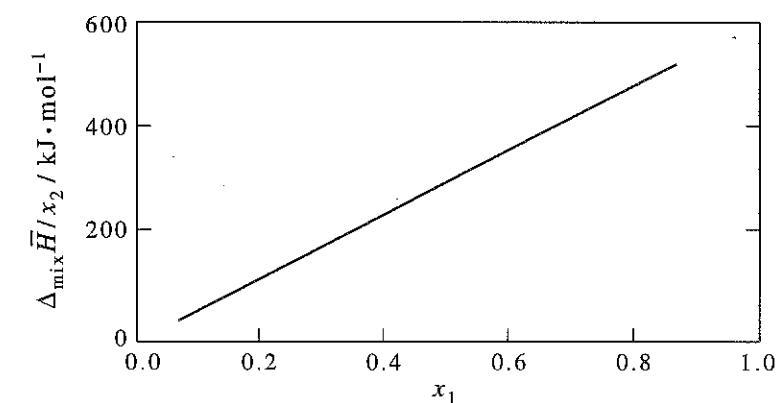


24-44. The molar enthalpies of mixing of solutions of tetrachloromethane (1) and cyclohexane (2) at 25°C are listed below.

$x_1$	$\Delta_{\text{mix}} \bar{H} / \text{J} \cdot \text{mol}^{-1}$
0.0657	37.8
0.2335	107.9
0.3495	134.9
0.4745	146.7
0.5955	141.6
0.7213	118.6
0.8529	73.6

Plot  $\Delta_{\text{mix}} \bar{H}$  against  $x_1 x_2$  according to Problem 24-37. Do tetrachloromethane and cyclohexane form a regular solution?

If tetrachloromethane and cyclohexane form a regular solution at 25°C, then a plot of  $\Delta_{\text{mix}} \bar{H}/x_2$  against  $x_1$  should be linear. The linearity of the following plot shows that they form a regular solution.

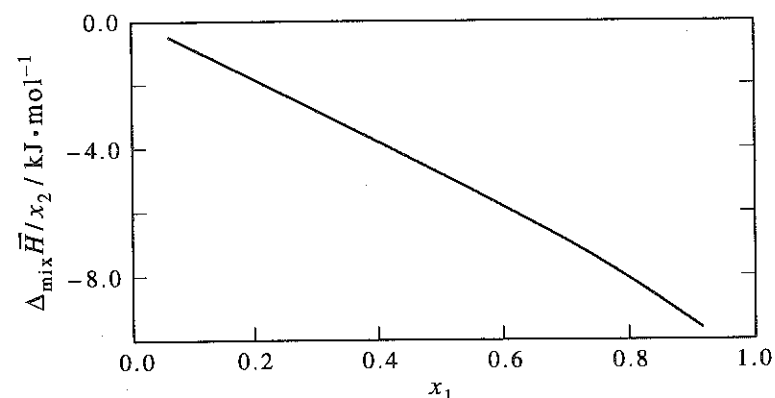


24-45. The molar enthalpies of mixing of solutions of tetrahydrofuran and trichloromethane at 25°C are listed below.

$x_{\text{THF}}$	$\Delta_{\text{mix}} \bar{H} / \text{J} \cdot \text{mol}^{-1}$
0.0568	-0.469
0.1802	-1.374
0.3301	-2.118
0.4508	-2.398
0.5702	-2.383
0.7432	-1.888
0.8231	-1.465
0.9162	-0.802

Do tetrahydrofuran and trichloromethane form a regular solution?

If tetrahydrofuran and trichloromethane form a regular solution at 25°C, then a plot of  $\Delta_{\text{mix}} \bar{H}/x_2$  against  $x_1$  should be linear. The nonlinearity of the following plot shows that they do not quite form a regular solution.



24-46. Derive the equation

$$x_1 d \ln \gamma_1 + x_2 d \ln \gamma_2 = 0$$

by starting with Equation 24.11. Use this equation to obtain the same result as in Example 24-8.

Equation 24.11 is

$$x_1 d\mu_1 + x_2 d\mu_2 = 0$$

Substitute  $\mu_j = \mu_j^* + RT \ln \gamma_j x_j$  for  $\mu_1$  and  $\mu_2$  to obtain

$$x_1 RT \left( \frac{dx_1}{x_1} + d \ln \gamma_1 \right) + x_2 RT \left( \frac{dx_2}{x_2} + d \ln \gamma_2 \right) = 0$$

or

$$RT(dx_1 + dx_2) + RTx_1 d \ln \gamma_1 + RTx_2 d \ln \gamma_2 = 0$$

But  $dx_1 + dx_2 = 0$  because  $x_1 + x_2 = 1$ , and so we have

$$x_1 d \ln \gamma_1 + x_2 d \ln \gamma_2 = 0$$

According to Example 24-8,

$$\gamma_1 = e^{\alpha x_2^2}$$

Therefore,

$$\begin{aligned} d \ln \gamma_2 &= -\frac{x_1}{x_2} d \ln \gamma_1 = -\frac{x_1}{x_2} (2\alpha x_2 dx_2) \\ &= -2\alpha(1-x_2)dx_2 \end{aligned}$$

Integration from  $x_2 = 1$  (where  $\gamma_2 = 1$ ) to arbitrary  $x_2$  gives

$$\begin{aligned} \ln \gamma_2 &= -2\alpha \int_1^{x_2} (1-x'_2) dx'_2 \\ &= -2\alpha \left( x_2 - 1 - \frac{x_2^2 - 1}{2} \right) = \alpha(1 - 2x_2 + x_2^2) \\ &= \alpha(1 - x_2)^2 = \alpha x_1^2 \end{aligned}$$

in agreement with Example 24-8.

24-47. The vapor pressure data for carbon disulfide in Table 24.1 can be curve fit by

$$P_1 = x_1 (514.5 \text{ torr}) e^{1.4967x_2^2 - 0.68175x_2^3}$$

Using the results of Example 24-7, show that the vapor pressure of dimethoxymethane is given by

$$P_2 = x_2 (587.7 \text{ torr}) e^{0.4741x_1^2 + 0.68175x_1^3}$$

Now plot  $P_2$  versus  $x_2$  and compare the result with the data in Table 24.1. Plot  $\bar{G}^E$  against  $x_1$ . Is the plot symmetric about a vertical line at  $x_1 = 1/2$ ? Do carbon disulfide and dimethoxymethane form a regular solution at 35.2°C?

According to Example 24-7, if

$$P_1 = x_2 P_1^* e^{\alpha x_2^2 + \beta x_2^3}$$

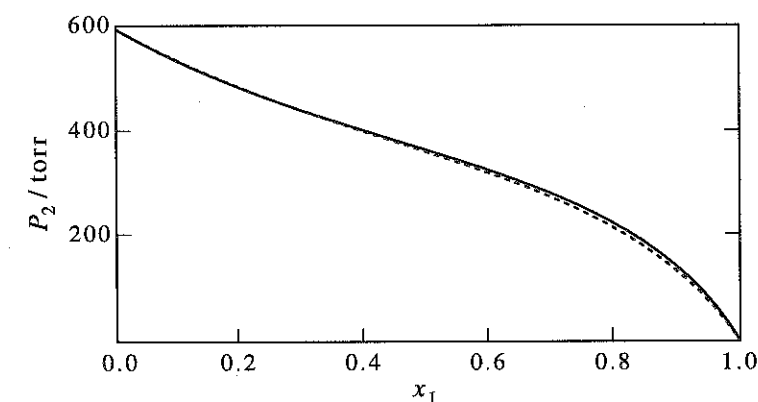
then

$$P_2 = x_2 P_2^* e^{(\alpha+3\beta/2)x_1^2 - \beta x_1^3}$$

Therefore, since  $\alpha = 1.4967$  and  $\beta = -0.68175$ ,

$$P_2 = x_2 P_2^* e^{0.4741x_1^2 + 0.68175x_1^3}$$

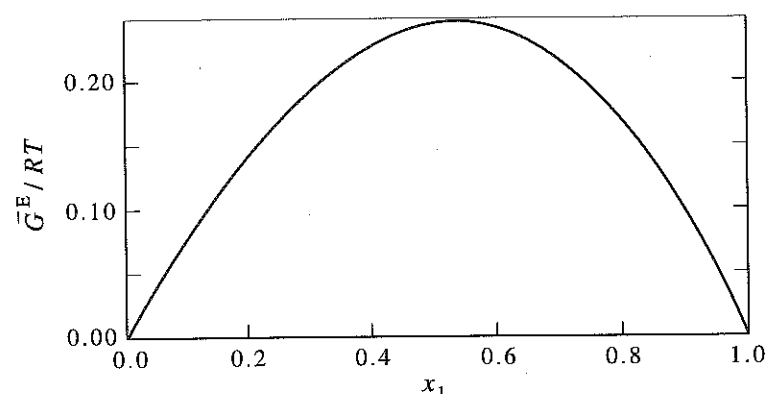
A comparison of  $P_2$  from Table 24.1 with that calculated from the above equation is shown below. The solid curve is the calculated curve and the dots represent the experimental data. The agreement is very good.



Now use Equation 24.51:

$$\begin{aligned}\bar{G}^E/RT &= x_1 \ln \gamma_1 + x_2 \ln \gamma_2 \\ &= x_1(1.4967x_2^2 - 0.68175x_2^3 + 0.4741x_1^2 + 0.68175x_1^3) \\ &= 0.8149x_1x_2(1 + 0.4183x_1)\end{aligned}$$

The following plot shows that  $\bar{G}^E$  is not symmetric about  $x_1 = x_2 = 1/2$ . Carbon disulfide and dimethoxymethane do not form a regular solution under the given conditions.



- 24-48.** A mixture of trichloromethane and acetone with  $x_{\text{acet}} = 0.713$  has a total vapor pressure of 220.5 torr at 28.2°C, and the mole fraction of acetone in the vapor is  $y_{\text{acet}} = 0.818$ . Given that the vapor pressure of pure trichloromethane at 28.2°C is 221.8 torr, calculate the activity and the activity coefficient (based upon a Raoult's law standard state) of trichloromethane in the mixture. Assume the vapor behaves ideally.

We have  $x_{\text{acet}} = 0.713$ ,  $y_{\text{acet}} = 0.818$ , and  $P_{\text{total}} = 220.5$  torr. Therefore,

$$P_{\text{tri}} = (1.000 - 0.818)(220.5 \text{ torr}) = 40.13 \text{ torr}$$

and

$$a_{\text{tri}}^{(R)} = \frac{P_{\text{tri}}}{P_{\text{tri}}^*} = \frac{40.13 \text{ torr}}{221.8 \text{ torr}} = 0.181$$

and

$$\gamma_{\text{tri}}^{(R)} = \frac{a_{\text{tri}}^{(R)}}{x_{\text{tri}}} = \frac{0.181}{1.000 - 0.713} = 0.631$$

- 24-49.** Consider a binary solution for which the vapor pressure (in torr) of one of the components (say component 1) is given empirically by

$$P_1 = 78.8x_1e^{0.65x_2^2+0.18x_2^3}$$

Calculate the activity and the activity coefficient of component 1 when  $x_1 = 0.25$  based on a solvent and a solute standard state.

$$a_1^{(R)} = \frac{P_1}{P_1^*} = x_1 e^{0.65x_2^2+0.18x_2^3}$$

When  $x_1 = 0.25$ ,  $a_1^{(R)} = 0.25e^{0.4416} = 0.39$  and  $\gamma_1^{(R)} = a_1^{(R)}/0.25 = 1.6$ . The activity based upon a Henry's law standard state is given by

$$a_1^{(H)} = \frac{P_1}{k_{H,1}} = \frac{x_1 P_1^* e^{0.65x_2^2+0.18x_2^3}}{P_1^* e^{0.65+0.18}} = \frac{0.39}{2.29} = 0.17$$

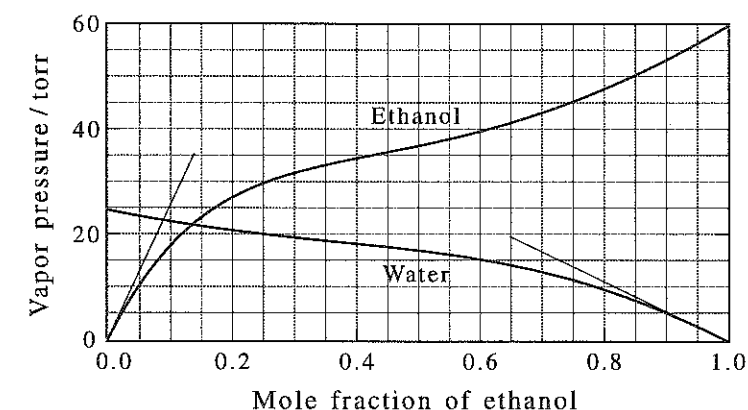
$$\text{and } \gamma_1^{(H)} = 0.17/0.25 = 0.68$$

- 24-50.** Some vapor pressure data for ethanol/water solutions at 25°C are listed below.

$x_{\text{ethanol}}$	$P_{\text{ethanol}}/\text{torr}$	$P_{\text{water}}/\text{torr}$
0.00	0.00	23.78
0.02	4.28	23.31
0.05	9.96	22.67
0.08	14.84	22.07
0.10	17.65	21.70
0.20	27.02	20.25
0.30	31.23	19.34
0.40	33.93	18.50
0.50	36.86	17.29
0.60	40.23	15.53
0.70	43.94	13.16
0.80	48.24	9.89
0.90	53.45	5.38
0.93	55.14	3.83
0.96	56.87	2.23
0.98	58.02	1.13
1.00	59.20	0.00

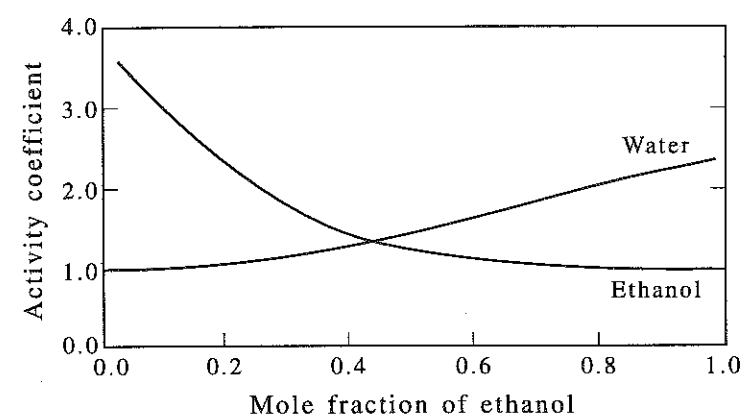
Plot these data to determine the Henry's law constant for ethanol in water and for water in ethanol at 25°C.

Henry's law constant of component  $j$  is given by the limiting slope of the vapor pressure of component  $j$  as  $x_j \rightarrow 0$ . The straight lines are shown in the following figure. The slopes of these lines give  $k_{H,\text{water}} \approx 20 \text{ torr}/0.35 = 57 \text{ torr}$  and  $k_{H,\text{eth}} \approx 25 \text{ torr}/0.10 = 250 \text{ torr}$



**24-51.** Using the data in Problem 24-50, plot the activity coefficients (based upon Raoult's law) of both ethanol and water against the mole fraction of ethanol.

The activity coefficients based upon Raoult's law are given by  $\gamma_j = P_j/x_j P_j^*$ , where all these quantities are given in the problem. The activities are shown in the following figure.

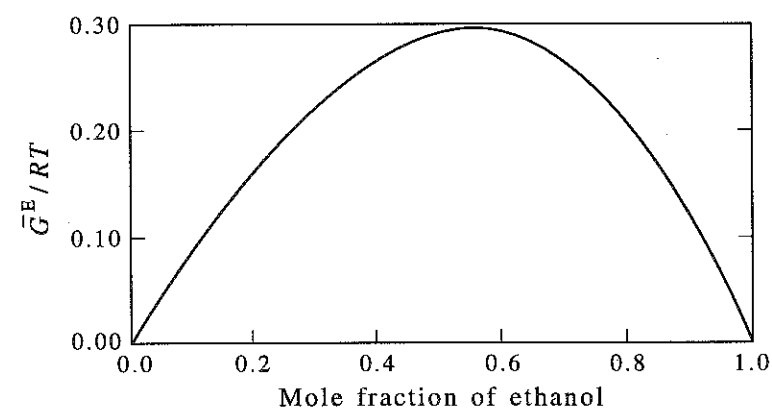


**24-52.** Using the data in Problem 24-50, plot  $\bar{G}^E/RT$  against  $x_{\text{H}_2\text{O}}$ . Is a water/ethanol solution at 25°C a regular solution?

According to Equation 24.51,

$$\frac{\bar{G}^E}{RT} = x_1 \ln \gamma_1 + x_2 \ln \gamma_2$$

The activity coefficients are calculated in Problem 24-51, and  $\bar{G}^E/RT$  is plotted against the mole fraction of water below. The plot is not symmetric about  $x_1 = x_2 = 1/2$ , and so water and ethanol do not form a regular solution under these conditions.

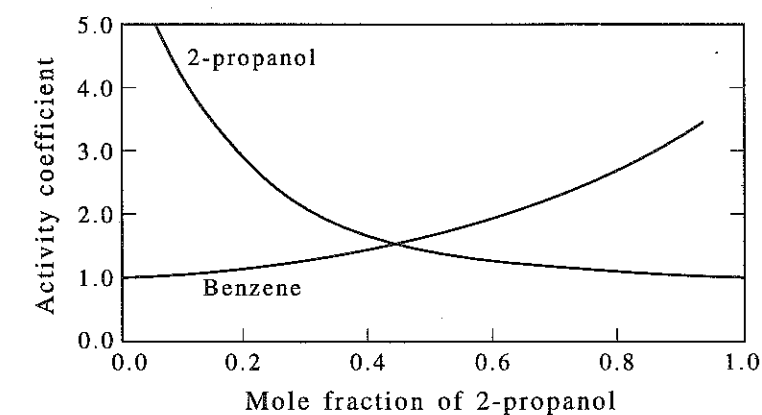
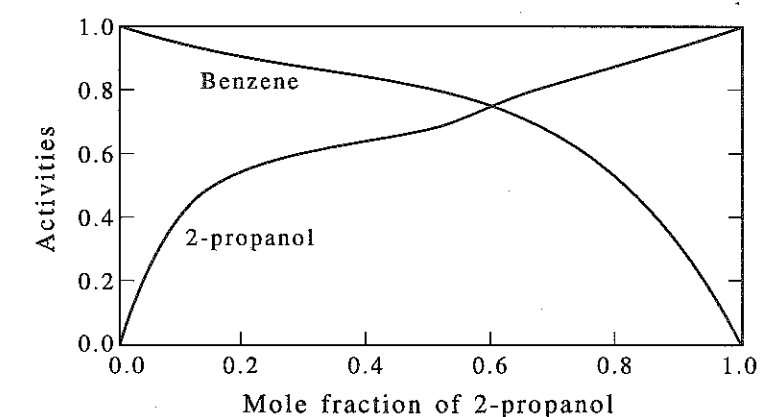


**24-53.** Some vapor pressure data for a 2-propanol/benzene solution at 25°C are

$x_{\text{2-propanol}}$	$P_{\text{2-propanol}}/\text{torr}$	$P_{\text{total}}/\text{torr}$
0.000	0.0	94.4
0.059	12.9	104.5
0.146	22.4	109.0
0.362	27.6	108.4
0.521	30.4	105.8
0.700	36.4	99.8
0.836	39.5	84.0
0.924	42.2	66.4
1.000	44.0	44.0

Plot the activities and the activity coefficients of 2-propanol and benzene relative to a Raoult's law standard state versus the mole fraction of 2-propanol.

The activity coefficients based upon Raoult's law are given by  $\gamma_j = P_j/x_j P_j^*$ , where all these quantities are given above. The activities and activity coefficients are shown in the following figures.

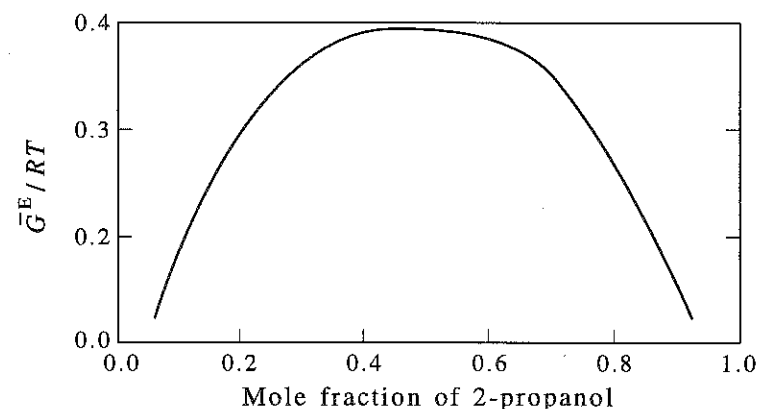


24-54. Using the data in Problem 24-53, plot  $\bar{G}^E/RT$  versus  $x_{2\text{-propanol}}$ .

According to Equation 24.51,

$$\frac{\bar{G}^E}{RT} = x_1 \ln \gamma_1 + x_2 \ln \gamma_2$$

The activity coefficients are calculated in Problem 24-53, and  $\bar{G}^E/RT$  is plotted against the mole fraction of 2-propanol below. The plot is not symmetric about  $x_1 = x_2 = 1/2$ , and so 2-propanol and benzene do not form a regular solution under these conditions.



24-55. Excess thermodynamic quantities are defined relative to the values the quantities would have if the pure components formed an ideal solution at the same given temperature and pressure. For example, we saw that (Equation 24.51)

$$\frac{\bar{G}^E}{RT} = \frac{G^E}{(n_1 + n_2)RT} = x_1 \ln \gamma_1 + x_2 \ln \gamma_2$$

Show that

$$\begin{aligned} \frac{\bar{S}^E}{R} &= \frac{\Delta S^E}{(n_1 + n_2)R} = -(x_1 \ln \gamma_1 + x_2 \ln \gamma_2) \\ &\quad - T \left( x_1 \frac{\partial \ln \gamma_1}{\partial T} + x_2 \frac{\partial \ln \gamma_2}{\partial T} \right) \end{aligned}$$

Use the relation  $S = -(\partial G / \partial T)_{P, n_1, n_2}$  to write

$$\begin{aligned} \bar{S}^E &= - \left( \frac{\partial \bar{G}^E}{\partial T} \right)_{P, x_1} = - \frac{\partial}{\partial T} [RT(x_1 \ln \gamma_1 + x_2 \ln \gamma_2)] \\ &= -R(x_1 \ln \gamma_1 + x_2 \ln \gamma_2) - RT \left( x_1 \frac{\partial \ln \gamma_1}{\partial T} + x_2 \frac{\partial \ln \gamma_2}{\partial T} \right)_P \end{aligned}$$

24-56. Show that

$$\bar{G}^E = \frac{G^E}{n_1 + n_2} = ux_1x_2$$

$$\bar{S}^E = \frac{S^E}{n_1 + n_2} = 0$$

and

$$\bar{H}^E = \frac{H^E}{n_1 + n_2} = ux_1x_2$$

for a regular solution (see Problem 24-37).

A regular solution is defined in Problem 24-37. For example,

$$\Delta_{\text{mix}} \bar{G} = RT(x_1 \ln x_1 + x_2 \ln x_2) + ux_1x_2$$

But the first terms on the right side of this equation are  $\Delta_{\text{mix}} \bar{G}^{\text{id}}$ , and so

$$\bar{G}^E = \Delta_{\text{mix}} \bar{G} - \Delta_{\text{mix}} \bar{G}^{\text{id}} = ux_1x_2$$

Similarly,

$$\begin{aligned} \bar{S}^E &= \Delta_{\text{mix}} \bar{S} - \Delta_{\text{mix}} \bar{S}^{\text{id}} = -R(x_1 \ln x_1 + x_2 \ln x_2) + R(x_1 \ln x_1 + x_2 \ln x_2) \\ &= 0 \end{aligned}$$

and  $\bar{G}^E = \bar{H}^E - T\bar{S}^E$  gives

$$\bar{H}^E = ux_1x_2$$

24-57. Example 24-7 expresses the vapor pressures of the two components of a binary solution as

$$P_1 = x_1 P_1^* e^{\alpha x_2^2 + \beta x_2^3}$$

and

$$P_2 = x_2 P_2^* e^{(\alpha + 3\beta/2)x_1^2 - \beta x_1^3}$$

Show that these expressions are equivalent to

$$\gamma_1 = e^{\alpha x_2^2 + \beta x_2^3} \quad \text{and} \quad \gamma_2 = e^{(\alpha + 3\beta/2)x_1^2 - \beta x_1^3}$$

Using these expressions for the activity coefficients, derive an expression for  $\bar{G}^E$  in terms of  $\alpha$  and  $\beta$ . Show that your expression reduces to that for  $\bar{G}^E$  for a regular solution.

Start with Equation 24.51

$$\bar{G}^E/RT = x_1 \ln \gamma_1 + x_2 \ln \gamma_2$$



and  $\gamma_j = P_j/x_j P_j^*$ . For  $P_1$  and  $P_2$  given in the problem

$$\gamma_1 = \frac{P_1}{x_1 P_1^*} = e^{\alpha x_2^2 + \beta x_2^3} \quad \text{and} \quad \gamma_2 = \frac{P_2}{x_1 P_2^*} = e^{(\alpha + 3\beta/2)x_1^2 - \beta x_1^3}$$

and so

$$\begin{aligned} \overline{G}^E/RT &= x_1(\alpha x_2^2 + \beta x_2^3) + x_2 \left[ \left( \alpha + \frac{3\beta}{2} \right) x_1^2 - \beta x_1^3 \right] \\ &= x_1 x_2 \left( \alpha x_2 + \beta x_2^2 + \alpha x_1 + \frac{3\beta}{2} x_1 - \beta x_1^2 \right) \\ &= x_1 x_2 \left[ \alpha(x_1 + x_2) + \frac{3\beta}{2} x_1 + \beta(x_2^2 - x_1^2) \right] \\ &= x_1 x_2 \left[ \alpha + \frac{3\beta}{2} x_1 + \beta(x_2 - x_1)(x_2 + x_1) \right] \\ &= x_1 x_2 \left[ \alpha + \beta \left( 1 - \frac{x_1}{2} \right) \right] \end{aligned}$$

This expression reduces to that of a regular solution when  $\beta = 0$ .

**24-58.** Prove that the maxima or minima of  $\Delta_{\text{mix}} \overline{G}$  defined in Problem 24-37 occur at  $x_1 = x_2 = 1/2$  for any value of  $RT/u$ . Now prove that

$$\begin{aligned} &> 0 \quad \text{for } RT/u > 0.50 \\ \frac{\partial^2 \Delta_{\text{mix}} \overline{G}}{\partial x_1^2} &= 0 \quad \text{for } RT/u = 0.50 \\ &< 0 \quad \text{for } RT/u < 0.50 \end{aligned}$$

at  $x_1 = x_2 = 1/2$ . Is this result consistent with the graphs you obtained in Problem 24-41?

Start with

$$\frac{\Delta_{\text{mix}} \overline{G}}{u} = \frac{RT}{u} (x_1 \ln x_1 + x_2 \ln x_2) + x_1 x_2$$

The maxima or minima are given by

$$\left( \frac{\partial \Delta_{\text{mix}} \overline{G}/u}{\partial x_1} \right) = \frac{RT}{u} [\ln x_1 + 1 - \ln(1 - x_2) - 1] + 1 - 2x_1 = 0$$

or by

$$\frac{RT}{u} \ln \frac{x_1}{1 - x_1} = 1 - 2x_1$$

Note that this equation is satisfied by  $x_1 = x_2 = 1/2$  for any value of  $RT/u$ .

$$\begin{aligned} \left( \frac{\partial^2 \Delta_{\text{mix}} \overline{G}/u}{\partial x_1^2} \right) &= \frac{RT}{u} \left( \frac{1}{x_1} + \frac{1}{1 - x_1} \right) - 2 \\ &= \frac{RT}{u} \left[ \frac{1}{x_1(1 - x_1)} \right] - 2 \\ &= \frac{4RT}{u} - 2 \end{aligned}$$

at  $x_1 = x_2 = 1/2$ . This expression is greater than zero when  $RT/u > 0.50$ , less than zero when  $RT/u < 0.50$ , and equal to zero when  $RT/u = 0.50$ .

**24-59.** Use the data in Table 24.1 to plot Figures 24.15 through 24.17.

Use the relations  $a_j^{(R)} = P_j/P_j^*$  and  $\gamma_j^{(R)} = P_j/x_j P_j^*$ . The results of the calculations are given below.

$x_1$	$P_{\text{CS}_2}/\text{torr}$	$P_{\text{dimeth}}/\text{torr}$	$a_{\text{CS}_2}^{(R)}$	$a_{\text{dimeth}}^{(R)}$	$\gamma_{\text{CS}_2}^{(R)}$	$\gamma_{\text{dimeth}}^{(R)}$	$\Delta G^E/\text{kJ}\cdot\text{mol}^{-1}$
0.0000	0.0	587.7	0.000	1.000	2.22	1.00	0.000
0.0489	54.5	558.3	0.106	0.950	2.17	1.00	0.037
0.1030	109.3	529.1	0.212	0.900	2.06	1.00	0.078
0.1640	159.5	500.4	0.310	0.851	1.89	1.02	0.120
0.2710	234.8	451.2	0.456	0.768	1.68	1.05	0.179
0.3470	277.6	412.7	0.540	0.706	1.55	1.08	0.204
0.4536	324.8	378.0	0.631	0.643	1.39	1.18	0.239
0.4946	340.2	360.8	0.661	0.614	1.34	1.21	0.242
0.5393	357.2	342.2	0.694	0.582	1.29	1.26	0.244
0.6071	381.9	313.3	0.742	0.533	1.22	1.36	0.242
0.6827	407.0	277.8	0.791	0.473	1.16	1.49	0.227
0.7377	424.3	250.1	0.825	0.426	1.12	1.62	0.209
0.7950	442.6	217.4	0.860	0.370	1.08	1.80	0.184
0.8445	458.1	184.9	0.890	0.315	1.05	2.02	0.154
0.9108	481.8	124.2	0.936	0.211	1.03	2.37	0.102
0.9554	501.0	65.1	0.974	0.111	1.02	2.48	0.059
1.0000	514.5	0.0	1.000	0.000	1.00	2.50	0.000