

HW 4 Key

16, 18, 20, 26
1, 26, 193

①



$$T_b = 60^\circ\text{C}$$

$$P_A = 3P_B$$

$$P_A^* = 550 \text{ torr}$$

$$P_B^* = 150 \text{ torr}$$



$$T_b = 40^\circ\text{C}$$

$$P_A = 2.5P_B$$

$$P_A^* = ?$$

$$P_B^* = 100 \text{ torr}$$

$$P_{\text{Tot}} = ?$$

First, find X_A, X_B for 1st container.

$$Y_A = \frac{P_A}{P_{\text{Tot}}} \Rightarrow Y_A P_{\text{Tot}} = P_A = X_A P_A^*$$

$$Y_A P_{\text{Tot}} = X_A P_A^* = P_A. \text{ Similarly, } Y_B P_{\text{Tot}} = X_B P_B^* = P_B$$

$$P_A = X_A P_A^*$$

$$3P_B = X_A P_A^*$$

$$P_B = \frac{X_A P_A^*}{3}$$

$$P_B = (1 - X_A) P_B^*$$

$$X_A P_A^* = 3(1 - X_A) P_B^*$$

$$X_A P_A^* = 3P_B^* - 3X_A P_B^*$$

$$X_A (P_A^* + 3P_B^*) = 3P_B^*$$

$$X_A = \frac{3P_B^*}{(P_A^* + 3P_B^*)} = \frac{3(150)}{(550 + 3(150))} = \underline{0.45}$$

$$\text{So } X_B = 1 - X_A = \underline{0.55}$$

Now to container 2. X_A, X_B will be the same.

$$P_A = X_A P_A^*$$

$$2.5P_B = X_A P_A^*$$

$$P_B = \frac{X_A P_A^*}{2.5}$$

$$P_B = X_B P_B^*$$

$$X_A P_A^* = 2.5(1 - X_A) P_B^*$$

$$P_A^* = \frac{2.5(1 - X_A) P_B^*}{X_A}$$

$$P_A^* = \frac{2.5(1-.45)(100)}{.45} = \boxed{305.56 \text{ torr}}$$

$$P_{\text{Tot}} = P_A^* X_A + P_B^* X_B$$

$$P_{\text{Tot}} = (305.56)(.45) + (100)(.55)$$

$$\boxed{P_{\text{Tot}} = 192.5 \text{ torr}}$$

	T(°C)	79.4	88	94	100	110
"B" → P [*] _{C₆H₆} (bar)		1.0	1.285	1.526	1.801	
"T" → P [*] _{C₇H₈} (bar)			0.508	0.616	0.742	1.0

$$X_B = \frac{P_T^* - P_{\text{Tot}}}{P_T^* - P_B^*}$$

$$Y_B = \frac{X_B P_B^*}{P_{\text{Tot}}}$$

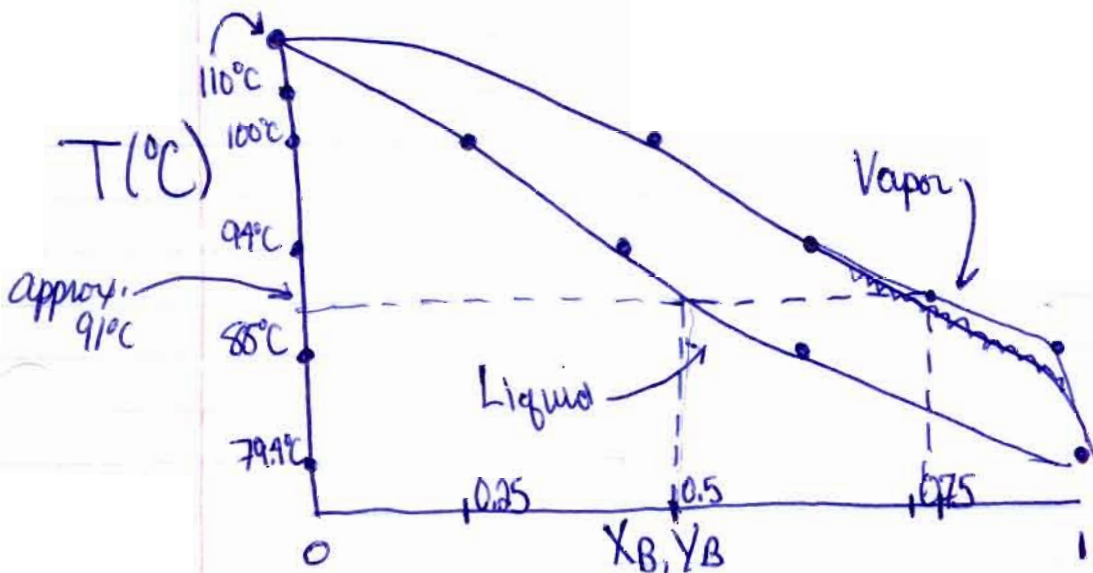
Select $P_{\text{Tot}} = 1 \text{ bar}$.

$$X_T = 1 - X_B$$

$$Y_T = 1 - Y_B$$

Adding ~~two~~ ⁴ more lines to the table, we have:

X _B	0.6332	0.4219	0.2436 †
X _T	0.3668	0.5781	0.7564
Y _B	0.8137	0.6439	0.4388 †
Y _T	0.1863	0.3560	0.5612



Using our plot, a 50/50 mole mix. would first start to boil at a $T = 91^\circ\text{C}$. The composition of first vapor bubble would be $y_B = 0.72$ (approx.), $y_T = 0.28$ (much in the lower boiling benzene).

③ BPT, FP↓, and Os.P. for a 1L solution of water w/ 10g NaCl.

1 L of water = 1 kg of water

$$1 \text{ L H}_2\text{O} \times \frac{1 \text{ g H}_2\text{O}}{1 \text{ mL H}_2\text{O}} \times \frac{1000 \text{ mL H}_2\text{O}}{1 \text{ L H}_2\text{O}} \times \frac{1 \text{ kg H}_2\text{O}}{1000 \text{ g H}_2\text{O}} = 1 \text{ kg of H}_2\text{O}.$$

$$10 \text{ g NaCl} \times \frac{1 \text{ mole NaCl}}{58.44 \text{ g NaCl}} = 0.1711 \text{ mole NaCl}$$

$$\text{Molality} = \frac{0.1711 \text{ moles NaCl}}{1 \text{ kg H}_2\text{O}} = 0.1711 \text{ m NaCl}$$

$$\text{Molarity} = \frac{0.1711 \text{ moles NaCl}}{1 \text{ L soln}} \approx 0.1711 \text{ M NaCl}$$

1 L soln \approx 1 L H₂O since low concentration

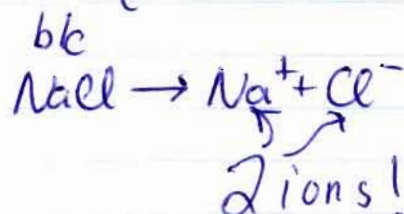
$$\Delta T_f = i K_f m \quad \text{where } i \equiv \text{van't Hoff Factor (how many particles)}$$

$$\Delta T_f = (2) \left(\frac{1.86 \text{ K} \cdot \text{kg}}{\text{mole}} \right) (0.1711 \text{ m}) \quad K_f \equiv \text{freezing pt dep. cons.}$$

$m \equiv$ solution molality

$i = 2$

$$\boxed{\Delta T_f = 0.637 \text{ K}} \rightarrow \boxed{T_f = -0.637^\circ\text{C}}$$



$$\Delta T_b = i K_b m$$

$$\Delta T_b = (2) \left(\frac{0.512 \text{ K} \cdot \text{kg}}{\text{mole}} \right) (0.1711 \text{ m})$$

$$\boxed{\Delta T_b = 0.175 \text{ K}} \rightarrow \boxed{T_b = 100.175^\circ\text{C}}$$

I just used 298K.

$$\Pi = iMRT$$

$$\Pi = (2)(0.1711 \text{ M}) \left(0.0821 \frac{\text{L}\cdot\text{atm}}{\text{K}\cdot\text{mol}}\right) (298 \text{ K})$$

$$\Pi = 8.37 \text{ atm}$$

④ Let's draw a diagram:

0.5g frog extract in 125 mL methanol

- 25 mL of soln spilled

Frog extract in 100 mL methanol

+ 2.05g sugar

Frog extract + 2.05g sugar in 100 mL MeOH

- 50 mL of soln spilled

Frog extract + Sugar + 50 mL MeOH

Data: 2ml sample which freezes at $T_f = -98.7^\circ\text{C}$.

MW sugar = 342 g/mol

0.7866 → $\rho_{\text{MeOH}} = 0.7866 \text{ g/mL}$

BP = 1.001 atm

MeOH f.p. = -97.95°C

$\Delta H_{\text{fus MeOH}} = 3.16 \text{ kJ/mol}$

VP pure MeOH = 121 Torr

$$\Delta T_{f, \text{soln}} = \Delta T_{f, \text{frog}} + \Delta T_{f, \text{sugar}}$$

$$\Delta T_{f, \text{soln}} = i K_f m_{\text{frog}} + i K_f m_{\text{sugar}}$$

$$0.75 \text{ K} = (1)(K_f) \left(\frac{\text{moles frog}}{\text{kg MeOH}} \right) + (1)(K_f) \left(\frac{\text{moles sugar}}{\text{kg MeOH}} \right)$$

Find K_f : $K_f = \frac{RT^2}{\Delta_{fus}H} \left(\frac{M}{1000 \text{ g} \cdot \text{kg}^{-1}} \right)$ CH_3OH

$$K_f = \frac{(8.3145 \text{ J/K} \cdot \text{mol})(-97.95 + 273.15 \text{ K})^2}{3.16 \times 10^3 \text{ J/mole}} \left(\frac{32 \text{ g/mole}}{1000 \text{ g/kg}} \right)$$

$$K_f = 2.58 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1}$$

Now we have:

$$0.75 \text{ K} = (1) (2.58 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1}) \left(\frac{\text{moles}_{\text{frag}}}{\text{kg}_{\text{MeOH}}} \right) + (1) (2.58 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1}) \left(\frac{\text{moles}_{\text{sugar}}}{\text{kg}_{\text{MeOH}}} \right)$$

$$0.75 \text{ K} = (1) (2.58 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1}) \left(\frac{\text{moles}_{\text{frag}}}{\text{kg}_{\text{MeOH}}} \right) + (1) (2.58 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1}) \left(\frac{2.05 \text{ g Sugar} \times \frac{1 \text{ mole}}{342 \text{ g}}}{\text{kg}_{\text{MeOH}}} \right)$$

blk frag was
diss. in
125 mL
MeOH

$$125 \text{ mL MeOH} \times \frac{0.7866 \text{ kg}}{1 \text{ mL}} \times \frac{1 \text{ kg}}{1000 \text{ g}}$$

$$100 \text{ mL} \left(\frac{0.7866}{1} \right) \left(\frac{1}{1000} \right)$$

blk sugar was only dissolved in 100 mL MeOH

$$0.75 \text{ K} = 2.58 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1} \left(\frac{\text{moles}_{\text{frag}} + 5.994 \times 10^{-3} \text{ moles}}{9.833 \times 10^{-2} \text{ kg} + 7.866 \times 10^{-2} \text{ kg}} \right)$$

$$0.75 \text{ K} = 26.2 \text{ K} \cdot \text{mol}^{-1} \cdot \text{moles}_{\text{frag}} + 0.197 \text{ K}$$

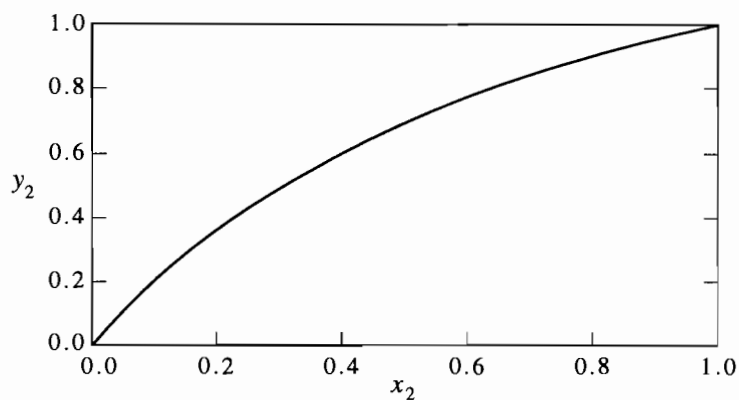
$$\text{moles}_{\text{frag}} = 0.553 \text{ K} \quad 0.0211$$

$$26.2 \text{ moles}_{\text{frag}} = \text{moles}_{\text{frag}}$$

$$\frac{0.5 \text{ g}}{0.0211 \text{ moles}} = \boxed{23.7 \text{ g/mole}}$$

seems low?

A plot of y_2 against x_2 is



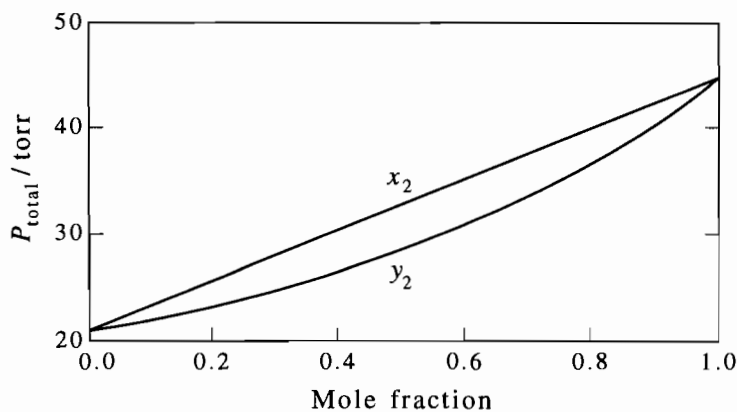
24-15. Use your results from Problem 24-14 to construct the pressure-composition diagram in Figure 24.4.

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

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_{total} as a function of x_2 . Now let y_2 vary from 0 to 1 to calculate x_2 and then P_{total} to give P_{total} as a function of y_2 . A plot of P_{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

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

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

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

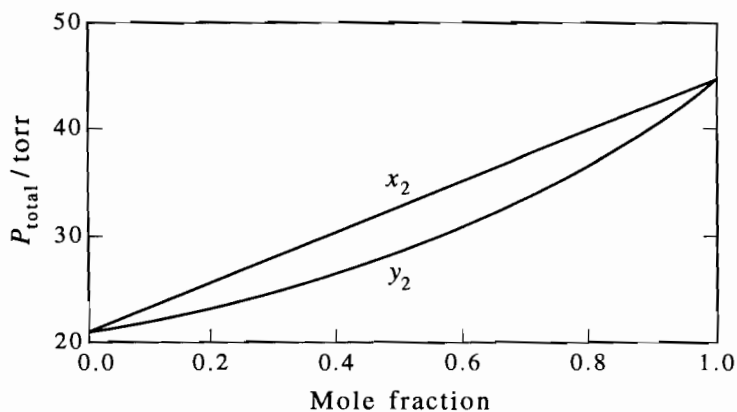
Substitute this result into

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

to get

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

The plots of P_{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.

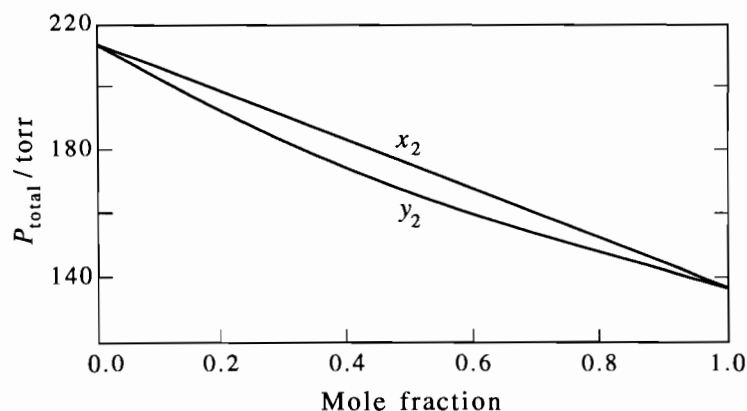
- 24-19.** Tetrachloromethane and trichloroethylene form essentially an ideal solution at 40°C at all concentrations. Given that the vapor pressure of tetrachloromethane and trichloroethylene at 40°C are 214 torr and 138 torr, respectively, plot the pressure-composition diagram for this system (see Problem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

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

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 15 molar solution implies that there are

$$(15 \text{ mol}\cdot\text{L}^{-1})(97.998 \text{ g}\cdot\text{mol}^{-1}) = 1470 \text{ g of phosphoric acid per liter of solution}$$

Therefore, the density of the solution is

$$\text{density} = \frac{1470 \text{ g}\cdot\text{L}^{-1}}{0.85} = 1700 \text{ g}\cdot\text{L}^{-1} = 1.7 \text{ g}\cdot\text{mL}^{-1}$$

25-4. Calculate the mole fraction of glucose in an aqueous solution that is $0.500 \text{ mol}\cdot\text{kg}^{-1}$ glucose.

There are 0.500 mol glucose per $\text{kg H}_2\text{O}$. so

$$x_2 = \frac{0.500 \text{ mol}}{0.500 \text{ mol} + \frac{1000 \text{ g H}_2\text{O}}{18.02 \text{ g}\cdot\text{mol}^{-1} \text{ H}_2\text{O}}} = 0.00893$$

25-5. Show that the relation between molarity and molality for a solution with a single solute is

$$c = \frac{(1000 \text{ mL}\cdot\text{L}^{-1})\rho m}{1000 \text{ g}\cdot\text{kg}^{-1} + mM_2}$$

where c is the molarity, m is the molality, ρ is the density of the solution in $\text{g}\cdot\text{mL}^{-1}$, and M_2 is the molar mass ($\text{g}\cdot\text{mol}^{-1}$) of the solute.

Consider a solution of a certain molality, m , containing 1000 g of solvent. The total mass of the solution is $1000 \text{ g}\cdot\text{kg}^{-1} + mM_2$ and its volume (in mL) is $(1000 \text{ g}\cdot\text{kg}^{-1} + mM_2)/\rho$, where ρ is the density of the the solution in $\text{g}\cdot\text{mL}^{-1}$. The volume of the solution in liters is $(1000 \text{ g}\cdot\text{kg}^{-1} + mM_2)/\rho(1000 \text{ mL}\cdot\text{L}^{-1})$ liters. There are m moles of solute per $(1000 \text{ g}\cdot\text{kg}^{-1} + mM_2)/\rho(1000 \text{ mL}\cdot\text{L}^{-1})$ liters, so the molarity is

$$c = \frac{(1000 \text{ mL}\cdot\text{L}^{-1})\rho m}{1000 \text{ g}\cdot\text{kg}^{-1} + mM_2}$$

25-6. The *CRC Handbook of Chemistry and Physics* has tables of “concentrative properties of aqueous solutions” for many solutions. Some entries for CsCl(s) are

$A/\%$	$\rho/\text{g}\cdot\text{mL}^{-1}$	$c/\text{mol}\cdot\text{L}^{-1}$
1.00	1.0058	0.060
5.00	1.0374	0.308
10.00	1.0798	0.641
20.00	1.1756	1.396
40.00	1.4226	3.380

where A is the mass percent of the solute, ρ is the density of the solution, and c is the molarity. Using these data, calculate the molality at each concentration.

This equation is similar to Equation 25.17 except for the negative sign, which occurs because boiling points of solutions are elevated whereas freezing points are lowered. The rest of the derivation follows Equations 25.18 through 25.23.

- 25–26.** Calculate the boiling point elevation constant for cyclohexane given that $T_{\text{vap}} = 354 \text{ K}$ and that $\Delta_{\text{vap}}\overline{H} = 29.97 \text{ kJ}\cdot\text{mol}^{-1}$.

Using the analog of Equation 25.23, we have

$$K_b = \frac{(84.161 \text{ g}\cdot\text{mol}^{-1})(8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(354 \text{ K})^2}{(1000 \text{ g}\cdot\text{kg}^{-1})(29.97 \times 10^3 \text{ J}\cdot\text{mol}^{-1})}$$

$$= 2.93 \text{ K}\cdot\text{kg}\cdot\text{mol}^{-1}$$

- 25–27.** A solution containing 1.470 g of dichlorobenzene in 50.00 g of benzene boils at 80.60°C at a pressure of 1.00 bar. The boiling point of pure benzene is 80.09°C and the molar enthalpy of vaporization of pure benzene is $32.0 \text{ kJ}\cdot\text{mol}^{-1}$. Determine the molecular mass of dichlorobenzene from these data.

The value of $\Delta_{\text{vap}}T$ is

$$\Delta_{\text{vap}}T = 80.60^\circ\text{C} - 80.09^\circ\text{C} = 0.51^\circ\text{C} = 0.51 \text{ K}$$

Using the analog of Equation 25.23, we have

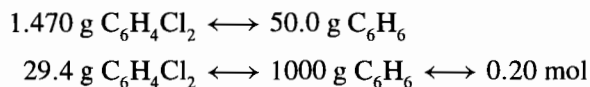
$$K_b = \frac{(78.108 \text{ g}\cdot\text{mol}^{-1})(8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(353.2 \text{ K})^2}{(1000 \text{ g}\cdot\text{kg}^{-1})(32.0 \times 10^3 \text{ J}\cdot\text{mol}^{-1})}$$

$$= 2.53 \text{ K}\cdot\text{kg}\cdot\text{mol}^{-1}$$

The molality is given by

$$m = \frac{\Delta_{\text{vap}}T}{K_b} = \frac{0.51 \text{ K}}{2.53 \text{ K}\cdot\text{kg}^{-1}\cdot\text{mol}^{-1}} = 0.20 \text{ mol}\cdot\text{kg}^{-1}$$

Therefore,



and so the molecular mass is 147.

- 25–28.** Consider the following phase diagram for a typical pure substance. Label the region corresponding to each phase. Illustrate how this diagram changes for a dilute solution of a nonvolatile solute.

The plot is essentially identical to the one obtained in Problem 25–37.

- 25–40.** Don Juan Pond in the Wright Valley of Antarctica freezes at -57°C . The major solute in the pond is CaCl_2 . Estimate the concentration of CaCl_2 in the pond water.

We say “estimate” because the concentration will be too large for Equation 25.45 to be quantitative. Nevertheless, we can “estimate” the molality to be

$$m \approx \frac{57 \text{ K}}{(3)(1.84 \text{ K}\cdot\text{kg}\cdot\text{mol}^{-1})} = 10 \text{ mol}\cdot\text{kg}^{-1}$$

where the factor of 3 in the denominator results because $\nu = 3$ for CaCl_2 .

- 25–41.** A solution of mercury(II) chloride is a poor conductor of electricity. A 40.7-g sample of HgCl_2 is dissolved in 100.0 g of water, and the freezing point of the solution is found to be -2.83°C . Explain why HgCl_2 in solution is a poor conductor of electricity.

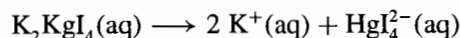
Because 40.7 g HgCl_2 corresponds to 0.150 mol HgCl_2 , the molality of the solution is $1.50 \text{ mol}\cdot\text{kg}^{-1}$. Using Equation 25.45, we find ν to be

$$\nu = \frac{\Delta T_{\text{fus}}}{K_f m} = \frac{2.83 \text{ K}}{(1.84 \text{ K}\cdot\text{kg}\cdot\text{mol}^{-1})(1.50 \text{ mol}\cdot\text{kg}^{-1})} = 1.02$$

This result indicates that HgCl_2 is not dissociated under these conditions, and so is a poor conductor of electricity.

- 25–42.** The freezing point of a 0.25-molal aqueous solution of Mayer’s reagent, K_2HgI_4 , is found to be -1.41°C . Suggest a possible dissociation reaction that takes place when K_2HgI_4 is dissolved in water.

Use Equation 25.45 to obtain $\nu = 3$. The equation for the dissociation reaction is



- 25–43.** Given the following freezing-point depression data, determine the number of ions produced per formula unit when the indicated substance is dissolved in water to produce a 1.00-molal solution.

Formula	$\Delta T/\text{K}$
$\text{PtCl}_2\cdot 4\text{NH}_3$	5.58
$\text{PtCl}_2\cdot 3\text{NH}_3$	3.72
$\text{PtCl}_2\cdot 2\text{NH}_3$	1.86
$\text{KPtCl}_3\cdot \text{NH}_3$	3.72
K_2PtCl_4	5.58

Interpret your results.

Use Equation 25.45 to obtain

formula	ν	ions
$\text{PtCl}_2 \cdot 4\text{NH}_3$	3	$\text{Pt}(\text{NH}_3)_4^{2+}$ 2 Cl^-
$\text{PtCl}_2 \cdot 3\text{NH}_3$	2	$\text{Pt}(\text{NH}_3)_3\text{Cl}^+$ Cl^-
$\text{PtCl}_2 \cdot 2\text{NH}_3$	1	$\text{Pt}(\text{NH}_3)_2\text{Cl}_2$
$\text{KPtCl}_3 \cdot \text{NH}_3$	2	K^+ $\text{Pt}(\text{NH}_3)\text{Cl}_3^-$
K_2PtCl_4	3	2 K^+ PtCl_4^{2-}

- 25-44. An aqueous solution of NaCl has an ionic strength of $0.315 \text{ mol} \cdot \text{L}^{-1}$. At what concentration will an aqueous solution of K_2SO_4 have the same ionic strength?

The ionic strength, I_c , equals c for a 1-1 electrolyte and $3c$ for a 2-1 electrolyte. Therefore, a solution of $\text{K}_2\text{SO}_4(\text{aq})$ would have an ionic strength of $0.315 \text{ mol} \cdot \text{L}^{-1}$ when its molarity is $0.105 \text{ mol} \cdot \text{L}^{-1}$.

- 25-45. Derive the "practical" formula for κ^2 given by Equation 25.53.

Start with

$$\kappa^2 = \frac{1}{\epsilon_0 \epsilon_r k_B T} \sum_{j=1}^s q_j^2 \frac{N_j}{V} = \frac{N_A e^2}{\epsilon_0 \epsilon_r k_B T} \sum_{j=1}^s z_j^2 \frac{n_j}{V}$$

Now

$$\frac{n_j}{V} = (1000 \text{ L} \cdot \text{m}^{-3}) c_j$$

because V , being in SI units, has units of m^3 . Therefore,

$$\kappa^2 = \frac{2e^2 N_A (1000 \text{ L} \cdot \text{m}^{-3})}{\epsilon_0 \epsilon_r k_B T} (I_c / \text{mol} \cdot \text{L}^{-1})$$

- 25-46. Some authors define ionic strength in terms of molality rather than molarity, in which case

$$I_m = \frac{1}{2} \sum_{j=1}^s z_j^2 m_j$$

Show that this definition modifies Equation 25.53 for dilute solutions to be

$$\kappa^2 = \frac{2e^2 N_A (1000 \text{ L} \cdot \text{m}^{-3}) \rho}{\epsilon_0 \epsilon_r k T} (I_m / \text{mol} \cdot \text{kg}^{-1})$$

where ρ is the density of the solvent (in $\text{g} \cdot \text{mL}^{-1}$).

For dilute solutions, $c = \rho m$ (see Problem 25-5), and so $I_c = \rho I_m$. Therefore,

$$\kappa^2 = \frac{2e^2 N_A (1000 \text{ L} \cdot \text{m}^{-3}) \rho}{\epsilon_0 \epsilon_r k T} (I_m / \text{mol} \cdot \text{kg}^{-1})$$