

1-

$$a) P_i = X_i K_i$$

$$P_{ch} = X_{ch} K_{ch} \text{ (dilute)}$$

$$34 = 0.2 K_{ch}$$

$$\Rightarrow K_{ch} = \boxed{170}$$

$$P_{Ac} = X_{Ac} K_{Ac} \text{ (dilute)}$$

$$42 = 0.2 K_{Ac} \Rightarrow K_{Ac} = \boxed{210}$$

$$b) X_{ch} = 0.2$$

$$a_{1,Ac} = \frac{P_{Ac}}{P_{Ac}^*} = \frac{270}{344} = 0.78$$

$$a_{1,Ac} = X_{1,Ac} \gamma_{1,Ac} \Rightarrow 0.78 = 0.8 \gamma_{1,Ac} \Rightarrow \gamma_{1,Ac} = \boxed{0.98}$$

$$c) X_{ch} = 0.8$$

$$a_{1,ch} = \frac{P_{ch}}{P_{ch}^*} = \frac{225}{293} = 0.77 \Rightarrow a_{1,ch} = X_{1,ch} \gamma_{1,ch}$$

$$\Rightarrow 0.77 = 0.8 \gamma_{1,ch} \Rightarrow \gamma_{1,ch} = \boxed{0.96}$$

d, e) For estimating the Henry Law Constant in part a we assumed that $\gamma = 1$, so we cannot find the activity coefficient γ_2 based on these data.

2-

The molar Gibbs energy of an ideal gas:

$$\bar{G} = \bar{G}^\circ + RT \ln \frac{P}{1 \text{ bar}}$$

In a mixture of ideal gases, we find that the system's partial molar Gibbs energy is equivalent to its chemical potential:

$$\bar{G}_i = \mu_i$$

$$\Rightarrow \bar{G}_i = \mu_i = \mu_i^\circ + RT \ln \frac{P_i}{1 \text{ bar}}$$

initial: two gases at the same T & P (gas 1 & gas 2)

$$G_{\text{initial}} = n_1 (\mu_1^\circ + RT \ln P) + n_2 (\mu_2^\circ + RT \ln P)$$

final: mixture of gas 1 and gas 2 [$P = P_1 + P_2$]

$$G_{\text{final}} = n_1 (\mu_1^\circ + RT \ln P_1) + n_2 (\mu_2^\circ + RT \ln P_2)$$

The Gibbs energy of mixing, $\Delta_{\text{mix}} G$:

$$\Delta_{\text{mix}} G = G_{\text{final}} - G_{\text{initial}}$$

$$\Rightarrow \Delta_{\text{mix}} G = n_1 RT \ln \frac{P_1}{P} + n_2 RT \ln \frac{P_2}{P}$$

as $P_i = x_i P$ & $x_i = n_i/n$:

$$\Delta_{\text{mix}} G = \overset{x_1 n}{\circlearrowleft n_1} RT \ln \left(\frac{P_1}{P} \right) + \overset{x_2 n}{\circlearrowleft n_2} RT \ln \left(\frac{P_2}{P} \right) \overset{x_2}{\circlearrowright}$$

$$\Rightarrow \Delta_{\text{mix}} G = nRT (x_1 \ln x_1 + x_2 \ln x_2) \checkmark$$

3.

$$\Delta T = K_b m \quad \Delta T = 0.3 \text{ K} \quad K_b = 2.53 \text{ K} \cdot \text{mol}^{-1} \cdot \text{Kg}$$

$$0.3 \text{ K} = 2.53 \text{ K} \cdot \text{mol}^{-1} \cdot \text{Kg} \times \frac{1.0 \text{ g} \times 1000 \text{ g/Kg} / M(\text{dinitrobenzene})}{50.0 \text{ g (benzene)}}$$

$$\Rightarrow M = 168.67 \text{ g/mol} \checkmark$$

$$4. \text{ Molarity (M)} = \frac{n_i (\# \text{ of moles of solute})}{\text{Volume of solution}} = \frac{n_i}{V_{\text{solvent}} + V_{\text{solute}}}$$

$$\text{Molality (m)} = \frac{n_i (\# \text{ of moles of solute})}{\text{weight of solvent in kg}} = \frac{n_i}{\rho_w \times V_w}$$

ex for a dilute solution $\Rightarrow V_{\text{solvent}} + V_{\text{solute}} \approx V_{\text{solvent}}$

$$\Rightarrow M = \frac{n_i}{V_w(\text{solvent})} \quad , \rho_w = 1.0$$

$$\Rightarrow m = \frac{n_i}{\rho_w V_w} \quad \Rightarrow m = M \checkmark$$

First calculate the mole fraction, molality, and molarity of lysozyme.

$$\text{Number of moles of lysozyme} = \frac{0.1 \text{ g}}{13930 \text{ g mol}^{-1}} = 7.17875 \times 10^{-6} \text{ mol}$$

$$\text{Number of moles of water} = \frac{50 \text{ g}}{18.02 \text{ g mol}^{-1}} = 2.7747 \text{ mol}$$

$$x_{\text{lysozyme}} = \frac{7.17875 \times 10^{-6} \text{ mol}}{7.17875 \times 10^{-6} \text{ mol} + 2.7747 \text{ mol}} = 2.5872 \times 10^{-6}$$

$$m = \frac{7.17875 \times 10^{-6} \text{ mol}}{50 \times 10^{-3} \text{ kg}} = 1.43575 \times 10^{-4} \text{ mol kg}^{-1}$$

For a dilute aqueous solution, the molality and molarity are numerically the same (see Problem 5.6). Therefore, $M = 1.43575 \times 10^{-4} \text{ mol L}^{-1}$.

Vapor pressure lowering:

$$\Delta P = x_{\text{lysozyme}} P_{\text{H}_2\text{O}}^* = (2.5872 \times 10^{-6}) (23.76 \text{ mmHg}) = 6.147 \times 10^{-5} \text{ mmHg}$$

Depression in freezing point:

$$\Delta T_f = K_f m = (1.86 \text{ K m}^{-1}) (1.43575 \times 10^{-4} \text{ m}) = 2.67 \times 10^{-4} \text{ K}$$

Elevation of boiling point:

$$\Delta T_b = K_b m = (0.51 \text{ K m}^{-1}) (1.43575 \times 10^{-4} \text{ m}) = 7.3 \times 10^{-5} \text{ K}$$

Osmotic pressure:

$$\begin{aligned} \pi &= MRT = (1.43575 \times 10^{-4} \text{ M}) (0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1}) (298 \text{ K}) \\ &= 3.51 \times 10^{-3} \text{ atm} \left(\frac{760 \text{ torr}}{1 \text{ atm}} \right) = 2.67 \text{ torr} \end{aligned}$$

Note that the only property that is readily measurable is the osmotic pressure.

6-

The absolute third-law entropy of the gas solution, S_f , can be calculated from the third-law entropy of the gases before they are mixed, S_i , and from the entropy of mixing, $\Delta_{\text{mix}}S$.

$$\begin{aligned} S_i &= S_{\text{CH}_4} + S_{\text{C}_2\text{H}_6} \\ &= (1 \text{ mol}) (186.19 \text{ J K}^{-1} \text{ mol}^{-1}) + (1 \text{ mol}) (229.49 \text{ J K}^{-1} \text{ mol}^{-1}) \\ &= 415.68 \text{ J K}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta_{\text{mix}}S &= -nR (x_{\text{CH}_4} \ln x_{\text{CH}_4} + x_{\text{C}_2\text{H}_6} \ln x_{\text{C}_2\text{H}_6}) \\ &= -(2 \text{ mol}) (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \left(\frac{1}{2} \ln \frac{1}{2} + \frac{1}{2} \ln \frac{1}{2} \right) \\ &= 11.526 \text{ J K}^{-1} \end{aligned}$$

$$S_f = S_i + \Delta_{\text{mix}}S = 415.68 \text{ J K}^{-1} + 11.526 \text{ J K}^{-1} = 427.21 \text{ J K}^{-1}$$

7-

$$\begin{aligned} \mu_{\text{ethanol}}(l) &= \mu_{\text{ethanol}}^*(l) + RT \ln x_{\text{ethanol}} \\ &= \mu_{\text{ethanol}}^*(l) + (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) (351.5 \text{ K}) \ln 0.40 \\ &= \mu_{\text{ethanol}}^*(l) - 2.7 \times 10^3 \text{ J mol}^{-1} \end{aligned}$$

The chemical potential of ethanol in solution is lower than the chemical potential of pure ethanol by $2.7 \times 10^3 \text{ J mol}^{-1}$.

(a) First calculate the vapor pressures of A and B using Raoult's law.

$$x_A = \frac{3.3 \text{ mol}}{3.3 \text{ mol} + 8.7 \text{ mol}} = 0.275$$

$$x_B = 1 - 0.275 = 0.725$$

$$P_A = x_A P_A^* = (0.275) (450 \text{ torr}) = 124 \text{ torr}$$

$$P_B = x_B P_B^* = (0.725) (732 \text{ torr}) = 531 \text{ torr}$$

The composition of the condensed liquid is the same as the composition of the vapor before condensation, the latter can be calculated from P_A and P_B .

$$\frac{P_A}{P_B} = \frac{124 \text{ torr}}{531 \text{ torr}} = \frac{x_A^v P_{\text{total}}}{x_B^v P_{\text{total}}} = \frac{x_A^v}{x_B^v}$$

$$\frac{x_A^v}{x_B^v} = 0.234$$

$$x_A^v = 0.234 x_B^v = 0.234 (1 - x_A^v)$$

$$1.234 x_A^v = 0.234$$

$$x_A^v = 0.19$$

$$x_B^v = 0.81$$

The total vapor pressure depends on the vapor pressures of A and B in a mixture, which in turn depends on the vapor pressures of pure A and B. With the total vapor pressure of the two mixtures known, a pair of simultaneous equations can be written in terms of the vapor pressures of pure A and B.

For the solution containing 1.2 moles of A and 2.3 moles of B,

$$x_A = \frac{1.2}{3.5} = 0.343$$

$$x_B = 1 - 0.343 = 0.657$$

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

$$331 \text{ mmHg} = 0.343 P_A^* + 0.657 P_B^*$$

Solve the last equation for P_A^* :

$$P_A^* = \frac{331 \text{ mmHg} - 0.657 P_B^*}{0.343} = 965 \text{ mmHg} - 1.92 P_B^* \quad (5.31.1)$$

Now consider the solution with the additional mole of B.

$$x_A = \frac{1.2}{4.5} = 0.267$$

$$x_B = 1 - 0.267 = 0.733$$

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

$$347 \text{ mmHg} = 0.267 P_A^* + 0.733 P_B^* \quad (5.31.2)$$

Substitute Eq. 5.31.1 into Eq. 5.31.2:

$$347 \text{ mmHg} = 0.267 (965 \text{ mmHg} - 1.92 P_B^*) + 0.733 P_B^*$$

$$0.220 P_B^* = 89.3 \text{ mmHg}$$

$$P_B^* = 406 \text{ mmHg} = 4.1 \times 10^2 \text{ mmHg}$$

Substitute the value of P_B^* into Eq. 5.31.1:

$$P_A^* = 965 \text{ mmHg} - 1.92 (406 \text{ mmHg}) = 1.9 \times 10^2 \text{ mmHg}$$

Before consumption of glucose

$$\begin{aligned} \text{Number of moles of glucose/mL of blood} &= \frac{(0.140 \text{ g}) \left(\frac{1 \text{ mol}}{180.16 \text{ g}} \right)}{100 \text{ mL}} \\ &= 7.771 \times 10^{-6} \text{ mol mL}^{-1} = 7.77 \times 10^{-6} \text{ mol mL}^{-1} \end{aligned}$$

$$\begin{aligned} \text{Total number of moles of glucose in blood} &= (7.771 \times 10^{-6} \text{ mol mL}^{-1}) (5.0 \times 10^3 \text{ mL}) \\ &= 3.9 \times 10^{-2} \text{ mol} \end{aligned}$$

$$\begin{aligned} \text{Total number of grams of glucose in blood} &= \left(\frac{0.140 \text{ g}}{100 \text{ mL}} \right) (5.0 \times 10^3 \text{ mL}) \\ &= 7.0 \text{ g} \end{aligned}$$

After consumption of glucose

$$\begin{aligned} \text{Number of moles of glucose/mL of blood} &= \frac{(0.240 \text{ g}) \left(\frac{1 \text{ mol}}{180.16 \text{ g}} \right)}{100 \text{ mL}} \\ &= 1.332 \times 10^{-5} \text{ mol mL}^{-1} = 1.33 \times 10^{-5} \text{ mol mL}^{-1} \end{aligned}$$

$$\begin{aligned} \text{Total number of moles of glucose in blood} &= (1.33 \times 10^{-5} \text{ mol mL}^{-1}) (5.0 \times 10^3 \text{ mL}) \\ &= 6.7 \times 10^{-2} \text{ mol} \end{aligned}$$

$$\begin{aligned} \text{Total number of grams of glucose in blood} &= \left(\frac{0.240 \text{ g}}{100 \text{ mL}} \right) (5.0 \times 10^3 \text{ mL}) \\ &= 12 \text{ g} \end{aligned}$$