

1) The partial molar volumes of two liquids A and B in a mixture in which the mole fraction of A is 0.485 are $285.32 \text{ cm}^3 \text{ mol}^{-1}$ and $197.14 \text{ cm}^3 \text{ mol}^{-1}$, respectively. The molar masses of A and B are 224.1 g mol^{-1} and 188.9 g mol^{-1} . What is the volume of a solution of mass 1.000 kg?

$$\text{Total volume } V = n_A V_A + n_B V_B = n(x_A V_A + x_B V_B)$$

$$\begin{aligned} \text{Total mass } m &= n_A M_A + n_B M_B \\ &= n(x_A M_A + (1-x_A) M_B) \quad \text{where } n = n_A + n_B \end{aligned}$$

$$\frac{m}{x_A M_A + (1-x_A) M_B} = n$$

$$n = \frac{1.000 \text{ kg}(10^3 \text{ g/kg})}{(0.4851) \times (224.1 \text{ g/mol}) + (1-0.4851) \times (188.9 \text{ g/mol})} = 4.855 \text{ mol}$$

$$V = n(x_A V_A + x_B V_B)$$

$$\begin{aligned} &= (4.855 \text{ mol}) \times [(0.4851) \times (285.32 \text{ cm}^3 \text{ mol}^{-1}) + (1-0.4851) \times (197.14 \text{ cm}^3 \text{ mol}^{-1})] \\ &= \boxed{937.7 \text{ cm}^3} \end{aligned}$$

2) The vapour pressure of benzene is 53.3 kPa at $60.6 \text{ }^\circ\text{C}$, but it fell to 49.2 kPa when 51.2 g of an involatile organic compound was dissolved in 500 g of benzene. Calculate the molar mass of the compound.

We assume that the solvent, benzene, is ideal and obeys Raoult's law.

Let B denote benzene and A the solute; then

$$p_B = x_B p_B^* \quad \text{and} \quad x_B = \frac{n_B}{n_A + n_B}$$

Hence $p_B = \frac{n_B p_B^*}{n_A + n_B}$; which solves to

$$n_A = \frac{n_B (p_B^* - p_B)}{p_B}$$

Then, Since $n_A = \frac{m_A}{M_A}$, where m_A is the mass of A present,

$$M_A = \frac{m_A p_B}{n_B (p_B^* - p_B)} = \frac{m_A M_B p_B}{m_B (p_B^* - p_B)}$$

From the data

$$M_A = \frac{(51.2 \text{ g}) \times (78.11 \text{ g mol}^{-1}) \times (49.2 \text{ kPa})}{(500 \text{ g}) \times (53.3 - 49.2) \text{ kPa}} = \boxed{96.0 \text{ g mol}^{-1}}$$

3) The addition of 200 g of a compound to 1000 g of benzene lowered the freezing point of the solvent by 3.50 K. Calculate the molar mass of the compound.

$$M_B = \frac{\text{mass of B}}{n_B} \quad [\text{B} = \text{compound}]$$

$$n_B = \text{mass of CCl}_4 \times b_B \quad [b_B = \text{molality of B}]$$

$$b_B = \frac{\Delta T}{K_f} \quad [5.37]; \text{ thus}$$

$$M_B = \frac{\text{mass of B} \times K_f}{\text{mass of CCl}_4 \times \Delta T} \quad K_f = 5.12 \text{ K}/(\text{mol kg}^{-1}) [\text{Table 5.2}]$$

$$M_B = \frac{(200 \text{ g}) \times (5.12 \text{ K kg mol}^{-1})}{(1.000 \text{ kg}) \times (3.50 \text{ K})} = \boxed{293 \text{ g mol}^{-1}}$$

4) The osmotic pressure of an aqueous solution at 298 K is 101.3 kPa. Calculate the freezing point of the solution.

$$\Delta T = K_f b_B [5.37] \quad b_B = \frac{n_B}{\text{mass of water}} \approx \frac{n_B}{V \rho} \quad [\text{dilute solution}]$$

$$\rho \approx 10^3 \text{ kg m}^{-3} [\text{density of solution} \approx \text{density of water}]$$

$$n_B \approx \frac{\Pi V}{RT} [5.40] \quad \Delta T \approx K_f \times \frac{\Pi}{RT \rho}$$

with $K_f = 1.86 \text{ K}/(\text{mol kg}^{-1})$ [Table 5.2]

$$\Delta T \approx \frac{(1.86 \text{ K kg mol}^{-1}) \times (101.3 \times 10^3 \text{ Pa})}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \times (10^3 \text{ kg m}^{-3})} = 0.076 \text{ K}$$

Therefore, the solution will freeze at about $\boxed{-0.08 \text{ }^\circ\text{C}}$.

Comment. Osmotic pressures are inherently large. Even dilute solutions with small freezing point depressions have large osmotic pressures.

5) Consider a container of volume 2.0 dm^3 that is divided into two compartments of equal size. In the left compartment there is nitrogen at 1.0 atm and $25 \text{ }^\circ\text{C}$; in the right compartment there is oxygen at the same temperature and pressure. Calculate the entropy and Gibbs energy of mixing when the partition is removed. Assume that the gases are perfect.

$$\Delta_{\text{mix}}G = nRT\{x_A \ln x_A + x_B \ln x_B\} [5.18] \quad x_A = x_B = 0.5, \quad n = \frac{pV}{RT}$$

Therefore,

$$\begin{aligned} \Delta_{\text{mix}}G &= (pV) \times \left(\frac{1}{2} \ln \frac{1}{2} + \frac{1}{2} \ln \frac{1}{2} \right) = -pV \ln 2 \\ &= (-1.0) \times (1.013 \times 10^5 \text{ Pa}) \times (2.0 \times 10^{-3} \text{ m}^3) \times (\ln 2) \\ &= -1.4 \times 10^2 \text{ J} = \boxed{-0.14 \text{ kJ}} \end{aligned}$$

$$\Delta_{\text{mix}}S = -nR\{x_A \ln x_A + x_B \ln x_B\} = \frac{-\Delta_{\text{mix}}G}{T} [5.19] = \frac{-0.14 \text{ kJ}}{298 \text{ K}} = \boxed{+0.47 \text{ JK}^{-1}}$$

6) The mole fraction of CO_2 in the atmosphere has risen from 0.000314 in 1962 to 0.000360 in 2005. Use Henry's law and the data in Table 5.1 to calculate the solubility (as a molality) of CO_2 in the ocean at $25 \text{ }^\circ\text{C}$.

With concentrations expressed in molalities, Henry's law [5.26] becomes $p_B = b_B K$.

Solving for b , the solubility, we have $b_B = \frac{p_B}{K}$.

$$(a) p_B = 0.000317 \times 101.3 \text{ kPa} = 0.321 \text{ kPa}$$

$$b = \frac{0.321 \text{ kPa}}{3.01 \times 10^3 \text{ kPa kg mol}^{-1}} = \boxed{0.107 \text{ mmol kg}^{-1}}$$

$$(b) p_B = 0.000375 \times 101.3 \text{ kPa} = 0.380 \text{ kPa}$$

$$b = \frac{0.380 \text{ kPa}}{3.01 \times 10^3 \text{ kPa kg mol}^{-1}} = \boxed{0.126 \text{ mmol kg}^{-1}}$$

7) Given that $p^*(\text{H}_2\text{O}) = 0.02308 \text{ atm}$ and $p(\text{H}_2\text{O}) = 0.02171 \text{ atm}$ in a solution in which 0.207 kg of a non-volatile solute ($M = 298 \text{ g mol}^{-1}$) is dissolved in 0.892 kg water at 293 K, calculate the activity and activity coefficient of water in the solution.

Let A = water and B = solute.

$$a_A = \frac{p_A}{p_A^*} [5.43] = \frac{0.02171 \text{ atm}}{0.02308 \text{ atm}} = \boxed{0.9406}$$

$$\gamma_A = \frac{a_A}{x_A} \text{ and } x_A = \frac{n_A}{n_A + n_B}$$

$$n_A = \frac{0.892 \text{ kg}}{0.01802 \text{ kg mol}^{-1}} = 49.50 \text{ mol} \quad n_B = \frac{0.207 \text{ kg}}{0.298 \text{ kg mol}^{-1}} = 0.859 \text{ mol}$$

$$x_A = \frac{49.50}{49.50 + 0.859} = 0.983 \quad \gamma_A = \frac{0.9406}{0.983} = \boxed{0.957}$$

8) Calculate the ionic strength of a solution that is 0.10 mol kg^{-1} in NaCl(aq) and 0.20 mol kg^{-1} in $\text{CuSO}_4(\text{aq})$.

$$I = \frac{1}{2} \sum (b_i / b^\ominus) z_i^2 [5.71]$$

and for an $M_p X_q$ salt, $(b_+ / b^\ominus) = p(b / b^\ominus)$, $(b_- / b^\ominus) = q(b / b^\ominus)$, so

$$I = \frac{1}{2} (pz_+^2 + qz_-^2) \left(\frac{b}{b^\ominus} \right)$$

$$I(\text{NaCl}) = \frac{1}{2} (1 \times 1 + 1 \times 1) \left(\frac{b}{b^\ominus} \right) = \left(\frac{b}{b^\ominus} \right)$$

$$I(\text{CaSO}_4) = \frac{1}{2} (1 \times 2^2 + 1 \times 2^2) \left(\frac{b}{b^\ominus} \right) = 4 \left(\frac{b}{b^\ominus} \right)$$

$$I = I(\text{NaCl}) + I(\text{CuSO}_4) = \left(\frac{b}{b^\ominus} \right) (\text{NaCl}) + 4 \left(\frac{b}{b^\ominus} \right) (\text{CuSO}_4)$$

$$= (0.10) + (4) \times (0.20) = \boxed{0.90}$$