Chapter 5 – New Exercises and Solutions

E5.1(c) 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 $cm^3\ mol^{-1}$ and 197.14 $cm^3\ mol^{-1}$, 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?

E5.1(c) Total volume $V = n_A V_A + n_B V_B = n(x_A V_A + x_B V_B)$

Total mass $m = n_A M_A + n_B M_B$

$$= n(x_A M_A + (1 - x_A)M_B) \quad \text{where } n = n_A + n_B$$

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

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

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

$$= (4.855\ \text{mol}) \times [(0.4851) \times (188.9\ \text{cm}^3\ \text{mol}^{-1}) + (1 - 0.4851) \times (197.14\ \text{cm}^3\ \text{mol}^{-1})]$$

$$= \boxed{937.7\ \text{cm}^3}$$

E5.2(c) At 20.0°C, the density of a 25.00 per cent by mass ethanol–water solution is 961.7 $kg\ m^{-3}$. Given that the partial molar volume of ethanol in the solution is 53.40 $cm^3\ mol^{-1}$, calculate the partial molar volume of the water.

E5.2(c) Let A denote water and B ethanol. The total volume of the solution is $V = n_A V_A + n_B V_B$

We know V_B; we need to determine n_A and n_B in order to solve for V_A.

Assume we have $100\ cm^3$ of solution; then the mass is

$$m = \rho V = (0.9617\ \text{g cm}^{-3}) \times (100\ \text{cm}^3) = 96.17\ \text{g}$$

of which $(0.2500) \times (96.17\ \text{g}) = 24.04\overline{3}\ \text{g}$ is ethanol and $(0.75) \times (96.17\ \text{g}) = 72.12\overline{7}\ \text{g}$ is water.

$$n_A = \frac{77.12\overline{7}\ \text{g}}{18.02\ \text{g mol}^{-1}} = 4.00\ \text{mol H}_2\text{O}$$

$$n_B = \frac{24.043\ \text{g}}{46.07\ \text{g mol}^{-1}} = 0.5219\ \text{mol ethanol}$$

$$\frac{V - n_B V_B}{n_A} = V_A = \frac{100\ \text{cm}^3 - (0.5219\ \text{mol}) \times (53.4\ \text{cm}^3\ \text{mol}^{-1})}{4.00\ \text{mol}} = \boxed{18.03\ \text{cm}^3}$$

E5.4(c) Predict the partial vapour pressure of HCl above its solution in liquid germanium tetrachloride of molality 0.050 $mol\ kg^{-1}$. For data, see Exercise 5.3a.

E5.4(c) In Exercise 5.3(a), the Henry's law constant was determined for concentrations expressed in mole fractions. Thus the concentration in molality must be converted to mole fraction.

$m(GeCl_4) = 1000\ g$, corresponding to

$$n(\mathrm{GeCl_4}) = \frac{1000\,g}{214.39\,g\,\mathrm{mol}^{-1}} = 4.664\,\mathrm{mol}, \quad n(\mathrm{HCl}) = 0.10\,\mathrm{mol}$$

Therefore, $x = \dfrac{0.050\ \mathrm{mol}}{(0.050\,\mathrm{mol}) + (4.664\,\mathrm{mol})} = 0.0106$

$K_B = 6.4\times10^3\ \mathrm{kPa}$ (Exercise 5.3(a)), $p = (0.0106\times 6.4\times10^3\ \mathrm{kPa}) = \boxed{68\,\mathrm{kPa}}$

E5.4(d) Predict the partial vapour pressure of the component B above its solution in A in Exercise 5.3b when the molality of B is 0.10 mol kg^{-1}. The molar mass of A is 74.1 g mol^{-1}.

E5.4(d) In exercise 5.3(b), the Henry's law constant was determined for concentrations expressed in mole fractions. Thus the concentration in molality must be converted to mole fraction.

$m(\mathrm{A}) = 1000$ g, corresponding to

$$n(\mathrm{A}) = \frac{1000\,\mathrm{g}}{74.1\ \mathrm{g\ mol}^{-1}} = 13.5\overline{0}\ \mathrm{mol} \qquad n(\mathrm{B}) = 0.10\ \mathrm{mol}$$

Therefore,

$$x_\mathrm{B} = \frac{0.10\ \mathrm{mol}}{0.10\ \mathrm{mol} + 13.5\overline{0}\ \mathrm{mol}} = 0.0073\overline{5}$$

using $K_\mathrm{B} = 8.2\times10^3$ kPa [exercise 5.3(b)]

$$p = 0.0073\overline{5}\times 8.2\times10^3\ \mathrm{kPa} = \boxed{60\ \mathrm{kPa}}$$

E5.5(c) The vapour pressure of benzene is 53.3 kPa at 60.6 °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.

E5.5(c) We assume that the solvent, benzene, is ideal and obeys Raoult's law.
Let B denote benzene and A the solute; then

$$p_\mathrm{B} = x_\mathrm{B}p_\mathrm{B}^* \quad \text{and} \quad x_\mathrm{B} = \frac{n_\mathrm{B}}{n_\mathrm{A}+n_\mathrm{B}}$$

Hence $p_\mathrm{B} = \dfrac{n_\mathrm{B}p_\mathrm{B}^*}{n_\mathrm{A}+n_\mathrm{B}}$; which solves to

$$n_\mathrm{A} = \frac{n_\mathrm{B}(p_\mathrm{B}^* - p_\mathrm{B})}{p_\mathrm{B}}$$

Then, Since $n_\mathrm{A} = \dfrac{m_\mathrm{A}}{M_\mathrm{A}}$, where m_A is the mass of A present,

$$M_\mathrm{A} = \frac{m_\mathrm{A}p_\mathrm{B}}{n_\mathrm{B}(p_\mathrm{B}^* - p_\mathrm{B})} = \frac{m_\mathrm{A}M_\mathrm{B}p_\mathrm{B}}{m_\mathrm{B}(p_\mathrm{B}^* - p_\mathrm{B})}$$

From the data

$$M_\mathrm{A} = \frac{(51.2\,g)\times(78.11\,\mathrm{g\,mol}^{-1})\times(49.2\ \mathrm{kPa})}{(500\,\mathrm{g})\times(53.3-49.2)\,\mathrm{kPa}} = \boxed{96.0\mathrm{g\ mol}^{-1}}$$

E5.6(c) 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.

E5.6(c) $M_{\mathrm{B}} = \dfrac{\text{mass of B}}{n_{\mathrm{B}}}$ [B = compound]

$$n_B = \text{mass of } \mathrm{CCl_4} \times b_{\mathrm{B}} \quad [b_{\mathrm{B}} = \text{molality of B}]$$

$$b_{\mathrm{B}} = \frac{\Delta T}{K_{\mathrm{f}}}\ [5.37];\text{thus}$$

$$M_{\mathrm{B}} = \frac{\text{mass of B} \times K_{\mathrm{f}}}{\text{mass of } \mathrm{CCl_4} \times \Delta T} \quad K_{\mathrm{f}} = 5.12\,\mathrm{K/(mol\,kg^{-1})}[\text{Table 5.2}]$$

$$M_{\mathrm{B}} = \frac{(200\,g) \times (5.12\,\mathrm{K\,kg\,mol^{-1}})}{(1.000\,\mathrm{kg}) \times (3.50\,\mathrm{K})} = \boxed{293\mathrm{g\ mol^{-1}}}$$

E5.7(c) The osmotic pressure of an aqueous solution at 298 K is 101.3 kPa. Calculate the freezing point of the solution.

E5.7(c) $\Delta T = K_{\mathrm{f}} b_{\mathrm{B}}[5.37] \quad b_{\mathrm{B}} = \dfrac{n_{\mathrm{B}}}{\text{mass of water}} \approx \dfrac{n_{\mathrm{B}}}{V\rho}$ [dilute solution]

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

$$n_{\mathrm{B}} \approx \frac{\Pi V}{RT}[5.40] \qquad \Delta T \approx K_{\mathrm{f}} \times \frac{\Pi}{RT\rho}$$

with $K_{\mathrm{f}} = 1.86\,\mathrm{K/(mol\,kg^{-1})}$ [Table 5.2]

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

Therefore, the solution will freeze at about $\boxed{-0.08\ °\mathrm{C}.}$

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

E5.8(c) Consider a container of volume 2.0 $\mathrm{dm^3}$ that is divided into two compartments of equal size. In the left compartment there is nitrogen at 1.0 atm and 25 °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.

E5.8(c) $\Delta_{\mathrm{mix}} G = nRT\{x_{\mathrm{A}} \ln x_{\mathrm{A}} + x_{\mathrm{B}} \ln x_{\mathrm{B}}\}[5.18] \quad x_{\mathrm{A}} = x_{\mathrm{B}} = 0.5, \quad n = \dfrac{pV}{RT}$

Therefore,

$$\Delta_{\mathrm{mix}} G = (pV) \times \left(\frac{1}{2}\ln\frac{1}{2} + \frac{1}{2}\ln\frac{1}{2}\right) = -pV\ln 2$$

$$= (-1.0) \times (1.013 \times 10^5\ \mathrm{Pa}) \times (2.0 \times 10^{-3}\ \mathrm{m^3}) \times (\ln 2)$$

$$= -1.4 \times 10^2\ \mathrm{J} = \boxed{-0.14\ \mathrm{kJ}}$$

$$\Delta_{\mathrm{mix}} S = -nR\{x_{\mathrm{A}} \ln x_{\mathrm{A}} + x_{\mathrm{B}} \ln x_{\mathrm{B}}\} = \frac{-\Delta_{\mathrm{mix}} G}{T}[5.19] = \frac{-0.14\,\mathrm{kJ}}{298\,\mathrm{K}} = \boxed{+0.47\ \mathrm{JK^{-1}}}$$

E5.9(c) Calculate the Gibbs energy, entropy, and enthalpy of mixing when 2.00 mol C_6H_{14} (hexane) is mixed with 3.00 mol C_7H_{16} (heptane) at 298 K; treat the solution as ideal.

E5.9(c) $\Delta_{\text{mix}}G = nRT\sum_{\text{J}} x_{\text{J}}\ln x_{\text{J}}$ [5.18] $\quad \Delta_{\text{mix}}S = -nR\sum_{\text{J}} x_{\text{J}}\ln x_{\text{J}}$ [5.19] $= \dfrac{-\Delta_{\text{mix}}G}{T}$

$$n = 2.00\,\text{mol} + 3.00\,\text{mol} = 5.00\,\text{mol}$$

$$x(\text{Hex}) = 0.400 \qquad x(\text{Hep}) = 0.600$$

Therefore,

$$\Delta_{\text{mix}}G = (5.00\text{ mol}) \times (8.314\text{ JK}^{-1}\text{ mol}^{-1}) \times (298\text{K}) \times (0.400\ln 0.400 + 0.600\ln 0.600)$$

$$= \boxed{-8.34\text{ kJ}}$$

$$\Delta_{\text{mix}}S = \frac{+8.34\text{ kJ}}{298\text{K}} = \boxed{+28.0\text{ JK}^{-1}}$$

$\Delta_{\text{mix}}H$ for an ideal solution is zero as it is for a solution of perfect gases [5.20]. It can be demonstrated from

$$\Delta_{\text{mix}}H = \Delta_{\text{mix}}G + T\Delta_{\text{mix}}S = (-8.34 \times 10^3\text{ J}) + (298\text{ K}) \times (28.0\text{ J K}^{-1}) \approx \boxed{0}$$

E5.10(c) What proportions of benzene and mesitylene, 1,3,5-trimethylbenzene, should be mixed (a) by mole fraction, (b) by mass in order to achieve the greatest entropy of mixing?

E5.10(c) Benzene and mesitylene form nearly ideal solutions, therefore eqn 5.19 applies.

$$\Delta_{\text{mix}}S = -nR(x_{\text{A}}\ln x_{\text{A}} + x_{\text{B}}\ln x_{\text{B}}) \text{ [5.19]}$$

We need to differentiate eqn 5.19 with respect to x_{A} and look for the value of x_{A} at which the derivative is zero. Since $x_{\text{B}} = 1 - x_{\text{A}}$, we need to differentiate

$$\Delta_{\text{mix}}S = -nR\{x_{\text{A}}\ln x_{\text{A}} + (1-x_{\text{A}})\ln(1-x_{\text{A}})\}$$

This gives $\left(\text{using } \dfrac{\text{d}\ln x}{\text{d}x} = \dfrac{1}{x}\right)$

$$\frac{\text{d}\Delta_{\text{mix}}S}{\text{d}x_{\text{A}}} = -nR\{\ln x_{\text{A}} + 1 - \ln(1-x_{\text{A}}) - 1\} = -nR\ln\frac{x_{\text{A}}}{1-x_{\text{A}}}$$

which is zero when $x_{\text{A}} = \frac{1}{2}$. Hence, the maximum entropy of mixing occurs for the preparation of a mixture that contains equal mole fractions of the two components.

(a) $$\frac{n(\text{Ben})}{n(\text{Mes})} = 1 = \frac{\left(\dfrac{m(\text{Ben})}{M(\text{Ben})}\right)}{\left(\dfrac{m(\text{Mes})}{M(\text{Mes})}\right)}$$

(b) $$\frac{m(\text{Ben})}{m(\text{Mes})} = \frac{M(\text{Ben})}{M(\text{Mes})} = \frac{78.11\,\text{g mol}^{-1}}{123.21\,\text{g mol}^{-1}} = \boxed{0.6340}$$

E5.11(c) 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 °C.

E5.11(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 × 101.3 kPa = 0.321 kPa

$$b = \frac{0.321\text{ kPa}}{3.01\times10^3\text{ kPa kg mol}^{-1}} = \boxed{0.107\text{ mmol kg}^{-1}}$$

(b) p_B = 0.000375 × 101.3 kPa = 0.380 kPa

$$b = \frac{0.380\text{ kPa}}{3.01\times10^3\text{ kPa kg mol}^{-1}} = \boxed{0.126\text{ mmol kg}^{-1}}$$

E5.12(c) A water carbonating plant is available for use in the home and operates by providing carbon dioxide at 7.2 atm. Estimate the molar concentration of the soda water it produces.

E5.12(c) As in Exercise 5.11(a), we have $b_B = \frac{p_B}{K} = \frac{7.2\times101.3\text{ kPa}}{3.01\times10^3\text{ kPa kg mol}^{-1}} = \boxed{0.24\text{ mol kg}^{-1}}$

Hence, the molality of the solution is about $\boxed{0.24\text{ mol kg}^{-1}}$ and, since molalities and molar concentrations for dilute aqueous solutions are approximately equal, the molar concentration is about $0.24\,\text{mol dm}^{-3}$.

E5.13(c) The enthalpy of fusion of napthalene is 18.80 kJ mol^{-1} and its melting point is 81°C. Calculate its ideal solubility in benzene at 25°C.

E5.13(c) The solubility in grams of anthracene per kg of benzene can be obtained from its mole fraction with use of the equation.

$$\ln x_B = \frac{\Delta_{\text{fus}}H}{R}\times\left(\frac{1}{T^*}-\frac{1}{T}\right)\text{[5.39; B, the solute, is naphthalene]}$$

$$=\left(\frac{18.8\times10^3\text{ J mol}^{-1}}{8.314\text{ J K}^{-1}\text{mol}^{-1}}\right)\times\left(\frac{1}{354.15\text{ K}}-\frac{1}{298.15\text{ K}}\right) = -1.20$$

Therefore, $x_B = e^{-1.20} = 0.301$

Since $x_B \ll 1, x(\text{naphthalene}) \approx \frac{n(\text{naphthalene})}{n(\text{benzene})}$

Therefore, in 1 kg of benzene,

$$n(\text{naphth.}) \approx x(\text{naphth.})\times\left(\frac{1000\text{ g}}{78.11\text{ g mol}^{-1}}\right) \approx (0.301)\times(12.80\text{ mol}) = 3.85\text{ mol}$$

The molality of the solution is therefore 3.85 mol kg^{-1}. Since $M = 128\text{ g mol}^{-1}$, 3.85 mol corresponds to $\boxed{\text{493 g naphthalene}}$ in 1 kg of benzene.

E5.15(c) Given that $p^*(H_2O) = 0.02308$ atm and $p(H_2O) = 0.02171$ atm in a solution in which 0.207 kg of a non-volatile solute ($M = 298\ \mathrm{g\ mol^{-1}}$) is dissolved in 0.892 kg water at 293 K, calculate the activity and activity coefficient of water in the solution.

E5.15(c) Let A = water and B = solute.

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

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

$$n_A = \frac{0.892\ \text{kg}}{0.01802\ \text{kg mol}^{-1}} = 49.5\bar{0}\ \text{mol} \quad n_B = \frac{0.207\ \text{kg}}{0.298\ \text{kg mol}^{-1}} = 0.859\ \text{mol}$$

$$x_A = \frac{49.5\bar{0}}{49.5\bar{0} + 0.859} = 0.983 \quad \gamma_A = \frac{0.9406}{0.983} = \boxed{0.957}$$

E5.16(c) Hexane and heptane form nearly ideal solutions. The boiling point of pure hexane is 69.0°C. Calculate the chemical potential of hexane relative to that of pure hexane when $x_{\text{hexane}} = 0.50$ at its boiling point. If the activity coefficient of hexane in this solution were actually 0.95 rather than 1.00, what would be its vapour pressure?

E5.16(c) B = Hexane $\quad \mu_B(l) = \mu^*_B(l) + RT \ln x_B$ [5.25, ideal solution]

$$RT \ln x_B = (8.314\ \text{JK}^{-1}\ \text{mol}^{-1}) \times (342.2\text{K}) \times (\ln 0.50) = \boxed{-197\bar{2}\ \text{J mol}^{-1}}$$

Thus, its chemical potential is lowered by this amount.

$$p_B = a_B p^*_B\ [5.43] = \gamma_B x_B p^*_B = (0.95) \times (0.50) \times (760\ \text{Torr}) = \boxed{361\ \text{Torr}}$$

Question. What is the lowering of the chemical potential in the nonideal solution with $\gamma = 0.95$?

E5.18(c) Calculate the ionic strength of a solution that is $0.10\ \mathrm{mol\ kg^{-1}}$ in NaCl(aq) and $0.20\ \mathrm{mol\ kg^{-1}}$ in $CaSO_4$(aq).

E5.18(c) $$I = \frac{1}{2}\sum (b_i / b^{\varnothing}) z_i^2 [5.71]$$

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

$$I = \frac{1}{2}\left(p z_+^2 + q z_-^2\right)\left(\frac{b}{b^{\varnothing}}\right)$$

$$I(\text{NaCl}) = \frac{1}{2}(1\times1+1\times1)\left(\frac{b}{b^{\varnothing}}\right) = \left(\frac{b}{b^{\varnothing}}\right)$$

$$I(\text{CaSO}_4) = \frac{1}{2}(1\times2^2+1\times2^2)\left(\frac{b}{b^{\varnothing}}\right) = 4\left(\frac{b}{b^{\varnothing}}\right)$$

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

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

Comment. Note that the strength of a solution of more than one electrolyte may be calculated by summing the ionic strengths of each electrolyte considered as a separate solution, as in the solution to this exercise, by summing the product $\frac{1}{2}\left(\frac{b^i}{b^\varnothing}\right)z_i^2$ for each individual ion as in the definition of I [5.71].

E5.20(c) Estimate the mean ionic activity coefficient and activity of a solution that is 0.040 mol kg^{-1} KF(aq) and 0.020 mol kg^{-1} $CaCl_2$(aq).

E5.20(c) These concentrations are sufficiently dilute for the Debye–Hückel limiting law to give a good approximate value for the mean ionic activity coefficient. Hence

$$\log\gamma_\pm = -|z_+z_-|AI^{1/2}[5.69]$$

$$I = \frac{1}{2}\sum_i z_i^2\left(\frac{b_i}{b^\varnothing}\right)[5.71] = \frac{1}{2}[(4\times 0.020) + (1\times 0.020) + (1\times 0.040) + (1\times 0.040)$$

$$= \boxed{0.0900}$$

$$\log\gamma_\pm = -2\times 1\times 0.509\times(0.090)^{1/2} = -0.30\overline{54};\quad \gamma_\pm = 0.49\overline{5} = \boxed{0.49}$$

E5.21(c) The mean activity coefficients of HCl in three dilute aqueous solutions at 25°C are 0.929 (at 5.0 mmol kg^{-1}), 0.905 (at 10.0 mmol kg^{-1}), and 0.830 (at 50.0 mmol kg^{-1}). Estimate the value of B in the extended Debye–Hückel law.

E5.21(c) $$\log\gamma_\pm = -\frac{A|z_+z_-|I^{1/2}}{1+BI^{1/2}}[5.72]$$

Solving for ***B***

$$B = -\left(\frac{1}{I^{1/2}} + \frac{A|z_+z_-|}{\log\gamma_\pm}\right)$$

For **HBr**, $I = \left(\frac{b}{b^\varnothing}\right)$ and $|z+z-| = 1$; so and $|z_+z_-|=1$; so

$$B = -\left(\frac{1}{(b/b^\varnothing)^{1/2}} + \frac{0.509}{\log\gamma_\pm}\right)$$

Hence, draw up the following table

$(b/b^\varnothing)$	5.0×10^{-3}	10.0×10^{-3}	50.0×10^{-3}
$\gamma_\pm$	0.929	0.905	0.830
B	1.77	1.74	1.81

The approximate constancy of B at about 1.77 indicates that the mean ionic activity coefficient of HCl obeys the extended Debye–Hückel law fairly well.