Exercise

5A.2(b) Let A stand for water and B for $MgSO_4(aq)$

$$V_J = \left(\frac{\partial V}{\partial n_J}\right)_{p,T,n'} \quad [5A.1] = \left(\frac{dv}{dx}\right)\left(\frac{dV}{dv}\right)\left(\frac{\partial x}{\partial n_J}\right)_{n'}$$

Now $x = \frac{b}{b^{\ominus}} = \frac{n_B}{n_A M_A b^{\ominus}}$ so $\left(\frac{\partial x}{\partial n_B}\right)_{n_A} = \frac{1}{n_A M_A b^{\ominus}}$

and $V_B = 2 \times 34.69 \times (x - 0.070) \frac{\text{cm}^3}{n_A M_A b^{\ominus}}$

Evaluate this expression for b = 0.050 mol kg^{-1} (x = 0.050), recalling that the original expression for v applies for 1.000 kg of water (*i.e.*, for $n_A M_A$ = 1.000 kg). The result is V_B = $\boxed{-1.4 \text{ cm}^3 \text{ mol}^{-1}}$.

The total volume consisting of 0.050 mol of $MgSO_4$ and 1.000 kg (55.49 mol) water is

$$V = 1001.21 + 34.69 \times (0.050\text{–}0.070)^2 = 1001.23 \text{ cm}^3 .$$

The total volume is also equal to

$$V = V_A n_A + V_B n_B \text{ [5A.3]} .$$

Therefore, $V_A = \frac{V - V_B n_B}{n_A} = \frac{1001.21 \text{ cm}^3 - (-1.4 \text{ cm}^3) \times (0.050 \text{ mol})}{55.49 \text{ mol}} = \boxed{18.04 \text{ cm}^3 \text{ mol}^{-1}}$

5A.4(b) The Gibbs energy of mixing perfect gases is

$$\Delta_{mix}G = nRT(x_A \ln x_A + x_B \ln x_B) \text{ [5A.16]} = pV(x_A \ln x_A + x_B \ln x_B) \text{ [perfect gas law]}$$

Because the compartments are of equal size, each contains half of the gas; therefore,

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

$$= -(100 \times 10^3 \text{ Pa}) \times (250 \text{ cm}^3)\left(\frac{1 \text{ m}^3}{10^6 \text{ cm}^3}\right) \times \ln 2 = -17.3 \text{ Pa m}^3 = \boxed{-17.3 \text{ J}}$$

$$\Delta_{mix}S = -nR(x_A \ln x_A + x_B \ln x_B) \text{ [5A.17]} = \frac{-\Delta_{mix}G}{T} = \frac{+17.3 \text{ J}}{273 \text{ K}} = \boxed{+0.635 \text{ J K}^{-1}}$$

5A.8(b) Let W denote water and E ethanol. The total volume of the solution is

$$V = n_W V_W + n_E V_E$$

We are given V_E, we need to determine n_W and n_E in order to solve for V_W, for

$$V_W = \frac{V - n_E V_E}{n_W}$$

Take 100 cm^3 of solution as a convenient sample. The mass of this sample is

$$m = \rho V = (0.9687 \text{ g cm}^{-3}) \times (100 \text{ cm}^3) = 96.87 \text{ g} .$$

80 per cent of this mass water and 20 per cent ethanol, so the moles of each component are

$$n_W = \frac{(0.80) \times (96.87 \text{ g})}{18.02 \text{ g mol}^{-1}} = 4.3 \text{ mol and } n_E = \frac{(0.20) \times (96.87 \text{ g})}{46.07 \text{ g mol}^{-1}} = 0.42 \text{ mol}^{-1} .$$

$$V_W = \frac{V - n_E V_E}{n_W} = \frac{100 \text{ cm}^3 - (0.42 \text{ mol}) \times (52.2 \text{ cm}^3 \text{ mol}^{-1})}{4.3 \text{ mol}} = \boxed{18 \text{ cm}^3 \text{ mol}^{-1}}$$

5B.1(b) In Exercise 5A.10(b), the Henry's law constant was determined for concentrations expressed in mole fractions; $K_B = 8.2\times10^3$ kPa. Thus the concentration must be converted from molality to mole fraction

$m_A = 1000$ g, corresponding to $n_A = \dfrac{1000\,\text{g}}{74.1\,\text{g mol}^{-1}} = 13.50\,\text{mol}$

Therefore $x_B = \dfrac{0.25\text{ mol}}{(0.25\,\text{mol}) + (13.50\,\text{mol})} = 0.018$

The pressure is

$p_B = K_B x_B$ [5A.23] $= (0.018) \times (8.2\times10^3 \text{ kPa}) = \boxed{1.5\times10^2 \text{ kPa}}$.

5B.6(b) **(i)** Benzene and ethylbenzene form nearly ideal solutions, so.

$\Delta_{mix}S = -nRT(x_A \ln x_A + x_B \ln x_B)$ [5A.17]

We need to differentiate eqn 5A.17 with respect to x_A and look for the value of x_A at which the derivative is zero. Since $x_B = 1 - x_A$, we need to differentiate

$\Delta_{mix}S = -nRT\{x_A \ln x_A + (1-x_A)\ln(1-x_A)\}$

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

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

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

(ii) Because entropy of mixing is maximized when $n_E = n_B$ (changing to notation specific to Benzene and Ethylbenzene)

$$\frac{m_E}{M_E} = \frac{m_B}{M_B}$$

This makes the mass ratio

$$\frac{m_B}{m_E} = \frac{M_B}{M_E} = \frac{78.11 \text{ g mol}^{-1}}{106.17 \text{ g mol}^{-1}} = \boxed{0.7357}$$

5B.7(b) The ideal solubility in terms of mole fraction is given by eqn 5B.15:

$$\ln x_{Pb} = \frac{\Delta_{fus}H}{R} \times \left(\frac{1}{T_f} - \frac{1}{T}\right)$$

$$= \left(\frac{5.2\times10^3 \text{ J mol}^{-1}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}}\right) \times \left(\frac{1}{600.\text{K}} - \frac{1}{553\text{K}}\right) = -0.089$$

Therefore, $x_{Pb} = e^{-0.089} = 0.92$.

$$x_{Pb} = \frac{n_{Pb}}{n_{Bi} + n_{Pb}} \quad \text{implying that} \quad n_{Pb} = \frac{n_{Bi}x_{Pb}}{1-x_{Pb}} = \frac{m_{Bi}}{M_{Bi}} \times \frac{x_{Pb}}{1-x_{Pb}}$$

Hence the amount of lead that dissolves in 1 kg of bismuth is

$$n_{Pb} = \frac{1000 \text{ g}}{209 \text{ g mol}^{-1}} \times \frac{0.92}{1-0.92} = \boxed{52 \text{ mol}}$$

or, in mass units, $m_{Pb} = n_{Pb}\times M_{Pb} = 52 \text{ mol} \times 207 \text{ g mol}^{-1} = 1.1\times10^4 \text{ g} = \boxed{11 \text{ kg}}$.

5B.9(b) In an ideal dilute solution the solvent (CCl_4, A) obeys Raoult's law [5A.21] and the solute (Br_2, B) obeys Henry's law [5A.23]; hence

$$p_A = x_A p^* = (0.934) \times (23\ \text{kPa}) = \boxed{21.\bar{5}\ \text{kPa}}$$

$$p_B = x_B K_B = (0.066) \times (73\ \text{kPa}) = \boxed{4.8\ \text{kPa}}$$

$$p_{\text{total}} = (21.\bar{5} + 4.8)\ \text{kPa} = \boxed{26.\bar{3}\ \text{kPa}}$$

The composition of the vapour in equilibrium with the liquid is

$$y_A = \frac{p_A}{p_{\text{total}}} = \frac{21.\bar{5}\ \text{kPa}}{23.\bar{3}\ \text{kPa}} = \boxed{0.82} \quad \text{and} \quad y_B = \frac{p_B}{p_{\text{total}}} = \frac{4.8\ \text{kPa}}{23.\bar{3}\ \text{kPa}} = \boxed{0.18}$$

5B.13(b) **(i)** If the solution is ideal, then the partial vapour pressures are given by Raoult's law [5A.21]:

$$p_B = x_B p_B^* = 0.50 \times 9.9\ \text{kPa} = 4.95\ \text{kPa}$$

$$p_T = x_T p_T^* = 0.50 \times 2.9\ \text{kPa} = 1.45\ \text{kPa}$$

The total pressure is

$$p_{\text{total}} = p_B + p_T = (4.95 + 1.45)\ \text{kPa} = \boxed{6.4\ \text{kPa}}\ .$$

(ii) The composition of the vapour is given by

$$y_B = \frac{p_B}{p_{\text{total}}} = \frac{4.95\ \text{kPa}}{6.4\ \text{kPa}} = \boxed{0.77}$$

and $$y_T = \frac{p_T}{p_{\text{total}}} = \frac{1.45\ \text{kPa}}{6.4\ \text{kPa}} = \boxed{0.23}$$

(iii) When only a few drops of liquid remain, the equimolar mixture is almost entirely vapour. Thus $y_B = y_T = 0.50$, which implies that

$$p_B = x_B p_B^* = p_T = x_T p_T^* = (1-x_B) p_T^*\ .$$

Solving for x_B yields

$$x_B = \frac{p_T^*}{p_B^* + p_T^*} = \frac{2.9\ \text{kPa}}{(9.9 + 2.9)\ \text{kPa}} = 0.23$$

The partial vapour pressures are

$$p_B = x_B p_B^* = 0.23 \times 9.9\ \text{kPa} = 2.24\ \text{kPa} = p_T\ [\text{vapour mixture is equimolar}] = p_{\text{total}}/2\ .$$

The total pressure is

$$p_{\text{total}} = 2p_B = \boxed{4.5\ \text{kPa}}\ .$$

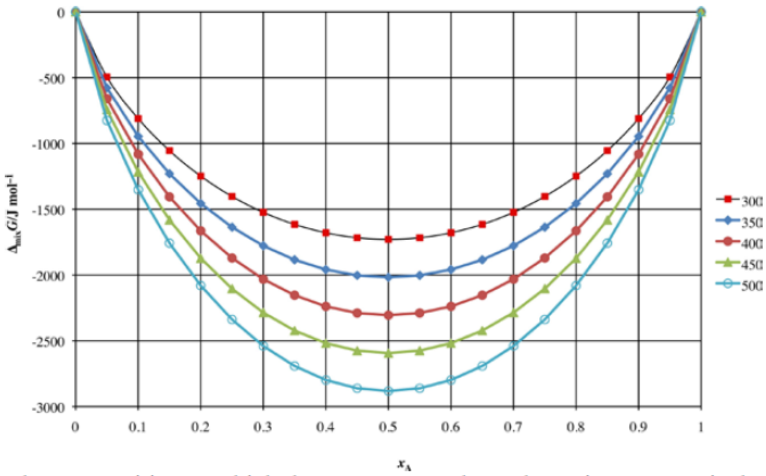
Problem

5B.12 The Gibbs energy of mixing an ideal solution is [5A.16]

$$\Delta_{\text{mix}}G = nRT(x_A \ln x_A + x_B \ln x_B)$$

The molar Gibbs energy of mixing is plotted against composition for several temperatures in Fig. 5B.4. The legend shows the temperature in kelvins.

Figure 5B.4



The composition at which the temperature dependence is strongest is the composition at which the function has its largest magnitude, namely $\boxed{x_A = x_B = 0.5}$.