5 Simple mixtures

5A The thermodynamic description of mixtures

Answers to discussion questions

5A.2 As noted in Topic 5A.1(b), $dG = dw_{add,max}$ (where w_{add} stands for additional (non-expansion) work) for systems at constant temperature and pressure. Therefore [5A.8]

$$dw_{add,max} = \mu_A dn_A + \mu_B dn_B + ...$$

Thus non-expansion work can arise from the changing composition of a system. Physically, it should not be surprising that at least *energy* can be changed by changing composition, by a chemical reaction transforming a species into one that is more or less favored energetically. In an electrochemical cell, where the reaction takes place at two distinct sites, the electrical work of transporting charge between the electrodes can be traced to changes in composition as products are formed from reactants.

5A.4 See Topic 5A.3(a). In both cases, the vapor pressure of a component in a solution is proportional to its concentration (mole fraction) in the solution, at least in the limit of low concentration:

$$p_J \propto x_J$$

If the proportionality constant is the component's vapor pressure as a pure substance, then Raoult's law is a good approximation [5A.21]. Substitution of Raoult's law into eqn 5A.20 for the chemical potential yields eqn 5A.22:

$$\mu_A = \mu_A{}^* + RT \ln x_A$$

If Raoult's law applies to both or all components of a mixture over a large range of composition, then we call the solution ideal. If, on the other hand, only the solvent obeys Raoult's law, and it may only obey it in the limit of mole fractions close to 1, we call the solution ideal-dilute if the solutes obey Henry's law [5A.23]. Substitution of Henry's law into eqn 5A.20 for solutes yields eqn 5E.8:

$$\mu_B = \mu_B^{\ominus} + RT \ln x_B \qquad \text{where} \qquad \mu_B^{\ominus} = \mu_B^* + RT \ln \frac{K_B}{p_B^*} \quad [5E.7]$$

Solutions to exercises

The partial molar volume is

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

Right away we see that $V_A = \boxed{0}$ because V is independent of n_A $[dx/dn_A = 0]$

$$V_B = (-22.5749 + 2 \times 0.56892x + 3 \times 0.01023x^2 + 4 \times 0.00234x^3)\left(\frac{cm^3}{mol}\right)$$

$$= \boxed{(-22.5749 + 1.13784x + 0.03069x^2 + 0.00936x^3)\ cm^3\ mol^{-1}}$$

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

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

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

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

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 $V_B = \boxed{-1.4\ cm^3\ mol^{-1}}$.

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

$$V = 1001.21 + 34.69 \times (0.050-0.070)^2 = 1001.23\ cm^3.$$

The total volume is also equal to
$$V = V_A n_A + V_B n_B \text{ [5A.3]} .$$
Therefore, $V_A = \dfrac{V - V_B n_B}{n_A} = \dfrac{1001.21 \text{ cm}^3 - (-1.4 \text{ cm}^3) \times (0.050 \text{ mol})}{55.49 \text{ mol}} = \boxed{18.\overline{04} \text{ cm}^3 \text{ mol}^{-1}}$

Question. V_A is essentially the same as the molar volume of pure water, but clearly V_B is not even approximately the molar volume of pure solid $MgSO_4$. What meaning can be ascribed to a negative partial molar volume?

5A.3(b) Use the Gibbs-Duhem equation [5A.13], replacing infinitesimal changes in chemical potential ($d\mu_J$) with small finite changes ($\delta\mu_J$)
$$\delta\mu_B \approx -\frac{n_A}{n_B}\delta\mu_A = -\frac{0.22 n_B}{n_B} \times (-15 \text{ J mol}^{-1}) = \boxed{+3.3 \text{ J mol}^{-1}}$$

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,
$$\Delta_{mix}G = (pV) \times \left(\frac{1}{2}\ln\frac{1}{2} + \frac{1}{2}\ln\frac{1}{2}\right) = -pV \ln 2$$
$$= -(100 \times 10^3 \text{ Pa}) \times (250 \text{ cm}^3)\left(\frac{1 \text{ m}^3}{10^6 \text{ cm}^3}\right) \times \ln 2 = -17.3 \text{ Pa m}^3 = \boxed{-17.3 \text{ J}}$$
$$\Delta_{mix}S = -nR(x_A \ln x_A + x_B \ln x_B) \text{ [5A.17]} = \frac{-\Delta_{mix}G}{T} = \frac{+17.3 \text{ J}}{273 \text{ K}} = \boxed{+0.635 \text{ J K}^{-1}}$$

5A.5(b) $\qquad \Delta_{mix}S = -nR\sum_J x_J \ln x_J$ [5A.17]

We need mole fractions:
$$x_J = \frac{n_J}{\sum_J n_J}$$

Since we have mass percentages, 100.0 g is a convenient sample size. The amounts of each component are
$$n_{N_2} = 75.52 \text{ g} \times \frac{1 \text{ mol}}{2 \times 14.007 \text{ g}} = 2.696 \text{ mol}$$
$$n_{O_2} = 23.15 \text{ g} \times \frac{1 \text{ mol}}{2 \times 15.999 \text{ g}} = 0.7235 \text{ mol}$$
$$n_{Ar} = 1.28 \text{ g} \times \frac{1 \text{ mol}}{39.95 \text{ g}} = 0.0320 \text{ mol}$$
$$n_{CO_2} = 0.046 \text{ g} \times \frac{1 \text{ mol}}{(12.011 + 2 \times 15.999) \text{ g}} = 0.00105 \text{ mol}$$

The mole fractions are
$$x_{N_2} = \frac{n_{N_2}}{n_{N_2} + n_{O_2} + n_{Ar} + n_{CO_2}} = \frac{2.696 \text{ mol}}{(2.696 + 0.7235 + 0.0320 + 0.00105) \text{ mol}} = 0.7809$$

Similarly, $x_{O_2} = 0.2096$, $x_{Ar} = 0.00928$, and $x_{CO_2} = 0.00030$.

Once we have mole fractions, the convenient sample size is for a total of one mole of gas:
$$\Delta_{mix}S = -R\sum_J x_J \ln x_J = -R\{(0.7809 \ln 0.7809) + (0.2096 \ln 0.2096)$$
$$+ (0.00928 \ln 0.00928) + (0.00030 \ln 0.00030)\}$$
$$= 0.5665R = +4.710 \text{ J K}^{-1} \text{ mol}^{-1}$$

From the data in Exercise 5A.5(a), the entropy of mixing was
$$\Delta_{mix}S = -R\sum_J x_J \ln x_J$$
$$= -R\{(0.781 \ln 0.781) + (0.210 \ln 0.210) + (0.0094 \ln 0.0094)\}$$
$$= 0.565R = +4.70 \text{ J K}^{-1} \text{ mol}^{-1}$$

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So the difference is

$$\Delta_{\text{mix}}S(\text{b}) - \Delta_{\text{mix}}S(\text{a}) = \boxed{0.001\overline{5}R} = \boxed{+0.01\overline{2} \text{ J K}^{-1} \text{ mol}^{-1}}$$

Comment. We can readily see that the data in this exercise (b) includes the CO_2 term, which contributes $-R(0.00030 \ln 0.00030) = 0.0025R$ to the entropy of mixing—more than the total difference. The fact that the mole fractions of the other components are slightly smaller in part (b) to make room for the small amount of CO_2 partly offsets the direct CO_2 term itself.

5A.6(b) Let 12 refer to 1,2-dimethylbenzene and 13 to 1,3-dimethylbenzene. Because the two components are structurally similar, we assume Raoult's Law [5A.21] applies.

$$p_{\text{total}} = p_{12} + p_{13} = x_{12}p_{12}^* + x_{13}p_{13}^* = (0.500)(20 + 18) \text{ kPa} = 19 \text{ kPa}.$$

The mole fractions in the vapor phase are the ratios of partial to total pressure:

$$x_{12,\text{vap}} = \frac{p_{12}}{p_{\text{total}}} = \frac{x_{\text{liq},12}p_{12}^*}{p_{\text{total}}} = \frac{(0.500)(20 \text{ kPa})}{19 \text{ kPa}} = \boxed{0.53} \quad \text{and} \quad x_{\text{vap},13} = \boxed{0.47}$$

5A.7(b) Total volume $V = n_A V_A + n_B V_B = n(x_A V_A + x_B V_B)$, where $n = n_A + n_B$
Total mass $m = n_A M_A + n_B M_B = n\{x_A M_A + (1-x_A)M_B\}$

So $\quad n = \dfrac{m}{x_A M_A + (1-x_A)M_B}$

$$= \frac{1.000 \times 10^3 \text{ g}}{(0.3713) \times (241.1 \text{g mol}^{-1}) + (1 - 0.3713) \times (198.2 \text{ g mol}^{-1})} = 4.670 \text{ mol}$$

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

and $\quad = (4.670 \text{ mol}) \times \{(0.3713) \times (188.2) + (1 - 0.3713) \times (176.14)\} \text{ cm}^3 \text{ mol}^{-1}$

$$= \boxed{843.5 \text{ cm}^3}$$

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

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

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

5A.9(b) Henry's law is [5A.23] $p_B = x_B K_B$, so check whether p_B / x_B is equal to a constant (K_B)

x	0.010	0.015	0.020
p/kPa	82.0	122.0	166.1
$(p/\text{kPa}) / x$	8.2×10^3	8.1×10^3	8.3×10^3

Hence, $K_B = p / x = \boxed{8.2 \times 10^3 \text{ kPa}}$ (average value).

5A.10(b) Refer to *Brief Illustration* 5A.4 and use the Henry's Law constant from Table 5A.1. Henry's law in terms of molal concentration is $p_B = b_B K_B$. So the molal solubility of methane in benzene at 25°C in equilibrium with 1.0 bar of methane is

$$b_{\text{CH}_4} = \frac{p_{\text{CH}_4}}{K_{\text{CH}_4}} = \frac{100 \text{ kPa}}{44.4 \times 10^3 \text{ kPa kg mol}^{-1}} = 2.2\overline{5} \times 10^{-3} \text{ mol kg}^{-1}$$

To find the molar solubility, we assume that the density of the solution is the same as that of pure benzene, given at a nearby temperature (20°C) in Table 0.1:

$$[\text{CH}_4] = b_{\text{CH}_4}\rho_{\text{benzene}} = 2.2\overline{5} \times 10^{-3} \text{ mol kg}^{-1} \times 0.879 \text{ kg dm}^{-3} = \boxed{2.0 \times 10^{-3} \text{ mol dm}^{-3}}$$

5A.11(b) With concentrations expressed in molalities, Henry's law [5A.23] becomes $p_B = b_B K_B$.

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Solving for b_B, the molality, we have $b_B = \dfrac{p_B}{K} = \dfrac{x_B p_{total}}{K}$,

where $p_{total} = 1$ atm $= 101.3$ kPa

For N_2, $K = 1.56 \times 10^5$ kPa kg mol^{-1} [Table 5A.1]

$$b = \frac{0.78 \times 101.3 \text{ kPa}}{1.56 \times 10^5 \text{ kPa kg mol}^{-1}} = \boxed{5.1 \times 10^{-4} \text{ mol kg}^{-1}}$$

For O_2, $K = 7.92 \times 10^4$ kPa kg mol^{-1} [Table 5A.1]

$$b = \frac{0.21 \times 101.3 \text{ kPa}}{7.92 \times 10^4 \text{ kPa kg mol}^{-1}} = \boxed{2.7 \times 10^{-4} \text{ mol kg}^{-1}}$$

5A.12(b) As in Exercise 5A.11(b), we have

$$b_B = \frac{p_B}{K} = \frac{2.0 \times 101.3 \text{ kPa}}{3.01 \times 10^3 \text{ kPa kg mol}^{-1}} = 0.067 \text{ mol kg}^{-1}$$

Hence, the molality of the solution is about 0.067 mol kg^{-1}. Since molalities and molar concentrations (molarities) for dilute aqueous solutions are numerically approximately equal, the molar concentration is about $\boxed{0.067 \text{ mol dm}^{-3}}$.

Solutions to problems

5A.2 $C = 1$; hence, according to the phase rule (eqn 4A.1) $F = C - P + 2 = 3 - P$

Since the tube is sealed there will always be some gaseous compound in equilibrium with the condensed phases. Thus when liquid begins to form upon melting, $P = 3$ (s, l, and g) and $F = 0$, corresponding to a definite melting temperature. At the transition to a normal liquid, $P = 3$ (l, l′, and g) as well, so again $F = 0$.

5A.4 Letting B stand for $CuSO_4$(aq), the partial molar volume of the dissolved salt is

$$V_B = \left(\frac{\partial V}{\partial n_B} \right)_{n_A} \quad [5A.1]$$

We will determine V_B by plotting V against n_B while holding n_A constant. We can find the volume from the density:

$$\rho = \frac{m_A + m_B}{V} \qquad \text{so} \qquad V = \frac{m_A + m_B}{\rho} .$$

The data include the composition of the solution expressed as mass percent. (That is, $m(CuSO_4)/g$, the mass in grams of B dissolved in 100 g solution, is numerically equal to w, defined as mass of B over total solution mass expressed as a percent). For our plot, we need n_B per *fixed amount* of A. Let us choose that fixed quantity to be $m_A = 1$ kg exactly, so n_B is numerically equal to the molal concentration. So

$$n_B = \frac{m_B}{M_B}$$

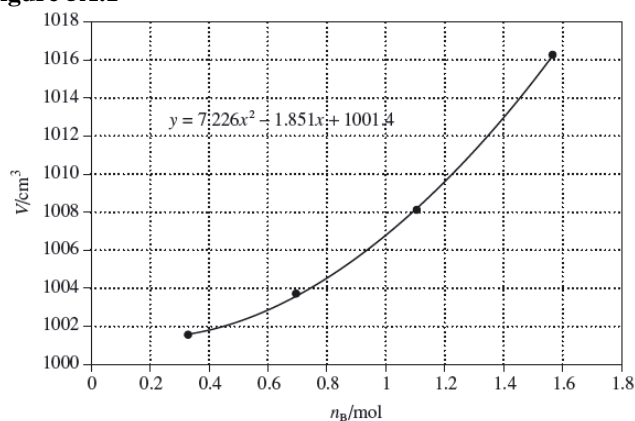such that $\dfrac{m_B}{m_A + m_B} \times 100 = w$.

Solve for m_B:

$$m_B = \frac{w m_A}{100 - w} .$$

Draw up the following table of values of m_B, n_B, and V at each data point, using $m_A = 1000$ g.

W	5	10	15	20
ρ /(g cm^{-3})	1.051	1.107	1.167	1.23
m_B/g	52.6	111.1	176.5	250.0
n_B/mol	0.330	0.696	1.106	1.566
V/cm^3	1001.6	1003.7	1008.1	1016.3
V_B/(cm^3 mol^{-1})	2.91	8.21	14.13	20.78

A plot V against n_B is shown in Figure 5A.1.

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Figure 5A.1

To find the partial molar volume, draw tangent lines to the curve at each of the data points and measure the slope of each tangent. Alternatively, fit the curve to a polynomial and differentiate the fit equation. A quadratic equation fits the data quite well

$$V/\text{cm}^3 = 7.226(n_B/\text{mol})^2 - 1.851(n_B/\text{mol}) + 1001.4 \,,$$

so

$$V_B / \text{cm}^3 = \left(\frac{\partial V / \text{cm}^3}{\partial n_B / \text{mol}} \right)_{n_A} = 2 \times 7.226 \times (n_B / \text{mol}) - 1.851$$

Comment. Selecting $m_A = 1000$ g is arbitrary. If you chose a different value for m_A, your table will have different values for m_B, n_B, and V; however, you should arrive at the same values for V_B.

5A.6 From *Example* 5A.1, we have

$$V_E/(\text{cm}^3 \text{ mol}^{-1}) = 54.6664 - 0.72788x + 0.084468x^2 \,,$$

where $x = n_E/\text{mol}$ mixed with 1.000 kg water. Thus, x is also equal to the numerical value of the molality. To find the minimum in V_E, differentiate it and set the derivative equal to zero:

$$\frac{dV_E(\text{cm}^3 \text{ mol}^{-1})}{dx} = -0.72788 + 2 \times 0.084468x = 0$$

Thus $\quad x = \dfrac{0.72788}{2 \times 0.084468} = 4.3086 \qquad$ so $\qquad b = \boxed{4.3086 \text{ mol kg}^{-1}}$

This value is consistent with Figure 5A.3 of the main text.

5B   The properties of solutions

Answers to discussion question

5B.2 All of the colligative properties result from the lowering of the chemical potential of the solvent due to the presence of the solute. This reduction takes the form $\mu_A = \mu_A^* + RT \ln x_A$ or $\mu_A = \mu_A^* + RT \ln a_A$, depending on whether or not the solution can be considered ideal. The lowering of the chemical potential results in a freezing point depression and a boiling point elevation as illustrated in Figure 5B.6 of the text. Both of these effects can be explained by the lowering of the vapour pressure of the solvent in solution due to the presence of the solute. The solute molecules get in the way of the solvent molecules, reducing their escaping tendency.

Solutions to exercises

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

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

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

The pressure is

$$p_B = K_B x_B \text{ [5A.23]} = (0.018) \times (8.2 \times 10^3 \text{ kPa}) = \boxed{1.5 \times 10^2 \text{ kPa}}.$$

5B.2(b) We assume that the solvent, 2-propanol, is ideal and obeys Raoult's law [5A.21].

$$x_A \text{ (solvent)} = \frac{p}{p^*} = \frac{49.62}{50.00} = 0.9924$$

Since $M_A(C_3H_8O) = 60.096 \text{ g mol}^{-1}$,

$$n_A = \frac{250 \text{ g}}{60.096 \text{ g mol}^{-1}} = 4.16 \text{ mol}$$

$$x_A = \frac{n_A}{n_A + n_B} \qquad \text{so} \qquad n_A + n_B = \frac{n_A}{x_A}.$$

Hence $n_B = n_A \left(\dfrac{1}{x_A} - 1 \right) = 4.16 \text{ mol} \times \left(\dfrac{1}{0.9924} - 1 \right) = 3.12 \times 10^{-2} \text{ mol}$

and $\quad M_B = \dfrac{m_B}{n_B} = \dfrac{8.69 \text{ g}}{3.12 \times 10^{-2} \text{ mol}} = \boxed{273 \text{ g mol}^{-1}}$

5B.3(b) Let B denote the compound and A the solvent, naphthalene. $K_f = 6.94 \text{ K kg mol}^{-1}$ [Table 5B.1]

$$M_B = \frac{m_B}{n_B}$$

$$n_B = m_A \, b_B \qquad \text{where} \qquad b_B = \frac{\Delta T}{K_f} \text{ [5B.13]}$$

Thus $\quad M_B = \dfrac{m_B K_f}{m_A \Delta T} = \dfrac{(5.00 \text{ g}) \times (6.94 \text{ K kg mol}^{-1})}{(0.250 \text{ kg}) \times (0.780 \text{ K})} = \boxed{178 \text{ g mol}^{-1}}$

5B.4(b) From the osmotic pressure, compute the concentration, and from the concentration the freezing point. According to the van't Hoff equation [5B.16], the osmotic pressure is

$$\Pi = [B]RT \qquad \text{so} \qquad [B] = \frac{\Pi}{RT} = \frac{n_B}{V_{soln}}$$

The expression for freezing point depression [5B.13] includes the molality b rather than the molarity [B]. In dilute solutions, the two concentration measures are readily related:

$$b = \frac{n_B}{m_A} \approx \frac{n_B}{V_{soln}\rho_{soln}} = \frac{[B]}{\rho_{soln}} = \frac{\Pi}{RT\rho_{soln}}$$

The freezing point depression is

$$\Delta T = K_f b \approx \frac{K_f \Pi}{RT\rho_{soln}} \qquad \text{where} \qquad K_f = 1.86 \text{ K mol}^{-1} \text{ kg [Table 5B.1]}$$

The density of a dilute aqueous solution is approximately that of water:

$$\rho \approx 1.0 \text{ g cm}^{-3} = 1.0 \times 10^3 \text{ kg m}^{-3}$$

So $\quad \Delta T \approx \dfrac{(1.86 \text{ K kg mol}^{-1}) \times (99 \times 10^3 \text{ Pa})}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (288 \text{ K}) \times (10^3 \text{ kg m}^{-3})} = 0.077 \text{ K}$

Therefore, the solution will freeze at about $\boxed{-0.077 °C}$.

$\quad \Delta_{mix}G = nRT \sum_J x_J \ln x_J \text{ [5A.16]} \qquad \text{and}$

$$\Delta_{mix}S = -nR \sum_J x_J \ln x_J \text{ [5A.17]} = \frac{-\Delta_{mix}G}{T}$$

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$$n = 2.00 \text{ mol} \qquad \text{and} \qquad x_{\text{hexane}} = x_{\text{heptane}} = 0.500$$

Therefore,

$$\Delta_{\text{mix}}G = (2.00 \text{ mol}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \times 2 \times (0.500 \ \ln 0.500)$$

$$= -3.43 \times 10^3 \text{ J} = \boxed{-3.43 \text{ kJ}}$$

and $\qquad \Delta_{\text{mix}}S = \dfrac{-\Delta_{\text{mix}}G}{T} = \dfrac{+3.43 \times 10^3}{298 \text{ K}} = \boxed{+11.5 \text{ J K}^{-1}}$

For an ideal solution, $\Delta_{\text{mix}}H = \boxed{0}$, just as it is for a mixture of perfect gases [5A.18]. It can be demonstrated from

$$\Delta_{\text{mix}}H = \Delta_{\text{mix}}G + T\Delta_{\text{mix}}S = \Delta_{\text{mix}}G + T\left(\frac{-\Delta_{\text{mix}}G}{T}\right) = 0$$

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

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

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

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

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

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

which is zero when $x_A = \boxed{\dfrac{1}{2}}$. 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 $\underline{B}$enzene and $\underline{E}$thylbenzene)

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

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:

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

$$= \left(\frac{5.2 \times 10^3 \text{ J mol}^{-1}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}}\right) \times \left(\frac{1}{600.\text{ K}} - \frac{1}{553 \text{ K}}\right) = -0.089$$

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

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

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

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

or, in mass units, $m_{\text{Pb}} = n_{\text{Pb}} \times M_{\text{Pb}} = 52 \text{ mol} \times 207 \text{ g mol}^{-1} = 1.1 \times 10^4 \text{ g} = \boxed{11 \text{ kg}}$.

Comment. A mixture of 11 kg of lead and 1 kg of bismuth would normally be regarded as a solution of bismuth in lead, not the other way around. It is unlikely that such a mixture could be regarded as an ideal dilute solution of lead in bismuth. Under such circumstances eqn 5B.15 ought to be considered suggestive at best, rather than quantitative.
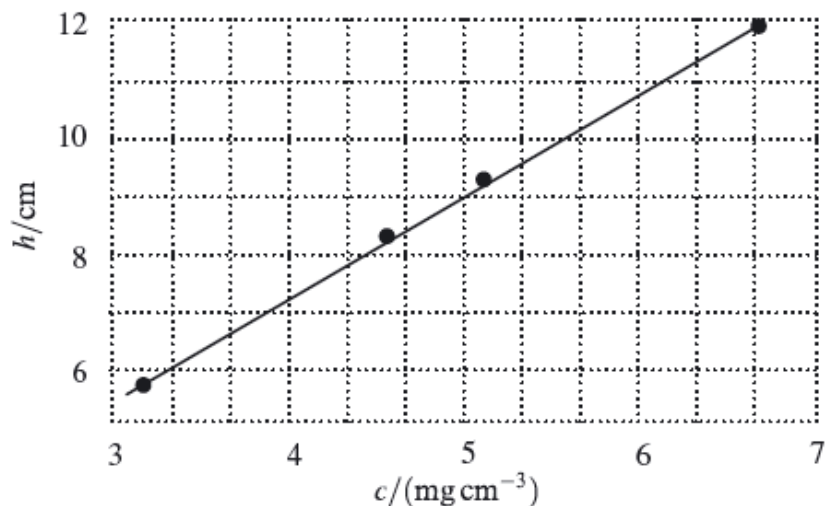
5B.8(b) The best value of the molar mass is obtained from values of the data extrapolated to zero concentration, since it is under this condition that the van't Hoff equation (5B.16) applies.

$$\Pi V = n_B RT \qquad \text{so} \qquad \Pi = \frac{mRT}{MV} = \frac{cRT}{M} \quad \text{where } c = m/V.$$

But the osmotic pressure is also equal to the hydrostatic pressure

$$\Pi = \rho g h \text{ [1A.1]} \quad \text{so} \qquad h = \left(\frac{RT}{\rho g M}\right) c$$

Figure 5B.1

Hence, plot h against c and identify the slope as $\dfrac{RT}{\rho g M}$. Figure 5B.1 shows the plot of the data. The slope of the line is 1.78 cm /(g dm^{-3}), so

$$\frac{RT}{\rho g M} = \frac{1.78 \text{ cm}}{\text{g dm}^{-3}} = 1.78 \text{ cm dm}^3 \text{ g}^{-1} = 1.78 \times 10^{-2} \text{ m}^4 \text{ kg}^{-1}$$

Therefore,

$$M = \frac{RT}{(\rho g) \times (1.78 \times 10^{-2} \text{ m}^4 \text{ kg}^{-1})}$$

$$= \frac{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (293 \text{ K})}{(1.000 \times 10^3 \text{ kg m}^{-3}) \times (9.81 \text{ m s}^{-2}) \times (1.78 \times 10^{-2} \text{ m}^4 \text{ kg}^{-1})} = \boxed{14.0 \text{ kg mol}^{-1}}$$

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

$$p_A = x_A p^* = (0.934) \times (23 \text{ kPa}) = \boxed{21.\overline{5} \text{ kPa}}$$
$$p_B = x_B K_B = (0.066) \times (73 \text{ kPa}) = \boxed{4.8 \text{ kPa}}$$
$$p_{\text{total}} = (21.\overline{5} + 4.8) \text{ kPa} = \boxed{26.\overline{3} \text{ kPa}}$$

The composition of the vapour in equilibrium with the liquid is

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

5B.10(b) Let subscript 12 denote the 1,2 isomer and 13 the 1,3 isomer. Assume that the structurally similar liquids obey Raoult's law [5A.21]. The partial pressures of the two liquids sum to 19 kPa.

$$p_{13} + p_{12} = p = x_{13} p_{13}^* + x_{12} p_{12}^* = x_{13} p_{13}^* + (1 - x_{13}) p_{12}^*$$

Solve for x_{13}:

$$x_{13} = \frac{p - p_{12}^*}{p_{13}^* - p_{12}^*} = \frac{(19 - 20) \text{ kPa}}{(18 - 20) \text{ kPa}} = \boxed{0.5}$$

and $\quad x_{12} = 1 - 0.5 = \boxed{0.5}$.

The vapour phase mole fractions are given by eqn 1A.8:

$$y_{13} = \frac{p_{13}}{p} = \frac{x_{13}p_{13}^*}{p} = \frac{(0.5) \times 18 \text{ kPa}}{19 \text{ kPa}} = \boxed{0.4\overline{7}}$$

and $\quad y_{12} = \frac{x_{12}p_{12}^*}{p} = \frac{(0.5) \times 20.0 \text{ kPa}}{50.7 \text{ kPa}} = \boxed{0.5\overline{3}}$.

5B.11(b) The partial vapour pressures are given by Raoult's law [5A.21]:

$$p_A = x_A p_A^* \qquad \text{and} \qquad p_B = x_B p_B^* = (1 - x_B)p_B^*.$$

Eqn 1A.8 relates these vapour pressures to the vapour-phase mole fractions:

$$y_A = \frac{p_A}{p_{\text{total}}} = \frac{x_A p_A^*}{x_A p_A^* + (1 - x_A)p_B^*}$$

Solve for x_A:

$$x_A p_A^* + (1 - x_A)p_B^* = \frac{x_A p_A^*}{y_A}$$

$$x_A \left(p_A^* - p_B^* - \frac{p_A^*}{y_A} \right) = -p_B^*$$

$$x_A = \frac{p_B^*}{p_B^* + \dfrac{p_A^*}{y_A} - p_A^*} = \frac{82.1 \text{ kPa}}{\left(82.1 + \dfrac{68.8}{0.621} - 68.8 \right) \text{ kPa}} = \boxed{0.662}$$

and $\quad x_B = 1 - x_A = 1 - 0.662 = \boxed{0.338}$.

The total vapour pressure is

$$p_{\text{total}} = x_A p_A^* + x_B p_B^* = 0.662 \times 68.8 \text{ kPa} + 0.338 \times 82.1 \text{ kPa} = \boxed{73.3 \text{ kPa}}.$$

5B.12(b) **(i)** If the solution is ideal, then the partial vapour pressures are given by Raoult's law [5A.21]:

$$p_A{}^\circ = x_A p_A^* = 0.4217 \times 110.1 \text{ kPa} = 46.4 \text{ kPa}$$

and $\quad p_B{}^\circ = x_B p_B^* = (1 - x_B)p_B^* = (1 - 0.4217) \times 76.5 \text{ kPa} = 44.2 \text{ kPa}$.

(Note the use of the symbol $^\circ$ to emphasize that these are idealized quantities; we do not yet know if they are the actual partial vapour pressures.) At the normal boiling temperature, the partial vapour pressures must add up to 1 atm (101.3 kPa). These ideal partial vapour pressures add up to only 90.7 kPa, so the $\boxed{\text{solution is not ideal}}$.

(ii) We actually do not have enough information to compute the initial composition of the vapour above the solution. The activities and activity coefficients are defined by the actual partial vapour pressures. We know only that the actual vapour pressures must sum to 101.3 kPa. We can make a further assumption that the proportions of the vapours are the same as given by Raoult's law. That is, we assume that

$$y_A = y_A{}^\circ = \frac{p_A{}^\circ}{p_A{}^\circ + p_B{}^\circ} = \frac{46.4 \text{ kPa}}{(46.4 + 44.2) \text{ kPa}} = \boxed{0.512}$$

and $\quad y_B = y_B{}^\circ = \dfrac{p_B{}^\circ}{p_A{}^\circ + p_B{}^\circ} = \dfrac{44.2 \text{ kPa}}{(46.4 + 44.2) \text{ kPa}} = \boxed{0.488}$.

By Eqn. 1A.8, the actual partial vapour pressures would then be

$$p_A = y_A p_{\text{total}} = 0.512 \times 101.3 \text{ kPa} = \boxed{51.9 \text{ kPa}}$$

and $\quad p_B = y_B p_{\text{total}} = 0.488 \times 101.3 \text{ kPa} = \boxed{49.4 \text{ kPa}}$.

To find the activity coefficients, note that

$$\gamma_A = \frac{p_A}{x_A p_A^*} = \frac{p_A}{p_A{}^\circ} = \frac{51.9 \text{ kPa}}{46.4 \text{ kPa}} = 1.117 \qquad \text{and} \qquad \gamma_B = \frac{49.4 \text{ kPa}}{44.2 \text{ kPa}} = 1.117$$

Comment. Assuming that the actual proportions of the vapours are the same as the ideal proportions begs the question (*i.e.*, arrives at the answer by assumption rather than calculation). The assumption is not unreasonable, though. It is equivalent to assuming that the activity coefficients of the two components are equal (when in principle they could be different). The facts that the difference between ideal and actual total pressure is relatively small (on the order of 10%), that non-ideal behavior is due to the **interaction** of the two components, and that the two components are present in comparable quantities combine to suggest that the error we make in making this assumption is fairly small.

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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
$$p_{total} = p_B + p_T = (4.95 + 1.45) \text{ kPa} = \boxed{6.4 \text{ kPa}} .$$
(ii) The composition of the vapour is given by
$$y_B = \frac{p_B}{p_{total}} = \frac{4.95 \text{ kPa}}{6.4 \text{ kPa}} = \boxed{0.77}$$
and
$$y_T = \frac{p_T}{p_{total}} = \frac{1.45 \text{ kPa}}{6.4 \text{ kPa}} = \boxed{0.23}$$

(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
$$p_B = x_B p_B^* = 0.23 \times 9.9 \text{ kPa} = 2.24 \text{ kPa} = p_T \text{ [vapour mixture is equimolar]} = p_{total}/2 .$$
The total pressure is
$$p_{total} = 2p_B = \boxed{4.5 \text{ kPa}} .$$
Comment. Notice that an equimolar liquid mixture yields a vapour composition directly proportional to the vapour pressures of the pure liquids. Conversely, an equimolar vapour mixture implies a liquid composition inversely proportional to those vapour pressures.

Solutions to problems

5B.2 The apparent molality is
$$b_{app} = \frac{\Delta T}{K_f} \text{ [5B.13]} = \frac{0.0703 \text{ K}}{1.86 \text{ K/(mol kg}^{-1})} = 0.0378 \text{ mol kg}^{-1}$$
Since the solution molality is nominally 0.0096 mol kg^{-1} in Th(NO$_3$)$_4$, each formula unit supplies $\frac{0.0378}{0.0096} \approx \boxed{4 \text{ ions}}$. (More careful data, as described in the original reference gives 5 to 6 ions.)

5B.4 **(a)** Let V_1^* be the molar volume of *pure* propionic acid and V_1 be its *partial* molar volume in the mixture (and V_2^* and V_2 the analogous quantities for oxane). The volume of an ideal mixture is additive
$$V^{ideal} = n_1 V_1^* + n_2 V_2^* ,$$
so the volume of a real mixture is
$$V = V^{ideal} + V^E .$$
We have an expression for excess molar volume in terms of mole fractions. To compute partial molar volumes, we need an expression for the excess volume as a function of moles
$$V^E = (n_1 + n_2)V_m^E = \frac{n_1 n_2}{n_1 + n_2}\left(a_0 + \frac{a_1(n_1 - n_2)}{n_1 + n_2} \right)$$
so
$$V = n_1 V_1^* + n_2 V_2^* + \frac{n_1 n_2}{n_1 + n_2}\left(a_0 + \frac{a_1(n_1 - n_2)}{n_1 + n_2} \right)$$
The partial molar volume of propionic acid is
$$V_1 = \left(\frac{\partial V}{\partial n_1} \right)_{n_2} = V_1^* + \frac{a_0 n_2^2}{(n_1 + n_2)^2} + \frac{a_1(3n_1 - n_2)n_2^2}{(n_1 + n_2)^3} = \boxed{V_1^* + a_0 x_2^2 + a_1(3x_1 - x_2)x_2^2}$$
That of oxane is
$$V_2 = \left(\frac{\partial V}{\partial n_2} \right)_{n_1} = V_2^* + \frac{a_0 n_1^2}{(n_1 + n_2)^2} + \frac{a_1(n_1^3 - 3n_1^2 n_2^2)}{(n_1 + n_2)^3} = \boxed{V_2^* + a_0 x_1^2 + a_1(x_1 - 3x_2)x_1^2}$$

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(b) We need the molar volumes of the pure liquids

$$V_1^* = \frac{M_1}{\rho_1} = \frac{74.08 \text{ g mol}^{-1}}{0.97174 \text{ g cm}^{-3}} = 76.23 \text{ cm}^3 \text{ mol}^{-1}$$

and $\quad V_2^* = \dfrac{M_2}{\rho_2} = \dfrac{86.13 \text{ g mol}^{-1}}{0.86398 \text{ g cm}^{-3}} = 99.69 \text{ cm}^3 \text{ mol}^{-1}$

In an equimolar mixture, the partial molar volume of propionic acid is

$$V_1 = 76.23 + (-2.4697) \times (0.5)^2 + (0.0608) \times \{3(0.5) - 0.5\} \times (0.5)^2 \text{ cm}^3 \text{ mol}^{-1}$$

$$= \boxed{75.63 \text{ cm}^3 \text{ mol}^{-1}}$$

and that of oxane is

$$V_2 = 99.69 + (-2.4697) \times (0.5)^2 + (0.0608) \times \{0.5 - 3(0.5)\} \times (0.5)^2 \text{ cm}^3 \text{ mol}^{-1}$$

$$= \boxed{99.06 \text{ cm}^3 \text{ mol}^{-1}}$$

5B.6   In this mixture, $x = 0.250$, so

$$G^E = RT(0.250)(1-0.250)\{0.4857 - 0.1077(0.500-1) + 0.0191(0.500-1)^2\} = 0.1021RT$$

Therefore, since

$$\Delta_{\text{mix}}G = \Delta_{\text{mix}}G^{\text{ideal}} + nG^E = nRT(x_A \ln x_A + x_B \ln x_B) + nG^E \text{ [5B.5 and 5A.16]}$$

$$\Delta_{\text{mix}}G = nRT(0.250 \ln 0.250 + 0.750 \ln 0.750) + 0.1021nRT = -0.460nRT$$

$$\Delta_{\text{mix}}G = -0.460 \times 4.00 \text{ mol} \times 8.3145 \text{ J mol}^{-1} \text{ K}^{-1} \times 303.15 \text{ K} = \boxed{-4.64 \text{ kJ mol}^{-1}}.$$

5B.8 $\mu_A = \left(\dfrac{\partial G}{\partial n_A}\right)_{n_B}$ [5A.4] $= \mu_A^{\text{ideal}} + \left(\dfrac{\partial}{\partial n_A}(nG^E)\right)_{n_B}$ [5B.5]   where $\mu_A^{\text{ideal}} = \mu_A^* + RT \ln x_A$ [5A.22]

$$\left(\frac{\partial nG^E}{\partial n_A}\right)_{n_B} = G^E + n\left(\frac{\partial G^E}{\partial n_A}\right)_{n_B} = G^E + n\left(\frac{\partial x_A}{\partial n_A}\right)_{n_B}\left(\frac{\partial G^E}{\partial x_A}\right)_{n_B}$$

where $\quad \left(\dfrac{\partial x_A}{\partial n_A}\right)_{n_B} = \dfrac{\partial}{\partial n_A}\left(\dfrac{n_A}{n_A + n_B}\right) = \dfrac{1}{n_A + n_B} - \dfrac{n_A}{(n_A + n_B)^2} = \dfrac{n_B}{(n_A + n_B)^2} = \dfrac{x_B}{n_A + n_B} = \dfrac{x_B}{n}$

Hence $\quad \left(\dfrac{\partial nG^E}{\partial n_A}\right)_{n_B} = G^E + x_B\left(\dfrac{\partial G^E}{\partial x_A}\right)_{n_B} = gRTx_A(1-x_A) + (1-x_A)gRT(1-2x_A)$
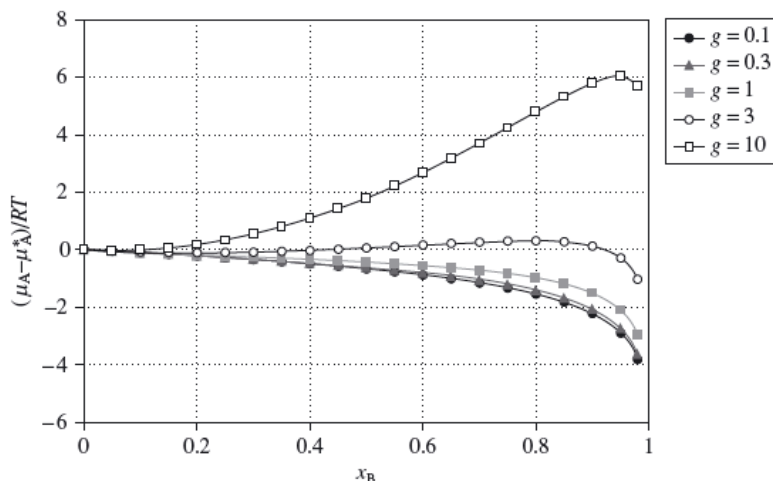
After expanding and collecting terms, we arrive at

$$\left(\frac{\partial nG^E}{\partial n_A}\right)_{n_B} = gRT(1-x_A)^2 = gRTx_B^2$$

Therefore, $\mu_A = \boxed{\mu_A^* + RT \ln x_A + gRTx_B^2}$

This function is plotted for several values of the parameter g in Figure 5B.2.

Figure 5B.2

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5B.10 By the van't Hoff equation [5B.16]

$$\Pi = [B]RT = \frac{cRT}{M}$$

Division by the standard acceleration of free fall, g, gives

$$\frac{\Pi}{g} = \frac{c(R/g)T}{M}$$

(a) This expression may be written in the form

$$\Pi' = \frac{cR'T}{M}$$

which has the same form as the van't Hoff equation, but the unit of osmotic pressure (Π') is now

$$\frac{\text{force / area}}{\text{length / time}^2} = \frac{(\text{mass length}) / (\text{area time}^2)}{\text{length / time}^2} = \frac{\text{mass}}{\text{area}}$$

This ratio can be specified in $g\ cm^{-2}$. Likewise, the constant of proportionality (R') would have the units of R/g.

$$\frac{\text{energy K}^{-1}\,\text{mol}^{-1}}{\text{length / time}^2} = \frac{(\text{mass length}^2 / \text{time}^2)\,\text{K}^{-1}\,\text{mol}^{-1}}{\text{length / time}^2} = \text{mass length K}^{-1}\,\text{mol}^{-1}$$

This result may be specified in $\boxed{\text{g cm K}^{-1}\,\text{mol}^{-1}}$.

$$R' = \frac{R}{g} = \frac{8.314\,47\,\text{J K}^{-1}\,\text{mol}^{-1}}{9.806\,65\,\text{m s}^{-2}}$$

$$= 0.847\,840\,\text{kg m K}^{-1}\,\text{mol}^{-1}\left(\frac{10^3\,\text{g}}{\text{kg}}\right) \times \left(\frac{10^2\,\text{cm}}{\text{m}}\right)$$

$$= \boxed{84\,784.0\,\text{g cm K}^{-1}\,\text{mol}^{-1}}$$

In the following we will drop the primes giving

$$\Pi = \frac{cRT}{M}$$

and use the Π units of $g\ cm^{-2}$ and the R units $g\ cm\ K^{-1}\ mol^{-1}$.

(b) By extrapolating the low concentration plot of Π / c versus c (Figure 5B.3(a)) to $c = 0$ we find the intercept $230\ g\ cm^{-2}/(g\ cm^{-3})$. In this limit the van't Hoff equation is valid so

Figure 5B.3(a)

Polyisobutylene in chlorobenzene at low concentrations
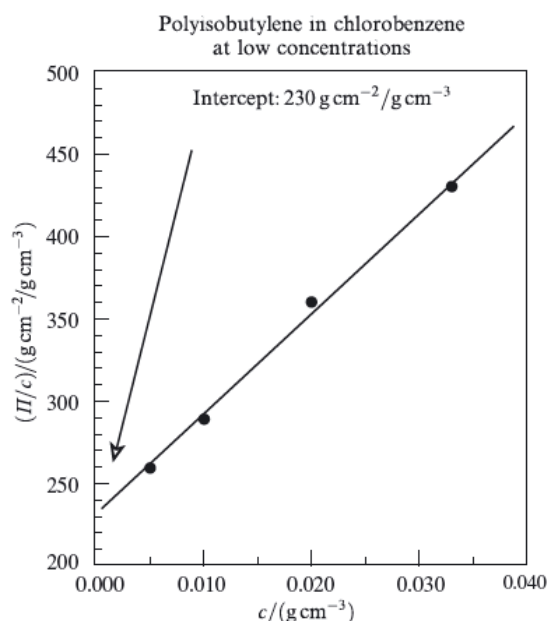
$$\frac{RT}{M} = \text{intercept} \quad\quad \text{or} \quad\quad M = \frac{RT}{\text{intercept}}$$

$$M = \frac{RT}{\text{intercept}} = \frac{(84\,784.0\,\text{g cm K}^{-1}\,\text{mol}^{-1}) \times (298.15\,\text{K})}{(230\,\text{g cm}^{-2})/(\text{g cm}^{-3})} = \boxed{1.1 \times 10^5\ \text{g mol}^{-1}}$$

(c) The plot of Π / c versus c for the full concentration range (Figure 5B.3(b)) is very nonlinear. We may conclude that the solvent is good. This may be due to the nonpolar nature of both solvent and solute.

Figure 5B.3(b)
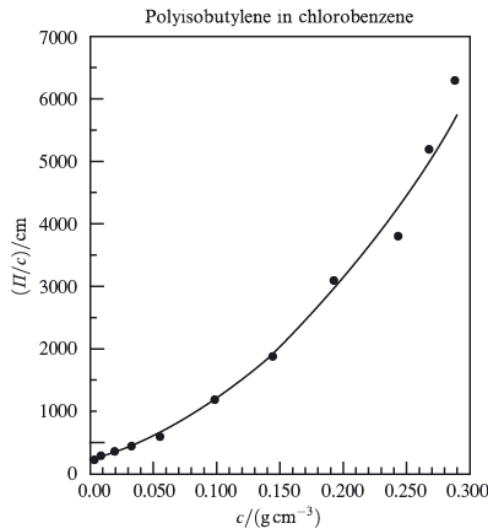
(d) The virial analogue to the van't Hoff equation (eqn. 5B.18) rearranges to

$$\Pi / c = (RT / M)(1 + B'c + C'c^2)$$

Since RT / M has been determined in part (b) by extrapolation to $c = 0$, it is best to determine the second and third virial coefficients with the linear regression fit

$$\frac{(\Pi / c)/(RT / M)^{-1}}{c} = B' + C'c$$

$R = 0.9791$.

$B' = \boxed{21.4\ \text{cm}^3\,\text{g}^{-1}}$; standard deviation $= 2.4\ \text{cm}^3\,\text{g}^{-1}$.

$C' = \boxed{211\ \text{cm}^6\,\text{g}^{-2}}$; standard deviation $= 15\ \text{cm}^6\,\text{g}^{-2}$.

(e) Using 1/4 for g and neglecting terms beyond the second power, we may write

$$\left(\frac{\Pi}{c}\right)^{1/2} = \left(\frac{RT}{M}\right)^{1/2}\left(1 + \frac{1}{2}B'c\right)$$

We can solve for B', then $g(B')^2 = C'$.

$$\frac{\left(\dfrac{\Pi}{c}\right)^{1/2}}{\left(\dfrac{RT}{M}\right)^{1/2}} - 1 = \frac{1}{2}B'c$$

RT / M has been determined above as 230 g cm^{-2}/(g cm^{-3}). We may analytically solve for B' from one of the data points, say, $\Pi / c = 430\,\text{g cm}^{-2} / \text{g cm}^{-3}$ at $c = 0.033$ g cm^{-3}.

$$\left(\frac{430\,\text{g cm}^{-2} / \text{g cm}^{-3}}{230\,\text{g cm}^{-2} / \text{g cm}^{-3}}\right)^{1/2} - 1 = \frac{1}{2}B' \times (0.033\ \text{g cm}^{-3})$$

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$$B' = \frac{2 \times (1.367 - 1)}{0.033 \text{ g cm}^{-3}} = 22 \text{ cm}^3 \text{ g}^{-1}$$

$$C' = g(B')^2 = 0.25 \times (22 \text{ cm}^3 \text{ g}^{-1})^2 = 12\overline{3} \text{ cm}^6 \text{ g}^{-2}$$

Better values of B' and C' can be obtained by plotting $\left(\frac{\Pi}{c}\right)^{1/2} / \left(\frac{RT}{M}\right)^{1/2}$ against c. This plot is shown in Figure 5B.3(c). The slope is 14 cm^3 g^{-1}. $B' = 2 \times$ slope $= \boxed{28 \text{ cm}^3 \text{ g}^{-1}}$. C' is then $\boxed{19\overline{6} \text{ cm}^6 \text{ g}^{-2}}$. The intercept of this plot should theoretically be 1.00, but it is in fact 0.916 with a standard deviation of 0.066. The overall consistency of the values of the parameters confirms that g is roughly 1/4 as assumed.

Figure 5B.3(c)
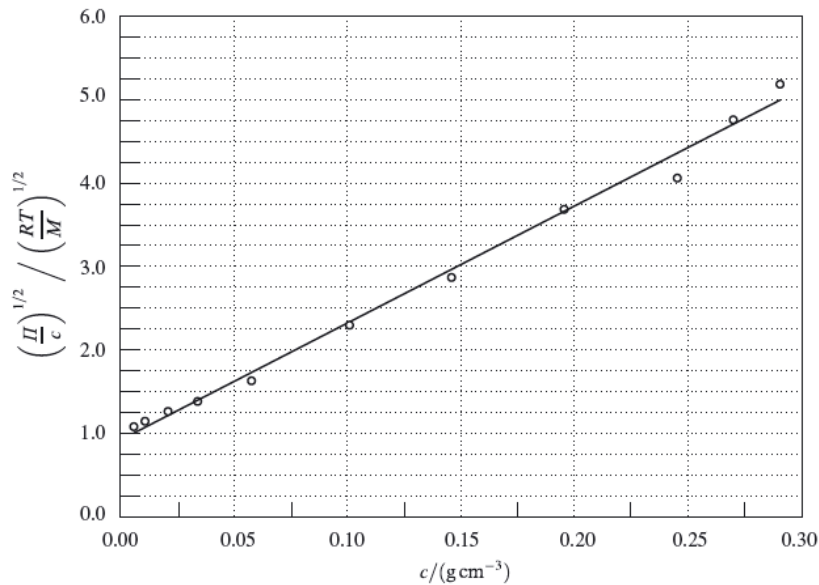
5B.12 The Gibbs energy of mixing an ideal solution is [5A.16]
$$\Delta_{mix}G = nRT(x_A \ln x_A + x_B \ln x_B)$$
The molar Gibbs energy of mixing is plotted against composition for several temperatures in Fig. 5B.4. The legend shows the temperature in kelvins.

Figure 5B.4
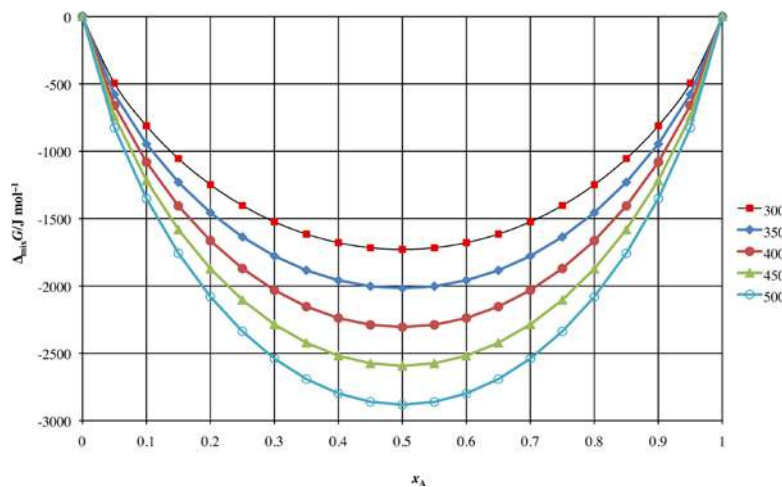
The composition at which the temperature dependence is strongest is the composition at which the function has its largest magnitude, namely $\boxed{x_A = x_B = 0.5}$.

5B.14 The theoretical solubility [5B.15] is

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

so
$$x_B = \exp\left(\frac{\Delta_{fus}H}{RT_f}\right)\exp\left(-\frac{\Delta_{fus}H}{RT}\right)$$

and
$$\frac{dx_B}{dT} = \boxed{\exp\left(\frac{\Delta_{fus}H}{RT_f}\right)\exp\left(-\frac{\Delta_{fus}H}{RT}\right)\times\left(\frac{\Delta_{fus}H}{RT^2}\right)}$$

This expression can be plotted as a function of temperature for various values of the enthalpy of fusion and the freezing temperature. The dependence on the freezing temperature is relatively uninteresting, though, since it enters into a factor that is independent of temperature, namely $\exp\left(\dfrac{\Delta_{fus}H}{RT_f}\right)$

So we will ignore the effect of the freezing temperature and simply plot dx_B/dT with this factor divided out. That is, in Figure 5B.5, we plot $f(T)$ vs. T for several values of $\Delta_{fus}H$ between 1 and 10 kJ mol^{-1}, where

$$f(T) = \exp\left(-\frac{\Delta_{fus}H}{RT}\right)\times\left(\frac{\Delta_{fus}H}{RT^2}\right)$$

Figure 5B.5
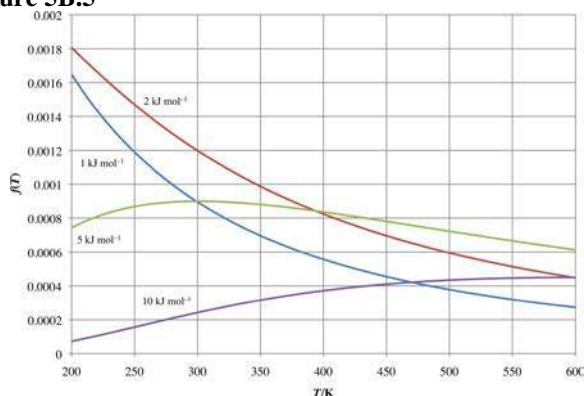
Note that the function does not appear to consistently as we increase $\Delta_{fus}H$. This apparent inconsistency would be removed, though, if we plotted over a temperature range that extended back to $T = 0$. The function has a maximum because the exponential factor increases toward a constant value of 1 with increasing temperature while the other factor decreases toward zero. The higher the value of $\Delta_{fus}H$. the higher the temperature at which $f(T)$ is maximal and the lower the value of that maximum value. For $\Delta_{fus}H = 1$ or 2 kJ mol^{-1}, the maximum occurs at temperatures lower than those shown and for $\Delta_{fus}H = 10$ kJ mol^{-1} it occurs at a higher temperature than those shown.

5C   Phase diagrams of binary systems

Answers to discussion question

5C.2   A low-boiling azeotrope has a boiling temperature lower than that of either component, so it is easier to get the molecules into the vapor phase than in a "normal" (non-azeotropic) mixture. Therefore, the liquid phase has less favorable intermolecular interactions than in a "normal" mixture, a sign that the components are less attracted to each other in the liquid phase than to molecules of their own kind. These intermolecular interactions are determined by factors such as dipole moment (polarity) and hydrogen bonding. Conversely, a high-boiling azeotrope has a boiling temperature higher than that of either component, so it is more difficult to get the molecules into the vapor phase. This reflects the relatively unusual situation of components that have more favorable intermolecular interactions with each other in the liquid phase than with molecules of their own kind. The concepts of ideal

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mixtures of liquids (in Topic 5A) and deviations from ideal behavior (in Topics 5B and 5E) will further define the behavior of "normal" (ideal) mixtures.

Solutions to exercises

5C.1(b)   Add the boiling point of A to the table at $x_A = y_A = 1$ and the boiling point of B at $x_B = y_B = 0$. Plot the boiling temperatures against liquid mole fractions and the same boiling temperatures against vapour mole fractions on the same plot.

The phase diagram is shown in Figure 5C.1. The phase boundary curves are polynomial fits to the data points.

Figure 5C.1
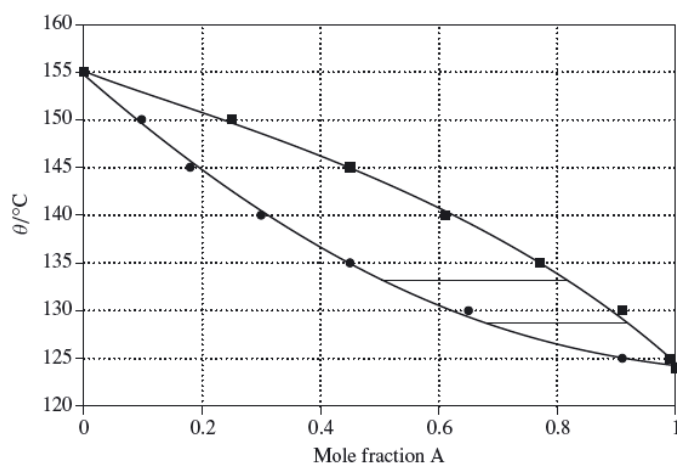
(i) Find $x_A = 0.50$ on the lower curve and draw a horizontal tie line to the upper curve. The mole fraction at that point is $\boxed{y_A = 0.82}$.

(ii) Find $x_A = 0.67$ (*i.e.*, $x_B = 0.33$) on the lower curve and draw a horizontal tie line to the upper curve. The mole fraction at that point is $\boxed{y_A = 0.91 \ (\textit{i.e.}, \ y_B = 0.09)}$.

5C.2(b)   The phase diagram is shown in Figure 5C.2.

Figure 5C.2
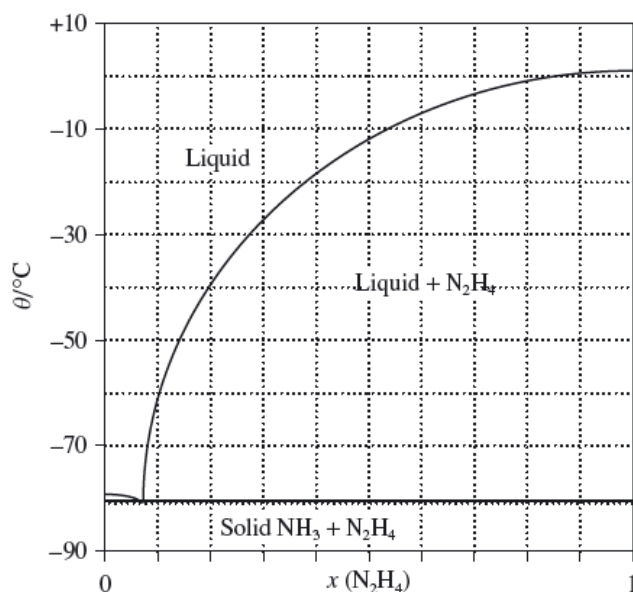
5C.3(b)   Refer to the figure given with the exercise. At the lowest temperature shown on the phase diagram, there are two liquid phases, a water-rich phase ($x_B = 0.07$) and a methylpropanol-rich phase ($x_B = 0.88$); the latter phase is about 10 times as abundant as the former (lever rule). On heating, the compositions of the two phases change, the water-rich phase increasing significantly in methylpropanol and the methylpropanol-rich phase more gradually increasing in water. (Note how the composition of the left side of the diagram changes more with temperature than the right.) The relative proportions of the phases continue to be given by the lever rule. Just before the isopleth intersects the phase boundary, the methylpropanol-rich phase ($x_B = 0.84$) is in equilibrium with a vanishingly small water-rich phase ($x_B = 0.3$). Then the phases merge, and the single-phase region is encountered with $x_B = 0.3$.

5C.4(b)   The feature that indicates incongruent melting (Topic 5C.4(c)) is circled in Figure 5C.3. The incongruent melting point is marked as T_1. The composition of the eutectic is $x_B \approx \boxed{0.58}$ and its melting point is labeled $\boxed{T_2}$.

Figure 5C.3
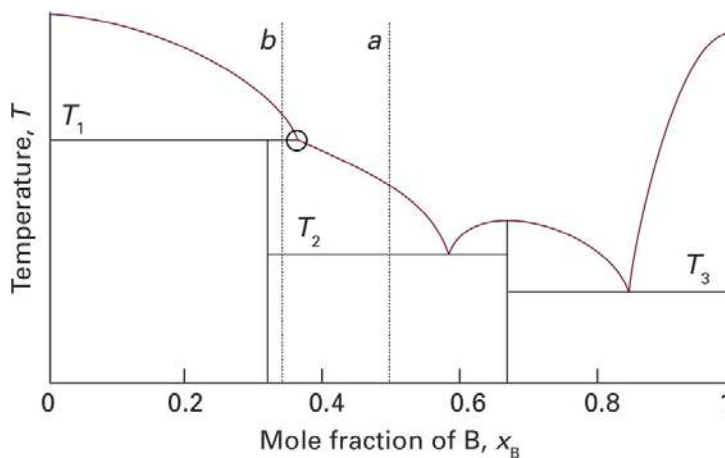
5C.5(b)   The cooling curves corresponding to the phase diagram in Figure 5C.4(a) are shown in Figure 5C.4(b). Note the breaks (abrupt change in slope) at temperatures corresponding to points a_1, b_1, and b_2. Also note the eutectic halts at a_2 and b_3.

Figure 5C.4
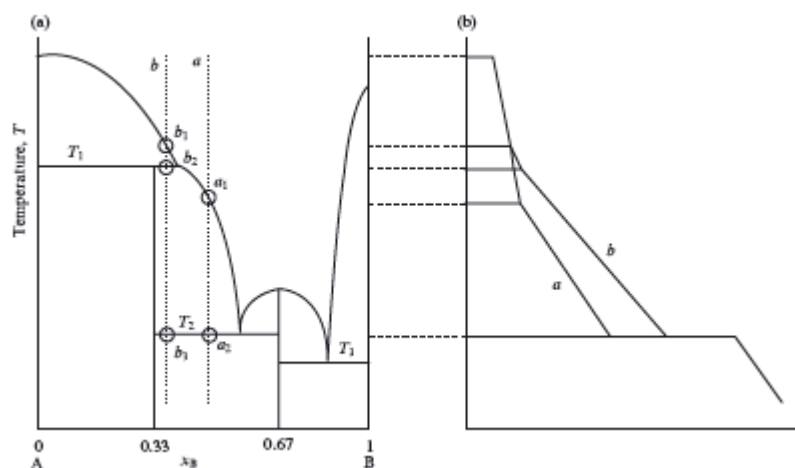
5C.6(b)   Refer to Figure 5C.5. Dotted horizontal lines have been drawn at the relevant temperatures.

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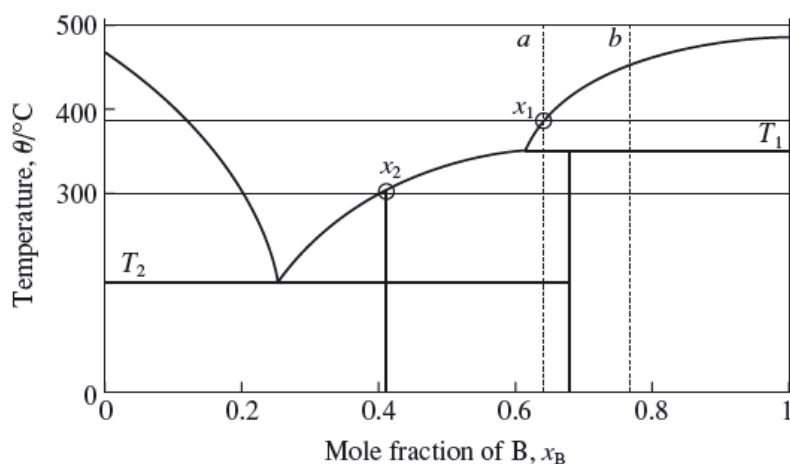
Figure 5C.5

(i) At 500°C, the phase diagram shows a single liquid phase at all compositions, so B is soluble in A in all proportions.

(ii) At 390°C, solid B exists in equilibrium with a liquid whose composition is circled and labeled x_1 on Figure 5.11. That composition is $x_B = x_1 = \boxed{0.63}$.

(iii) At point x_2, two phases coexist: solid AB_2 and a liquid mixture of A and B with mole fraction $x_B = x_2 = 0.41$. Although the liquid does not contain any AB_2 units, we can think of the liquid as a mixture of dissociated AB_2 in A. Call the amount (moles) of the compound n_c and that of free A n_a. Thus, the amount of A (regardless of whether free or in the compound) is

$$n_A = n_a + n_c ,$$

and the amount of B is

$$n_B = 2n_c .$$

The mole fraction of B is

$$x_B = x_2 = \frac{n_B}{n_A + n_B} = \frac{2n_c}{(n_a + n_c) + 2n_c} = \frac{2n_c}{n_a + 3n_c}$$

Rearrange this relationship, collecting terms in n_c on one side and n_a on the other:

$$n_a x_2 = n_c(2 - 3x_2) .$$

The mole ratio of compound to free A is given by

$$\frac{n_c}{n_a} = \frac{x_2}{2 - 3x_2} = \frac{0.41}{2 - 3 \times 0.41} = \boxed{0.53} .$$

5C.7(b) The phase diagram is shown in Figure 5C.6. Point symbols are plotted at the given data points. The lines are schematic at best.

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Figure 5C.6
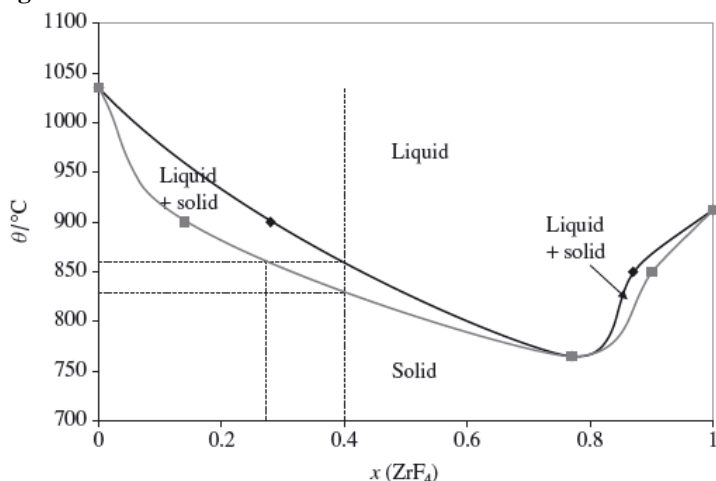
At 860°C, a solid solution with $x(ZrF_4) = 0.27$ appears. The solid solution continues to form, and its ZrF_4 content increases until it reaches $x(ZrF_4) = 0.40$ at 830°C. At that temperature and below, the entire sample is solid.

5C.8(b) The phase diagram for this system (Figure 5C.7) is very similar to that for the system methyl ethyl ether and diborane of Exercise 5C.7(a). The regions of the diagram contain analogous substances. The mixture in this Exercise has a diborane mole fraction of 0.80. Follow this isopleth down to see that crystallization begins at about 123 K. The liquid in equilibrium with the solid becomes progressively richer in diborane until the liquid composition reaches 0.90 at 104 K. Below that temperature the system is a mixture of solid compound and solid diborane.

Figure 5C.7
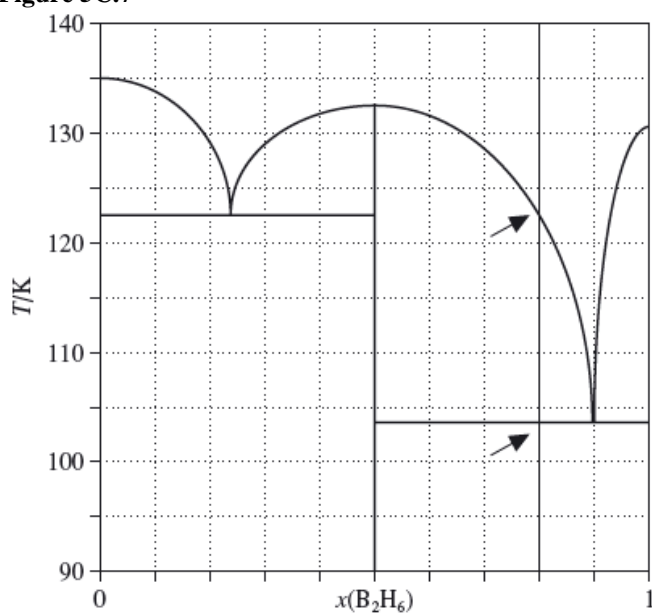
5C.9(b) The cooling curves are sketched in Figure 5C.8. Note the breaks and halts. The breaks correspond to changes in the rate of cooling due to the freezing out of a solid which releases its heat of fusion and thus slows down the cooling process. The halts correspond to the existence of three phases and hence no variance until one of the phases disappears.

Figure 5C.8
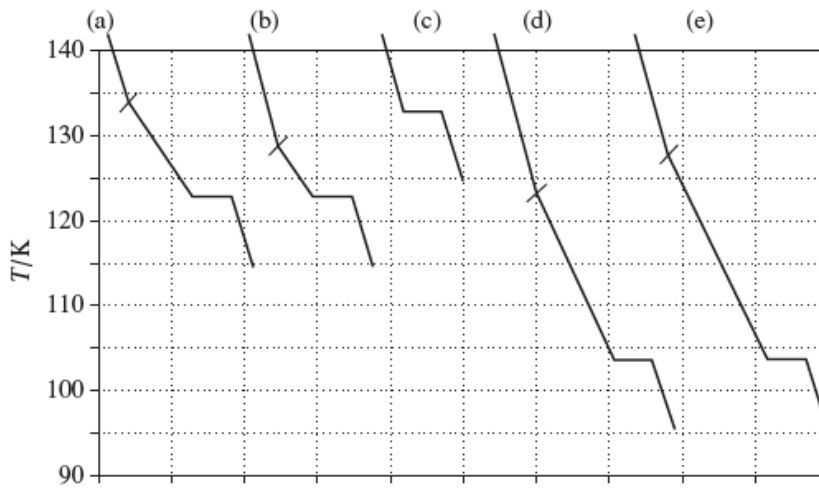
**5C.10(b)** The phase diagram is sketched in Figure 5C.9.

Figure 5C.9
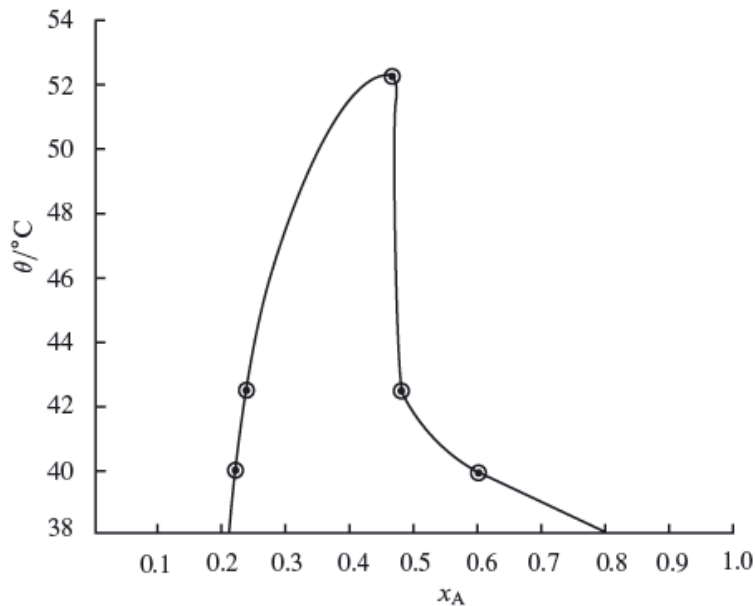
(i) When x_A falls to 0.47, a second liquid phase appears. The amount of new phase increases as x_A falls and the amount of original phase decreases until, at $x_A = 0.314$, only one liquid remains.

(ii) The mixture has a single liquid phase at all compositions.

Solutions to problems

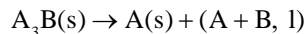**5C.2**   (a) The phase diagram is shown in Figure 5C.10.

Figure 5C.10
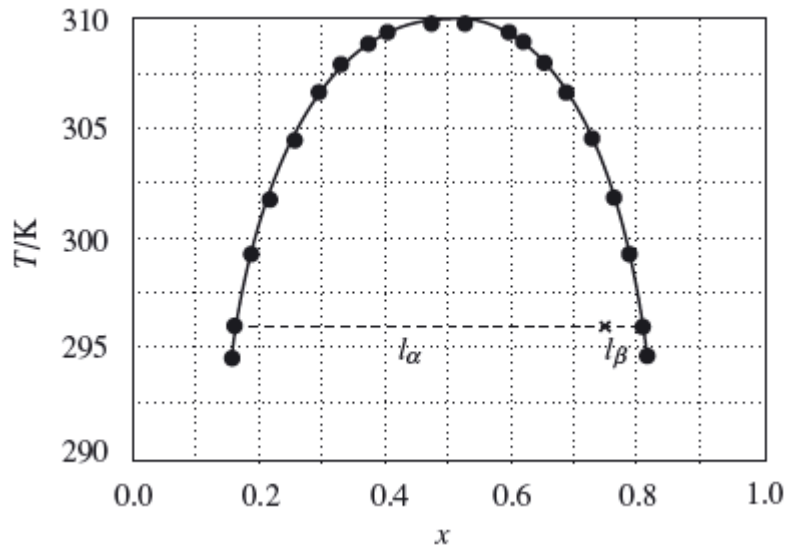
(b) We need not interpolate data, for 296.0 K is a temperature for which we have experimental data. The mole fraction of N, N-dimethylacetamide in the heptane-rich phase (call the point α, at the left of the tie line) is 0.168 and in the acetamide-rich phase (β, at right) 0.804. The proportions of the two phases are in an inverse ratio of the distance their mole fractions are from the composition point in question, according to the lever rule. That is

$$n_\alpha / n_\beta = l_\beta / l_\alpha = (0.804 - 0.750) / (0.750 - 0.168) = \boxed{0.093}$$

The smooth curve through the data crosses $x = 0.750$ at $\boxed{302.5 \text{ K}}$, the temperature at which the heptane-rich phase will vanish.

5C.4 Figure 5C.11 displays the phase diagram. $\boxed{\text{A compound with probable formula A}_3\text{B exists}}$. It melts incongruently at 700 °C , undergoing the peritectic reaction

$$A_3B(s) \rightarrow A(s) + (A + B, \, l)$$

The proportions of A and B in the product are dependent upon the overall composition and the temperature. A eutectic exists at 400°C and $x_B = 0.83$.

Figure 5C.11
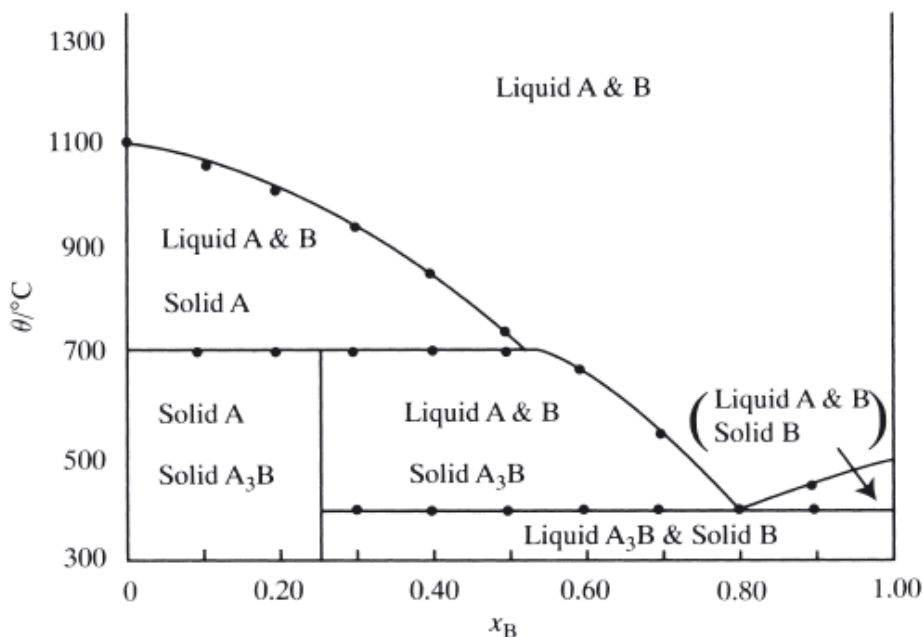
5C.6 The information has been used to construct the phase diagram in Figure 5C.12(a). In $MgCu_2$ the mass percentage of Mg is

$$(100) \times \frac{24.3}{24.3 + 127} = \boxed{16}$$

and in Mg_2Cu it is

$$(100) \times \frac{48.6}{48.6 + 63.5} = \boxed{43}.$$

The initial point is a_1, corresponding to a single-phase liquid system. At a_2 (at 720°C) $MgCu_2$ begins to come out of solution and the liquid becomes richer in Mg, moving toward e_2. At a_3 there is solid $MgCu_2$ + liquid of composition e_2 (33 per cent by mass of Mg). This solution freezes without further change. The cooling curve will resemble that shown in Figure 5C.12(b).

Figure 5C.12
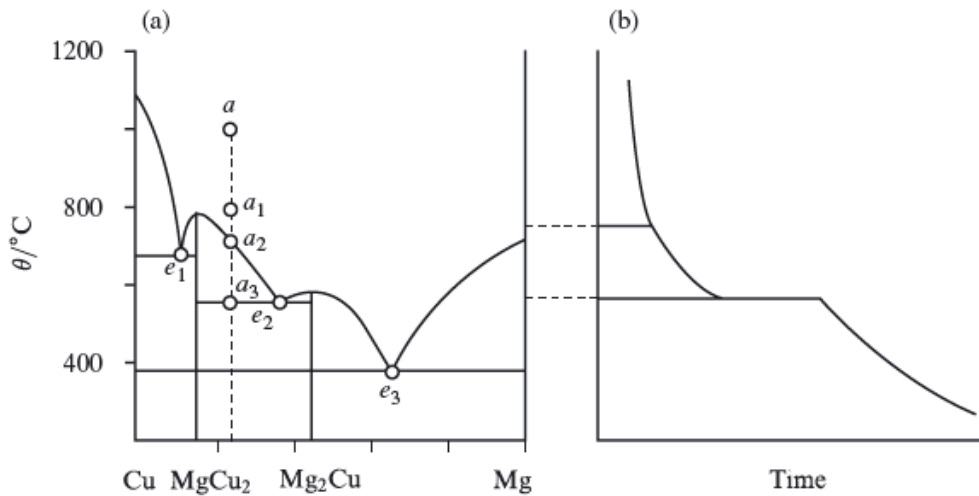
5C.8 The data are plotted in Figure 5C.13. At 360°C, $K_2FeCl_4(s)$ appears. The solution becomes richer in $FeCl_2$ until the temperature reaches 351°C, at which point $KFeCl_3(s)$ also appears. Below 351°C the system is a mixture of $K_2FeCl_4(s)$ and $KFeCl_3(s)$.

Figure 5C.13
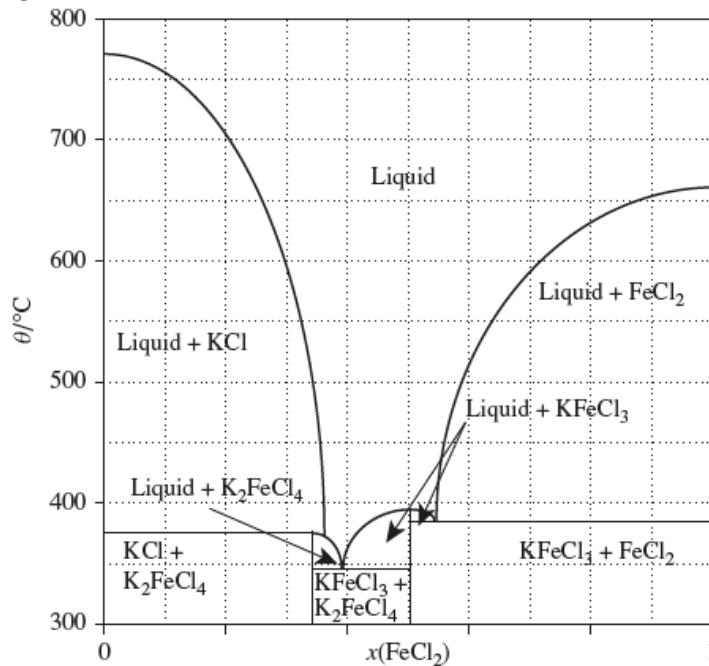
5C.10 Equation 5C.5 is

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$$p = \frac{p_A^* p_B^*}{p_A^* + (p_B^* - p_A^*) y_A}$$

First divide both sides by p_A^* to express the pressure in units of p_A^*. Next, divide both numerator and denominator by p_B^* to see if the right hand side can be expressed as a function of the ratio p_A^* / p_B^* rather than of each vapor pressure separately:

$$p / p_A^* = \frac{1}{p_A^* / p_B^* + (1 - p_A^* / p_B^*) y_A}$$

The plot of p / p_A^* vs. y_A at several values of the vapor pressure ratio is shown in Figure 5C.4 of the main text.
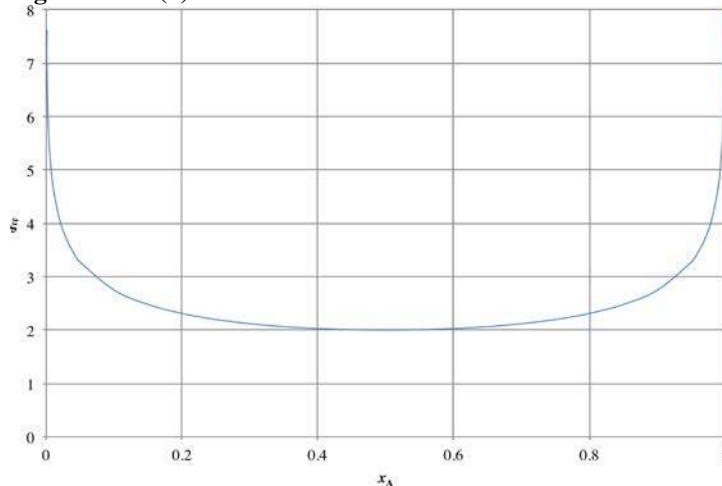
5C.12 Equation 5C.7 is

$$\ln \frac{x_A}{1 - x_A} = -\xi(1 - 2x_A) = \xi(2x_A - 1)$$

The simplest way to construct a plot of ξ vs. x_A is to isolate ξ:

$$\xi = \frac{\ln \dfrac{x_A}{1 - x_A}}{2x_A - 1}$$

A plot based on this equation is shown in Figure 5C.14(a).

Figure 5C.14(a)

 (a) The graphical method described in section 5C.3(b) and illustrated in the main text's Figure 5C.19 is also shown below in Figure 5C.14(b). Here the left-hand side of eqn 5C.7 is plotted as the bold curve, and the lighter lines are the right-hand side for $\xi = 1, 2, 3,$ and 5. Small squares are placed where the curve intersects one of the lines. Note that the curve intersects **every** line at $x_A = \frac{1}{2}$, the composition at which H^E is maximized. For values of $\xi \leq 2$, that is the only point of intersection; for values of $\xi > 2$, there are two additional points of intersection arranged at equal distance from $x_A = \frac{1}{2}$.

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Figure 5C.14(b)
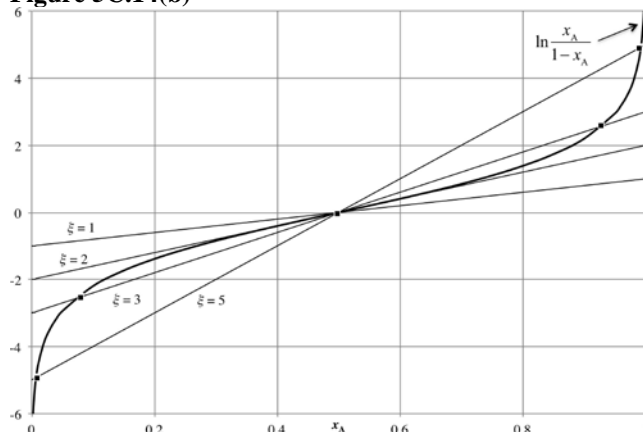
The root $x_A = \frac{1}{2}$ is unlike the other roots of eqn 5C.7 in several respects. The graphical approach shows that it is a root for all values of ξ. That fact can be confirmed by inspection by substituting $x_A = \frac{1}{2}$ into eqn 5C.7, leading to $0 = 0$ for any finite value of ξ. For $\xi > 2$, that root of eqn 5C.7 is a maximum in the Gibbs energy, not a minimum, as can be seen in Figure 5C.18 of the main text. However, in the equation obtained by isolating ξ, $x_A = \frac{1}{2}$ leads only to $\xi = 2$. That equation yields an indeterminate form for $x_A = \frac{1}{2}$, but application of L'Hospital's rule yields

$$\lim_{x \to \frac{1}{2}} \frac{\ln \dfrac{x_A}{1-x_A}}{2x_A - 1} = \lim_{x \to \frac{1}{2}} \frac{\ln x_A - \ln(1-x_A)}{2x_A - 1} = \lim_{x \to \frac{1}{2}} \frac{x_A^{-1} - (-x_A)^{-1}}{2} = \frac{2+2}{2} = 2$$

(b) One method of numerical solution is illustrated by the following cells from a spreadsheet. Set up one column to represent x_A, one for the left-hand side of eqn 5C.7, and one for the right-hand side (with variable). From the cells shown here, it is apparent that

$\ln \dfrac{x_A}{1-x_A} < 7(2x_A - 1)$ when $x_A = 0.9980$ or 0.9985, but $\ln \dfrac{x_A}{1-x_A} > 7(2x_A - 1)$ when $x_A = 0.9990$. Therefore, the value of x_A when the two sides were equal lies somewhere between 0.9985 and 0.9990, or, to three decimal places, at 0.999. Therefore, a root of eqn 5C.7 when $\xi = 7$ is $x_A = 0.999$.

x	ln(x/(1-x))	7(2x–1)
0.998	6.213	6.972
0.9985	6.501	6.979
0.999	6.907	6.986

5D Phase diagrams of ternary systems

Answers to discussion question

5D.2   The lever rule [5C.6] applies in a ternary system, but with an important caveat. The tie lines along which the rule applies are experimentally determined, not necessarily horizontal lines or lines parallel to any edge of the triangular diagram. Thus the lever rule applies, but as a practical matter it can be used only in the vicinity of plotted tie lines. (By contrast, recall that the lever rule in a binary phase diagram could be applied within a two-phase region simply by drawing a horizontal line to the appropriate phase boundaries.) See Topic 5D.2(a) and Figure 5D.4 of the main text.

Solutions to exercises

5D.1(b)   The ordered triples (x_A, x_B, x_C) are plotted in Figure 5D.1. The vertices of the triangular phase diagram are labeled for the component that is pure at that vertex. For example, the top of the diagram is pure A: (1, 0, 0). As a reminder, at the edge opposite a labeled vertex, that

component's mole fraction is zero. For example, the base of the diagram represents compositions $(0, x_B, x_C)$.

Figure 5D.1
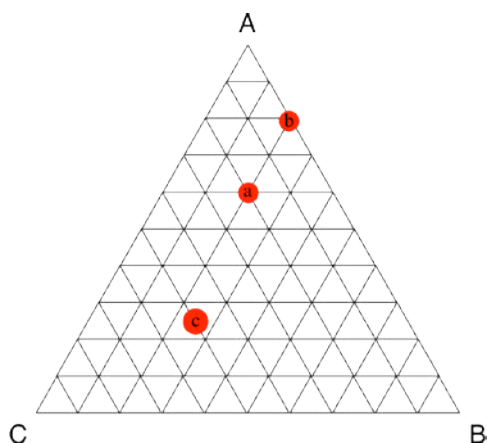
5D.2(b) Note that the compositions are given in mass percentages, not mole percentages, so we simply convert to moles before plotting. Assume a convenient sample size, such as 100 g, making the numerical values of the mass percentages equal to masses in grams:

(i) NaCl: $\qquad 33\text{ g} \times \dfrac{1\text{ mol}}{58.44\text{ g}} = 0.56\overline{5}\text{ mol}$

$Na_2SO_4 \cdot 10H_2O$: $\qquad 33\text{ g} \times \dfrac{1\text{ mol}}{322.21\text{ g}} = 0.10\overline{2}\text{ mol}$

H_2O: $\qquad 34\text{ g} \times \dfrac{1\text{ mol}}{18.016\text{ g}} = 1.8\overline{9}\text{ mol}$

To get mole fractions, divide these amounts by the total amount of 2.55 mol:

$$x(\text{NaCl}) = \frac{0.56\overline{5}\text{ mol}}{2.55\text{ mol}} = 0.22$$

$$x\,(Na_2SO_4 \cdot 10H_2O) = 0.040 \qquad x(H_2O) = 0.74$$

This composition is point a in Figure 5D.2.

(ii) We want to plot a line representing equal masses of salt with varying amounts of water. One point on that line has no water. Compute the mole fractions that correspond to the amounts of salt computed in part (a) with no water. In that case, the total amount is:

$$n_{\text{total}} = (0.56\overline{5} + 0.10\overline{2})\text{ mol} = 0.66\overline{7}\text{ mol}$$

so $\qquad x(\text{NaCl}) = \dfrac{0.56\overline{5}\text{ mol}}{0.66\overline{7}\text{ mol}} = 0.85 \qquad$ and $\qquad x\,(Na_2SO_4 \cdot 10H_2O) = 0.15$

Plot this point on the edge opposite the vertex labeled H_2O. The other extreme has the salts in the same proportions, but in amounts negligible compared to that of water, so the other end of this line lies at the vertex labeled H_2O. The line is labeled b on Figure 5D.2, and note that it goes through point (a) as it must.

Figure 5D.2

NaCl

H₂O   Na₂SO₄·10H₂O
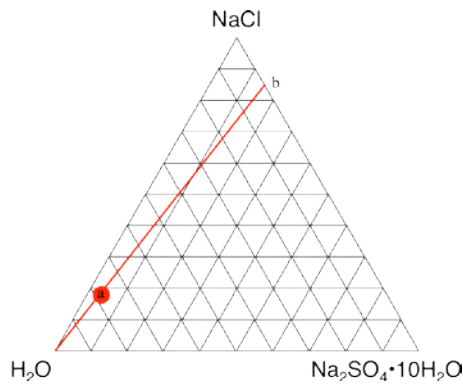
5D.3(b)   First convert to moles and find composition by mole fraction.

H_2O (W): $55.0 \text{ g} \times \dfrac{1 \text{ mol}}{18.016 \text{ g}} = 3.05 \text{ mol}$

$CHCl_3$ (C): $8.8 \text{ g} \times \dfrac{1 \text{ mol}}{119.4 \text{ g}} = 0.074 \text{ mol}$

CH_3COOH (A): $3.7 \text{ g} \times \dfrac{1 \text{ mol}}{60.05 \text{ g}} = 0.062 \text{ mol}$

To get mole fractions, divide these amounts by the total amount of 3.19 mol:

$$x_W = \frac{3.05 \text{ mol}}{3.19 \text{ mol}} = 0.958 \qquad x_C = 0.023 \qquad\qquad x_A = 0.019$$

This point is plotted in Figure 5D.3; it is very close to the label W in the original Figure 5D.4 of the main text. One phase is present, since our point lies outside the phase-boundary arc (to the left of it).

(i) If water is added to our mixture, the composition changes from our point along the very short line connecting it to the vertex labeled W. The system remains in a single phase.
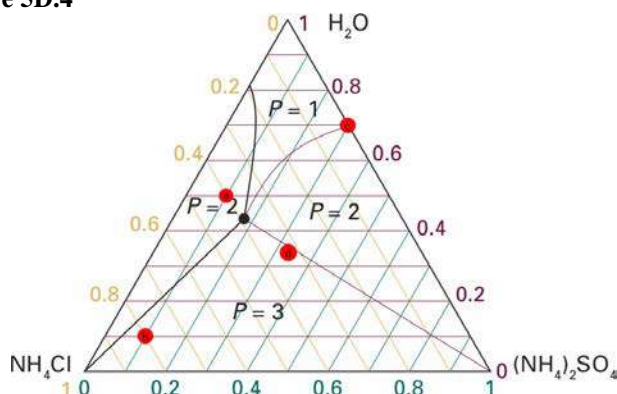
(ii) If acetic acid is added to our mixture, the composition changes from our point along the line connecting it to the vertex labeled A. The system remains in a single phase.

Figure 5D.3
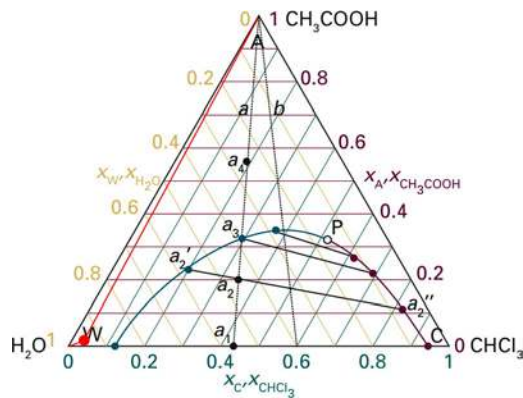
5D.4(b)   The phase diagram showing the four given compositions is shown in Figure 5D.4.

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Figure 5D.4

Point (a) is in a two-phase region and point (b) in a three-phase region. Point (c) is practically in a single-phase region; that is, it is on the border between a single-phase and a two-phase region, so there would be a vanishingly small amount of a second phase present. Finally, point (d), for which all three components are present in nearly equal amounts, is in a three-phase region (although very near the border with a two-phase region).

5D.5(b) **(i)** Note the line in Figure 5D. 5 that runs from the water-NH_4Cl edge near $x(NH_4Cl) = 0.2$ (the point that represents a saturated aqueous solution of NH_4Cl) to the $(NH_4)_2SO_4$ vertex. Traveling along that line from the edge to the vertex represents adding $(NH_4)_2SO_4$ to a saturated aqueous solution of NH_4Cl. Note that it traverses the single-phase region at first. That is, the added $(NH_4)_2SO_4$ dissolves and does not cause NH_4Cl to precipitate out. If one starts with saturated aqueous NH_4Cl with solid NH_4Cl in excess, then the starting point is a bit further down on the water-NH_4Cl edge, for example at $x(NH_4Cl) = 0.3$. Adding $(NH_4)_2SO_4$ to such a solution would take one from that point to the $(NH_4)_2SO_4$ vertex. Initially, the system remains in the two-phase region, but eventually a single-phase region is reached. Note that the line intersects the single-phase region at a higher NH_4Cl-water ratio and even a higher overall $x(NH_4Cl)$ than that of saturated aqueous NH_4Cl. (That is, there is not only more NH_4Cl relative to water at that intersection point, but NH_4Cl is a larger fraction of the saturated **three**-component solution than it was in the saturated **two**-component system of water and NH_4Cl.) So here too, the effect of adding $(NH_4)_2SO_4$ is to make additional NH_4Cl dissolve, at least at first.

Figure 5D.5
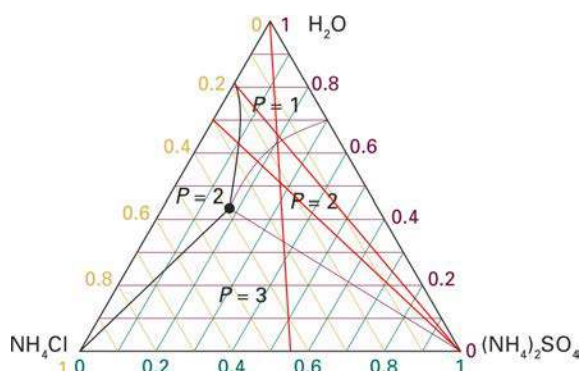
(ii) First convert to moles for a convenient sample size, such as 100 g, and find composition by mole fraction.

NH_4Cl:
$$25\ \text{g} \times \frac{1\ \text{mol}}{53.49\ \text{g}} = 0.46\overline{7}\ \text{mol}$$

$(NH_4)_2SO_4$:
$$75\ \text{g} \times \frac{1\ \text{mol}}{132.15\ \text{g}} = 0.56\overline{8}\ \text{mol}$$

To get mole fractions, divide these amounts by the total amount of 1.03 mol:

$$x(NH_4Cl) = \frac{0.46\overline{7}\ \text{mol}}{1.03\ \text{mol}} = 0.45 \qquad x((NH_4)_2SO_4) = 0.55$$

So the system's starting point is on the baseline of the triangle, and the path it traverses joins the initial point on the baseline to the H$_2$O vertex. As soon as water is introduced, a third (saturated aqueous) phase is formed in equilibrium with two solid phases. As more water is added, one of the solid phases disappears, and the two remaining phases consist of a saturated aqueous phase and a solid rich in (NH$_4$)$_2$SO$_4$. Eventually, as still more water is added, that solid phase also disappears, leaving a single aqueous phase at x(H$_2$O) ≥ 0.63.

Solutions to problem

5D.2   **(i)** The phase diagram is shown in Figure 5D.6.

Figure 5D.6
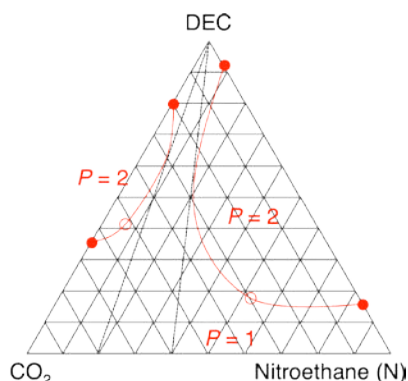
(ii) Lines from the baseline (the CO$_2$-nitroethane edge) to the DEC vertex represent compositions obtained by adding DEC to a CO$_2$-nitroethane mixture. Such lines that avoid two-phase regions represent compositions of CO$_2$ and nitroethane to which addition of DEC can cause no phase separation. The range of such CO$_2$-nitroethane compositions can be found by drawing lines from the DEC vertex to the baseline **tangent** to the two-phase arcs. On Figure 5.26, the dashed lines are tangent to the two two-phase regions, and they intersect the baseline at $x = 0.2$ and $x = 0.4$ (where x is mole fraction of nitroethane). So binary CO$_2$-nitroethane compositions between these would show no phase separation if DEC is added to them in any amount. (Keep in mind, though, that the phase boundaries here are sketched, not plotted, so the tangent lines are only approximate.)

5E   Activities

Answers to discussion question

5E.2   Raoult's law [5A.21] assumes that the vapor pressure of a solvent in solution (or of a liquid in a mixture of liquids) is simply its pure-substance vapor pressure multiplied by its mole fraction in the mixture. That is, it assumes that the intermolecular interactions that produce equilibrium between pure liquid and vapor are unchanged except for the fact that only a fraction of the molecules in the liquid are molecules of the species of interest. In effect, Raoult's law predicts vapor pressure based on pure-liquid vapor pressure and composition (mole fraction):

$p_A = p_A^* x_A$

For real solutions, on the other hand, we modify Raoult's law to say, in effect, whatever the vapor pressure *really* is, let us use that to define an "effective" mole fraction. Raoult's law implies

$$\frac{p_A}{p_A^*} = x_A$$

We modify this relationship to define activity:

$$\frac{p_A}{p_A^*} = a_A \quad [5E.2]$$

Solutions to exercises

5E.1(b) Let A = water and B = solute.

$$a_A = \frac{p_A}{p_A^*} \; [5E.2] = \frac{0.02239 \text{ atm}}{0.02308 \text{ atm}} = \boxed{0.9701}$$

$$\gamma_A = \frac{a_A}{x_A} [5E.4] \text{ and } x_A = \frac{n_A}{n_A + n_B}$$

$$n_A = \frac{920 \text{ g}}{18.02 \text{ g mol}^{-1}} = 51.1 \text{ mol} \quad n_B = \frac{122 \text{ g}}{241 \text{ g mol}^{-1}} = 0.506 \text{ mol}$$

So $\quad x_A = \dfrac{51.1}{51.1 + 0.506} = 0.990 \quad$ and $\quad \gamma_A = \dfrac{0.9701}{0.990} = \boxed{0.980}$

5E.2(b) From eqn 1A.8 (partial pressures) and y_A we can compute the partial pressures:

$$y_A = \frac{p_A}{p_A + p_B} = \frac{p_A}{101.3 \text{ kPa}} = 0.314$$

So $\quad p_A = 101.3 \text{ kPa} \times 0.314 = 31.8 \text{ kPa}$
and $\quad p_B = 101.3 \text{ kPa} - 31.8 \text{ kPa} = 69.5 \text{ kPa}$

$$a_A = \frac{p_A}{p_A^*} \; [5E.2] = \frac{31.8 \text{ kPa}}{73.0 \text{ kPa}} = \boxed{0.436} \quad \text{and} \quad a_B = \frac{p_B}{p_B^*} = \frac{69.5 \text{ kPa}}{92.1 \text{ kPa}} = \boxed{0.755}$$

$$\gamma_A = \frac{a_A}{x_A} \; [5E.4] = \frac{0.436}{0.220} = \boxed{1.98} \quad \text{and} \quad \gamma_B = \frac{a_B}{x_B} = \frac{0.755}{0.780} = \boxed{0.967}$$

5E.3(b) The biological standard state is defined as pH 7, which implies $a_{H^+} = 10^{-7}$. All other activities in the biological standard state are unity, just as in the chemical standard state; in the chemical standard state, $a_{H^+} = 1 = 10^0$ as well (which implies pH 0). As a result, the biological standard molar Gibbs function for H$^+$ is lower than that of the chemical standard by 7 RT ln 10 [5E.16], which is equal to 39.96 kJ mol^{-1} at 25°C [*Brief illustration* 5E.3]. For the given reaction, the standard Gibbs energy is

$$\Delta G^{\ominus} = \Delta_f G^{\ominus}(B) + 4\Delta_f G^{\ominus}(H^+) - 2\Delta_f G^{\ominus}(A)$$

The biological standard is

$$\Delta G^{\oplus} = \Delta_f G^{\oplus}(B) + 4\Delta_f G^{\oplus}(H^+) - 2\Delta_f G^{\oplus}(A)$$
$$= \Delta_f G^{\ominus}(B) + 4\{\Delta_f G^{\ominus}(H^+) - 39.96 \text{ kJ mol}^{-1}\} - 2\Delta_f G^{\ominus}(A)$$
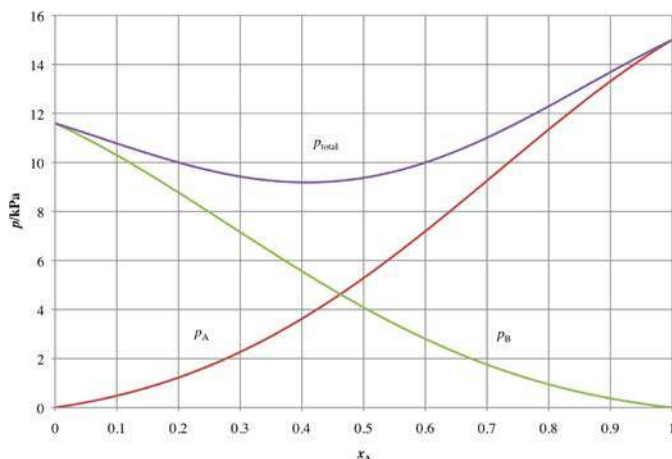
Comparing the two, we have

$$\Delta G^{\oplus} - \Delta G^{\ominus} = -4 \times 39.96 \text{ kJ mol}^{-1} = \boxed{-159.84 \text{ kJ mol}^{-1}}$$

5E.4(b) The partial pressures of both components are given by eqn 5E.19

$$p_J = p_J^* x_J e^{\xi(1-x_J)^2}$$

The total pressure is the sum of the two partial pressures. The vapor-pressure diagram is plotted in Figure 5E.1.

Figure 5E.1

Comment. The figure shows that upon adding the other component to either pure component, the vapor pressure falls (as is evident from the fact that the total pressure decreases as one moves from either edge of the graph). This is consistent with the physical interpretation given in Topic 5E.3: negative ξ corresponds to exothermic mixing, reflecting favorable interactions between the components.

Solutions to problems

5E.2
$$\phi = -\frac{x_A}{x_B}\ln a_A = -\frac{\ln a_A}{r} \tag{a}$$

Therefore, $\mathrm{d}\phi = -\frac{1}{r}\mathrm{d}\ln a_A + \frac{1}{r^2}\ln a_A \mathrm{d}r$

and $\quad \mathrm{d}\ln a_A = \frac{1}{r}\ln a_A \mathrm{d}r - r\mathrm{d}\phi$. $\tag{b}$

Now the Gibbs–Duhem equation [5A.12a], implies
$$x_A\mathrm{d}\mu_A + x_B\mathrm{d}\mu_B = 0 .$$
Since $\mu = \mu^* + RT\ln a$,
$$x_A \,\mathrm{d}\ln a_A + x_B \,\mathrm{d}\ln a_B = 0 .$$
Therefore $\mathrm{d}\ln a_B = -\dfrac{x_A}{x_B}\mathrm{d}\ln a_A = -\dfrac{\mathrm{d}\ln a_A}{r} = -\dfrac{1}{r^2}\ln a_A\ \mathrm{d}r + \mathrm{d}\phi$ [from (b)]

$$= \frac{\phi}{r}\mathrm{d}r + \mathrm{d}\phi\ \text{[from (a)]} = \phi\ \mathrm{d}\ln r + \mathrm{d}\phi$$

Subtract $\mathrm{d}\ln r$ from both sides, to obtain
$$\mathrm{d}\ln\frac{a_B}{r} = (\phi-1)\,\mathrm{d}\ln r + \mathrm{d}\phi = \frac{(\phi-1)}{r}\mathrm{d}r + \mathrm{d}\phi .$$

Integrate both sides of the equality from pure A (where $r = 0$) to an arbitrary composition:
$$\int \mathrm{d}\ln\frac{a_B}{r} = \int \frac{(\phi-1)}{r}\mathrm{d}r + \int \mathrm{d}\phi$$

The lower limit of the left-hand integral is:
$$\lim_{r\to 0}\ln\left(\frac{a_B}{r}\right) = \lim_{r\to 0}\ln\left(\frac{\gamma_B x_B}{r}\right) = \lim_{r\to 0}\ln(\gamma_B x_A) = \ln 1 = 0 ,$$

leaving the desired expression
$$\ln\frac{a_B}{r} = \boxed{\phi - \phi(0) + \int_0^r \left(\frac{\phi-1}{r}\right)\mathrm{d}r}$$

5E.4 The partial pressure compared to its pure substance value, according to eqn 5E.19, is
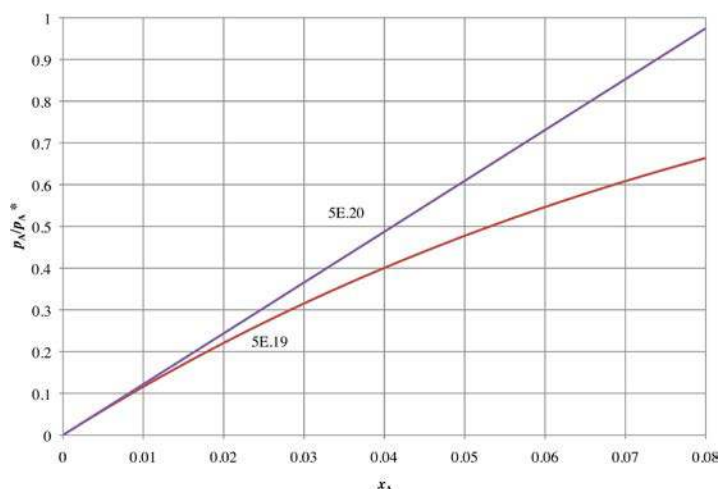$$p_A / p_A^* = x_A \mathrm{e}^{\xi(1-x_A)^2}$$
For small x_A, this becomes approximately [5E.20]
$$p_A / p_A^* \approx x_A \mathrm{e}^{\xi}$$

Certainly one would not expect this expression to hold over the entire range of compositions. In fact, the two equations differ pretty quickly, particularly for relatively large values of ξ. These two equations are plotted against x_A in Figure 5E.2.

Figure 5E.2

At $x_A > \boxed{0.019}$, eqn 5E.20 exceeds 5E.19 by more than 10 per cent.

5F   The activities of ions

Answers to discussion question

5F.2   The Debye-Hückel theory of electrolyte solutions formulates deviations from ideal behavior (essentially, deviations due to electrostatic interactions) in terms of the work of charging the ions. The assumption is that the solute particles would behave ideally if they were not charged, and the difference in chemical potential between real and ideal behavior amounts to the work of putting electrical charges onto the ions. (Recall [Topic 3C.1(e)] that the Gibbs function is associated with maximum non-expansion work.) To find the work of charging, the distribution of ions must be found, and that is done using the shielded Coulomb potential [5F.15], which takes into account the ionic strength of the solution and the dielectric constant of the solvent. Details of the derivation are found in Topic 5F.2 (particularly in the *Justifications*). The Debye-Hückel limiting law [5F.19b] (valid only for dilute solutions because of some truncated series expansions) gives a mean ionic activity coefficient that depends on the charges of the ions involved, the ionic strength of the solution, and on a constant [5F.20] that takes into account solvent properties and temperature.

Solutions to exercises

5F.1(b)   The definition of ionic strength is

$$I = \frac{1}{2} \sum_i \left(\frac{b_i}{b^\ominus} \right) z_i^2 \quad \text{[5F.9]}$$

and if b is the molal concentration of an M_pX_q salt, the molal concentrations of the ions are

$$b_M = p \times b \qquad \text{and} \qquad b_X = q \times b \ .$$

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

For $K_3[Fe(CN)_6]$ $\ I = \frac{1}{2} (3 \times 1^2 + 1 \times 3^2) \left(\frac{b}{b^\ominus} \right) = 6 \left(\frac{b}{b^\ominus} \right)$

For KCl and NaBr (and any other compound of monovalent ions)

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

Thus, for this mixture

$$I = I(K_3[Fe(CN)_6]) + I(KCl) + I(NaBr)$$

$$= 6\left(\frac{b(K_3[Fe(CN)_6])}{b^{\ominus}}\right) + \frac{b(KCl)}{b^{\ominus}} + \frac{b(NaBr)}{b^{\ominus}}$$

$$= (6) \times (0.040) + (0.030) + (0.050) = \boxed{0.320}$$

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 $\frac{1}{2}\left(\frac{b_i}{b^{\ominus}}\right)z_i^2$ for each individual ion as in the definition of I [5F.9].

Question. Can you establish that the comment holds for this exercise? Note that the term for K^+ in a sum over ions includes ions from two different salts.

5F.2(b) The original KNO_3 solution has an ionic strength of 0.110. (For compounds of monovalent ions, the ionic strength is numerically equal to the molal concentration, as shown in Exercise 5F.1(b).) Therefore, the ionic strengths of the added salts must be 0.890.

(i) The salt to be added is monovalent, so an additional 0.890 mol kg^{-1} must be dissolved. The mass that must be added is therefore

$$(0.500 \text{ kg}) \times (0.890 \text{ mol kg}^{-1}) \times (101.11 \text{ g mol}^{-1}) = \boxed{45.0 \text{ g}}.$$

(ii) For $Ba(NO_3)_2$ $\qquad I = \frac{1}{2}(1 \times 2^2 + 2 \times 1^2)\left(\frac{b}{b^{\ominus}}\right)$ [5F.9]$= 3\left(\frac{b}{b^{\ominus}}\right)$

Therefore, the solution should be made 0.890 mol kg^{-1}/3 = 0.297 mol kg^{-1} in $Ba(NO_3)_2$. The mass that should be added to 500 g of the solution is therefore

$$(0.500 \text{ kg}) \times (0.297 \text{ mol kg}^{-1}) \times (261.32 \text{ g mol}^{-1}) = \boxed{38.8 \text{ g}}.$$

5F.3(b) The solution is dilute, so use the Debye–Hückel limiting law.

$$\log \gamma_{\pm} = -|z_+ z_-| A I^{1/2} \text{ [5F.8]}$$

$$I = \frac{1}{2}\sum_i \left(\frac{b_i}{b^{\ominus}}\right)z_i^2 \text{[5F.9]} = \frac{1}{2}\{(0.020 \times 1^2) + (0.020 \times 1^2) + (0.035 \times 2^2) + (2 \times 0.035 \times 1^2)\}$$

$$= 0.125$$

For NaCl:

$$\log \gamma_{\pm} = -1 \times 1 \times 0.509 \times (0.125)^{1/2} = -0.180 \qquad \text{so} \qquad \gamma_{\pm} = \boxed{0.66}.$$

The activities of the ions are

$$a(Na^+) = a(Cl^-) = \gamma_{\pm} b/b^{\circ} = 0.66 \times 0.020 = \boxed{0.013}$$

Question: What are the activity coefficients and activities of $Ca(NO_3)_2$ in the same solution?

5F.4(b) The extended Debye–Hückel law [5F.11a] is

$$\log \gamma_{\pm} = -\frac{A|z_+ z_-| I^{1/2}}{1 + BI^{1/2}}$$

Solving for B.

$$B = -\left(\frac{1}{I^{1/2}} + \frac{A|z_+ z_-|}{\log \gamma_{\pm}}\right) = -\left(\frac{1}{(b/b^{\ominus})^{1/2}} + \frac{0.509}{\log \gamma_{\pm}}\right)$$

Draw up the following table

b / (mol kg^{-1})	5.0×10^{-3}	10.0×10^{-3}	50.0×10^{-3}
$\gamma_{\pm}$	0.927	0.902	0.816
B	1.32	1.36	1.29

The values of B are reasonably constant, illustrating that the extended law fits these activity coefficients with $B = \boxed{1.3}$.
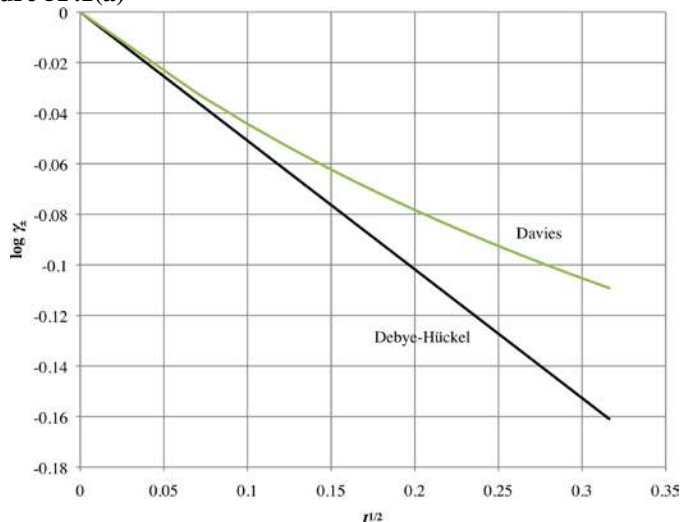
Solutions to problem

5F.2   Specialized to 1,1 electrolytes, the Davies equation with $C = 0$ and Debye-Hückel limiting law are, respectively

$$\log \gamma_\pm = -\frac{AI^{1/2}}{1 + BI^{1/2}} \ [5F.11b] \qquad \text{and}$$

$$\log \gamma_\pm = -0.509 I^{1/2} [5F.8] = -0.509 \left(\frac{b}{b^{\ominus}}\right)^{1/2} [5F.9]$$

Figure 5F.1(a) shows a plot of $\log \gamma_\pm$ vs. $I^{1/2}$ for both equations.

Figure 5F.1(a)

It is clear that the values plotted differ by about 50% at the right side of the figure; however, note that the values plotted are $\log \gamma_\pm$ and not $\gamma_\pm$. Figure 5F.1(b) shows a plot of $\gamma_\pm$ vs. $I^{1/2}$ for both equations. Toward the right side of this graph, one can see that the values plotted differ by about 10%. To be exact, for $I < \boxed{0.086}$, the limiting law predicts activity coefficients within 10% of those predicted by the extended law.
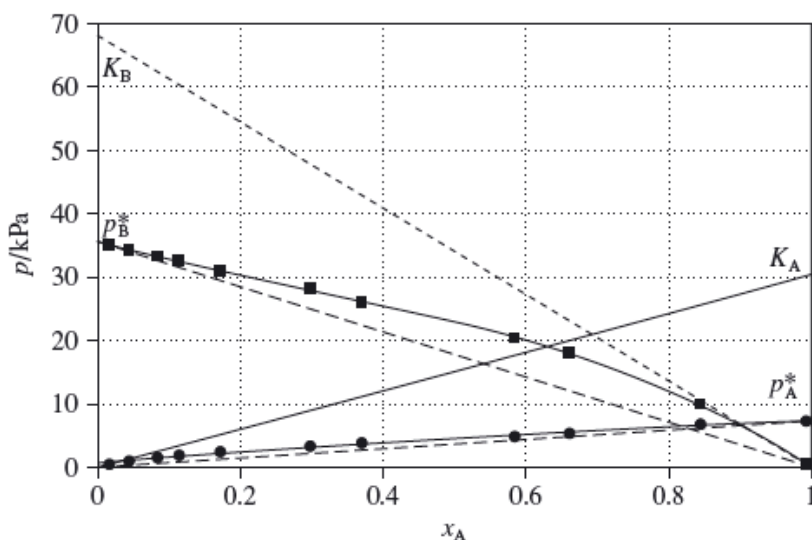
Figure 5F.1(b)
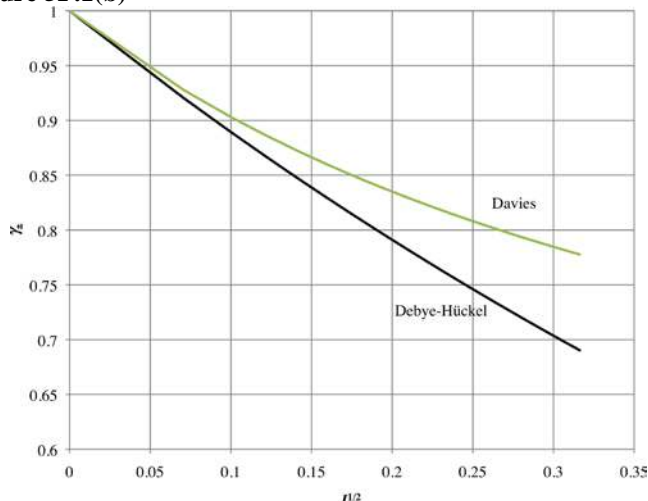
Integrated activities

5.2   The data are plotted in Figure I5.1. The dotted lines correspond to Henry's law vapour pressures and the dashed lines to Raoult's law; the solid curves represent the experimental data.

Figure I5.1

On a Raoult's law basis, $a = \dfrac{p}{p^*}$ [5E.2] and $a = \gamma x$ [5E.4], so $\gamma = \dfrac{p}{xp^*}$. On a Henry's law

basis, $a = \dfrac{p}{K}$ [5E.10], so $\gamma = \dfrac{p}{xK}$. The vapour pressures of the pure components are not given in the table of data, so we extrapolate the experimental data to obtain $p^*_A = 7.3$ kPa and $p^*_B = 35.6$ kPa. The Henry's law constant for benzene is determined by extrapolating the low-B data to $x_B = 1$, $i.e.$, to $x_A = 0$. (The Henry's law constant for acetic acid can also be determined by extrapolating the low-A data to $x_A = 1$) The values obtained are $K_B = 68.1$ kPa and $K_A = 30.3$ kPa. Then draw up the following table based on the partial pressures given in the data.

x_A	0.016	0.0439	0.0835	0.1138	0.1714
p_A/kPa	0.484	0.967	1.535	1.89	2.45
p_A/kPa	35.05	34.29	33.28	32.64	30.9
a_A(R)	0.066	0.132	0.210	0.259	0.336 $[p_A/p^*_A]$
a_B(R)	0.985	0.963	0.935	0.917	0.868 $[p_B/p^*_B]$
γ_A(R)	4.144	3.017	2.518	2.275	1.958 $[p_A/x_Ap^*_A]$
γ_B(R)	1.001	1.007	1.020	1.035	1.048 $[p_B/x_Bp^*_B]$
a_B(H)	0.515	0.504	0.489	0.479	0.454 $[p_B/K_B]$
γ_B(H)	0.523	0.527	0.533	0.541	0.548 $[p_B/x_BK_B]$

x_A	0.2973	0.3696	0.5834	0.6604	0.8437	0.9931
p_A/kPa	3.31	3.83	4.84	5.36	6.76	7.29
p_A/kPa	28.16	26.08	20.42	18.01	10	0.47
a_A(R)	0.453	0.525	0.663	0.734	0.926	0.999
a_B(R)	0.791	0.733	0.574	0.506	0.281	0.013
γ_A(R)	1.525	1.420	1.136	1.112	1.098	1.006
γ_B(R)	1.126	1.162	1.377	1.490	1.797	1.913
a_B(H)	0.414	0.383	0.300	0.264	0.147	0.007
γ_B(H)	0.588	0.607	0.720	0.779	0.939	1.000

G^E is defined [5B.5] as

$$G^E = \Delta_{mix}G - \Delta_{mix}G^{ideal} = nRT(x_A \ln a_A + x_B \ln a_B) - nRT(x_A \ln x_A + x_B \ln x_B)$$

and with $a = \gamma x$

$$G^E = nRT(x_A \ln \gamma_A + x_B \ln \gamma_B).$$

For $n = 1$, we can draw up the following table from the information above and

$$RT = 8.3145 \text{ J mol}^{-1} \text{ K}^{-1} \times 323 \text{ K} = 2.69 \times 10^3 \text{ J mol}^{-1} = 2.69 \text{ kJ mol}^{-1}.$$

x_A	0.016	0.0439	0.0835	0.1138	0.1714
$x_A \ln \gamma_A$	0.023	0.0485	0.077	0.094	0.115
$x_b \ln \gamma_B$(R)	0.001	0.0071	0.018	0.030	0.038

G^E / kJ mol^{-1}	0.0626	0.1492	0.256	0.332	0.413

x_A	0.2973	0.3696	0.5834	0.6604	0.8437	0.9931
$x_A \ln \gamma_A$	0.125	0.129	0.075	0.070	0.079	0.006
$x_b \ln \gamma_B(R)$	0.083	0.095	0.133	0.135	0.092	0.004
G^E / kJ mol^{-1}	0.560	0.602	0.558	0.551	0.457	0.027

Question. In this problem both A and B were treated as solvents, but only B as a solute. Extend the table by including a row for $\gamma_A(H)$.

5.4 $p_A = a_A p_A^* $ [5E.2] $= \gamma_A x_A p_A^*$ [5E.4]

so $\qquad \gamma_A = \dfrac{p_A}{x_A p_A^*} = \dfrac{y_A p}{x_A p_A^*}$

Sample calculation at 80 K:

$$\gamma(O_2) = \frac{0.11 \times 100\,\text{kPa}}{0.34 \times 225\,\text{Torr}} \times \left(\frac{760\,\text{Torr}}{101.325\,\text{kPa}}\right) = 1.079$$

Summary

T/K	77.3	78	80	82	84	86	88	90.2
$\gamma(O_2)$	—	0.877	1.079	1.039	0.995	0.993	0.990	0.987

To within the experimental uncertainties the solution appears to be ideal ($\gamma = 1$). The low value at 78 K may be caused by nonideality; however, the larger relative uncertainty in $y(O_2)$ is probably the origin of the low value.

A temperature–composition diagram is shown in Figure I5.2(a). The near ideality of this solution is, however, best shown in the pressure–composition diagram of Figure I5.2(b). The liquid line is essentially a straight line as predicted for an ideal solution.
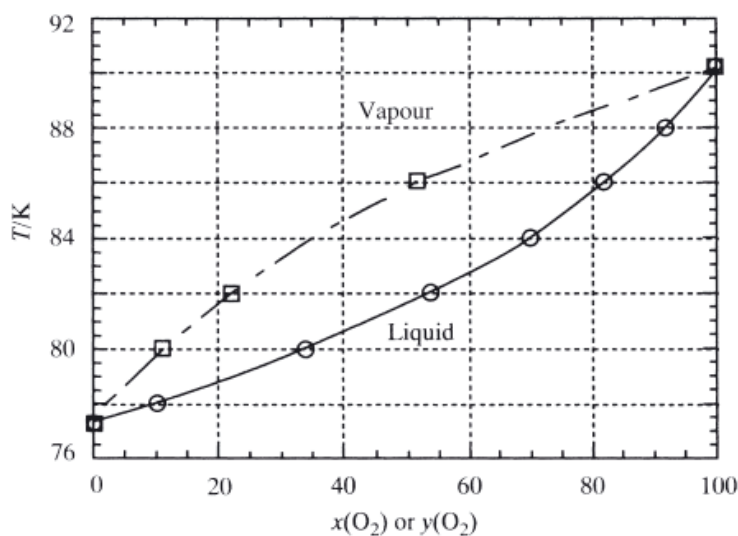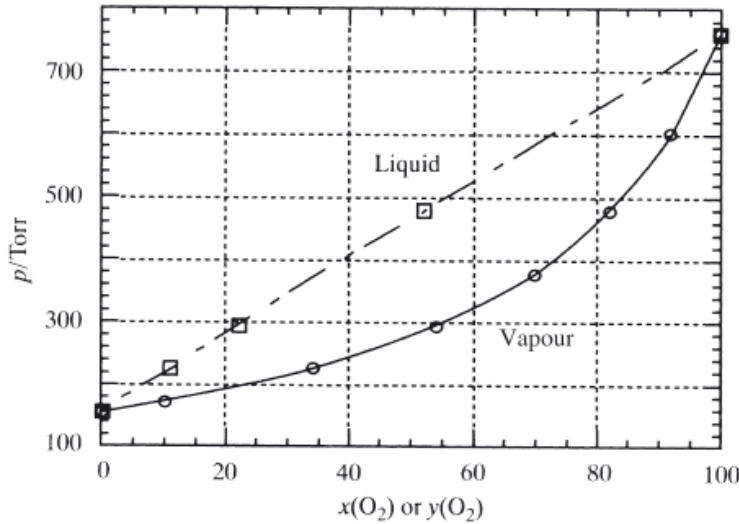
Figure I5.2(a)

Figure I5.2(b)

5.6 The Gibbs-Duhem equation applies to any partial molar quantity, so we start, as in Example 5A.2, with

$$n_A\, dV_A + n_B\, dV_B = 0$$

Hence $dV_B = -\dfrac{n_A}{n_B}dV_A$

Therefore, by integration,

$$V_B(x_A,x_B) - V_B(0,1) = \int_{V_B(0,1)}^{V_B(x_A,x_B)} dV_B = -\int_{V_A(0,1)}^{V_A(x_A,x_B)} \frac{n_A}{n_B}dV_A = -\int_{V_A(0,1)}^{V_A(x_A,x_B)} \frac{nx_A dV_A}{n(1-x_A)}$$

The notation V_B^* means the molar volume of pure B, which is the same as the partial molar volume of B when $x_B = 1$. Therefore,

$$V_B(x_A,x_B) = V_B^* - \int_{V_A(0,1)}^{V_A(x_A,x_B)} \frac{x_A dV_A}{1-x_A}.$$

We must now plot $x_A/(1 - x_A)$ against V_A and estimate the integral. That means we must first find the partial molar volumes of chloroform (V_A) that corresponds to various chloroform mole fractions (x_A). At constant temperature and pressure,

$$V_A = \left(\frac{\partial V}{\partial n_A}\right)_{n_B} \text{[5A.1]} = \left(\frac{\partial (nV_m)}{\partial (nx_A)}\right)_{n_B} \text{ where } n = n_A + n_B \text{ is the total number of moles.}$$

Thus, V_A is the tangent line to the curve of a plot of V vs. n_A for a constant value of n_B. For convenience, let $n_B = 1$ mol. Then we can draw up a table of V, n, and n_A values using the V_m, x_A data given and the relationship

$$x_A = \frac{n_A}{n} = \frac{n_A}{n_A + 1\text{ mol}}.$$

Solving for n_A yields $n_A = \dfrac{x_A}{1-x_A} \times 1\text{ mol}$

x_A	0	0.194	0.385	0.559	0.788	0.889	1
$V_m/(\text{cm}^3\text{ mol}^{-1})$	73.99	75.29	76.5	77.55	79.08	79.82	80.67
n_A/mol	0	0.241	0.626	1.268	3.717	8.009	
n/mol	1	1.241	1.626	2.268	4.717	9.009	
V/cm^3	73.99	93.41	124.4	175.9	373.0	719.1	

Figure I5.3(a)
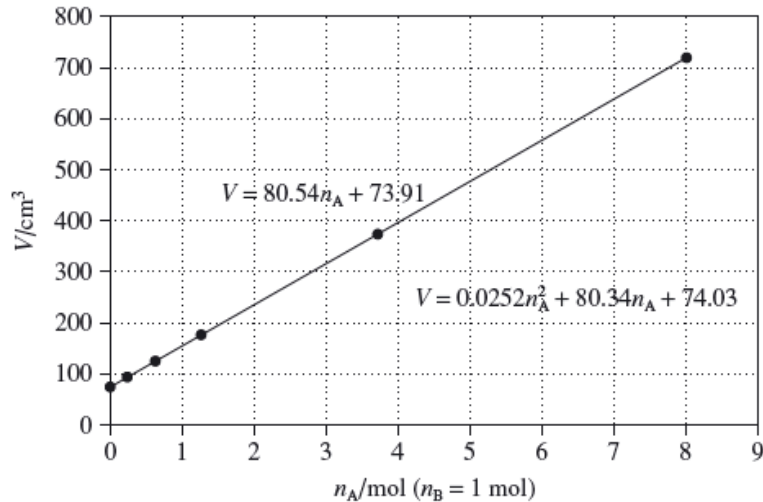
In Figure I5.3(a), we plot V against n_A. Both linear and quadratic fits to the data are shown. The data fit a straight line quite well; however, the slope of a straight line is constant, which would imply V_A is constant (at 80.54 cm^3 mol^{-1}) over this range of compositions. We require some variation in V_A, so we use the quadratic fit,

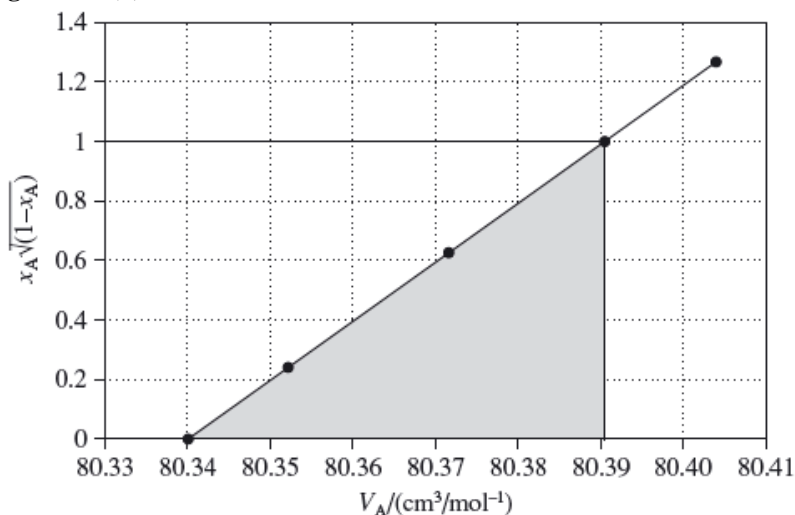$$V/\text{cm}^3 = 0.0252(n_A/\text{mol})^2 + 80.34(n_A/\text{mol}) + 74.03 \,,$$

which leads to

$$V_A = \left(\frac{\partial V}{\partial n_A}\right)_{n_B} = \{2 \times 0.0252(n_A / \text{mol}) + 80.34\} \text{ cm}^3 \text{ mol}^{-1}$$

Finally, we can draw up the table, including $x_A = 0.500$

x_A	0	0.194	0.385	0.500	0.559	0.788	0.889
$V_A/(\text{cm}^3 \text{ mol}^{-1})$	80.34	80.35	80.37	80.39	80.40	80.53	80.74

For the present purpose we integrate up to $V_A(0.5,0.5) = 84.39$ cm^3 mol^{-1}.

Figure I5.3(b)

The points are plotted in Figure I5.3(b), and the area required is 0.025 cm^3 mol^{-1}. Hence,

$$V_B(0.5,0.5) = 73.99 \text{ cm}^3 \text{ mol}^{-1} - 0.025 \text{ cm}^3 \text{ mol}^{-1} = \boxed{73.96 \text{ cm}^3 \text{ mol}^{-1}}.$$

Comment. The integral derived at the start of this problem is most useful for computing the partial molar quantity of one component given that of the other. In this case, the data given were overall molar volumes, from which we had to compute V_A before we could apply the integral to compute V_B. In such a case, it would have been easier to compute V_B directly in the same way we computed V_A.

5.8 In this case it is convenient to rewrite the Henry's law expression as

$$\text{mass of N}_2 = p_{N_2} \times \text{mass of H}_2\text{O} \times K_{N_2}$$

(1) At $p_{N_2} = 0.78 \times 4.0$ atm $= 3.1$ atm

mass of $N_2 = 3.1$ atm $\times 100$ g $H_2O \times 0.18$ μg N_2 / (g H_2O atm) $= \boxed{56 \ \mu\text{g N}_2}$

(2) At $p_{N_2} = 0.78$ atm, mass of $N_2 = \boxed{14 \ \mu\text{g N}_2}$

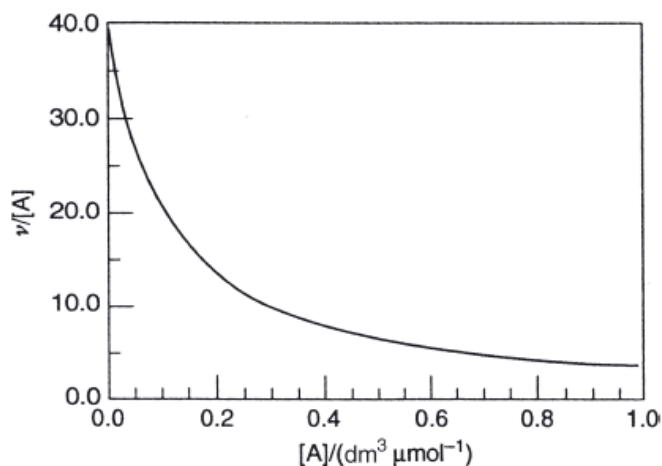(3) In fatty tissue the increase in N_2 concentration from 1 atm to 4 atm is

$$4 \times (56 - 14)\mu\text{g N}_2 = \boxed{1.7 \times 10^2 \ \mu\text{g N}_2}$$

5.10 **(a)** The sum has just one term, so

$$\frac{v}{[A]_{\text{out}}} = \frac{NK}{1 + K[A]_{\text{out}}} = \frac{4.0 \times 10^7 \ \text{dm}^3 \ \text{mol}^{-1}}{1 + (1.0 \times 10^7 \ \text{dm}^3 \ \text{mol}^{-1})[A]_{\text{out}}} = \frac{40 \ \text{dm}^3 \ \mu\text{mol}^{-1}}{1 + (10 \ \text{dm}^3 \ \mu\text{mol}^{-1})[A]_{\text{out}}}$$

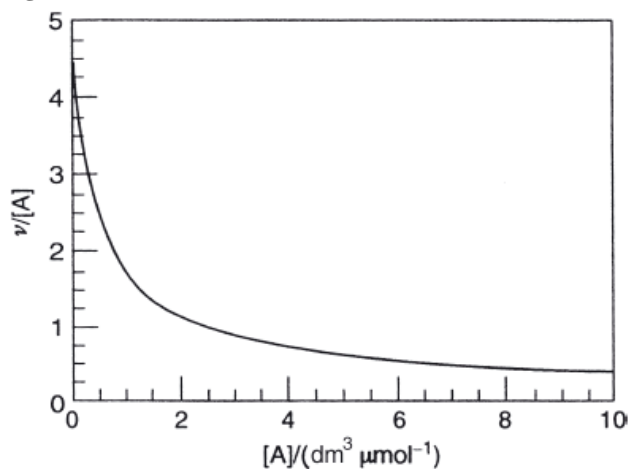The plot is shown in Figure I5.4(a).

Figure I5.4(a)

(b) There are two terms in the sum here

$$\frac{v}{[A]_{\text{out}}} = \frac{4 \times (1 \times 10^5 \ \text{dm}^3 \ \text{mol}^{-1})}{1 + (1 \times 10^5 \ \text{dm}^3 \ \text{mol}^{-1}) \times [A]_{\text{out}}} + \frac{2 \times (2 \times 10^6 \ \text{dm}^3 \ \text{mol}^{-1})}{1 + (2 \times 10^6 \ \text{dm}^3 \ \text{mol}^{-1}) \times [A]_{\text{out}}}$$

$$= \frac{0.4 \ \text{dm}^3 \ \mu\text{mol}^{-1}}{1 + (0.1 \ \text{dm}^3 \ \mu\text{mol}^{-1}) \times [A]_{\text{out}}} + \frac{4 \ \text{dm}^3 \ \mu\text{mol}^{-1}}{1 + (2 \ \text{dm}^3 \ \mu\text{mol}^{-1}) \times [A]_{\text{out}}}$$

The plot is shown in Figure I5.4(b).

Figure I5.4(b)

5.12 Kevlar is a polyaromatic amide. Phenyl groups provide aromaticity and a planar, rigid structure. The amide group is expected to be like the peptide bond that connects amino acid residues within protein molecules. This group is also planar because resonance produces

partial double bond character between the carbon and nitrogen atoms. There is a substantial energy barrier preventing free rotation about the CN bond. The two bulky phenyl groups on the ends of an amide group are trans because steric hinderance makes the cis conformation unfavourable. See Figure I5.5(a).

Figure I5.5(a)
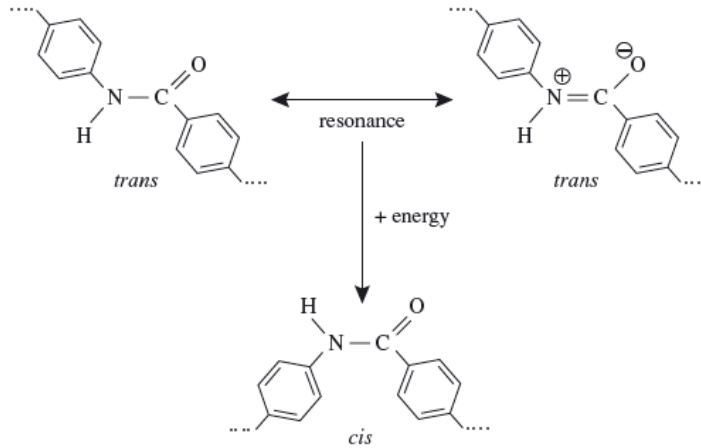
The flatness of the Kevlar polymeric molecule makes it possible to process the material so that many molecules with parallel alignment form highly ordered, untangled crystal bundles. The alignment makes possible both considerable van der Waals attractions between adjacent molecules and for strong hydrogen bonding between the polar amide groups on adjacent molecules. These bonding forces create the high thermal stability and mechanical strength observed in Kevlar. See Figure I5.5(b).

Figure I5.5(b)
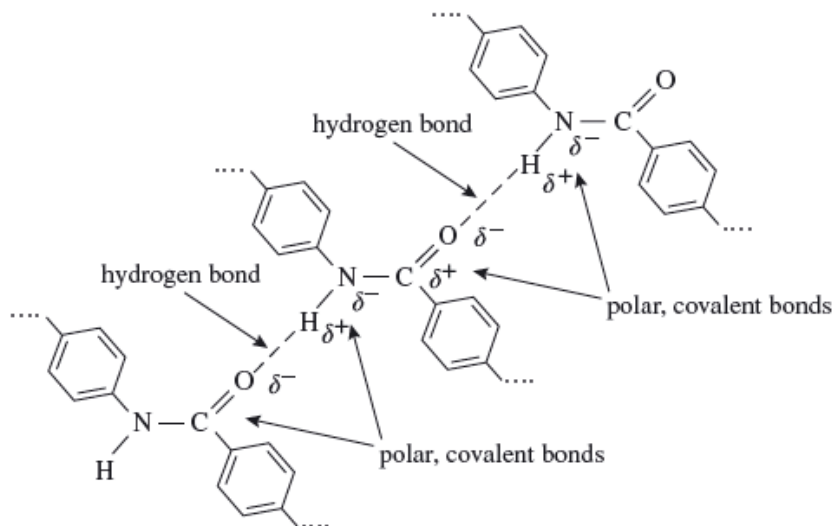
Kevlar is able to absorb great quantities of energy, such as the kinetic energy of a speeding bullet, through hydrogen bond breakage and the transition to the cis conformation.