

## 7 Simple mixtures

### Solutions to exercises

#### Discussion questions

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- E7.1(b)** For a component in an ideal solution, Raoult's law is:  $p = xp^*$ . For real solutions, the activity,  $a$ , replaces the mole fraction,  $x$ , and Raoult's law becomes  $p = ap^*$ .
- E7.2(b)** All the colligative properties are a result of 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 Fig. 7.20 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.
- E7.3(b)** The activity of a solute is that property which determines how the chemical potential of the solute varies from its value in a specified reference state. This is seen from the relation  $\mu = \mu^\ominus + RT \ln a$ , where  $\mu^\ominus$  is the value of the chemical potential in the reference state. The reference state is either the hypothetical state where the pure solute obeys Henry's law (if the solute is volatile) or the hypothetical state where the solute at unit molality obeys Henry's law (if the solute is involatile). The activity of the solute can then be defined as that physical property which makes the above relation true. It can be interpreted as an effective concentration.

#### Numerical exercises

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- E7.4(b)** Total volume  $V = n_A V_A + n_B V_B = n(x_A V_A + x_B V_B)$   
Total mass  $m = n_A M_A + n_B M_B$   
 $= n(x_A M_A + (1 - x_A) M_B)$  where  $n = n_A + n_B$   
$$\frac{m}{x_A M_A + (1 - x_A) M_B} = n$$
$$n = \frac{1.000 \text{ kg}(10^3 \text{ g/kg})}{(0.3713) \times (241.1 \text{ g/mol}) + (1 - 0.3713) \times (198.2 \text{ g/mol})} = 4.670\bar{1} \text{ mol}$$
$$V = n(x_A V_A + x_B V_B)$$
$$= (4.670\bar{1} \text{ mol}) \times [(0.3713) \times (188.2 \text{ cm}^3 \text{ mol}^{-1}) + (1 - 0.3713) \times (176.14 \text{ cm}^3 \text{ mol}^{-1})]$$
$$= \boxed{843.5 \text{ cm}^3}$$
- E7.5(b)** Let A denote water and B ethanol. The total volume of the solution is  $V = n_A V_A + n_B V_B$   
We know  $V_B$ ; we need to determine  $n_A$  and  $n_B$  in order to solve for  $V_A$ .  
Assume we have  $100 \text{ cm}^3$  of solution; then the mass is  
$$m = \rho V = (0.9687 \text{ g cm}^{-3}) \times (100 \text{ cm}^3) = 96.87 \text{ g}$$
  
of which  $(0.20) \times (96.87 \text{ g}) = 19.\overline{374} \text{ g}$  is ethanol and  $(0.80) \times (96.87 \text{ g}) = 77.\overline{496} \text{ g}$  is water.  
$$n_A = \frac{77.\overline{496} \text{ g}}{18.02 \text{ g mol}^{-1}} = 4.3\bar{0} \text{ mol H}_2\text{O}$$
$$n_B = \frac{19.\overline{374} \text{ g}}{46.07 \text{ g mol}^{-1}} = 0.42\bar{05} \text{ mol ethanol}$$

$$\frac{V - n_B V_B}{n_A} = V_A = \frac{100 \text{ cm}^3 - (0.4205 \text{ mol}) \times (52.2 \text{ cm}^3 \text{ mol}^{-1})}{4.30 \text{ mol}} = 18.15 \text{ cm}^3$$

$$= \boxed{18 \text{ cm}^3}$$

**E7.6(b)** Check that  $p_B/x_B = \text{a constant } (K_B)$

$x_B$	0.010	0.015	0.020
$(p_B/x_B)/\text{kPa}$	$8.2 \times 10^3$	$8.1 \times 10^3$	$8.3 \times 10^3$

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

**E7.7(b)** In exercise 7.6(b), the Henry's law constant was determined for concentrations expressed in mole fractions. Thus the concentration in molality must be converted to mole fraction.

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

$$n(\text{A}) = \frac{1000 \text{ g}}{74.1 \text{ g mol}^{-1}} = 13.50 \text{ mol} \quad n(\text{B}) = 0.25 \text{ mol}$$

Therefore,

$$x_B = \frac{0.25 \text{ mol}}{0.25 \text{ mol} + 13.50 \text{ mol}} = 0.0182$$

using  $K_B = 8.2 \times 10^3 \text{ kPa}$  [exercise 7.6(b)]

$$p = 0.0182 \times 8.2 \times 10^3 \text{ kPa} = \boxed{1.5 \times 10^2 \text{ kPa}}$$

**E7.8(b)**

$$K_f = \frac{RT^*2M}{\Delta_{\text{fus}}H} = \frac{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times (354 \text{ K})^2 \times 0.12818 \text{ kg mol}^{-1}}{18.80 \times 10^3 \text{ J mol}^{-1}}$$

$$= \boxed{7.1 \text{ K kg mol}^{-1}}$$

$$K_b = \frac{RT^*2M}{\Delta_{\text{vap}}H} = \frac{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times (490.9 \text{ K})^2 \times 0.12818 \text{ kg mol}^{-1}}{51.51 \times 10^3 \text{ J mol}^{-1}}$$

$$= \boxed{4.99 \text{ K kg mol}^{-1}}$$

**E7.9(b)** We assume that the solvent, 2-propanol, is ideal and obeys Raoult's law.

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

$$M_A(\text{C}_3\text{H}_8\text{O}) = 60.096 \text{ g mol}^{-1}$$

$$n_A = \frac{250 \text{ g}}{60.096 \text{ g mol}^{-1}} = 4.1600 \text{ mol}$$

$$x_A = \frac{n_A}{n_A + n_B} \quad n_A + n_B = \frac{n_A}{x_A}$$

$$\begin{aligned}
 n_B &= n_A \left( \frac{1}{x_A} - 1 \right) \\
 &= 4.1600 \text{ mol} \left( \frac{1}{0.9924} - 1 \right) = 3.186 \times 10^{-2} \text{ mol} \\
 M_B &= \frac{8.69 \text{ g}}{3.186 \times 10^{-2} \text{ mol}} = 273 \text{ g mol}^{-1} = \boxed{270 \text{ g mol}^{-1}}
 \end{aligned}$$

**E7.10(b)**  $K_f = 6.94$  for naphthalene

$$\begin{aligned}
 M_B &= \frac{\text{mass of B}}{n_B} \\
 n_B &= \text{mass of naphthalene} \cdot b_B \\
 b_B &= \frac{\Delta T}{K_f} \quad \text{so} \quad M_B = \frac{(\text{mass of B}) \times K_f}{(\text{mass of naphthalene}) \times \Delta T} \\
 M_B &= \frac{(5.00 \text{ g}) \times (6.94 \text{ K kg mol}^{-1})}{(0.250 \text{ kg}) \times (0.780 \text{ K})} = \boxed{178 \text{ g mol}^{-1}}
 \end{aligned}$$

**E7.11(b)**  $\Delta T = K_f b_B$  and  $b_B = \frac{n_B}{\text{mass of water}} = \frac{n_B}{V\rho}$

$$\begin{aligned}
 \rho &= 10^3 \text{ kg m}^{-3} \quad (\text{density of solution} \approx \text{density of water}) \\
 n_B &= \frac{\Pi V}{RT} \quad \Delta T = K_f \frac{\Pi}{RT\rho} \quad K_f = 1.86 \text{ K mol}^{-1} \text{ kg} \\
 \Delta T &= \frac{(1.86 \text{ K kg mol}^{-1}) \times (99 \times 10^3 \text{ Pa})}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (288 \text{ K}) \times (10^3 \text{ kg m}^{-3})} = 7.7 \times 10^{-2} \text{ K} \\
 T_f &= \boxed{-0.077^\circ\text{C}}
 \end{aligned}$$

**E7.12(b)**  $\Delta_{\text{mix}}G = nRT(x_A \ln x_A + x_B \ln x_B)$

$$\begin{aligned}
 n_{\text{Ar}} &= n_{\text{Ne}}, \quad x_{\text{Ar}} = x_{\text{Ne}} = 0.5, \quad n = n_{\text{Ar}} + n_{\text{Ne}} = \frac{pV}{RT} \\
 \Delta_{\text{mix}}G &= pV \left( \frac{1}{2} \ln \frac{1}{2} + \frac{1}{2} \ln \frac{1}{2} \right) = -pV \ln 2 \\
 &= -(100 \times 10^3 \text{ Pa}) \times (0.250 \text{ L}) \left( \frac{1 \text{ m}^3}{10^3 \text{ L}} \right) \ln 2 \\
 &= -17.3 \text{ Pa m}^3 = -17.3 \text{ J} \quad \Delta_{\text{mix}}S = \frac{-\Delta_{\text{mix}}G}{T} = \frac{17.3 \text{ J}}{273 \text{ K}} = \boxed{6.34 \times 10^{-2} \text{ J K}^{-1}}
 \end{aligned}$$

**E7.13(b)**  $\Delta_{\text{mix}}G = nRT \sum_J x_J \ln x_J$  [7.18]  $\Delta_{\text{mix}}S = -nR \sum_J x_J \ln x_J$  [7.19] =  $\frac{-\Delta_{\text{mix}}G}{T}$

$$n = 1.00 \text{ mol} + 1.00 \text{ mol} = 2.00 \text{ mol}$$

$$x(\text{Hex}) = x(\text{Hep}) = 0.500$$

Therefore,

$$\begin{aligned}
 \Delta_{\text{mix}}G &= (2.00 \text{ mol}) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \times (0.500 \ln 0.500 + 0.500 \ln 0.500) \\
 &= \boxed{-3.43 \text{ kJ}}
 \end{aligned}$$

$$\Delta_{\text{mix}}S = \frac{+3.43 \text{ kJ}}{298 \text{ K}} = \boxed{+11.5 \text{ J K}^{-1}}$$

$\Delta_{\text{mix}}H$  for an ideal solution is zero as it is for a solution of perfect gases [7.20]. It can be demonstrated from

$$\Delta_{\text{mix}}H = \Delta_{\text{mix}}G + T \Delta_{\text{mix}}S = (-3.43 \times 10^3 \text{ J}) + (298 \text{ K}) \times (11.5 \text{ J K}^{-1}) = \boxed{0}$$

**E7.14(b)** Benzene and ethylbenzene form nearly ideal solutions, so

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

To find maximum  $\Delta_{\text{mix}}S$ , differentiate with respect to  $x_A$  and find value of  $x_A$  at which the derivative is zero.

Note that  $x_B = 1 - x_A$  so

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

$$\text{use } \frac{d \ln x}{dx} = \frac{1}{x}$$

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

$$= 0 \quad \text{when } x_A = \frac{1}{2}$$

Thus the maximum entropy of mixing is attained by mixing equal molar amounts of two components.

$$\frac{n_B}{n_E} = \boxed{1} = \frac{m_B/M_B}{m_E/M_E} \quad \frac{m_E}{m_B} = \frac{M_E}{M_B} = \frac{106.169}{78.115} = 1.3591$$

$$\frac{m_B}{m_E} = \boxed{0.7358}$$

**E7.15(b)** Assume Henry's law [7.26] applies; therefore, with  $K(\text{N}_2) = 6.51 \times 10^7 \text{ Torr}$  and  $K(\text{O}_2) = 3.30 \times 10^7 \text{ Torr}$ , as in Exercise 7.14, the amount of dissolved gas in 1 kg of water is

$$n(\text{N}_2) = \left( \frac{10^3 \text{ g}}{18.02 \text{ g mol}^{-1}} \right) \times \left( \frac{p(\text{N}_2)}{6.51 \times 10^7 \text{ Torr}} \right) = (8.52 \times 10^{-7} \text{ mol}) \times (p/\text{Torr})$$

For  $p(\text{N}_2) = xp$  and  $p = 760 \text{ Torr}$

$$n(\text{N}_2) = (8.52 \times 10^{-7} \text{ mol}) \times (x) \times (760) = x(6.48 \times 10^{-4} \text{ mol})$$

and, with  $x = 0.78$

$$n(\text{N}_2) = (0.78) \times (6.48 \times 10^{-4} \text{ mol}) = 5.1 \times 10^{-4} \text{ mol} = 0.51 \text{ mmol}$$

The molality of the solution is therefore approximately  $\boxed{0.51 \text{ mmol kg}^{-1}}$  in  $\text{N}_2$ . Similarly, for oxygen,

$$n(\text{O}_2) = \left( \frac{10^3 \text{ g}}{18.02 \text{ g mol}^{-1}} \right) \times \left( \frac{p(\text{O}_2)}{3.30 \times 10^7 \text{ Torr}} \right) = (1.68 \times 10^{-6} \text{ mol}) \times (p/\text{Torr})$$

For  $p(\text{O}_2) = xp$  and  $p = 760 \text{ Torr}$

$$n(\text{O}_2) = (1.68 \times 10^{-6} \text{ mol}) \times (x) \times (760) = x(1.28 \text{ mmol})$$

and when  $x = 0.21$ ,  $n(\text{O}_2) \approx 0.27 \text{ mmol}$ . Hence the solution will be  $\boxed{0.27 \text{ mmol kg}^{-1}}$  in  $\text{O}_2$ .

**E7.16(b)** Use  $n(\text{CO}_2) = (4.4 \times 10^{-5} \text{ mol}) \times (p/\text{Torr})$ ,  $p = 2.0(760 \text{ Torr}) = 1520 \text{ Torr}$

$$n(\text{CO}_2) = (4.4 \times 10^{-5} \text{ mol}) \times (1520) = 0.067 \text{ mol}$$

The molality will be about  $0.067 \text{ mol kg}^{-1}$  and, since molalities and molar concentration for dilute aqueous solutions are approximately equal, the molar concentration is about  $0.067 \text{ mol L}^{-1}$

**E7.17(b)**  $M(\text{glucose}) = 180.16 \text{ g mol}^{-1}$

$$\Delta T = K_f b_B \quad K_f = 1.86 \text{ K kg mol}^{-1}$$

$$\Delta T = (1.86 \text{ K kg mol}^{-1}) \times \left( \frac{10 \text{ g}/180.16 \text{ g mol}^{-1}}{0.200 \text{ kg}} \right) = 0.52 \text{ K}$$

Freezing point will be  $0^\circ\text{C} - 0.52^\circ\text{C} = -0.52^\circ\text{C}$

**E7.18(b)** The procedure here is identical to Exercise 7.18(a).

$$\begin{aligned} \ln x_B &= \frac{\Delta_{\text{fus}}H}{R} \times \left( \frac{1}{T^*} - \frac{1}{T} \right) \quad [7.39; \text{B, the solute, is lead}] \\ &= \left( \frac{5.2 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \right) \times \left( \frac{1}{600 \text{ K}} - \frac{1}{553 \text{ K}} \right) \\ &= -0.088\bar{6}, \quad \text{implying that } x_B = 0.92 \end{aligned}$$

$$x_B = \frac{n(\text{Pb})}{n(\text{Pb}) + n(\text{Bi})}, \quad \text{implying that } n(\text{Pb}) = \frac{x_B n(\text{Bi})}{1 - x_B}$$

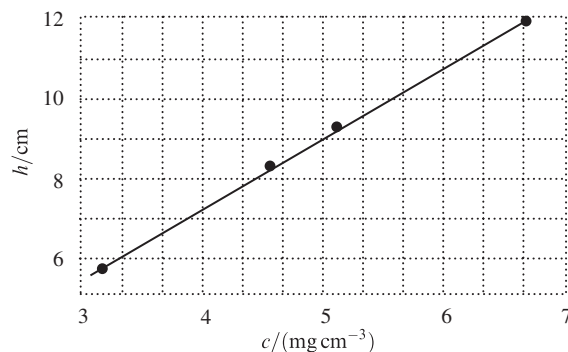
$$\text{For 1 kg of bismuth, } n(\text{Bi}) = \frac{1000 \text{ g}}{208.98 \text{ g mol}^{-1}} = 4.785 \text{ mol}$$

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

$$n(\text{Pb}) = \frac{(0.92) \times (4.785 \text{ mol})}{1 - 0.92} = 55 \text{ mol}, \quad \text{or } \boxed{11 \text{ kg}}$$

**Comment.** It is highly unlikely that a solution of 11 kg of lead and 1 kg of bismuth could in any sense be considered ideal. The assumptions upon which eqn 7.39 is based are not likely to apply. The answer above must then be considered an order of magnitude result only.

**E7.19(b)** Proceed as in Exercise 7.19(a). The data are plotted in Fig. 7.1, and the slope of the line is  $1.78 \text{ cm}/(\text{mg cm}^{-3}) = 1.78 \text{ cm}/(\text{g L}^{-1}) = 1.78 \times 10^{-2} \text{ m}^4 \text{ kg}^{-1}$ .



**Figure 7.1**

Therefore,

$$M = \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (293.15 \text{ K})}{(1.000 \times 10^3 \text{ kg m}^{-3}) \times (9.81 \text{ m s}^{-2}) \times (1.78 \times 10^{-2} \text{ m}^4 \text{ kg}^{-1})} = \boxed{14.0 \text{ kg mol}^{-1}}$$

**E7.20(b)** Let A = water and B = solute.

$$a_A = \frac{p_A}{p_A^*} [42] = \frac{0.02239 \text{ atm}}{0.02308 \text{ atm}} = \boxed{0.9701}$$

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

$$n_A = \frac{0.920 \text{ kg}}{0.01802 \text{ kg mol}^{-1}} = 51.05 \text{ mol} \quad n_B = \frac{0.122 \text{ kg}}{0.241 \text{ kg mol}^{-1}} = 0.506 \text{ mol}$$

$$x_A = \frac{51.05}{51.05 + 0.506} = 0.990 \quad \gamma_A = \frac{0.9701}{0.990} = \boxed{0.980}$$

**E7.21(b)** B = Benzene  $\mu_B(l) = \mu_B^*(l) + RT \ln x_B$  [7.50, ideal solution]

$$RT \ln x_B = (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (353.3 \text{ K}) \times (\ln 0.30) = \boxed{-3536 \text{ J mol}^{-1}}$$

Thus, its chemical potential is lowered by this amount.

$$p_B = a_B p_B^* [42] = \gamma_B x_B p_B^* = (0.93) \times (0.30) \times (760 \text{ Torr}) = \boxed{212 \text{ Torr}}$$

**Question.** What is the lowering of the chemical potential in the nonideal solution with  $\gamma = 0.93$ ?

**E7.22(b)** 
$$y_A = \frac{p_A}{p_A + p_B} = \frac{p_A}{760 \text{ Torr}} = 0.314$$

$$p_A = (760 \text{ Torr}) \times (0.314) = 238.64 \text{ Torr}$$

$$p_B = 760 \text{ Torr} - 238.64 \text{ Torr} = 521.36 \text{ Torr}$$

$$a_A = \frac{p_A}{p_A^*} = \frac{238.64 \text{ Torr}}{(73.0 \times 10^3 \text{ Pa}) \times \left(\frac{1 \text{ atm}}{101325 \text{ Pa}}\right) \times \left(\frac{760 \text{ Torr}}{\text{atm}}\right)} = \boxed{0.436}$$

$$a_B = \frac{p_B}{p_B^*} = \frac{521.36 \text{ Torr}}{(92.1 \times 10^3 \text{ Pa}) \times \left(\frac{1 \text{ atm}}{101325 \text{ Pa}}\right) \times \left(\frac{760 \text{ Torr}}{\text{atm}}\right)} = \boxed{0.755}$$

$$\gamma_A = \frac{a_A}{x_A} = \frac{0.436}{0.220} = \boxed{1.98}$$

$$\gamma_B = \frac{a_B}{x_B} = \frac{0.755}{0.780} = \boxed{0.968}$$

## Solutions to problems

### Solutions to numerical problems

**P7.3**

$$V_{\text{salt}} = \left(\frac{\partial V}{\partial b}\right)_{\text{H}_2\text{O}} \text{ mol}^{-1} \text{ [Problem 7.2]}$$

$$= 69.38(b - 0.070) \text{ cm}^3 \text{ mol}^{-1} \quad \text{with } b \equiv b/(\text{mol kg}^{-1})$$

Therefore, at  $b = 0.050 \text{ mol kg}^{-1}$ ,  $V_{\text{salt}} = \boxed{-1.4 \text{ cm}^3 \text{ mol}^{-1}}$

The total volume at this molality is

$$V = (1001.21) + (34.69) \times (0.02)^2 \text{ cm}^3 = 1001.22 \text{ cm}^3$$

Hence, as in Problem 7.2,

$$V(\text{H}_2\text{O}) = \frac{(1001.22 \text{ cm}^3) - (0.050 \text{ mol}) \times (-1.4 \text{ cm}^3 \text{ mol}^{-1})}{55.49 \text{ mol}} = \boxed{18.04 \text{ cm}^3 \text{ mol}^{-1}}$$

**Question.** What meaning can be ascribed to a negative partial molar volume?

**P7.5**

Let E denote ethanol and W denote water; then

$$V = n_E V_E + n_W V_W \quad [7.3]$$

For a 50 per cent mixture by mass,  $m_E = m_W$ , implying that

$$n_E M_E = n_W M_W, \quad \text{or} \quad n_W = \frac{n_E M_E}{M_W}$$

$$\text{Hence, } V = n_E V_E + \frac{n_E M_E V_W}{M_W}$$

$$\text{which solves to } n_E = \frac{V}{V_E + \frac{M_E V_W}{M_W}}, \quad n_W = \frac{M_E V}{V_E M_W + M_E V_W}$$

$$\text{Furthermore, } x_E = \frac{n_E}{n_E + n_W} = \frac{1}{1 + \frac{M_E}{M_W}}$$

Since  $M_E = 46.07 \text{ g mol}^{-1}$  and  $M_W = 18.02 \text{ g mol}^{-1}$ ,  $\frac{M_E}{M_W} = 2.557$ . Therefore

$$x_E = 0.2811, \quad x_W = 1 - x_E = 0.7189$$

At this composition

$$V_E = 56.0 \text{ cm}^3 \text{ mol}^{-1} \quad V_W = 17.5 \text{ cm}^3 \text{ mol}^{-1} \quad [\text{Fig. 7.1 of the text}]$$

$$\text{Therefore, } n_E = \frac{100 \text{ cm}^3}{(56.0 \text{ cm}^3 \text{ mol}^{-1}) + (2.557) \times (17.5 \text{ cm}^3 \text{ mol}^{-1})} = 0.993 \text{ mol}$$

$$n_W = (2.557) \times (0.993 \text{ mol}) = 2.54 \text{ mol}$$

The fact that these amounts correspond to a mixture containing 50 per cent by mass of both components is easily checked as follows

$$m_E = n_E M_E = (0.993 \text{ mol}) \times (46.07 \text{ g mol}^{-1}) = 45.7 \text{ g ethanol}$$

$$m_W = n_W M_W = (2.54 \text{ mol}) \times (18.02 \text{ g mol}^{-1}) = 45.7 \text{ g water}$$

At 20°C the densities of ethanol and water are,  $\rho_E = 0.789 \text{ g cm}^{-3}$ ,  $\rho_W = 0.997 \text{ g cm}^{-3}$ . Hence,

$$V_E = \frac{m_E}{\rho_E} = \frac{45.7 \text{ g}}{0.789 \text{ g cm}^{-3}} = \boxed{57.9 \text{ cm}^3} \text{ of ethanol}$$

$$V_W = \frac{m_W}{\rho_W} = \frac{45.7 \text{ g}}{0.997 \text{ g cm}^{-3}} = \boxed{45.8 \text{ cm}^3} \text{ of water}$$

The change in volume upon adding a small amount of ethanol can be approximated by

$$\Delta V = \int dV \approx \int V_E dn_E \approx V_E \Delta n_E$$

where we have assumed that both  $V_E$  and  $V_W$  are constant over this small range of  $n_E$ . Hence

$$\Delta V \approx (56.0 \text{ cm}^3 \text{ mol}^{-1}) \times \left( \frac{(1.00 \text{ cm}^3) \times (0.789 \text{ g cm}^{-3})}{(46.07 \text{ g mol}^{-1})} \right) = \boxed{+0.96 \text{ cm}^3}$$

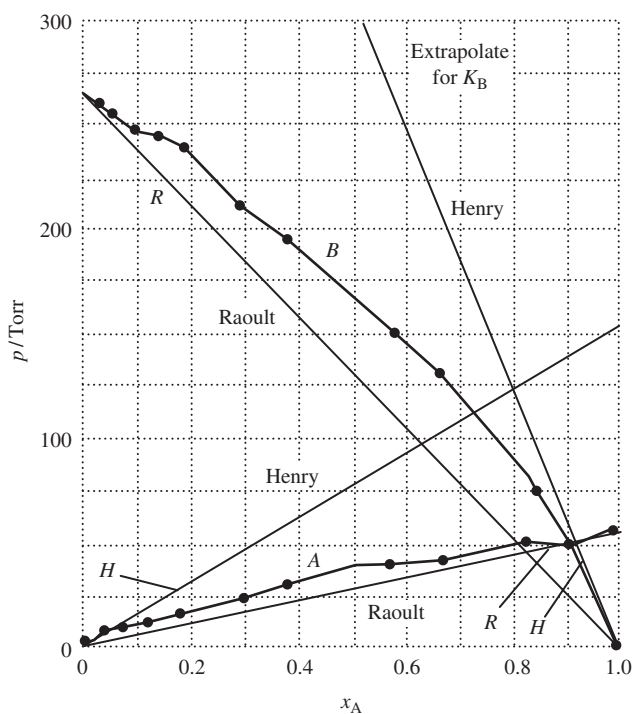
**P7.7**

$$m_B = \frac{\Delta T}{K_f} = \frac{0.0703 \text{ K}}{1.86 \text{ K}/(\text{mol kg}^{-1})} = 0.0378 \text{ mol kg}^{-1}$$

Since the solution molality is nominally  $0.0096 \text{ mol kg}^{-1}$  in  $\text{Th}(\text{NO}_3)_4$ , each formula unit supplies  $\frac{0.0378}{0.0096} \approx \boxed{4 \text{ ions}}$ . (More careful data, as described in the original reference gives  $\nu \approx 5$  to 6.)

**P7.9**

The data are plotted in Figure 7.2. The regions where the vapor pressure curves show approximate straight lines are denoted R for Raoult and H for Henry. A and B denote acetic acid and benzene respectively.



**Figure 7.2**

As in Problem 7.8, we need to form  $\gamma_A = \frac{p_A}{x_A p_A^*}$  and  $\gamma_B = \frac{p_B}{x_B p_B^*}$  for the Raoult's law activity coefficients and  $\gamma_B = \frac{p_B}{x_B K}$  for the activity coefficient of benzene on a Henry's law basis, with  $K$  determined by extrapolation. We use  $p_A^* = 55 \text{ Torr}$ ,  $p_B^* = 264 \text{ Torr}$  and  $K_B^* = 600 \text{ Torr}$  to draw up



the following table:

$x_A$	0	0.2	0.4	0.6	0.8	1.0
$p_A/\text{Torr}$	0	20	30	38	50	55
$p_B/\text{Torr}$	264	228	190	150	93	0
$a_A(\text{R})$	0	0.36	0.55	0.69	0.91	$1.00[p_A/p_A^*]$
$a_B(\text{R})$	1.00	0.86	0.72	0.57	0.35	$0[p_B/p_B^*]$
$\gamma_A(\text{R})$	—	1.82	1.36	1.15	1.14	$1.00[p_A/x_A p_A^*]$
$\gamma_B(\text{R})$	1.00	1.08	1.20	1.42	1.76	$-[p_B/x_B p_B^*]$
$a_B(\text{H})$	0.44	0.38	0.32	0.25	0.16	$0[p_B/K_B]$
$\gamma_B(\text{H})$	0.44	0.48	0.53	0.63	0.78	$1.00[p_B/x_B K_B]$

$G^E$  is defined as [Section 7.4]:

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

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  $RT = 2.69 \text{ kJ mol}^{-1}$ :

$x_A$	0	0.2	0.4	0.6	0.8	1.0
$x_A \ln \gamma_A$	0	0.12	0.12	0.08	0.10	0
$x_B \ln \gamma_B$	0	0.06	0.11	0.14	0.11	0
$G^E/(\text{kJ mol}^{-1})$	0	0.48	0.62	0.59	0.56	0

**P7.11** (a) The volume of an ideal mixture is

$$V_{\text{ideal}} = n_1 V_{\text{m},1} + n_2 V_{\text{m},2}$$

so the volume of a real mixture is

$$V = V_{\text{ideal}} + V^E$$

We have an expression for excess molar volume in terms of mole fractions. To compute partial molar volumes, we need an expression for the actual excess volume as a function of moles

$$V^E = (n_1 + n_2) V_{\text{m}}^E = \frac{n_1 n_2}{n_1 + n_2} \left( a_0 + \frac{a_1(n_1 - n_2)}{n_1 + n_2} \right)$$

$$\text{so } V = n_1 V_{\text{m},1} + n_2 V_{\text{m},2} + \frac{n_1 n_2}{n_1 + n_2} \left( a_0 + \frac{a_1(n_1 - n_2)}{n_1 + n_2} \right)$$

The partial molar volume of propionic acid is

$$V_1 = \left( \frac{\partial V}{\partial n_1} \right)_{p,T,n_2} = V_{\text{m},1} + \frac{a_0 n_2^2}{(n_1 + n_2)^2} + \frac{a_1(3n_1 - n_2)n_2^2}{(n_1 + n_2)^3}$$

$$\boxed{V_1 = V_{\text{m},1} + a_0 x_2^2 + a_1(3x_1 - x_2)x_2^2}$$

That of oxane is

$$\boxed{V_2 = V_{\text{m},2} + a_0 x_1^2 + a_1(x_1 - 3x_2)x_1^2}$$

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

$$V_{m,1} = \frac{M_1}{\rho_1} = \frac{74.08 \text{ g mol}^{-1}}{0.97174 \text{ g cm}^{-3}} = 76.23 \text{ cm}^3 \text{ mol}^{-1}$$

$$\text{and } V_{m,2} = \frac{86.13 \text{ g mol}^{-1}}{0.86398 \text{ g cm}^{-3}} = 99.69 \text{ cm}^3 \text{ mol}^{-1}$$

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

$$\begin{aligned} V_1 &= 76.23 + (-2.4697) \times (0.500)^2 + (0.0608) \times [3(0.5) - 0.5] \times (0.5)^2 \text{ cm}^3 \text{ mol}^{-1} \\ &= \boxed{75.63 \text{ cm}^3 \text{ mol}^{-1}} \end{aligned}$$

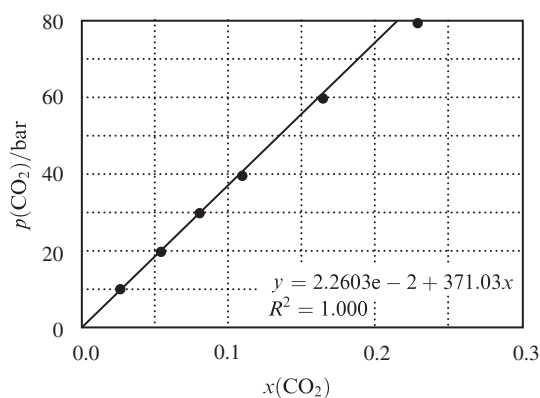
and that of oxane is

$$\begin{aligned} V_2 &= 99.69 + (-2.4697) \times (0.500)^2 + (0.0608) \times [0.5 - 3(0.5)] \times (0.5)^2 \text{ cm}^3 \text{ mol}^{-1} \\ &= \boxed{99.06 \text{ cm}^3 \text{ mol}^{-1}} \end{aligned}$$

**P7.13** Henry's law constant is the slope of a plot of  $p_B$  versus  $x_B$  in the limit of zero  $x_B$  (Fig. 7.3). The partial pressures of  $\text{CO}_2$  are almost but not quite equal to the total pressures reported above

$$p_{\text{CO}_2} = p y_{\text{CO}_2} = p(1 - y_{\text{cyc}})$$

Linear regression of the low-pressure points gives  $K_H = \boxed{371 \text{ bar}}$



**Figure 7.3**

The activity of a solute is

$$a_B = \frac{p_B}{K_H} = x_B \gamma_B$$

so the activity coefficient is

$$\gamma_B = \frac{p_B}{x_B K_H} = \frac{y_B p}{x_B K_H}$$

where the last equality applies Dalton's law of partial pressures to the vapour phase. A spreadsheet applied this equation to the above data to yield

$p/\text{bar}$	$y_{\text{cyc}}$	$x_{\text{cyc}}$	$\gamma_{\text{CO}_2}$
10.0	0.0267	0.9741	1.01
20.0	0.0149	0.9464	0.99
30.0	0.0112	0.9204	1.00
40.0	0.00947	0.892	0.99
60.0	0.00835	0.836	0.98
80.0	0.00921	0.773	0.94

**P7.16**  $G^E = RTx(1-x)\{0.4857 - 0.1077(2x-1) + 0.0191(2x-1)^2\}$

with  $x = 0.25$  gives  $G^E = 0.1021RT$ . Therefore, since

$$\Delta_{\text{mix}}G(\text{actual}) = \Delta_{\text{mix}}G(\text{ideal}) + nG^E$$

$$\begin{aligned} \Delta_{\text{mix}}G &= nRT(x_A \ln x_A + x_B \ln x_B) + nG^E = nRT(0.25 \ln 0.25 + 0.75 \ln 0.75) + nG^E \\ &= -0.562nRT + 0.1021nRT = -0.460nRT \end{aligned}$$

Since  $n = 4$  mol and  $RT = (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (303.15 \text{ K}) = 2.52 \text{ kJ mol}^{-1}$ ,

$$\Delta_{\text{mix}}G = (-0.460) \times (4 \text{ mol}) \times (2.52 \text{ kJ mol}^{-1}) = \boxed{-4.6 \text{ kJ}}$$

### Solutions to theoretical problems

**P7.18**  $x_A d\mu_A + x_B d\mu_B = 0$  [7.11, Gibbs–Duhem equation]

Therefore, after dividing through by  $dx_A$

$$x_A \left( \frac{\partial \mu_A}{\partial x_A} \right)_{p,T} + x_B \left( \frac{\partial \mu_B}{\partial x_A} \right)_{p,T} = 0$$

or, since  $dx_B = -dx_A$ , as  $x_A + x_B = 1$

$$x_A \left( \frac{\partial \mu_A}{\partial x_A} \right)_{p,T} - x_B \left( \frac{\partial \mu_B}{\partial x_B} \right)_{p,T} = 0$$

$$\text{or, } \left( \frac{\partial \mu_A}{\partial \ln x_A} \right)_{p,T} = \left( \frac{\partial \mu_B}{\partial \ln x_B} \right)_{p,T} \left[ d \ln x = \frac{dx}{x} \right]$$

$$\text{Then, since } \mu = \mu^\ominus + RT \ln \frac{f}{p^\ominus}, \left( \frac{\partial \ln f_A}{\partial \ln x_A} \right)_{p,T} = \left( \frac{\partial \ln f_B}{\partial \ln x_B} \right)_{p,T}$$

$$\text{On replacing } f \text{ by } p, \left( \frac{\partial \ln p_A}{\partial \ln x_A} \right)_{p,T} = \left( \frac{\partial \ln p_B}{\partial \ln x_B} \right)_{p,T}$$

If A satisfies Raoult's law, we can write  $p_A = x_A p_A^*$ , which implies that

$$\left( \frac{\partial \ln p_A}{\partial \ln x_A} \right)_{p,T} = \frac{\partial \ln x_A}{\partial \ln x_A} + \frac{\partial \ln p_A^*}{\partial \ln x_A} = 1 + 0$$

$$\text{Therefore, } \left( \frac{\partial \ln p_B}{\partial \ln x_B} \right)_{p,T} = 1$$

which is satisfied if  $p_B = x_B p_B^*$  (by integration, or inspection). Hence, if A satisfies Raoult's law, so does B.

**P7.20**  $\ln x_A = \frac{-\Delta_{\text{fus}}G}{RT}$  (Section 7.5 analogous to equation for  $\ln x_B$  used in derivation of eqn 7.39)

$$\frac{d \ln x_A}{dT} = -\frac{1}{R} \times \frac{d}{dT} \left( \frac{\Delta_{\text{fus}}G}{T} \right) = \boxed{\frac{\Delta_{\text{fus}}H}{RT^2}} \quad [\text{Gibbs-Helmholtz equation}]$$

$$\int_1^{x_A} d \ln x_A = \int_{T^*}^T \frac{\Delta_{\text{fus}}H}{RT^2} dT \approx \frac{\Delta_{\text{fus}}H}{R} \int_{T^*}^T \frac{dT}{T^2}$$

$$\boxed{\ln x_A = \frac{-\Delta_{\text{fus}}H}{R} \times \left( \frac{1}{T} - \frac{1}{T^*} \right)}$$

The approximations  $\ln x_A \approx -x_B$  and  $T \approx T^*$  then lead to eqns 33 and 36, as in the text.

**P7.22** Retrace the argument leading to eqn 7.40 of the text. Exactly the same process applies with  $a_A$  in place of  $x_A$ . At equilibrium

$$\mu_A^*(p) = \mu_A(x_A, p + \Pi)$$

which implies that, with  $\mu = \mu^* + RT \ln a$  for a real solution,

$$\mu_A^*(p) = \mu_A^*(p + \Pi) + RT \ln a_A = \mu_A^*(p) + \int_p^{p+\Pi} V_m dp + RT \ln a_A$$

and hence that  $\int_p^{p+\Pi} V_m dp = -RT \ln a_A$

For an incompressible solution, the integral evaluates to  $\Pi V_m$ , so  $\Pi V_m = -RT \ln a_A$

In terms of the osmotic coefficient  $\phi$  (Problem 7.21)

$$\Pi V_m = r\phi RT \quad r = \frac{x_B}{x_A} = \frac{n_B}{n_A} \quad \phi = -\frac{x_A}{x_B} \ln a_A = -\frac{1}{r} \ln a_A$$

For a dilute solution,  $n_A V_m \approx V$

Hence,  $\Pi V = n_B \phi RT$

and therefore, with  $[B] = \frac{n_B}{V}$   $\boxed{\Pi = \phi[B]RT}$

### Solutions to applications

**P7.24** By the van't Hoff equation [7.40]

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

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 ( $\Pi'$ ) 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  $\text{g cm}^{-2}$ . 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  $\boxed{\text{g cm K}^{-1} \text{ mol}^{-1}}$

$$\begin{aligned} R' &= \frac{R}{g} = \frac{8.31451 \text{ J K}^{-1} \text{ mol}^{-1}}{9.80665 \text{ m s}^{-2}} \\ &= 0.847844 \text{ kg m K}^{-1} \text{ mol}^{-1} \left( \frac{10^3 \text{ g}}{\text{kg}} \right) \times \left( \frac{10^2 \text{ cm}}{\text{m}} \right) \end{aligned}$$

$$\boxed{R' = 84784.4 \text{ g cm K}^{-1} \text{ mol}^{-1}}$$

In the following we will drop the primes giving

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

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

- (b) By extrapolating the low concentration plot of  $\Pi/c$  versus  $c$  (Fig. 7.4 (a)) to  $c = 0$  we find the intercept  $230 \text{ g cm}^{-2}/\text{g cm}^{-3}$ . In this limit van't Hoff equation is valid so

$$\begin{aligned} \frac{RT}{\bar{M}_n} &= \text{intercept} \quad \text{or} \quad \bar{M}_n = \frac{RT}{\text{intercept}} \\ \bar{M}_n &= \frac{(84784.4 \text{ g cm K}^{-1} \text{ mol}^{-1}) \times (298.15 \text{ K})}{(230 \text{ g cm}^{-2})/(\text{g cm}^{-3})} \end{aligned}$$

$$\boxed{\bar{M}_n = 1.1 \times 10^5 \text{ g mol}^{-1}}$$

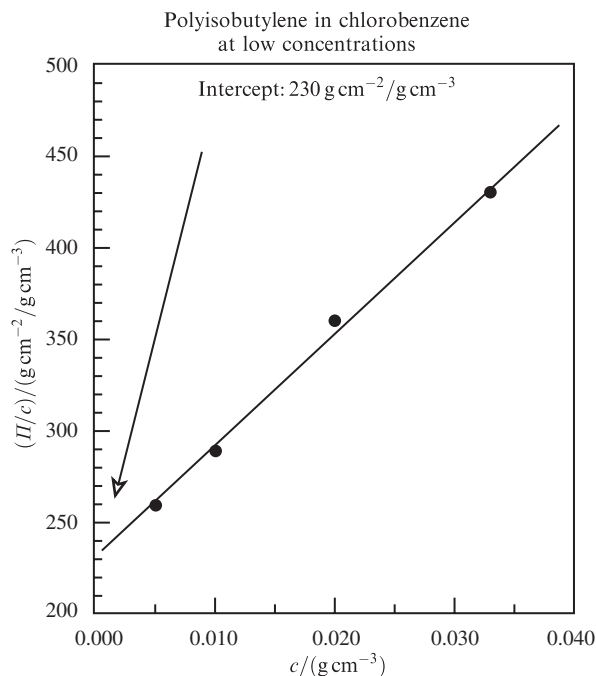


Figure 7.4(a)

- (c) The plot of  $\Pi/c$  versus  $c$  for the full concentration range (Fig. 7.4(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.

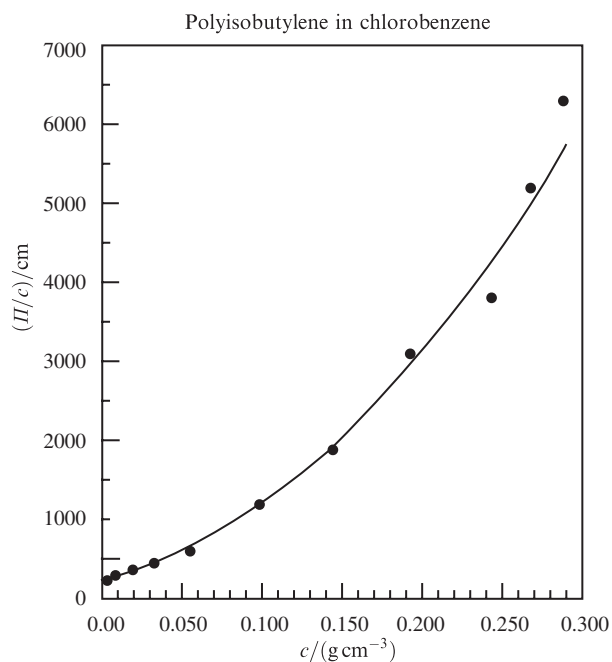


Figure 7.4(b)

(d)  $\Pi/c = (RT/\overline{M}_n)(1 + B'c + C'c^2)$

Since  $RT/\overline{M}_n$  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

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

$$R = 0.9791$$

$B' = 21.4 \text{ cm}^3 \text{ g}^{-1},$	standard deviation = $2.4 \text{ cm}^3 \text{ g}^{-1}$
$C' = 211 \text{ cm}^6 \text{ g}^{-2},$	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

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

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

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

$RT/\bar{M}_n$  has been determined above as  $230 \text{ g cm}^{-2}/\text{g cm}^{-3}$ . 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  $c = 0.033 \text{ g cm}^{-3}$ .

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

$$B' = \frac{2 \times (1.367 - 1)}{0.033 \text{ g cm}^{-3}} = 22.2 \text{ cm}^3 \text{ g}^{-1}$$

$$C' = g(B')^2 = 0.25 \times (22.2 \text{ cm}^3 \text{ g}^{-1})^2 = 123 \text{ cm}^6 \text{ g}^{-2}$$

Better values of  $B'$  and  $C'$  can be obtained by plotting  $\left(\frac{\Pi}{c}\right)^{1/2} / \left(\frac{RT}{\bar{M}_n}\right)^{1/2}$  against  $c$ . This plot is shown in Fig. 7.4(c). The slope is  $14.03 \text{ cm}^3 \text{ g}^{-1}$ .  $B' = 2 \times \text{slope} = 28.0 \text{ cm}^3 \text{ g}^{-1}$ .  $C'$  is then  $196 \text{ cm}^6 \text{ g}^{-2}$ . 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.

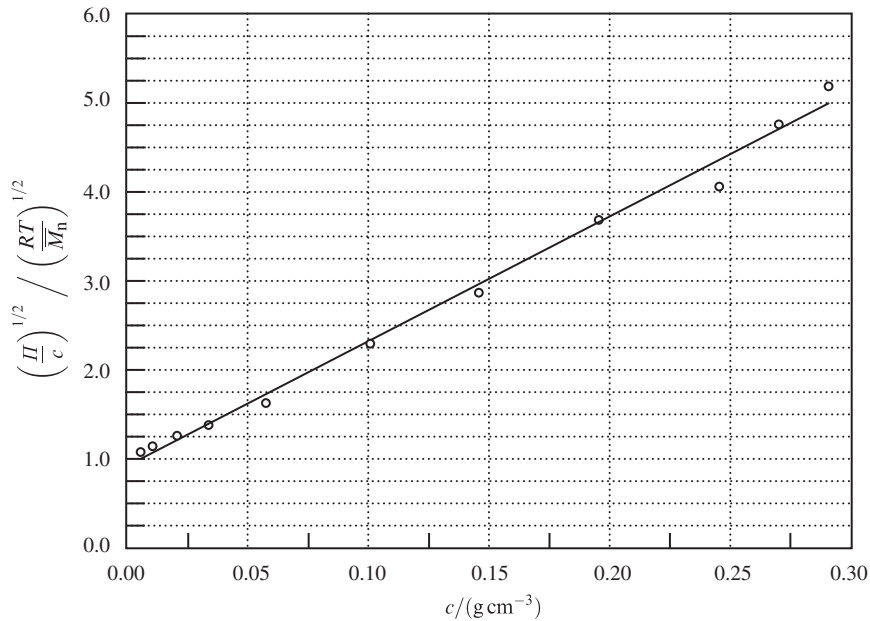


Figure 7.4(c)