

# 8 Phase diagrams

## Solutions to exercises

### Discussion questions

**E8.1(b)** What factors determine the number of theoretical plates required to achieve a desired degree of separation in fractional distillation?

The principal factor is the shape of the two-phase liquid-vapor region in the phase diagram (usually a temperature-composition diagram). The closer the liquid and vapour lines are to each other, the more theoretical plates needed. See Fig. 8.15 of the text. But the presence of an azeotrope could prevent the desired degree of separation from being achieved. Incomplete miscibility of the components at specific concentrations could also affect the number of plates required.

**E8.2(b)** See Figs 8.1(a) and 8.1(b).

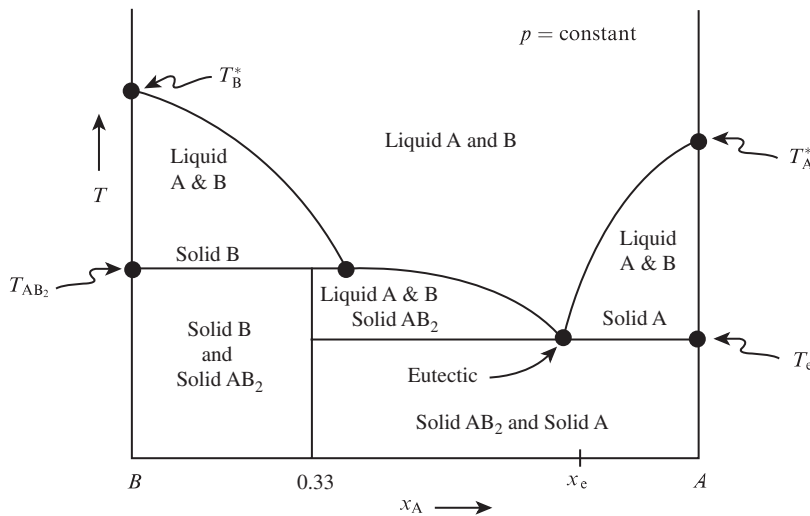


Figure 8.1(a)

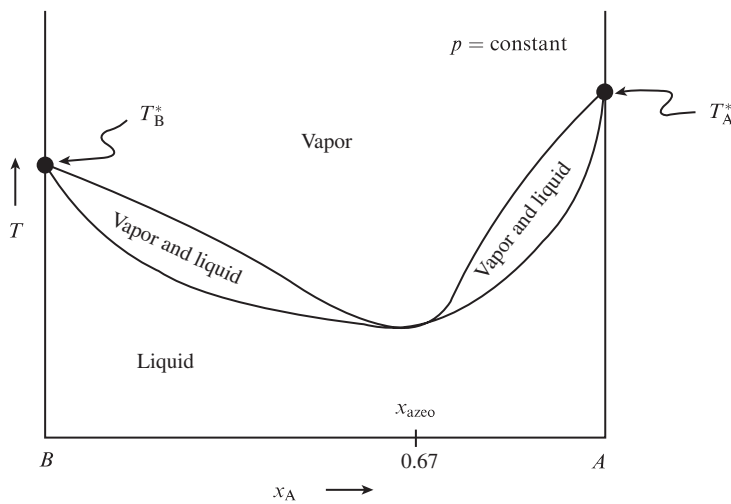
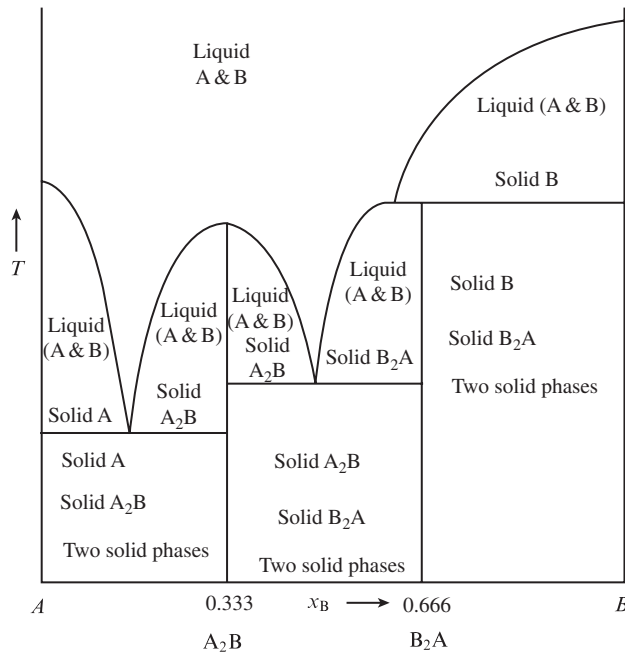


Figure 8.1(b)

**E8.3(b)** See Fig. 8.2.



**Figure 8.2**

**Numerical exercises**

**E8.4(b)**

$$p = p_A + p_B = x_A p_A^* + (1 - x_A) p_B^*$$

$$x_A = \frac{p - p_B^*}{p_A^* - p_B^*}$$

$$x_A = \frac{19 \text{ kPa} - 18 \text{ kPa}}{20 \text{ kPa} - 18 \text{ kPa}} = \boxed{0.5} \quad \text{A is 1,2-dimethylbenzene}$$

$$y_A = \frac{x_A p_A^*}{p_B^* + (p_A^* - p_B^*) x_A} = \frac{(0.5) \times (20 \text{ kPa})}{18 \text{ kPa} + (20 \text{ kPa} - 18 \text{ kPa}) 0.5} = 0.526 \approx \boxed{0.5}$$

$$y_B = 1 - 0.526 = 0.474 \approx 0.5$$

**E8.5(b)**

$$p_A = y_A p = 0.612 p = x_A p_A^* = x_A (68.8 \text{ kPa})$$

$$p_B = y_B p = (1 - y_A) p = 0.388 p = x_B p_B^* = (1 - x_A) \times 82.1 \text{ kPa}$$

$$\frac{y_A p}{y_B p} = \frac{x_A p_A^*}{x_B p_B^*} \quad \text{and} \quad \frac{0.612}{0.388} = \frac{68.8 x_A}{82.1 (1 - x_A)}$$

$$(0.388) \times (68.8) x_A = (0.612) \times (82.1) - (0.612) \times (82.1) x_A$$

$$26.694 x_A = 50.245 - 50.245 x_A$$

$$x_A = \frac{50.245}{26.694 + 50.245} = \boxed{0.653} \quad x_B = 1 - 0.653 = \boxed{0.347}$$

$$p = x_A p_A^* + x_B p_B^* = (0.653) \times (68.8 \text{ kPa}) + (0.347) \times (82.1 \text{ kPa}) = \boxed{73.4 \text{ kPa}}$$

- E8.6(b)** (a) If Raoult's law holds, the solution is ideal.

$$p_A = x_A p_A^* = (0.4217) \times (110.1 \text{ kPa}) = 46.43 \text{ kPa}$$

$$p_B = x_B p_B^* = (1 - 0.4217) \times (94.93 \text{ kPa}) = 54.90 \text{ kPa}$$

$$p = p_A + p_B = (46.43 + 54.90) \text{ kPa} = 101.33 \text{ kPa} = 1.000 \text{ atm}$$

Therefore, Raoult's law correctly predicts the pressure of the boiling liquid and the solution is ideal.

(b)  $y_A = \frac{p_A}{p} = \frac{46.43 \text{ kPa}}{101.33 \text{ kPa}} = \boxed{0.4582}$

$$y_B = 1 - y_A = 1.000 - 0.4582 = \boxed{0.5418}$$

- E8.7(b)** Let B = benzene and T = toluene. Since the solution is equimolar  $z_B = z_T = 0.500$

- (a) Initially  $x_B = z_B$  and  $x_T = z_T$ ; thus

$$p = x_B p_B^* + x_T p_T^* \text{ [8.3]} = (0.500) \times (74 \text{ Torr}) + (0.500) \times (22 \text{ Torr}) \\ = 37 \text{ Torr} + 11 \text{ Torr} = \boxed{48 \text{ Torr}}$$

(b)  $y_B = \frac{p_B}{p} \text{ [4]} = \frac{37 \text{ Torr}}{48 \text{ Torr}} = \boxed{0.77}$        $y_T = 1 - 0.77 = \boxed{0.23}$

- (c) Near the end of the distillation

$$y_B = z_B = 0.500 \quad \text{and} \quad y_T = z_T = 0.500$$

Equation 5 may be solved for  $x_A$  [A = benzene = B here]

$$x_B = \frac{y_B p_T^*}{p_B^* + (p_T^* - p_B^*) y_B} = \frac{(0.500) \times (22 \text{ Torr})}{(75 \text{ Torr}) + (22 - 74) \text{ Torr} \times (0.500)} = 0.23$$

$$x_T = 1 - 0.23 = 0.77$$

This result for the special case of  $z_B = z_T = 0.500$  could have been obtained directly by realizing that

$$y_B(\text{initial}) = x_T(\text{final}) \quad y_T(\text{initial}) = x_B(\text{final})$$

$$p(\text{final}) = x_B p_B^* + x_T p_T^* = (0.23) \times (74 \text{ Torr}) + (0.77) \times (22 \text{ Torr}) = \boxed{34 \text{ Torr}}$$

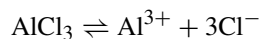
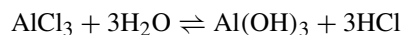
Thus in the course of the distillation the vapour pressure fell from 48 Torr to 34 Torr.

- E8.8(b)** See the phase diagram in Fig. 8.3.

(a)  $y_A = \boxed{0.81}$

(b)  $x_A = \boxed{0.67}$        $y_A = \boxed{0.925}$

- E8.9(b)**  $\text{Al}^{3+}$ ,  $\text{H}^+$ ,  $\text{AlCl}_3$ ,  $\text{Al}(\text{OH})_3$ ,  $\text{OH}^-$ ,  $\text{Cl}^-$ ,  $\text{H}_2\text{O}$  giving seven species. There are also three equilibria



and one condition of electrical neutrality

$$[\text{H}^+] + 3[\text{Al}^{3+}] = [\text{OH}^-] + [\text{Cl}^-]$$

Hence, the number of independent components is

$$C = 7 - (3 + 1) = \boxed{3}$$

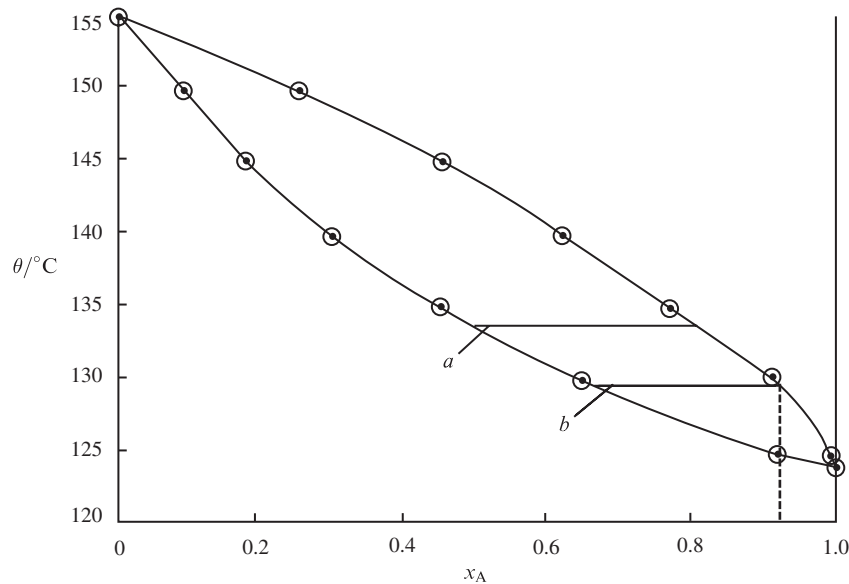


Figure 8.3

**E8.10(b)**  $\text{NH}_4\text{Cl}(\text{s}) \rightleftharpoons \text{NH}_3(\text{g}) + \text{HCl}(\text{g})$

(a) For this system  $C = 1$  [Example 8.1] and  $P = 2$  (s and g).

(b) If ammonia is added before heating,  $C = 2$  (because  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_3$  are now independent) and  $P = 2$  (s and g).

**E8.11(b)** (a) Still  $C = 2$  ( $\text{Na}_2\text{SO}_4$ ,  $\text{H}_2\text{O}$ ), but now there is no solid phase present, so  $P = 2$  (liquid solution, vapour).

(b) The variance is  $F = 2 - 2 + 2 = 2$ . We are free to change any two of the three variables, amount of dissolved salt, pressure, or temperature, but not the third. If we change the amount of dissolved salt and the pressure, the temperature is fixed by the equilibrium condition between the two phases.

**E8.12(b)** See Fig. 8.4.

**E8.13(b)** See Fig. 8.5. The phase diagram should be labelled as in Fig. 8.5. (a) Solid Ag with dissolved Sn begins to precipitate at  $a_1$ , and the sample solidifies completely at  $a_2$ . (b) Solid Ag with dissolved Sn begins to precipitate at  $b_1$ , and the liquid becomes richer in Sn. The peritectic reaction occurs at  $b_2$ , and as cooling continues  $\text{Ag}_3\text{Sn}$  is precipitated and the liquid becomes richer in Sn. At  $b_3$  the system has its eutectic composition (e) and freezes without further change.

**E8.14(b)** See Fig. 8.6. The feature denoting incongruent melting is circled. Arrows on the tie line indicate the decomposition products. There are two eutectics: one at  $x_B = 0.53$ ,  $T = T_2$ ; another at  $x_B = 0.82$ ,  $T = T_3$ .

**E8.15(b)** The cooling curves corresponding to the phase diagram in Fig. 8.7(a) are shown in Fig. 8.7(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  $b_3$ .

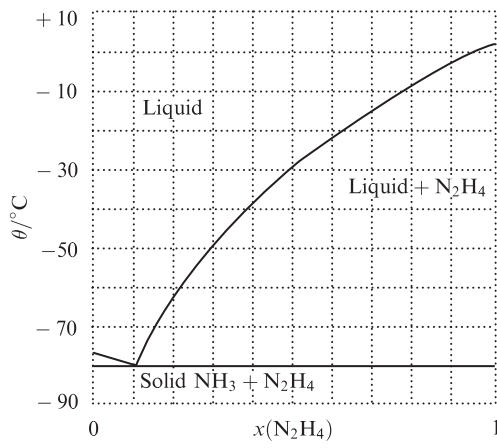


Figure 8.4

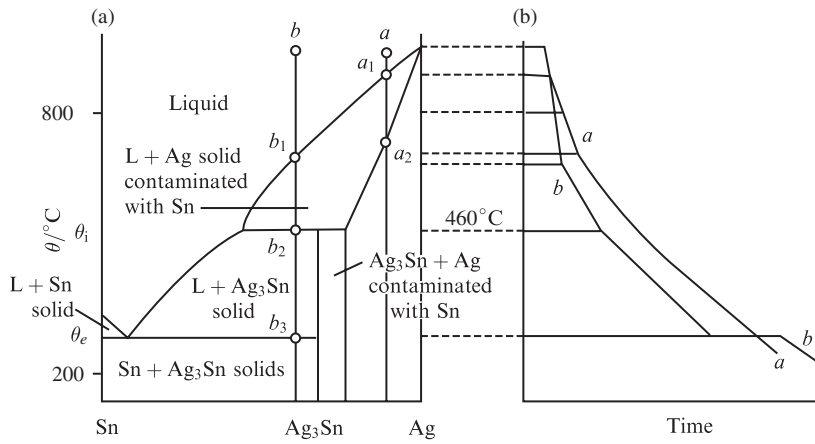


Figure 8.5

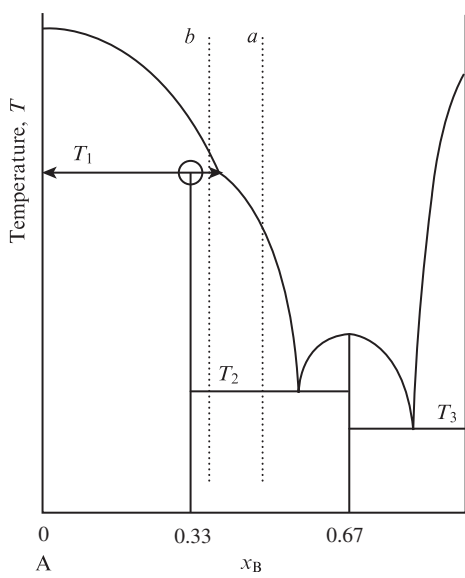


Figure 8.6

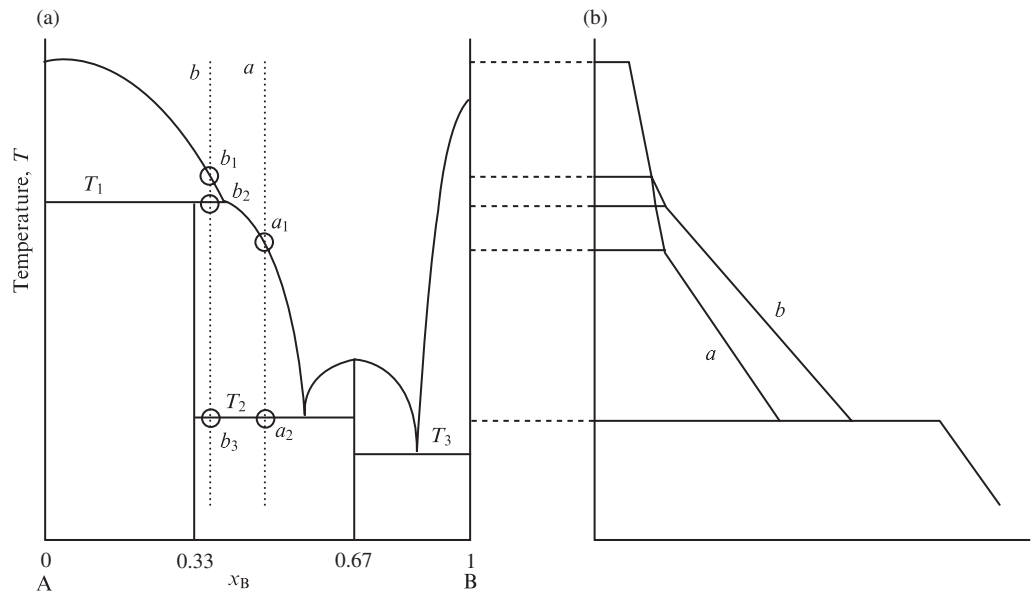


Figure 8.7

**E8.16(b)** Rough estimates based on Fig. 8.37 of the text are

(a)  $x_B \approx 0.75$     (b)  $x_{AB_2} \approx 0.8$     (c)  $x_{AB_2} \approx 0.6$

**E8.17(b)** The phase diagram is shown in Fig. 8.8. The given data points are circled. The lines are schematic at best.

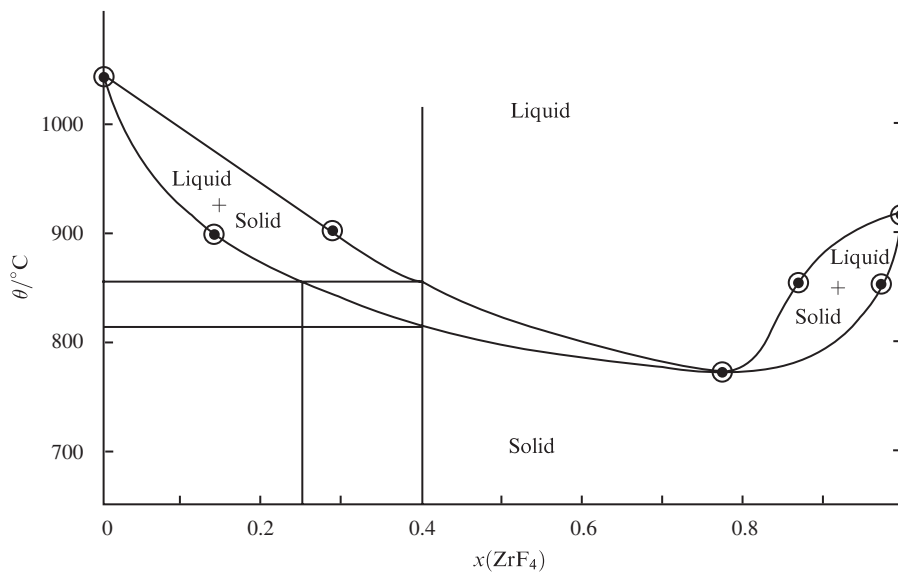


Figure 8.8

A solid solution with  $x(\text{ZrF}_4) = 0.24$  appears at  $855^\circ\text{C}$ . The solid solution continues to form, and its  $\text{ZrF}_4$  content increases until it reaches  $x(\text{ZrF}_4) = 0.40$  and  $820^\circ\text{C}$ . At that temperature, the entire sample is solid.

- E8.18(b)** The phase diagram for this system (Fig. 8.9) is very similar to that for the system methyl ethyl ether and diborane of Exercise 8.12(a). (See the *Student's Solutions Manual*.) The regions of the diagram contain analogous substances. The solid compound begins to crystallize at 120 K. The liquid becomes progressively richer in diborane until the liquid composition reaches 0.90 at 104 K. At that point the liquid disappears as heat is removed. Below 104 K the system is a mixture of solid compound and solid diborane.

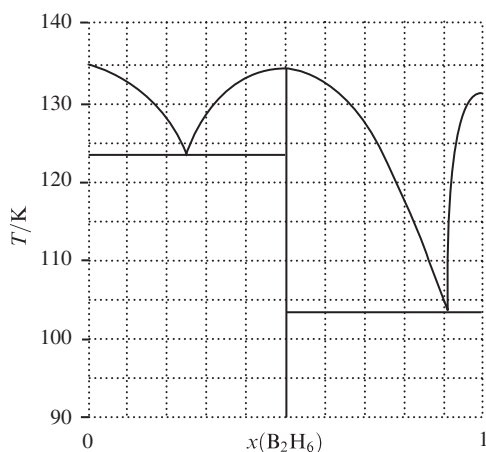


Figure 8.9

- E8.19** Refer to the phase diagram in the solution to Exercise 8.17(a). (See the *Student's Solutions Manual*.) The cooling curves are sketched in Fig. 8.10.

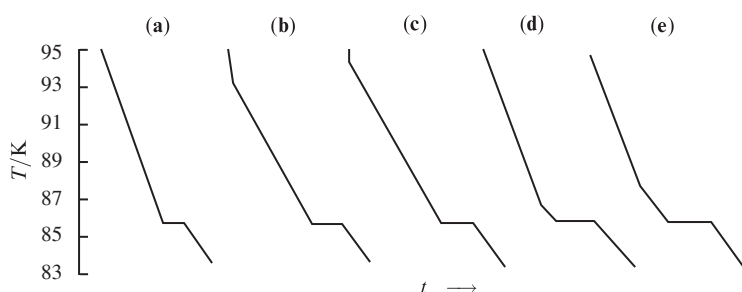


Figure 8.10

- E8.20**
- (a) 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.
  - (b) The mixture has a single liquid phase at all compositions.  
The phase diagram is sketched in Fig. 8.11.

## Solutions to problems

### Solutions to numerical problems

- P8.2**
- (a) The phase diagram is shown in Fig. 8.12.
  - (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 ( $\alpha$ , at the left of the phase diagram) is 0.168 and in the acetamide-rich phase ( $\beta$ , at right) 0.804. The proportions of the two

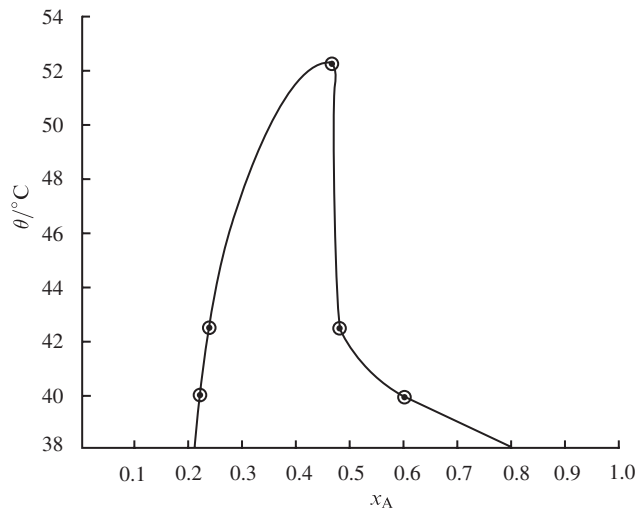


Figure 8.11

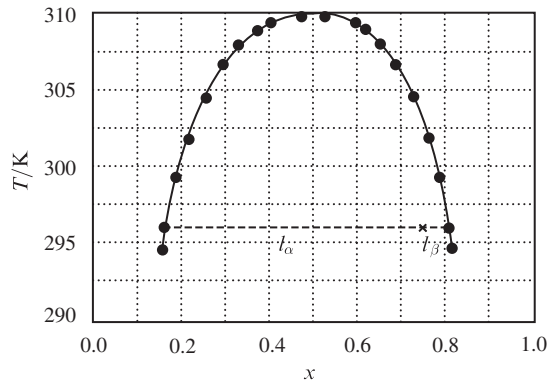


Figure 8.12

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 point at which the heptane-rich phase will vanish.

**P8.6** See Fig. 8.13(a). The number of distinct chemical species (as opposed to components) and phases present at the indicated points are, respectively

$$b(3, 2), d(2, 2), e(4, 3), f(4, 3), g(4, 3), k(2, 2)$$

[Liquid A and solid A are here considered distinct species.]

The cooling curves are shown in Fig. 8.13(b).

**P8.8** The information has been used to construct the phase diagram in Fig. 8.14(a). In  $\text{MgCu}_2$  the mass percentage of Mg is  $(100) \times \frac{24.3}{24.3 + 127} = \boxed{16}$ , and in  $\text{Mg}_2\text{Cu}$  it is  $(100) \times \frac{48.6}{48.6 + 63.5} = \boxed{43}$ . The initial point is  $a_1$ , corresponding to a liquid single-phase system. At  $a_2$  (at  $720^\circ\text{C}$ )  $\text{MgCu}_2$  begins to come out of solution and the liquid becomes richer in Mg, moving toward  $e_2$ . At  $a_3$  there is solid



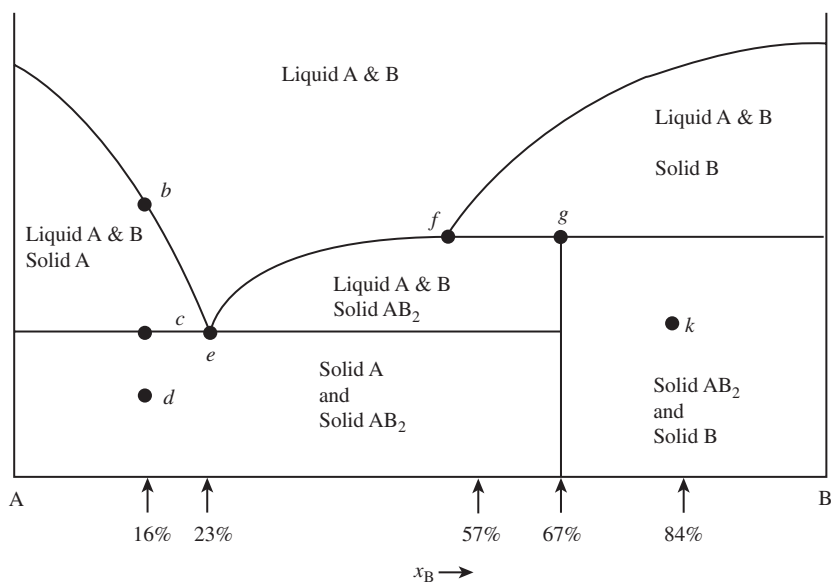


Figure 8.13(a)

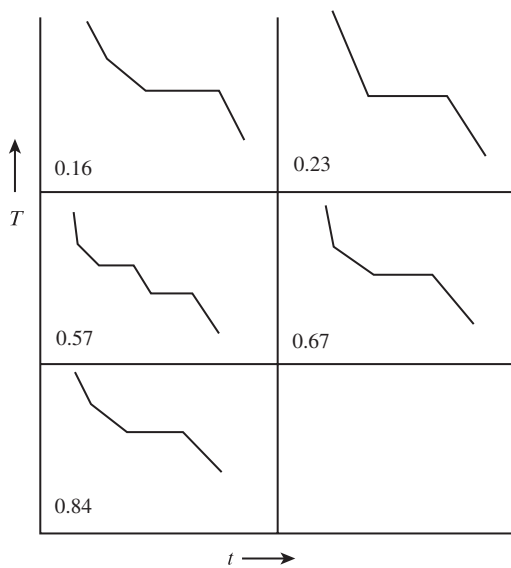


Figure 8.13(b)

$\text{MgCu}_2$  + 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 Fig. 8.14(b).

**P8.10** (a) **eutectic:** 40.2 at % Si at 1268°C      **eutectic:** 69.4 at % Si at 1030°C      [8.6]

**congruent melting compounds:**  $\text{Ca}_2\text{Si}$  mp = 1314°C  
 $\text{CaSi}$  mp = 1324°C      [8.7]

**incongruent melting compound:**  $\text{CaSi}_2$  mp = 1040°C      melts into  $\text{CaSi}(s)$  and liquid (68 at % Si)

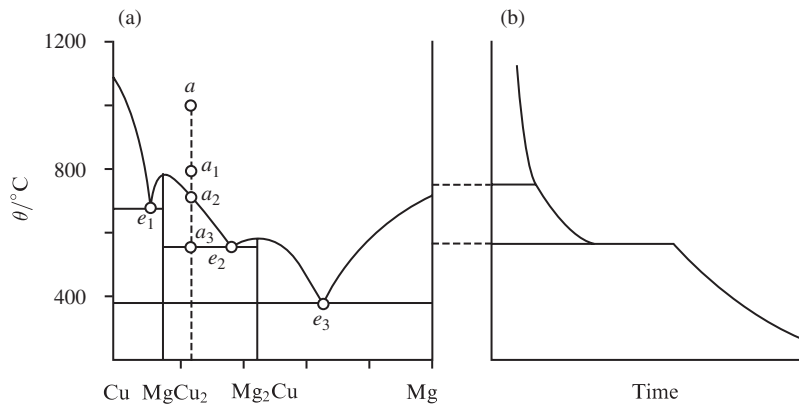


Figure 8.14

- (b) At 1000°C the phases at equilibrium will be Ca(s) and liquid (13 at % Si). The lever rule gives the relative amounts:

$$\frac{n_{Ca}}{n_{liq}} = \frac{l_{liq}}{l_{Ca}} = \frac{0.2 - 0}{0.2 - 0.13} = 2.86$$

- (c) When an 80 at % Si melt it cooled in a manner that maintains equilibrium, Si(s) begins to appear at about 1250°C. Further cooling causes more Si(s) to freeze out of the melt so that the melt becomes more concentrated in Ca. There is a 69.4 at % Si eutectic at 1030°C. Just before the eutectic is reached, the lever rule says that the relative amounts of the Si(s) and liquid (69.4% Si) phases are:

$$\frac{n_{Si}}{n_{liq}} = \frac{l_{liq}}{l_{Si}} = \frac{0.80 - 0.694}{1.0 - 0.80} = 0.53 = \text{relative amounts at } T \text{ slightly higher than } 1030^\circ\text{C}$$

Just before 1030°C, the Si(s) is 34.6 mol% of the total heterogeneous mixture; the eutectic liquid is 65.4 mol%.

At the eutectic temperature a third phase appears - CaSi<sub>2</sub>(s). As the melt cools at this temperature both Si(s) and CaSi<sub>2</sub>(s) freeze out of the melt while the concentration of the melt remains constant. At a temperature slightly below 1030°C all the melt will have frozen to Si(s) and CaSi<sub>2</sub>(s) with the relative amounts:

$$\begin{aligned} \frac{n_{Si}}{n_{CaSi_2}} &= \frac{l_{CaSi_2}}{l_{Si}} = \frac{0.80 - 0.667}{1.0 - 0.80} \\ &= 0.665 = \text{relative amounts at } T \text{ slightly higher than } 1030^\circ\text{C} \end{aligned}$$

Just under 1030°C, the Si(s) is 39.9 mol% of the total heterogeneous mixture; the CaSi<sub>2</sub>(s) is 60.1 mol%.

A graph of mol% Si(s) and mol% CaSi<sub>2</sub>(s) vs. mol% eutectic liquid is a convenient way to show relative amounts of the three phases as the eutectic liquid freezes. Equations for the graph are derived with the law of conservation of mass. For the silicon mass,

$$n \cdot z_{Si} = n_{liq} \cdot w_{Si} + n_{Si} \cdot x_{Si} + n_{CaSi_2} \cdot y_{Si}$$

where  $n$  = total number of moles.

$$\begin{aligned}
 w_{\text{Si}} &= \text{Si fraction in eutectic liquid} = 0.694 \\
 x_{\text{Si}} &= \text{Si fraction in Si(s)} = 1.000 \\
 y_{\text{Si}} &= \text{Si fraction in CaSi}_2\text{(s)} = 0.667 \\
 z_{\text{Si}} &= \text{Si fraction in melt} = 0.800
 \end{aligned}$$

This equation may be rewritten in mole fractions of each phase by dividing by  $n$ :

$$z_{\text{Si}} = (\text{mol fraction liq}) \cdot w_{\text{Si}} + (\text{mol fraction Si}) \cdot x_{\text{Si}} + (\text{mol fraction CaSi}_2) \cdot y_{\text{Si}}$$

Since,  $(\text{mol fraction liq}) + (\text{mol fraction Si}) + (\text{mol fraction CaSi}_2) = 1$

or  $(\text{mol fraction CaSi}_2) = 1 - (\text{mol fraction liq} + \text{mol fraction Si})$ , we may write :

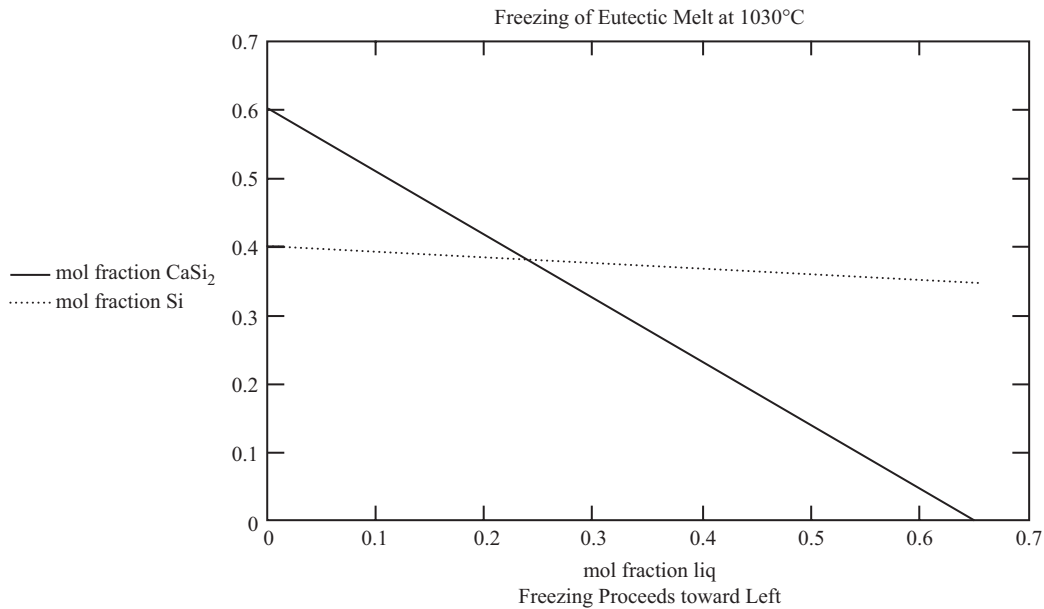
$$\begin{aligned}
 z_{\text{Si}} &= (\text{mol fraction liq}) \cdot w_{\text{Si}} + (\text{mol fraction Si}) \cdot x_{\text{Si}} \\
 &\quad + [1 - (\text{mol fraction liq} + \text{mol fraction Si})] \cdot y_{\text{Si}}
 \end{aligned}$$

Solving for mol fraction Si:

$$\text{mol fraction Si} := \frac{(z_{\text{Si}} - y_{\text{Si}}) - (w_{\text{Si}} - y_{\text{Si}})(\text{mol fraction liq})}{x_{\text{Si}} - y_{\text{Si}}}$$

$$\text{mol fraction CaSi}_2 := 1 - (\text{mol fraction liq} + \text{mol fraction Si})$$

These two eqns are used to prepare plots of the mol fraction of Si and the mol fraction of CaSi<sub>2</sub> against the mol fraction of the melt in the range 0–0.65.



**Figure 8.15**

### Solutions to theoretical problems

**P8.12**

The general condition of equilibrium in an isolated system is  $dS = 0$ . Hence, if  $\alpha$  and  $\beta$  constitute an isolated system, which are in thermal contact with each other

$$dS = dS_{\alpha} + dS_{\beta} = 0 \tag{a}$$

Entropy is an additive property and may be expressed in terms of  $U$  and  $V$ .

$$S = S(U, V)$$

The implication of this problem is that energy in the form of heat may be transferred from one phase to another, but that the phases are mechanically rigid, and hence their volumes are constant. Thus,  $dV = 0$ , and

$$dS = \left( \frac{\partial S_\alpha}{\partial U_\alpha} \right)_V dU_\alpha + \left( \frac{\partial S_\beta}{\partial U_\beta} \right)_V dU_\beta = \frac{1}{T_\alpha} dU_\alpha + \frac{1}{T_\beta} dU_\beta \quad [5.4]$$

But,  $dU_\alpha = -dU_\beta$ ; therefore  $\frac{1}{T_\alpha} = \frac{1}{T_\beta}$  or  $T_\alpha = T_\beta$

### Solutions to applications

**P8.14**  $C = 1$ ; hence,  $F = C - P + 2 = 3 - P$

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  $F = 0$ .

**P8.16** The temperature-composition lines can be calculated from the formula for the depression of freezing point [7.33].

$$\Delta T \approx \frac{RT^{*2}x_B}{\Delta_{\text{fus}}H}$$

For bismuth

$$\frac{RT^{*2}}{\Delta_{\text{fus}}H} = \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (544.5 \text{ K})^2}{10.88 \times 10^3 \text{ J mol}^{-1}} = 227 \text{ K}$$

For cadmium

$$\frac{RT^{*2}}{\Delta_{\text{fus}}H} = \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (594 \text{ K})^2}{6.07 \times 10^3 \text{ J mol}^{-1}} = 483 \text{ K}$$

We can use these constants to construct the following tables

$x(\text{Cd})$	0.1	0.2	0.3	0.4	
$\Delta T/\text{K}$	22.7	45.4	68.1	90.8	$(\Delta T = x(\text{Cd}) \times 227 \text{ K})$
$T_i/\text{K}$	522	499	476	454	$(T_i = T_f^* - \Delta T)$
$x(\text{Bi})$	0.1	0.2	0.3	0.4	
$\Delta T/\text{K}$	48.3	96.6	145	193	$(\Delta T = x(\text{Bi}) \times 483 \text{ K})$
$T_i/\text{K}$	546	497	449	401	$(T_i = T_f^* - \Delta T)$

These points are plotted in Fig. 8.16(a).

The eutectic temperature and concentration are located by extrapolation of the plotted freezing point lines until they intersect at  $e$ , which corresponds to  $T_E \approx 400 \text{ K}$  and  $x_E(\text{Cd}) \approx 0.60$ .

Liquid at  $a$  cools without separation of a solid until  $a'$  is reached (at 476 K). Solid Bi then separates, and the liquid becomes richer in Cd. At  $a'''$  (400 K) the composition is pure solid Bi + liquid of composition  $x(\text{Bi}) = 0.4$ . The whole mass then solidifies to solid Bi + solid Cd.

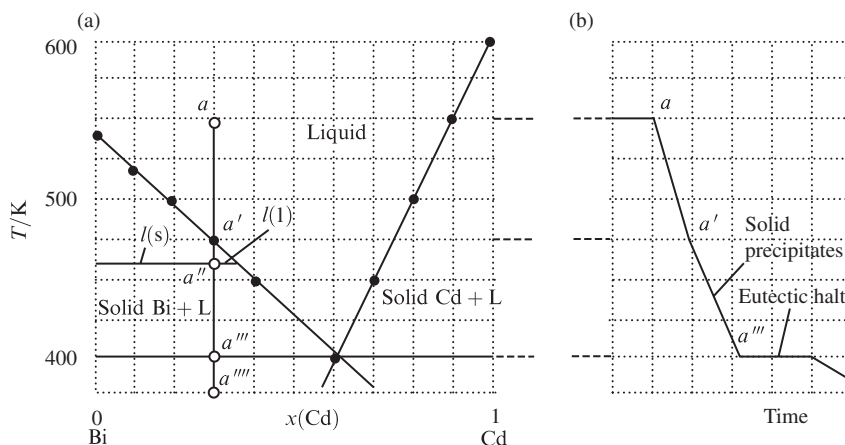


Figure 8.16

- (a) At 460 K (point  $a''$ ),  $\frac{n(l)}{n(s)} = \frac{l(s)}{l(l)} \approx \boxed{5}$  by the lever rule.
- (b) At 375 K (point  $a''''$ ) there is no liquid. The cooling curve is shown in Fig. 8.16(b).

**Comment.** The experimental values of  $T_E$  and  $x_E(\text{Cd})$  are 417 K and 0.55. The extrapolated values can be considered to be remarkably close to the experimental ones when one considers that the formulas employed apply only to dilute (ideal) solutions.

- P8.17** (a) The data are plotted in Fig. 8.17.

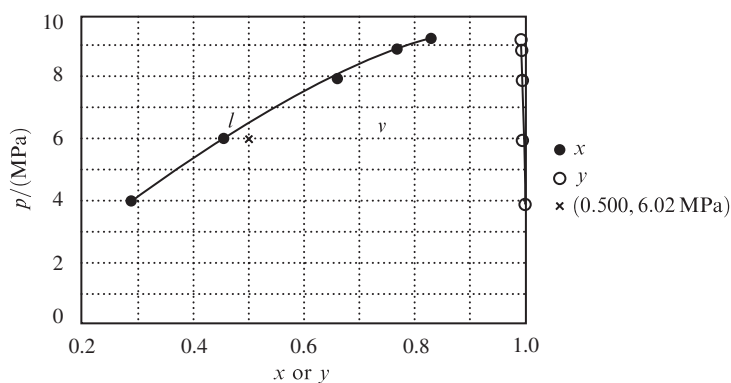


Figure 8.17

- (b) We need not interpolate data, for 6.02 MPa is a pressure for which we have experimental data. The mole fraction of  $\text{CO}_2$  in the liquid phase is 0.4541 and in the vapour phase 0.9980. 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

$$\frac{n_{\text{liq}}}{n_{\text{vap}}} = \frac{v}{l} = \frac{0.9980 - 0.5000}{0.5000 - 0.4541} = \boxed{10.85}$$

- P8.19** (a) As the solutions become either pure methanol ( $x_{\text{methanol}} = 1$ ) or pure TAME ( $x_{\text{methanol}} = 0$ ), the activity coefficients should become equal to 1 (Table 7.3). This means that the extremes in the range of  $\ln \gamma(x)$  curves should approach zero as they do in the above plot (Fig. 8.18(a)).

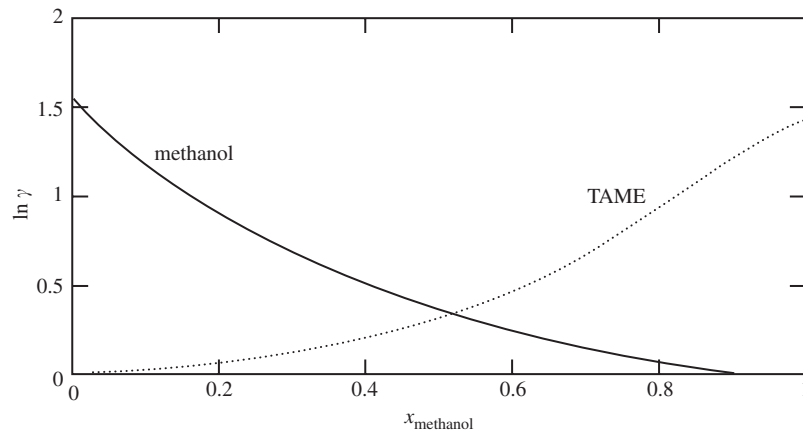


Figure 8.18(a)

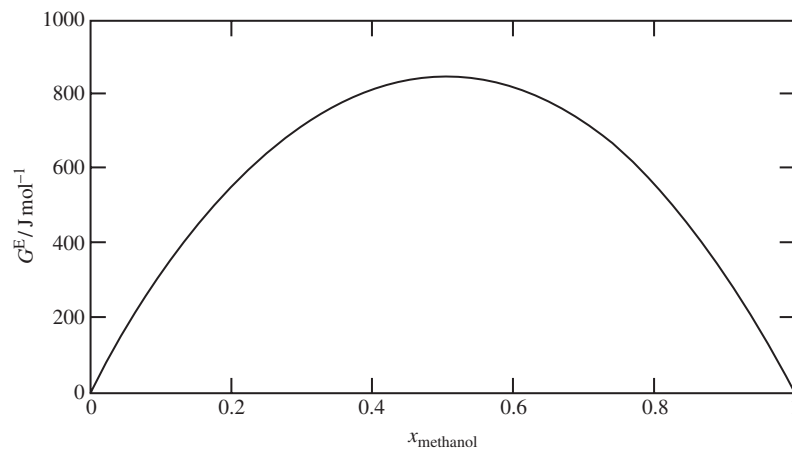


Figure 8.18(b)

- (b) The large positive deviation of  $G^E$  from the ideal mixture ( $G_{\text{ideal}}^E = 0$ , Section 7.4) indicates that the mixing process is unfavorable. This may originate from the breakage of relatively strong methanol hydrogen bonding upon solution formation.

$G^E$  for a regular solution is expected to be symmetrical about the point  $x_{\text{methanol}} = 0.5$ . Visual inspection of the  $G^E(x_{\text{methanol}})$  plot reveals that methanol/TAME solutions are approximately “regular”. The symmetry expectation can be demonstrated by remembering that  $H_m^E = Wx_Ax_B$  and  $S^E = 0$  for a regular solution (Section 7.4b). Then, for a regular solution  $G_m^E = H_m^E - TS_m^E = H^E = Wx_Ax_B$ , which is symmetrical about  $x = 0.5$  in the sense that  $G_m^E$  at  $x = 0.5 - \delta$  equals  $G_m^E$  at  $x = 0.5 + \delta$ .

- (c) Azeotrope composition and vapor pressure:

$$x_{\text{methanol}} = y_{\text{methanol}} = 0.682$$

$$P = 11.59 \text{ kPa}$$

when  $x_{\text{methanol}} = 0.2$ ,  $P = 10.00 \text{ kPa}$ .

- (d) The vapor pressure plot shows positive deviations from ideality. The escaping tendency is stronger than that of an ideal solution.

To get the Henry’s law constants, estimate values for the targets of  $P_{\text{methanol}}$  at  $x_{\text{methanol}} = 0$  and  $P_{\text{TAME}}$  at  $x_{\text{methanol}} = 1$ .

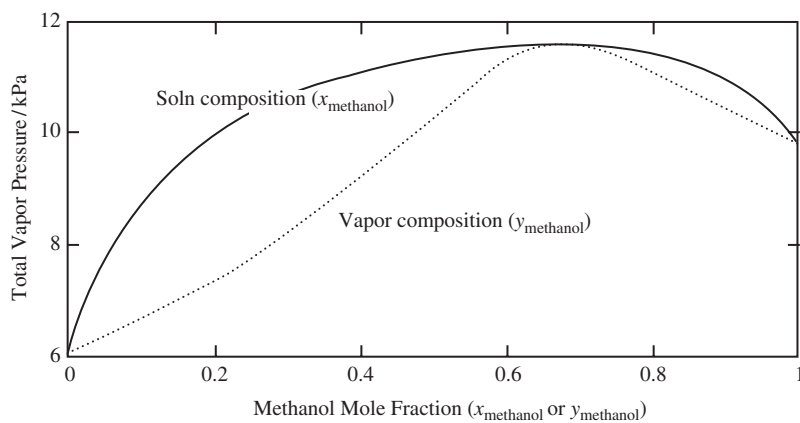


Figure 8.18(c)

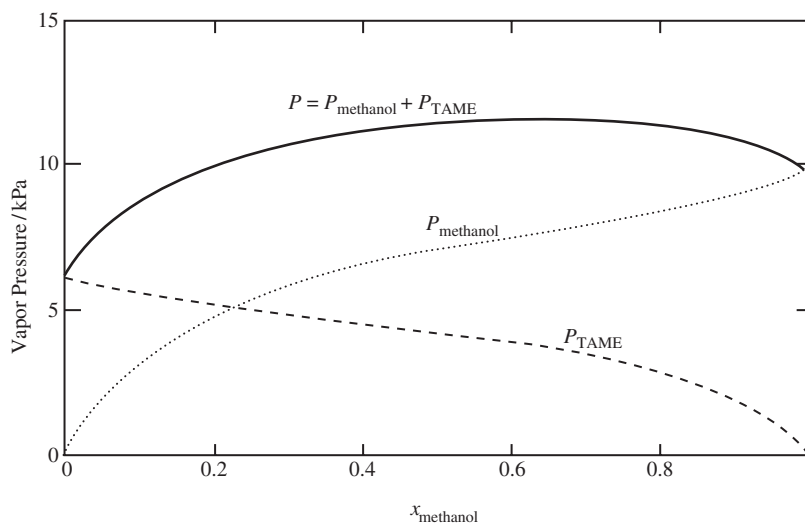


Figure 8.18(d)

For methanol in TAME (eqn 7.26):

$$K_{\text{methanol}} = \left( \frac{dP_{\text{methanol}}}{dx_{\text{methanol}}} \right)_{x_{\text{methanol}}=0} = 45.1 \text{ kPa}$$

For TAME in methanol:

$$K_{\text{TAME}} = \left( \frac{dP_{\text{TAME}}}{dx_{\text{TAME}}} \right)_{x_{\text{TAME}}=0} = - \left( \frac{dP_{\text{TAME}}}{dx_{\text{methanol}}} \right)_{x_{\text{methanol}}=1} = 25.3 \text{ kPa}$$

- (e) According to eqn 6.3, the vapor pressure should increase when the applied pressure is increased.  
For TAME:

$$\begin{aligned} P &= P^* e^{V_m \Delta P / RT} \\ &= (6.09 \text{ kPa}) e^{(131.78 \text{ cm}^3 \text{ mol}^{-1})(2.0 \text{ bar}) / [(83.1451 \text{ cm}^3 \text{ bar K}^{-1} \text{ mol}^{-1})(288.15 \text{ K})]} \\ &= 6.16 \text{ kPa} \end{aligned}$$

The applied pressure increases the vapor pressure by about 1%, molecules have been “squeezed” out of the liquid phase and into the gas phase but only to a slight extent.