Chem 401—Physical Chemistry
Chapter 6 Homework Solutions

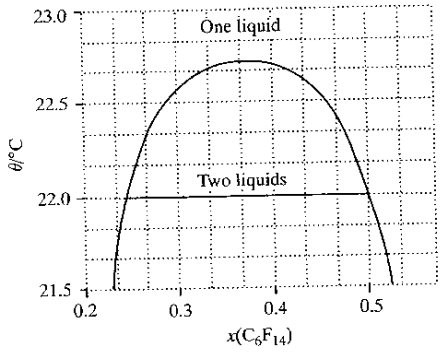

Figure 6.10

Solutions to problems

Solutions to numerical problems

P6.2 **(a)** The phase diagram is shown in Figure 6.11.

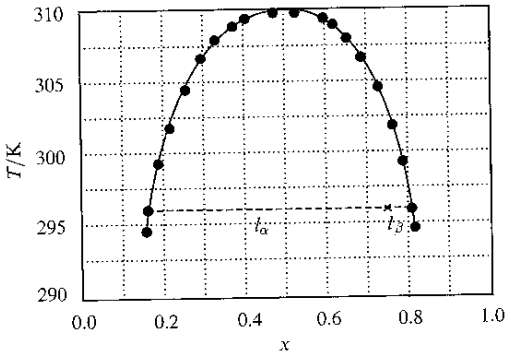

Figure 6.11

(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 (α, at the left of the phase diagram) 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 point at which the heptane-rich phase will vanish.

P6.4 The phase diagram is shown in Figure 6.12(a). The values of x_S corresponding to the three compounds are: (1) P_4S_3, 0.43; (2) P_4S_7, 0.64; (3) P_4S_{10}, 0.71.

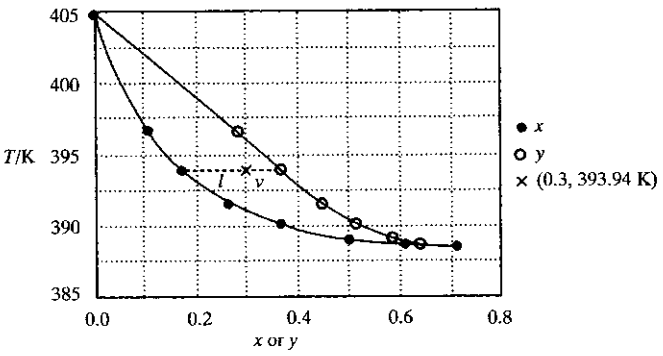

Figure 6.12

to the lever rule, the proportions of the two phases are in an inverse ratio of the distances their mole fractions are from the composition point in question. That is,

$$\frac{n_{\text{liq}}}{n_{\text{vap}}} = \frac{v}{l} = \frac{0.3691 - 0.300}{0.300 - 0.1700} = \boxed{0.532}.$$

P6.3

$$p_A = a_A p_A^* = \gamma_A x_A p_A^* \text{ [5.45]}.$$

$$\gamma_A = \frac{p_A}{x_A p_A^*} = \frac{y_A p}{x_A p_A^*}.$$

Sample calculation at 80 K:

$$\gamma_{O_2}(80\text{ K}) = \frac{0.11(100\text{ kPa})}{0.34(225\text{ Torr})}\left(\frac{760\text{ Torr}}{101.325\text{ kPa}}\right),$$

$$\gamma_{O_2}(80\text{ K}) = 1.079.$$

Summary:

T/K	77.3	78	80	82	84	86	88	90.2
γ_{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 Fig. 6.13(a). The near ideality of this solution is, however, best shown in the pressure–composition diagram of Fig. 6.13(b). The liquid line is essentially a straight line as predicted for an ideal solution.

P6.5

A compound with probable formula A_3B exists. It melts incongruently at 700°C, undergoing the peritectic reaction

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

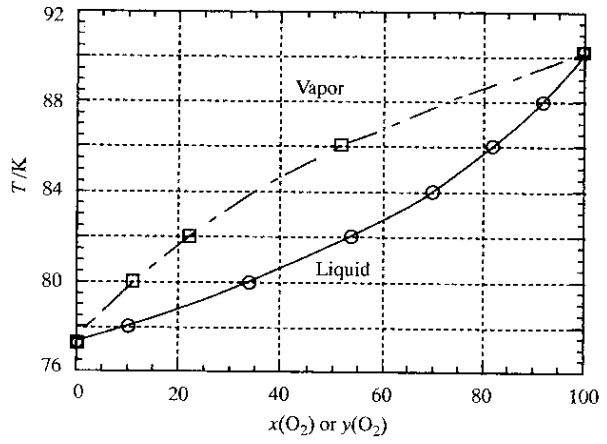

Figure 6.13(a)

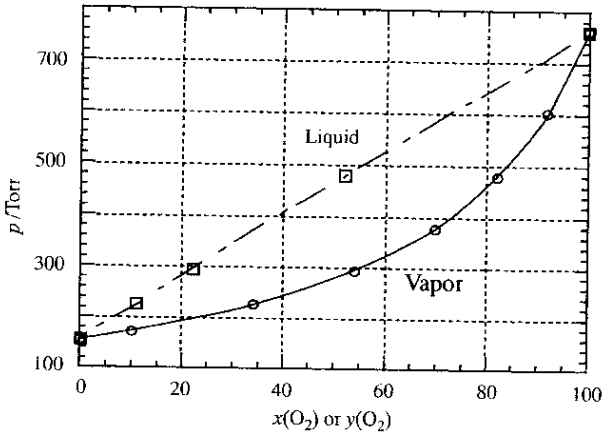

Figure 6.13(b)

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 $x_B \approx 0.83$. See Fig. 6.14.

P6.7 The information has been used to construct the phase diagram in Fig. 6.15(a). In $MgCu_2$ the mass percentage of Mg is $(100) \times \dfrac{24.3}{24.3 + 127} = \boxed{16}$, and in Mg_2Cu it is $(100) \times \dfrac{48.6}{48.6 + 63.5} = \boxed{43}$. The initial point is a_1, corresponding to a liquid single-phase system. At a_2 (at 720°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 Fig. 6.15(b).

P6.9 **(a)** **Eutectic**: 40.2 at% Si at 1268°C, **Eutectic**: 69.4 at% Si at 1030°C.

Congruent melting compounds: Ca_2Si mp = 1314°C
CaSi mp = 1324°C

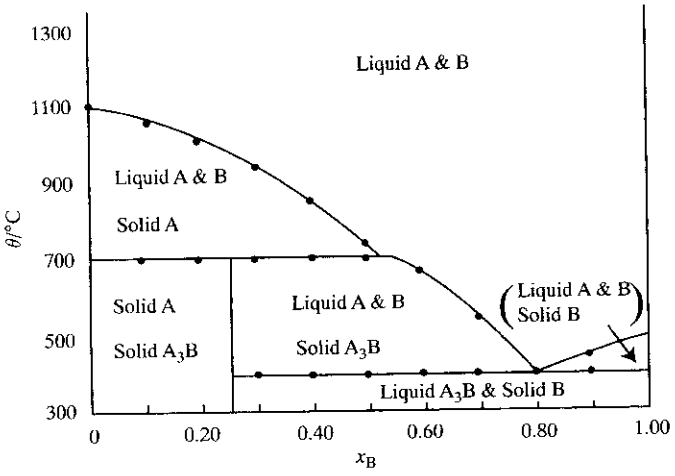

Figure 6.14

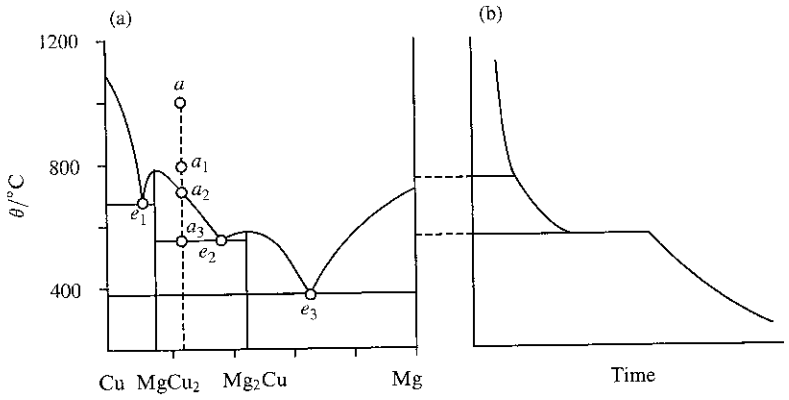

Figure 6.15

Incongruent melting compound: $CaSi_2$ mp = 1040°C melts into CaSi(s) and liquid (68 at% Si).

(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:

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

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—$CaSi_2$(s). As the melt cools at this temperature, both Si(s) and $CaSi_2$(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 $CaSi_2$(s) with the relative amounts:

$$\frac{n_{Si}}{n_{CaSi_2}} = \frac{l_{CaSi_2}}{l_{Si}} = \frac{0.80 - 0.667}{1.0 - 0.80}$$

$$= \boxed{0.665 = \text{relative amounts of } T \text{ slightly higher than } 1030°C}.$$

Just under 1030°C, the Si(s) is 39.9 mol% of the total heterogeneous mixture; the $CaSi_2$(s) is 60.1 mol%.

A graph of mol% Si(s) and mol% $CaSi_2$ (s) vs. mol% eutectic liquid is a convenient way to show relative amounts of the three phases as the eutectic liquid freezes. See Fig. 6.16. Equations for the graph are derived with the law of conservation of mass. For the silicon mass,

$$nz_{Si} = n_{liq}w_{Si} + n_{Si}x_{Si} + n_{CaSi_2}y_{Si}$$

where n = total number of moles.

w_{Si} = Si fraction in eutectic liquid = 0.694
x_{Si} = Si fraction in Si(s) = 1.000
y_{Si} = Si fraction in $CaSi_2$(s) = 0.667
z_{Si} = Si fraction in melt = 0.800

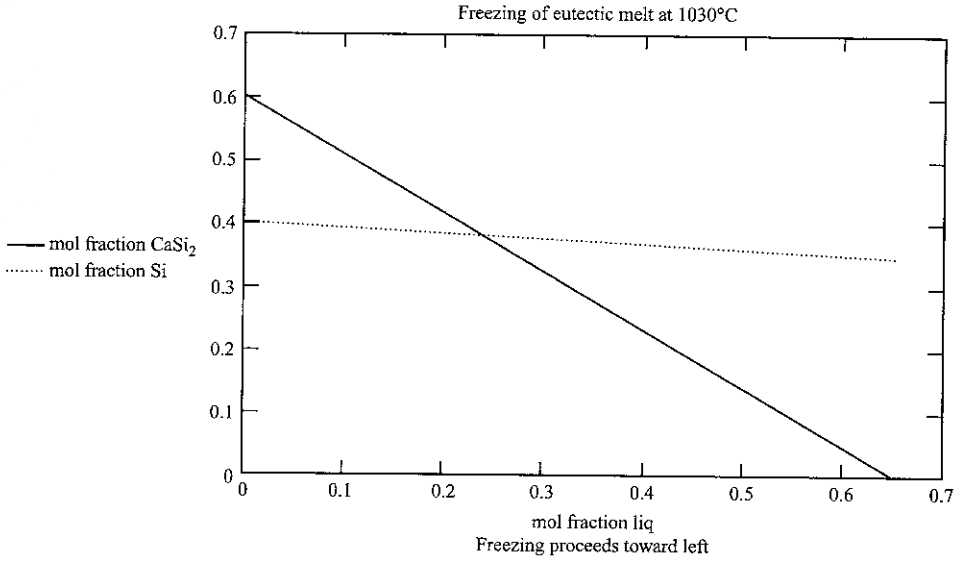

Figure 6.16

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

$$z_{Si} = (\text{mol fraction liq})w_{Si} + (\text{mol fraction Si})x_{Si} + (\text{mol fraction } CaSi_2)y_{Si}.$$

Since, (mol fraction liq) + (mol fraction Si) + (mol fraction $CaSi_2$) = 1
or (mol fraction $CaSi_2$) = 1 − (mol fraction liq + mol fraction Si), we may write:

$$z_{Si} = (\text{mol fraction liq})w_{Si} + (\text{mol fraction Si})x_{Si} + [1 - (\text{mol fraction liq} + \text{mol fraction Si})]y_{Si}.$$

Solving for mol fraction Si:

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

$$\text{mol fraction } CaSi_2 := 1 - (\text{mol fraction liq} + \text{mol fraction Si}).$$

These two eqns are used to prepare plots of the mol fraction of Si and mol fraction of $CaSi_2$ against the mol fraction of the melt in the range 0–0.65.

Solutions to theoretical problems

P6.11 The general condition of equilibrium in an isolated system is $dS = 0$. Hence, if α and β 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

$$dS = \left(\frac{\partial S_\alpha}{\partial U_\alpha}\right)_V dU_\alpha + \left(\frac{\partial S_\beta}{\partial U_\beta}\right)_V dU_\beta = \frac{1}{T_\alpha} dU_\alpha + \frac{1}{T_\beta} dU_\beta \text{ [3.45].}$$

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

Solutions to applications

P6.13 **(i)** Below a denaturant concentration of 0.1 only the native and unfolded forms are stable.

(ii) At denaturant concentration of 0.15 only the native form is stable below a temperature of about 0.70. At temperature 0.70 the native and molten-globule forms are at equilibrium. Heating above 0.70 causes all native forms to become molten-globules. At temperature 0.90, equilibrium between