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CHAPTER 10

PHASE DIAGRAMS

PROBLEM SOLUTIONS

Solubility Limit

10.1 (a) We are asked to determine how much sugar will dissolve in 1000 g of water at 80°C. From the solubility limit curve in Figure 10.1, at 80°C the maximum concentration of sugar in the syrup is about 74 wt%. It is now possible to calculate the mass of sugar using Equation 5.3 as

$$C_{\text{sugar}}(\text{wt\%}) = \frac{m_{\text{sugar}}}{m_{\text{sugar}} + m_{\text{water}}} \times 100$$

$$74 \text{ wt\%} = \frac{m_{\text{sugar}}}{m_{\text{sugar}} + 1000 \text{ g}} \times 100$$

Solving for m_{sugar} yields $m_{\text{sugar}} = 2846 \text{ g}$

- (b) Again using this same plot, at 20°C the solubility limit (or the concentration of the saturated solution) is about 64 wt% sugar.
- (c) The mass of sugar in this saturated solution at 20° C (m'_{sugar}) may also be calculated using Equation 5.3 as follows:

$$64 \text{ wt\%} = \frac{m'_{\text{sugar}}}{m'_{\text{sugar}} + 1000 \text{ g}} \times 100$$

which yields a value for m'_{sugar} of 1778 g. Subtracting the latter from the former of these sugar concentrations yields the amount of sugar that precipitated out of the solution upon cooling m''_{sugar} ; that is

$$m"_{\text{sugar}} = m_{\text{sugar}} - m'_{\text{sugar}} = 2846 \text{ g} - 1778 \text{ g} = 1068 \text{ g}$$

- 10.2 (a) From Figure 10.7, the maximum solubility of Pb in Sn at 100°C corresponds to the position of the β –(α + β) phase boundary at this temperature, or to about 1 wt% Pb.
- (b) From this same figure, the maximum solubility of Sn in Pb corresponds to the position of the α –(α + β) phase boundary at this temperature, or about 5 wt% Sn.

Microstructure

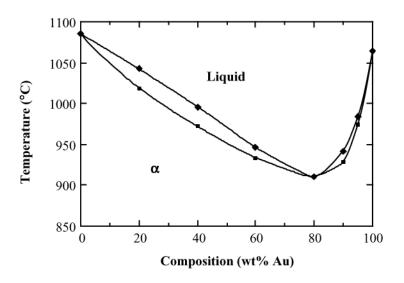
10.3 Three variables that determine the microstructure of an alloy are (1) the alloying elements present, (2) the concentrations of these alloying elements, and (3) the heat treatment of the alloy.

Phase Equilibria

- 10.4 In order for a system to exist in a state of equilibrium the free energy must be a minimum for some specified combination of temperature, pressure, and composition.
 - 10.5 This problem asks us to consider a specimen of ice I which is at -10°C and 1 atm pressure.
- (a) In order to determine the pressure at which melting occurs at this temperature, we move vertically at this temperature until we cross the Ice I-Liquid phase boundary of Figure 10.38. This occurs at approximately 570 atm; thus the pressure of the specimen must be raised from 1 to 570 atm.
- (b) In order to determine the pressure at which sublimation occurs at this temperature, we move vertically downward from 1 atm until we cross the Ice I-Vapor phase boundary of Figure 10.38. This intersection occurs at approximately 0.0023 atm.
- 10.6 The melting and boiling temperatures for ice I at a pressure of 0.01 atm may be determined by moving horizontally across the pressure-temperature diagram of Figure 10.38 at this pressure. The temperature corresponding to the intersection of the Ice I-Liquid phase boundary is the melting temperature, which is approximately 1°C. On the other hand, the boiling temperature is at the intersection of the horizontal line with the Liquid-Vapor phase boundary-approximately 28°C.

Binary Isomorphous Systems

10.7 The copper-gold phase diagram is constructed below.



Interpretation of Phase Diagrams

- 10.8 This problem asks that we cite the phase or phases present for several alloys at specified temperatures.
- (a) For an alloy composed of 15 wt% Sn-85 wt% Pb and at 100°C, from Figure 10.7, α and β phases are present, and

$$C_{\alpha} = 5 \text{ wt% Sn-95 wt% Pb}$$
 $C_{\beta} = 98 \text{ wt% Sn-2 wt% Pb}$

- (b) For an alloy composed of 25 wt% Pb-75 wt% Mg and at 425°C, from Figure 10.18, only the α phase is present; its composition is 25 wt% Pb-75 wt% Mg.
- (c) For an alloy composed of 85 wt% Ag-15 wt% Cu and at 800°C, from Figure 10.6, β and liquid phases are present, and

$$C_{\beta} = 92 \text{ wt% Ag-8 wt% Cu}$$

 $C_{L} = 77 \text{ wt% Ag-23 wt% Cu}$

(d) For an alloy composed of 55 wt% Zn-45 wt% Cu and at 600°C, from Figure 10.17, β and γ phases are present, and

$$C_{\beta} = 51$$
 wt% Zn-49 wt% Cu
 $C_{\gamma} = 58$ wt% Zn-42 wt% Cu

(e) For an alloy composed of 1.25 kg Sn and 14 kg Pb and at 200°C, we must first determine the Sn and Pb concentrations (using Equation 5.3), as

$$C_{\text{Sn}} = \frac{1.25 \text{ kg}}{1.25 \text{ kg} + 14 \text{ kg}} \times 100 = 8.2 \text{ wt}\%$$

$$C_{\text{Pb}} = \frac{14 \text{ kg}}{1.25 \text{ kg} + 14 \text{ kg}} \times 100 = 91.8 \text{ wt}\%$$

From Figure 10.7, only the α phase is present; its composition is 8.2 wt% Sn-91.8 wt% Pb.

(f) For an alloy composed of 7.6 lb_m Cu and 114.4 lb_m Zn and at 600°C, we must first determine the Cu and Zn concentrations (using Equation 5.3), as

$$C_{\text{Cu}} = \frac{7.6 \text{ lb}_{\text{m}}}{7.6 \text{ lb}_{\text{m}} + 144.4 \text{ lb}_{\text{m}}} \times 100 = 5.0 \text{ wt}\%$$

$$C_{\rm Zn} = \frac{144.4 \text{ lb}_{\rm m}}{7.6 \text{ lb}_{\rm m} + 144.4 \text{ lb}_{\rm m}} \times 100 = 95.0 \text{ wt}\%$$

From Figure 10.17, only the L phase is present; its composition is 95.0 wt% Zn-5.0 wt% Cu

(g) For an alloy composed of 21.7 mol Mg and 35.4 mol Pb and at 350°C, it is necessary to determine the Mg and Pb concentrations in weight percent. However, we must first compute the masses of Mg and Pb (in grams) using a rearranged form of Equation 5.4:

$$m_{Pb} = n_{m_{Pb}} A_{Pb} = (35.4 \text{ mol})(207.2 \text{ g/mol}) = 7335 \text{ g}$$

$$m_{\text{Mg}}' = n_{m_{\text{Mg}}} A_{\text{Mg}} = (21.7 \text{ mol})(24.3 \text{ g/mol}) = 527 \text{ g}$$

Now, using Equation 5.3, concentrations of Pb and Mg are determined as follows:

$$C_{\text{Pb}} = \frac{7335 \text{ g}}{7335 \text{ g} + 527 \text{ g}} \times 100 = 93 \text{ wt}\%$$

$$C_{\text{Mg}} = \frac{527 \text{ g}}{7335 \text{ g} + 527 \text{ g}} \times 100 = 7 \text{ wt}\%$$

From Figure 10.18, L and $\mathrm{Mg}_2\mathrm{Pb}$ phases are present, and

$$C_L = 94 \text{ wt}\% \text{ Pb} - 6 \text{ wt}\% \text{ Mg}$$

$$C_{\text{Mg}_{2}\text{Pb}} = 81 \text{ wt\% Pb} - 19 \text{ wt\% Mg}$$

(h) For an alloy composed of 4.2 mol Cu and 1.1 mol Ag and at 900°C, it is necessary to determine the Cu and Ag concentrations in weight percent. However, we must first compute the masses of Cu and Ag (in grams) using a rearranged form of Equation 5.4:

$$m_{\text{Cu}}' = n_{m_{\text{Cu}}} A_{\text{Cu}} = (4.2 \text{ mol})(63.55 \text{ g/mol}) = 266.9 \text{ g}$$

$$m_{Ag} = n_{m_{Ag}} A_{Ag} = (1.1 \text{ mol})(107.87 \text{ g/mol}) = 118.7 \text{ g}$$

Now, using Equation 5.3, concentrations of Cu and Ag are determined as follows:

$$C_{\text{Cu}} = \frac{266.9 \text{ g}}{266.9 \text{ g} + 118.7 \text{ g}} \times 100 = 69.2 \text{ wt}\%$$

$$C_{\text{Ag}} = \frac{118.7 \text{ g}}{266.9 \text{ g} + 118.7 \text{ g}} \times 100 = 30.8 \text{ wt}\%$$

From Figure 10.6, α and liquid phases are present; and

$$C_{\alpha} = 8 \text{ wt% Ag-92 w% Cu}$$

 $C_{I} = 45 \text{ wt% Ag-55 wt% Cu}$

- 10.9 It *is possible* to have a Cu-Ag alloy, which at equilibrium consists of a β phase of composition 92 wt% Ag-8 wt% Cu and a liquid phase of composition 76 wt% Ag-24 wt% Cu. From Figure 10.6 a horizontal tie line can be constructed across the $\beta + L$ phase region at about 800°C which intersects the $L-(\beta + L)$ phase boundary at 76 wt% Ag, and also the $(\beta + L)-\beta$ phase boundary at 92 wt% Ag.
- 10.10 It *is possible* to have a Cu-Ag alloy, which at equilibrium consists of an α phase of composition 4 wt% Ag-96 wt% Cu and a β phase of composition 95 wt% Ag-5 wt% Cu. From Figure 10.6 a horizontal tie can be constructed across the $\alpha + \beta$ region at 690°C which intersects the $\alpha (\alpha + \beta)$ phase boundary at 4 wt% Ag, and also the $(\alpha + \beta) \beta$ phase boundary at 95 wt% Ag.
- 10.11 Upon heating a lead-tin alloy of composition 30 wt% Sn-70 wt% Pb from 150°C and utilizing Figure 10.7:
- (a) The first liquid forms at the temperature at which a vertical line at this composition intersects the eutectic isotherm--i.e., at 183°C.
- (b) The composition of this liquid phase corresponds to the intersection with the $(\alpha + L)$ -L phase boundary, of a tie line constructed across the $\alpha + L$ phase region just above this eutectic isotherm--i.e., $C_L = 61.9$ wt% Sn.
- (c) Complete melting of the alloy occurs at the intersection of this same vertical line at 30 wt% Sn with the $(\alpha + L)$ -L phase boundary--i.e., at about 260°C.
- (d) The composition of the last solid remaining prior to complete melting corresponds to the intersection with α –(α + L) phase boundary, of the tie line constructed across the α + L phase region at 260°C--i.e., C_{α} is about 13 wt% Sn.
 - 10.12 Upon cooling a 50 wt% Ni-50 wt% Cu alloy from 1400°C and utilizing Figure 10.2a:
- (a) The first solid phase forms at the temperature at which a vertical line at this composition intersects the L–($\alpha + L$) phase boundary--i.e., at about 1320°C.
- (b) The composition of this solid phase corresponds to the intersection with the L-(α + L) phase boundary, of a tie line constructed across the α + L phase region at 1320°C--i.e., C_{α} = 62 wt% Ni-38 wt% Cu.
- (c) Complete solidification of the alloy occurs at the intersection of this same vertical line at 50 wt% Ni with the $(\alpha + L)$ - α phase boundary--i.e., at about 1270°C.
- (d) The composition of the last liquid phase remaining prior to complete solidification corresponds to the intersection with the L-(α + L) boundary, of the tie line constructed across the α + L phase region at 1270°C--i.e., C_L is about 37 wt% Ni-63 wt% Cu.

10.13 This problem asks us to determine the phases present and their concentrations at several temperatures, as an alloy of composition 52 wt% Zn-48 wt% Cu is cooled. From Figure 10.17:

At 1000°C, a liquid phase is present; $W_L = 1.0$

At 800°C, the β phase is present, and $W_{\beta} = 1.0$

At 500°C, β and γ phases are present, and

$$W_{\gamma} = \frac{C_0 - C_{\beta}}{C_{\gamma} - C_{\beta}} = \frac{52 - 49}{58 - 49} = 0.33$$

$$W_{\beta} = 1.00 - 0.33 = 0.67$$

At 300°C, the β' and γ phases are present, and

$$W_{\beta'} = \frac{C_{\gamma} - C_0}{C_{\gamma} - C_{\beta'}} = \frac{59 - 52}{59 - 50} = 0.78$$

$$W_{\gamma} = 1.00 - 0.78 = 0.22$$

10.14 This problem asks that we determine the phase mass fractions for the alloys and temperatures in Problem 10.8.

(a)
$$W_{\alpha} = \frac{C_{\beta} - C_{0}}{C_{\beta} - C_{\alpha}} = \frac{98 - 15}{98 - 5} = 0.89$$

$$W_{\beta} = \frac{C_0 - C_{\alpha}}{C_{\beta} - C_{\alpha}} = \frac{15 - 5}{98 - 5} = 0.11$$

(b)
$$W_{\alpha} = 1.0$$

(c)
$$W_{\beta} = \frac{C_0 - C_L}{C_{\beta} - C_L} = \frac{85 - 77}{92 - 77} = 0.53$$

$$W_L = \frac{C_{\beta} - C_0}{C_{\beta} - C_L} = \frac{92 - 85}{92 - 77} = 0.47$$

(d)
$$W_{\beta} = \frac{C_{\gamma} - C_{0}}{C_{\gamma} - C_{\beta}} = \frac{58 - 55}{58 - 51} = 0.43$$

$$W_{\gamma} = \frac{C_0 - C_{\beta}}{C_{\gamma} - C_{\beta}} = \frac{55 - 51}{58 - 51} = 0.57$$

(e)
$$W_{\alpha} = 1.0$$

(f)
$$W_L = 1.0$$

(g)
$$W_{\text{Mg}_2\text{Pb}} = \frac{C_{\text{L}} - C_0}{C_{\text{L}} - C_{\text{Mg}_2\text{Pb}}} = \frac{94 - 93}{94 - 81} = 0.08$$

$$W_L = \frac{C_0 - C_{\text{Mg}_2\text{Pb}}}{C_L - C_{\text{Mg}_2\text{Pb}}} = \frac{93 - 81}{94 - 81} = 0.92$$

(h)
$$W_{\alpha} = \frac{C_L - C_0}{C_L - C_{\alpha}} = \frac{45 - 30.8}{45 - 8} = 0.38$$

$$W_L = \frac{C_0 - C_{\alpha}}{C_L - C_{\alpha}} = \frac{30.8 - 8}{45 - 8} = 0.62$$

10.15 (a) This part of the problem calls for us to cite the temperature to which a 90 wt% Pb-10 wt% Sn alloy must be heated in order to have 50% liquid. Probably the easiest way to solve this problem is by trial and error--that is, on the Pb-Sn phase diagram (Figure 10.7), moving vertically at the given composition, through the α + L region until the tie-line lengths on both sides of the given composition are the same. This occurs at approximately 300°C (570°F).

(b) We can also produce a 50% liquid solution at 250°C, by adding Sn to the alloy. At 250°C and within the $\alpha + L$ phase region

$$C_{\alpha} = 13 \text{ wt\% Sn-87 wt\% Pb}$$

 $C_{I} = 39 \text{ wt\% Sn-61 wt\% Pb}$

Let C_0 be the new alloy composition to give $W_{\alpha} = W_L = 0.5$. Then,

$$W_{\alpha} = 0.5 = \frac{C_L - C_0}{C_L - C_{\alpha}} = \frac{39 - C_0}{39 - 13}$$

And solving for C_0 gives 26 wt% Sn. Now, let $m_{\rm Sn}$ be the mass of Sn added to the alloy to achieve this new composition. The amount of Sn in the original alloy is

$$(0.10)(1.5 \text{ kg}) = 0.15 \text{ kg}$$

Then, using a modified form of Equation 5.3

$$\left[\frac{0.15 \text{ kg} + m_{\text{Sn}}}{1.5 \text{ kg} + m_{\text{Sn}}} \right] \times 100 = 26$$

And, solving for m_{Sn} (the mass of tin to be added), yields $m_{\text{Sn}} = 0.324$ kg.

- 10.16 (a) This portion of the problem asks that we calculate, for a Pb-Mg alloy, the mass of lead in 7.5 kg of the solid α phase at 300°C just below the solubility limit. From Figure 10.18, the solubility limit for the α phase at 300°C corresponds to the position (composition) of the α - α + Mg₂Pb phase boundary at this temperature, which is about 17 wt% Pb. Therefore, the mass of Pb in the alloy is just (0.17)(7.5 kg) = 1.3 kg.
- (b) At 400°C, the solubility limit of the α phase increases to approximately 32 wt% Pb. In order to determine the additional amount of Pb that may be added ($m_{\mathrm{Pb'}}$), we utilize a modified form of Equation 5.3 as

$$C_{\text{Pb}} = 32 \text{ wt\%} = \frac{1.3 \text{ kg} + m_{\text{Pb'}}}{7.5 \text{ kg} + m_{\text{Pb'}}} \times 100$$

Solving for $m_{\text{Pb'}}$ yields $m_{\text{Pb'}} = 1.62 \text{ kg.}$

- 10.17 (a) In order to determine the temperature of a 65 wt% Ni-35 wt% Cu alloy for which α and liquid phases are present with the α phase of composition 70 wt% Ni, we need to construct a tie line across the $\alpha + L$ phase region of Figure 10.2a that intersects the solidus line at 70 wt% Ni; this is possible at about 1340°C.
- (b) The composition of the liquid phase at this temperature is determined from the intersection of this same tie line with liquidus line, which corresponds to about 59 wt% Ni.
- (c) The mass fractions of the two phases are determined using the lever rule, Equations 10.1 and 10.2 with $C_0 = 65$ wt% Ni, $C_L = 59$ wt% Ni, and $C_\alpha = 70$ wt% Ni, as

$$W_{\alpha} = \frac{C_0 - C_L}{C_{\alpha} - C_L} = \frac{65 - 59}{70 - 59} = 0.55$$

$$W_L = \frac{C_{\alpha} - C_0}{C_{\alpha} - C_I} = \frac{70 - 65}{70 - 59} = 0.45$$

- 10.18 (a) We are given that the mass fractions of α and liquid phases are both 0.5 for a 40 wt% Pb-60 wt% Mg alloy and are asked to estimate the temperature of the alloy. Using the appropriate phase diagram, Figure 10.18, by trial and error with a ruler, a tie line within the $\alpha + L$ phase region that is divided in half for an alloy of this composition exists at about 540°C.
- (b) We are now asked to determine the compositions of the two phases. This is accomplished by noting the intersections of this tie line with both the solidus and liquidus lines. From these intersections, $C_{\alpha} = 26$ wt% Pb, and $C_{I} = 54$ wt% Pb.
- 10.19 The problem is to solve for compositions at the phase boundaries for both α and β phases (i.e., C_{α} and C_{β}). We may set up two independent lever rule expressions, one for each composition, in terms of C_{α} and C_{β} as follows:

$$W_{\alpha 1} = 0.57 = \frac{C_{\beta} - C_{01}}{C_{\beta} - C_{\alpha}} = \frac{C_{\beta} - 60}{C_{\beta} - C_{\alpha}}$$

$$W_{\alpha 2} = 0.14 = \frac{C_{\beta} - C_{02}}{C_{\beta} - C_{\alpha}} = \frac{C_{\beta} - 30}{C_{\beta} - C_{\alpha}}$$

In these expressions, compositions are given in wt% of A. Solving for C_{α} and C_{β} from these equations, yield

$$C_{\alpha} = 90 \text{ (or } 90 \text{ wt\% A-10 wt\% B)}$$

$$C_{\beta} = 20.2 \text{ (or } 20.2 \text{ wt% A-79.8 wt% B)}$$

10.20 For this problem, we are asked to determine the composition of the α phase given that

$$C_0 = 55$$
 (or 55 wt% B-45 wt% A)

$$C_{\beta} = 90 \text{ (or } 90 \text{ wt% B-10 wt% A)}$$

$$W_{\alpha} = W_{\beta} = 0.5$$

If we set up the lever rule for W_{α}

$$W_{\alpha} = 0.5 = \frac{C_{\beta} - C_{0}}{C_{\beta} - C_{\alpha}} = \frac{90 - 55}{90 - C_{\alpha}}$$

And solving for C_{α}

$$C_{G} = 20 \text{ (or } 20 \text{ wt\% B-80 wt\% A)}$$

10.21 Yes, it is possible to have a Cu-Ag alloy of composition 20 wt% Ag-80 wt% Cu which consists of mass fractions $W_{\alpha} = 0.80$ and $W_{L} = 0.20$. Using the appropriate phase diagram, Figure 10.6, by trial and error with a ruler, the tie-line segments within the α + L phase region are proportioned such that

$$W_{\alpha} = 0.8 = \frac{C_L - C_0}{C_L - C_{\alpha}}$$

for $C_0 = 20$ wt% Ag. This occurs at about 800°C.

10.22 It is *not possible* to have a 50 wt% Pb-50 wt% Mg alloy that has masses of 5.13 kg and 0.57 kg for the α and Mg₂Pb phases, respectively. In order to demonstrate this, it is first necessary to determine the mass fraction of each phase as:

$$W_{\alpha} = \frac{m_{\alpha}}{m_{\alpha} + m_{\text{Mg}_{2}\text{Pb}}} = \frac{5.13 \text{ kg}}{5.13 \text{ kg} + 0.57 \text{ kg}} = 0.90$$

$$W_{\text{Mg}_2\text{Pb}} = 1.00 - 0.90 = 0.10$$

Now, if we apply the lever rule expression for W_{α}

$$W_{\alpha} = \frac{C_{\text{Mg}_2\text{Pb}} - C_0}{C_{\text{Mg}_2\text{Pb}} - C_{\alpha}}$$

Since the Mg_2Pb phase exists only at 81 wt% Pb, and $C_0 = 50$ wt% Pb

$$W_{\alpha} = 0.90 = \frac{81 - 50}{81 - C_{\alpha}}$$

Solving for C_{α} from this expression yields $C_{\alpha} = 46.6$ wt% Pb. From Figure 10.18, the maximum concentration of Pb in the α phase in the $\alpha + Mg_2$ Pb phase field is about 42 wt% Pb. Therefore, this alloy is not possible.

10.23 This portion of the problem asks that we derive Equation 10.6a, which is used to convert from phase weight fraction to phase volume fraction. Volume fraction of phase α , V_{α} , is defined by Equation 10.5 as

$$V_{\alpha} = \frac{v_{\alpha}}{v_{\alpha} + v_{\beta}} \tag{10.S1}$$

where v_{α} and v_{β} are the volumes of the respective phases in the alloy. Furthermore, the density of each phase is equal to the ratio of its mass and volume, or upon rearrangement

$$v_{\alpha} = \frac{m_{\alpha}}{\rho_{\alpha}} \tag{10.S2a}$$

$$v_{\beta} = \frac{m_{\beta}}{\rho_{\beta}} \tag{10.S2b}$$

Substitution of these expressions into Equation 10.S1 leads to

$$V_{\alpha} = \frac{\frac{m_{\alpha}}{\rho_{\alpha}}}{\frac{m_{\alpha}}{\rho_{\alpha}} + \frac{m_{\beta}}{\rho_{\beta}}}$$
(10.S3)

in which m's and ρ 's denote masses and densities, respectively. Now, the mass fractions of the α and β phases (i.e., W_{α} and W_{β}) are defined in terms of the phase masses as

$$W_{\alpha} = \frac{m_{\alpha}}{m_{\alpha} + m_{\beta}} \tag{10.S4a}$$

$$W_{\beta} = \frac{m_{\beta}}{m_{\alpha} + m_{\beta}} \tag{10.S4b}$$

Which, upon rearrangement yield

$$m_{\alpha} = W_{\alpha} \left(m_{\alpha} + m_{\beta} \right) \tag{10.S5a}$$

$$m_{\mathbf{B}} = W_{\mathbf{B}} \left(m_{\alpha} + m_{\mathbf{B}} \right) \tag{10.S5b}$$

Incorporation of these relationships into Equation 10.S3 leads to

$$V_{\alpha} = \frac{\frac{W_{\alpha} (m_{\alpha} + m_{\beta})}{\rho_{\alpha}}}{\frac{W_{\alpha} (m_{\alpha} + m_{\beta})}{\rho_{\alpha}} + \frac{W_{\beta} (m_{\alpha} + m_{\beta})}{\rho_{\beta}}}$$

$$V_{\alpha} = \frac{\frac{W_{\alpha}}{\rho_{\alpha}}}{\frac{W_{\alpha}}{\rho_{\alpha}} + \frac{W_{\beta}}{\rho_{\beta}}}$$
(10.S6)

which is the desired equation.

For this portion of the problem we are asked to derive Equation 10.7a, which is used to convert from phase volume fraction to mass fraction. Mass fraction of the α phase is defined as

$$W_{\alpha} = \frac{m_{\alpha}}{m_{\alpha} + m_{\beta}} \tag{10.S7}$$

From Equations 10.S2a and 10.S2b

$$m_{\alpha} = v_{\alpha} \rho_{\alpha}$$
 (10.S8a)

$$m_{\beta} = v_{\beta} \rho_{\beta} \tag{10.88b}$$

Substitution of these expressions into Equation 10.S7 yields

$$W_{\alpha} = \frac{v_{\alpha} \rho_{\alpha}}{v_{\alpha} \rho_{\alpha} + v_{\beta} \rho_{\beta}}$$
 (10.S9)

From Equation 10.5 and its equivalent for V_{β} the following may be written:

$$v_{\alpha} = V_{\alpha} \left(v_{\alpha} + v_{\beta} \right) \tag{10.S10a}$$

$$v_{\beta} = V_{\beta} (v_{\alpha} + v_{\beta}) \tag{10.S10b}$$

Substitution of Equations 10.S10a and 10.S10b into Equation 10.S9 yields

$$W_{\alpha} = \frac{V_{\alpha}(v_{\alpha} + v_{\beta})\rho_{\alpha}}{V_{\alpha}(v_{\alpha} + v_{\beta})\rho_{\alpha} + V_{\beta}(v_{\alpha} + v_{\beta})\rho_{\beta}}$$

$$W_{\alpha} = \frac{V_{\alpha} \rho_{\alpha}}{V_{\alpha} \rho_{\alpha} + V_{\beta} \rho_{\beta}}$$
 (10.S11)

which is the desired expression.

10.24 This problem asks that we determine the phase volume fractions for the alloys and temperatures in Problems 10.8a, b, and d. This is accomplished by using the technique illustrated in Example Problem 10.3, and also the results of Problems 10.8 and 10.14.

(a) This is a Sn-Pb alloy at 100°C, wherein

$$C_{\alpha} = 5$$
 wt% Sn-95 wt% Pb
 $C_{\beta} = 98$ wt% Sn-2 wt% Pb
 $W_{\alpha} = 0.89$
 $W_{\beta} = 0.11$
 $\rho_{\text{Sn}} = 7.29 \text{ g/cm}^3$
 $\rho_{\text{Pb}} = 11.27 \text{ g/cm}^3$

Using these data it is first necessary to compute the densities of the α and β phases using Equation 5.10a.

Thus

$$\rho_{\alpha} = \frac{100}{\frac{C_{\text{Sn}(\alpha)}}{\rho_{\text{Sn}}} + \frac{C_{\text{Pb}(\alpha)}}{\rho_{\text{Pb}}}}$$

$$= \frac{100}{\frac{5}{7.29 \text{ g/cm}^3} + \frac{95}{11.27 \text{ g/cm}^3}} = 10.97 \text{ g/cm}^3$$

$$\rho_{\beta} = \frac{100}{\frac{C_{\text{Sn }(\beta)}}{\rho_{\text{Sn}}} + \frac{C_{\text{Pb}(\beta)}}{\rho_{\text{Pb}}}}$$

$$= \frac{100}{\frac{98}{7.29 \text{ g/cm}^3} + \frac{2}{11.27 \text{ g/cm}^3}} = 7.34 \text{ g/cm}^3$$

Now we may determine the V_{α} and V_{β} values using Equation 10.6. Thus,

$$V_{\alpha} = \frac{\frac{W_{\alpha}}{\rho_{\alpha}}}{\frac{W_{\alpha}}{\rho_{\alpha}} + \frac{W_{\beta}}{\rho_{\beta}}}$$

$$= \frac{\frac{0.89}{10.97 \text{ g/cm}^3}}{\frac{0.89}{10.97 \text{ g/cm}^3} + \frac{0.11}{7.34 \text{ g/cm}^3}} = 0.84$$

$$V_{\beta} = \frac{\frac{W_{\beta}}{\rho_{\beta}}}{\frac{W_{\alpha}}{\rho_{\alpha}} + \frac{W_{\beta}}{\rho_{\beta}}}$$

$$= \frac{\frac{0.11}{7.34 \text{ g/cm}^3}}{\frac{0.89}{10.97 \text{ g/cm}^3} + \frac{0.11}{7.34 \text{ g/cm}^3}} = 0.16$$

- (b) This is a Pb-Mg alloy at 425°C, wherein only the α phase is present. Therefore, $V_{\alpha} = 1.0$.
- (d) This is a Zn-Cu alloy at 600°C, wherein

$$C_{\beta} = 51 \text{ wt% Zn-49 wt% Cu}$$
 $C_{\gamma} = 58 \text{ wt% Zn-42 wt% Cu}$
 $W_{\beta} = 0.43$
 $W_{\gamma} = 0.57$
 $\rho_{\text{Zn}} = 6.67 \text{ g/cm}^3$
 $\rho_{\text{Cu}} = 8.68 \text{ g/cm}^3$

Using these data it is first necessary to compute the densities of the β and γ phases using Equation 5.10a. Thus

$$\rho_{\beta} = \frac{100}{\frac{C_{\text{Zn }(\beta)}}{\rho_{\text{Zn}}} + \frac{C_{\text{Cu }(\beta)}}{\rho_{\text{Cu}}}}$$

$$= \frac{100}{\frac{51}{6.67 \text{ g/cm}^3} + \frac{49}{8.68 \text{ g/cm}^3}} = 7.52 \text{ g/cm}^3$$

$$\rho_{\gamma} = \frac{100}{\frac{C_{\text{Zn }(\gamma)}}{\rho_{\text{Zn}}} + \frac{C_{\text{Cu }(\gamma)}}{\rho_{\text{Cu}}}}$$

$$= \frac{100}{\frac{58}{6.67 \text{ g/cm}^3} + \frac{42}{8.68 \text{ g/cm}^3}} = 7.39 \text{ g/cm}^3$$

Now we may determine the V_{β} and V_{γ} values using Equation 10.6. Thus,

$$V_{\beta} = \frac{\frac{W_{\beta}}{\rho_{\beta}}}{\frac{W_{\beta}}{\rho_{\beta}} + \frac{W_{\gamma}}{\rho_{\gamma}}}$$

$$= \frac{\frac{0.43}{7.52 \text{ g/cm}^3}}{\frac{0.43}{7.52 \text{ g/cm}^3} + \frac{0.57}{7.39 \text{ g/cm}^3}} = 0.43$$

$$V_{\gamma} = \frac{\frac{W_{\gamma}}{\rho_{\gamma}}}{\frac{W_{\beta}}{\rho_{\beta}} + \frac{W_{\gamma}}{\rho_{\gamma}}}$$

$$= \frac{\frac{0.57}{7.39 \text{ g/cm}^3}}{\frac{0.43}{7.52 \text{ g/cm}^3} + \frac{0.57}{7.39 \text{ g/cm}^3}} = 0.57$$

Development of Microstructure in Isomorphous Alloys

10.25 (a) Coring is the phenomenon whereby concentration gradients exist across grains in polycrystalline alloys, with higher concentrations of the component having the lower melting temperature at the grain boundaries.

It occurs, during solidification, as a consequence of cooling rates that are too rapid to allow for the maintenance of the equilibrium composition of the solid phase.

(b) One undesirable consequence of a cored structure is that, upon heating, the grain boundary regions will melt first and at a temperature below the equilibrium phase boundary from the phase diagram; this melting results in a loss in mechanical integrity of the alloy.

Mechanical Properties of Isomorphous Alloys

10.26 This problem asks if a noncold-worked Cu-Ni solid solution alloy is possible having a minimum tensile strength of 380 MPa (55,000 psi) and also a ductility of at least 45%EL. From Figure 10.5a, a tensile strength greater than 380 MPa is possible for compositions between about 34 and 87 wt% Ni. On the other hand, according to Figure 10.5b, ductilities greater than 45%EL exist for compositions less than about 7 wt% and greater than about 71 wt% Ni. Therefore, the stipulated criteria are met for all compositions between 71 and 87 wt% Ni.

Binary Eutectic Systems

10.27 We are asked to determine the approximate temperature from which a Pb-Mg alloy was quenched, given the mass fractions of α and Mg₂Pb phases. We can write a lever-rule expression for the mass fraction of the α phase as

$$W_{\alpha} = 0.65 = \frac{C_{\text{Mg}_2\text{Pb}} - C_0}{C_{\text{Mg}_2\text{Pb}} - C_{\alpha}}$$

The value of C_0 is stated as 45 wt% Pb-55 wt% Mg, and $C_{\rm Mg_2Pb}$ is 81 wt% Pb-19 wt% Mg, which is independent of temperature (Figure 10.18); thus,

$$0.65 = \frac{81 - 45}{81 - C_{\alpha}}$$

which yields

$$C_{\alpha} = 25.6 \text{ wt}\% \text{ Pb}$$

The temperature at which the α –(α + Mg₂Pb) phase boundary (Figure 10.18) has a value of 25.6 wt% Pb is about 360°C (680°F).

Development of Microstructure in Eutectic Alloys

10.28 Upon solidification, an alloy of eutectic composition forms a microstructure consisting of alternating layers of the two solid phases because during the solidification atomic diffusion must occur, and with this layered configuration the diffusion path length for the atoms is a minimum.

10.29 A "phase" is a homogeneous portion of the system having uniform physical and chemical characteristics, whereas a "microconstituent" is an identifiable element of the microstructure (that may consist of more than one phase).

10.30 This problem asks if it is possible to have a Mg-Pb alloy for which the mass fractions of primary α and total α are 0.60 and 0.85, respectively, at 460°C. In order to make this determination we need to set up the appropriate lever rule expression for each of these quantities. From Figure 10.18 and at 460°C, $C_{\alpha} = 41$ wt% Pb, $C_{\text{Mg }_{2}\text{Pb}} = 81$ wt% Pb, and $C_{\text{eutectic}} = 67$ wt% Pb.

For primary α

$$W_{\alpha'} = \frac{C_{\text{eutectic}} - C_0}{C_{\text{eutectic}} - C_{\alpha}} = \frac{67 - C_0}{67 - 41} = 0.60$$

Solving for C_0 gives $C_0 = 51.4$ wt% Pb.

Now the analogous expression for total α

$$W_{\alpha} = \frac{C_{\text{Mg}_{2}\text{Pb}} - C_{0}}{C_{\text{Mg}_{2}\text{Pb}} - C_{\alpha}} = \frac{81 - C_{0}}{81 - 41} = 0.85$$

which yields a value of 47 wt% Pb for C_0 . Therefore, since these two C_0 values are different, this alloy is *not* possible.

10.31 This problem asks if it is possible to have a Pb-Sn alloy for which the masses of primary β and total β are 2.21 and 2.53 kg, respectively in 2.8 kg total of the alloy at 180° C. In order to make this determination we first need to convert these masses to mass fractions. Thus,

$$W_{\beta'} = \frac{2.21 \text{ kg}}{2.8 \text{ kg}} = 0.789$$

$$W_{\beta} = \frac{2.53 \text{ kg}}{2.8 \text{ kg}} = 0.904$$

Next it is necessary to set up the appropriate lever rule expression for each of these quantities. From Figure 10.7 and at 180°C, $C_{\alpha} = 18.3$ wt% Sn, $C_{\beta} = 97.8$ wt% Sn, and $C_{\text{eutectic}} = 61.9$ wt% Sn.

For primary β

$$W_{\beta'} = \frac{C_0 - C_{\text{eutectic}}}{C_B - C_{\text{eutectic}}} = \frac{C_0 - 61.9}{97.8 - 61.9} = 0.789$$

And solving for C_0 gives $C_0 = 90.2$ wt% Sn.

Now the analogous expression for total β

$$W_{\beta} = \frac{C_0 - C_{\alpha}}{C_{\beta} - C_{\alpha}} = \frac{C_0 - 18.3}{97.8 - 18.3} = 0.904$$

And this value of C_0 is also 90.2 wt% Sn. Therefore, since these two C_0 values are identical, this alloy is possible.

10.32 (a) This portion of the problem asks that we determine the mass fractions of α and β phases for an 80 wt% Sn-20 wt% Pb alloy (at 180°C). In order to do this it is necessary to employ the lever rule using a tie line that extends entirely across the $\alpha+\beta$ phase field. From Figure 10.7 and at 180°C, $C_{\alpha}=18.3$ wt% Sn, $C_{\beta}=97.8$ wt% Sn, and $C_{\rm eutectic}=61.9$ wt% Sn. Therefore, the two lever-rule expressions are as follows:

$$W_{\alpha} = \frac{C_{\beta} - C_{0}}{C_{\beta} - C_{\alpha}} = \frac{97.8 - 80}{97.8 - 18.3} = 0.224$$

$$W_{\beta} = \frac{C_0 - C_{\alpha}}{C_{\beta} - C_{\alpha}} = \frac{80 - 18.3}{97.8 - 18.3} = 0.776$$

(b) Now it is necessary to determine the mass fractions of primary β and eutectic microconstituents for this same alloy. This requires that we utilize the lever rule and a tie line that extends from the maximum solubility of Pb in the β phase at 180°C (i.e., 97.8 wt% Sn) to the eutectic composition (61.9 wt% Sn). Thus

$$W_{\beta'} = \frac{C_0 - C_{\text{eutectic}}}{C_{\beta} - C_{\text{eutectic}}} = \frac{80.0 - 61.9}{97.8 - 61.9} = 0.504$$

$$W_{\rm e} = \frac{C_{\rm \beta} - C_{\rm 0}}{C_{\rm \beta} - C_{\rm eutectic}} = \frac{97.8 - 80.0}{97.8 - 61.9} = 0.496$$

(c) And, finally, we are asked to compute the mass fraction of eutectic β , $W_{e\beta}$. This quantity is simply the difference between the mass fractions of total β and primary β as

$$W_{e\beta} = W_{\beta} - W_{\beta'} = 0.776 - 0.504 = 0.272$$

10.33 This problem asks that we determine the composition of a Cu-Ag alloy at 775°C given that $W_{\alpha'}=0.73$ and $W_{\rm eutectic}=0.27$. Since there is a primary α microconstituent present, we know that the alloy composition, C_0 is between 8.0 and 71.9 wt% Ag (Figure 10.6). Furthermore, this figure also indicates that $C_{\alpha}=8.0$ wt% Ag and $C_{\rm eutectic}=71.9$ wt% Ag. Applying the appropriate lever rule expression for $W_{\alpha'}$

$$W_{\alpha'} = \frac{C_{\text{eutectic}} - C_0}{C_{\text{eutectic}} - C_{\alpha}} = \frac{71.9 - C_0}{71.9 - 8.0} = 0.73$$

and solving for C_0 yields $C_0 = 25.2$ wt% Ag.

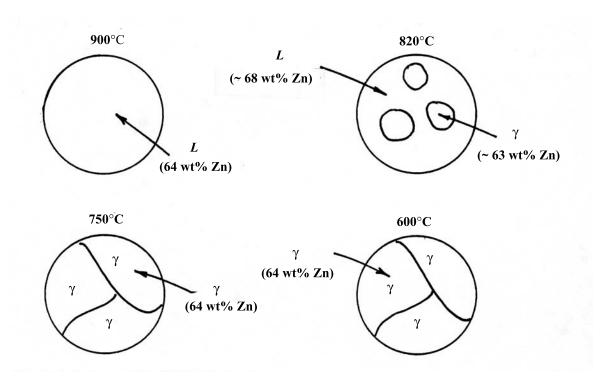
10.34 We are given a hypothetical eutectic phase diagram for which $C_{\rm eutectic} = 64$ wt% B, $C_{\alpha} = 12$ wt% B at the eutectic temperature, and also that $W_{\beta'} = 0.367$ and $W_{\beta} = 0.768$; from this we are asked to determine the composition of the alloy. Let us write lever rule expressions for $W_{\beta'}$ and W_{β}

$$W_{\beta} = \frac{C_0 - C_{\alpha}}{C_{\beta} - C_{\alpha}} = \frac{C_0 - 12}{C_{\beta} - 12} = 0.768$$

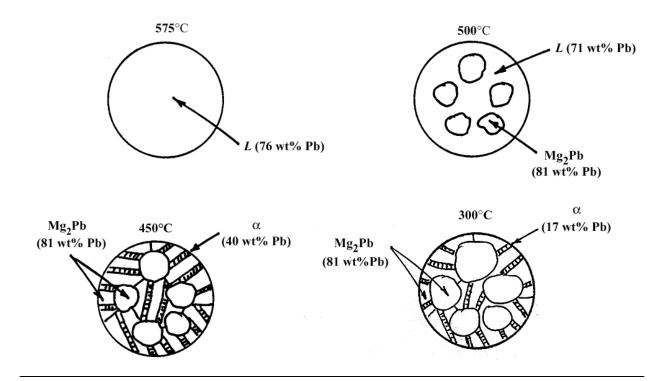
$$W_{\beta'} = \frac{C_0 - C_{\text{eutectic}}}{C_{\beta} - C_{\text{eutectic}}} = \frac{C_0 - 64}{C_{\beta} - 64} = 0.367$$

Thus, we have two simultaneous equations with C_0 and C_{β} as unknowns. Solving them for C_0 gives $C_0 = 75$ wt% B.

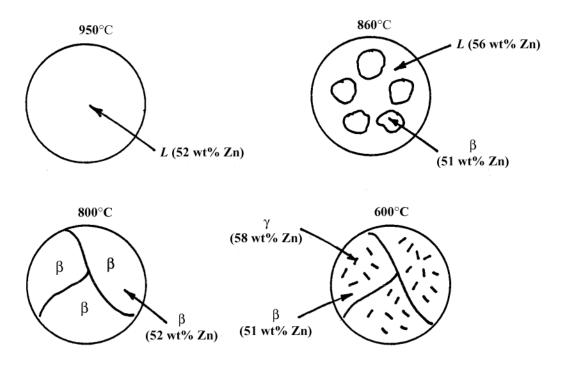
10.35 Schematic sketches of the microstructures that would be observed for an 64 wt% Zn-36 wt% Cu alloy at temperatures of 900°C, 820°C, 750°C, and 600°C are shown below. The phase compositions are also indicated.



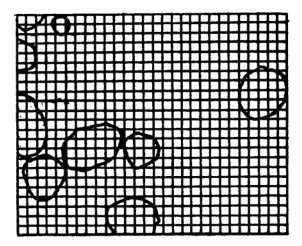
10.36 Schematic sketches of the microstructures that would be observed for a 76 wt% Pb-24 wt% Mg alloy at temperatures of 575°C, 500°C, 450°C, and 300°C are shown below. The phase compositions are also indicated.



10.37 Schematic sketches of the microstructures that would be observed for a 52 wt% Zn-48 wt% Cu alloy at temperatures of 950°C, 860°C, 800°C, and 600°C are shown below. The phase compositions are also indicated.



10.38 We are asked in this problem to estimate the composition of the Pb-Sn alloy which microstructure is shown in Figure 10.15. Primary α and eutectic microconstituents are present in the photomicrograph, and it is given that their densities are 11.2 and 8.7 g/cm³, respectively. Below is shown a square grid network onto which is superimposed outlines of the primary α phase areas.



The area fraction of this primary α phase may be determined by counting squares. There are a total of 644 squares, and of these, approximately 104 lie within the primary α phase particles. Thus, the area fraction of primary α is 104/644 = 0.16, which is also assumed to be the volume fraction.

We now want to convert the volume fractions into mass fractions in order to employ the lever rule to the Pb-Sn phase diagram. To do this, it is necessary to utilize Equations 10.7a and 10.7b as follows:

$$W_{\alpha'} = \frac{V_{\alpha'} \, \rho_{\alpha'}}{V_{\alpha'} \, \rho_{\alpha'} + V_{\text{eutectic}} \, \rho_{\text{eutectic}}}$$

$$= \frac{(0.16)(11.2 \text{ g/cm}^3)}{(0.16)(11.2 \text{ g/cm}^3) + (0.84)(8.7 \text{ g/cm}^3)} = 0.197$$

$$W_{\text{eutectic}} = \frac{V_{\text{eutectic}} \rho_{\text{eutectic}}}{V_{\alpha'} \rho_{\alpha'} + V_{\text{eutectic}} \rho_{\text{eutectic}}}$$

$$= \frac{(0.84)(8.7 \text{ g/cm}^3)}{(0.16)(11.2 \text{ g/cm}^3) + (0.84)(8.7 \text{ g/cm}^3)} = 0.803$$

From Figure 10.7, we want to use the lever rule and a tie-line that extends from the eutectic composition (61.9 wt% Sn) to the α -(α + β) phase boundary at 180°C (about 18.3 wt% Sn). Accordingly

$$W_{\alpha'} = 0.197 = \frac{61.9 - C_0}{61.9 - 18.3}$$

wherein C_0 is the alloy composition (in wt% Sn). Solving for C_0 yields $C_0 = 53.3$ wt% Sn. This value is in good agreement with the actual composition—viz. 50 wt% Sn.

Equilibrium Diagrams Having Intermediate Phases or Compounds

10.39 This problem gives us the compositions in weight percent for the two intermetallic compounds AB and AB₂, and then asks us to identify element B if element A is potassium. Probably the easiest way to solve this problem is to first compute the ratio of the atomic weights of these two elements using Equation 5.6a; then, since we know the atomic weight of potassium (39.10 g/mol), it is possible to determine the atomic weight of element B, from which an identification may be made.

First of all, consider the AB intermetallic compound; inasmuch as it contains the same numbers of A and B atoms, its composition in atomic percent is 50 at% A-50 at% B. Equation 5.6a may be written in the form:

$$C_{\rm B}' = \frac{C_{\rm B}A_{\rm A}}{C_{\rm A}A_{\rm B} + C_{\rm B}A_{\rm A}} \times 100$$

where A_A and A_B are the atomic weights for elements A and B, and C_A and C_B are their compositions in weight percent. For this AB compound, and making the appropriate substitutions in the above equation leads to

50 at% B =
$$\frac{(65.7 \text{ wt% B})(A_A)}{(34.3 \text{ wt% A})(A_B) + (65.7 \text{ wt% B})(A_A)} \times 100$$

Now, solving this expression yields,

$$A_{\rm B} = 1.916 \, A_{\rm A}$$

Since potassium is element A and it has an atomic weight of 39.10 g/mol, the atomic weight of element B is just

$$A_{\mathbf{B}} = (1.916)(39.10 \text{ g/mol}) = 74.92 \text{ g/mol}$$

Upon consultation of the period table of the elements (Figure 2.6) we note that arsenic has an atomic weight of 74.92 g/mol; therefore, element B is arsenic.

Congruent Phase Transformations Eutectoid and Peritectic Reactions

10.40 The principal difference between congruent and incongruent phase transformations is that for congruent no compositional changes occur with any of the phases that are involved in the transformation. For incongruent there will be compositional alterations of the phases.

10.41 In this problem we are asked to specify temperature-composition points for all eutectics, eutectoids, peritectics, and congruent phase transformations for the tin-gold system.

There are two eutectics on this phase diagram. One exists at 10 wt% Au-90 wt% Sn and 217°C. The reaction upon cooling is

$$L \rightarrow \alpha + \beta$$

The other eutectic exists at 80 wt% Au-20 wt% Sn and 280°C. This reaction upon cooling is

$$L \rightarrow \delta + \zeta$$

There are three peritectics. One exists at 30 wt% Au-70 wt% Sn and 252°C. Its reaction upon cooling is as follows:

$$L + \gamma \rightarrow \beta$$

The second peritectic exists at 45 wt% Au-55 wt% Sn and 309°C. This reaction upon cooling is

$$L + \delta \rightarrow \gamma$$

The third peritectic exists at 92 wt% Au-8 wt% Sn and 490°C. This reaction upon cooling is

$$L + \eta \rightarrow \zeta$$

There is one congruent melting point at 62.5 wt% Au-37.5 wt% Sn and 418°C. Its reaction upon cooling is

$$L \rightarrow \delta$$

No eutectoids are present.

10.42 In this problem we are asked to specify temperature-composition points for all eutectics, eutectoids, peritectics, and congruent phase transformations for a portion of the aluminum-copper phase diagram.

There is one eutectic on this phase diagram, which exists at 8.3 wt% Al-91.7 wt% Cu and 1036°C. Its reaction upon cooling is

$$L \rightarrow \alpha + \beta$$

There are four eutectoids for this system. One exists at 11.8 wt% Al-88.2 wt% Cu and 565°C. This reaction upon cooling is

$$\beta \rightarrow \alpha + \gamma_2$$

Another eutectoid exists at 15.4 wt% Al-84.6 wt% Cu and 964°C. For cooling the reaction is

$$\chi \rightarrow \beta + \gamma_1$$

A third eutectoid exists at 15.5 wt% Al-84.5 wt% Cu and 786°C. For cooling the reaction is

$$\gamma_1 \rightarrow \beta + \gamma_2$$

The other eutectoid exists at 23.5 wt% Al-76.5 wt% Cu and 560°C. For cooling the reaction is

$$\epsilon_2 \rightarrow \delta + \zeta_1$$

There are four peritectics on this phase diagram. One exists at 15.3 wt% Al-84.7 wt% Cu and 1037°C. The reaction upon cooling is

$$\beta + L \rightarrow \chi$$

Another peritectic exists at 17 wt% Al-83 wt% Cu and 1021°C. It's cooling reaction is

$$\chi + L \rightarrow \gamma_1$$

Another peritectic exists at 20.5 wt% Al-79.5 wt% Cu and 961°C. The reaction upon cooling is

$$\gamma_1 + L \rightarrow \epsilon_1$$

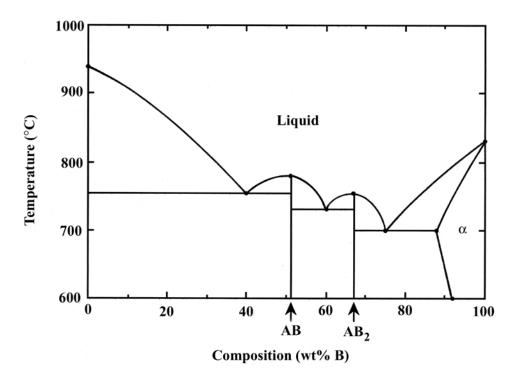
Another peritectic exists at 28.4 wt% Al-71.6 wt% Cu and 626°C. The reaction upon cooling is

$$\varepsilon_2 + L \rightarrow \eta_1$$

There is a single congruent melting point that exists at 12.5 wt% Al-87.5 wt% Cu and 1049°C. The reaction upon cooling is

$$L \rightarrow \beta$$

10.43 Below is shown the phase diagram for these two A and B metals.



Ceramic Phase Diagrams

10.44 There is only one eutectic for the portion of the $\rm ZrO_2$ -CaO system shown in Figure 10.23, which, upon cooling, is

Liquid
$$\rightarrow$$
 cubic ZrO₂ + CaZrO₃

There are two eutectoids, which reactions are as follows:

tetragonal
$$\rightarrow$$
 monoclinic ZrO_2 + cubic ZrO_2

cubic
$$\rightarrow$$
 monoclinic ZrO₂ + CaZr₄O₉

10.45 (a) For this portion of the problem we are to determine the type of vacancy defect that is produced on the Al_2O_3 -rich side of the spinel phase field (Figure 10.22) and the percentage of these vacancies at the maximum nonstoichiometry (82 mol% Al_2O_3). On the alumina-rich side of this phase field, there is an excess of Al^{3+} ions, which means that some of the Al^{3+} ions substitute for Mg^{2+} ions. In order to maintain charge neutrality, Mg^{2+} vacancies are formed, and for every Mg^{2+} vacancy formed, two Al^{3+} ions substitute for three Mg^{2+} ions.

Now, we will calculate the percentage of Mg^{2+} vacancies that exist at 82 mol% $\mathrm{Al_2O_3}$. Let us arbitrarily choose as our basis 50 MgO- $\mathrm{Al_2O_3}$ units of the stoichiometric material, which consists of 50 Mg²⁺ ions and 100 Al^{3+} ions. Furthermore, let us designate the number of Mg²⁺ vacancies as x, which means that 2x Al³⁺ ions have been added and 3x Mg²⁺ ions have been removed (two of which are filled with Al^{3+} ions). Using our 50 MgO- $\mathrm{Al_2O_3}$ unit basis, the number of moles of $\mathrm{Al_2O_3}$ in the nonstoichiometric material is (100 + 2x)/2; similarly the number of moles of MgO is (50 - 3x). Thus, the expression for the mol% of $\mathrm{Al_2O_3}$ is just

$$\text{mol% Al}_2 O_3 = \left[\frac{\frac{100 + 2x}{2}}{\frac{100 + 2x}{2} + (50 - 3x)} \right] \times 100$$

If we solve for x when the mol% of $Al_2O_3 = 82$, then x = 12.1. Thus, adding 2x or (2)(12.1) = 24.2 Al^{3+} ions to the original material consisting of 100 Al^{3+} and 50 Mg^{2+} ions will produce 12.1 Mg^{2+} vacancies. Therefore, the percentage of vacancies is just

% vacancies =
$$\frac{12.1}{100 + 50} \times 100 = 8.1\%$$

(b) Now, we are asked to make the same determinations for the MgO-rich side of the spinel phase field, for 39 mol% Al_2O_3 . In this case, Mg^{2+} ions are substituting for Al^{3+} ions. Since the Mg^{2+} ion has a lower charge than the Al^{3+} ion, in order to maintain charge neutrality, negative charges must be eliminated, which may be accomplished by introducing O^{2-} vacancies. For every 2 Mg^{2+} ions that substitute for 2 Al^{3+} ions, one O^{2-} vacancy is formed.

Now, we will calculate the percentage of O^{2-} vacancies that exist at 39 mol% Al_2O_3 . Let us arbitrarily choose as our basis 50 MgO- Al_2O_3 units of the stoichiometric material which consists of 50 Mg²⁺ ions 100 Al^{3+} ions. Furthermore, let us designate the number of O^{2-} vacancies as y, which means that $2y \, Mg^{2+}$ ions have been added and $2y \, Al^{3+}$ ions have been removed. Using our 50 MgO- Al_2O_3 unit basis, the number of moles of Al_2O_3 in the nonstoichiometric material is (100 - 2y)/2; similarly the number of moles of MgO is (50 + 2y). Thus, the expression for the mol% of Al_2O_3 is just

$$\text{mol% Al}_2 O_3 = \left[\frac{\frac{100 - 2y}{2}}{\frac{100 - 2y}{2} + (50 + 2y)} \right] \times 100$$

If we solve for y when the mol% of $Al_2O_3 = 39$, then y = 7.91. Thus, $7.91 O^{2-}$ vacancies are produced in the original material that had $200 O^{2-}$ ions. Therefore, the percentage of vacancies is just

% vacancies =
$$\frac{7.91}{200} \times 100 = 3.96\%$$

10.46 (a) The chemical formula for kaolinite clay may also be written as $Al_2O_3-2SiO_2-2H_2O$. Thus, if we remove the chemical water, the formula becomes $Al_2O_3-2SiO_2$. The formula weight for Al_2O_3 is just (2)(26.98 g/mol) + (3)(16.00 g/mol) = 101.96 g/mol; and for SiO_2 the formula weight is 28.09 g/mol + (2)(16.00 g/mol) = 60.09 g/mol. Thus, the composition of this product, in terms of the concentration of Al_2O_3 , $C_{Al_2O_3}$, in weight percent is just

$$C_{\text{Al}_2\text{O}_3} = \frac{101.96 \text{ g/mol}}{101.96 \text{ g/mol} + (2)(60.09 \text{ g/mol})} \times 100 = 45.9 \text{ wt}\%$$

(b) The liquidus and solidus temperatures for this material as determined from the ${\rm SiO_2-Al_2O_3}$ phase diagram, Figure 10.24, are 1800°C and 1587°C, respectively.

Gibbs Phase Rule

10.47 We are asked to specify the value of F for Gibbs phase rule at points A, B, and C on the pressure-temperature diagram for H_2O . Gibbs phase rule in general form is

$$P + F = C + N$$

For this system, the number of components, C, is 1, whereas N, the number of noncompositional variables, is 2--viz. temperature and pressure. Thus, the phase rule now becomes

$$P + F = 1 + 2 = 3$$

Or

$$F = 3 - P$$

where P is the number of phases present at equilibrium.

At point A, only a single (liquid) phase is present (i.e., P = 1), or

$$F = 3 - P = 3 - 1 = 2$$

which means that both temperature and pressure are necessary to define the system.

At point B which is on the phase boundary between liquid and vapor phases, two phases are in equilibrium (P=2); hence

$$F = 3 - P = 3 - 2 = 1$$

Or that we need to specify the value of either temperature or pressure, which determines the value of the other (pressure or temperature).

And, finally, at point C, three phases are present—viz. ice I, vapor, and liquid—and the number of degrees of freedom is zero since

$$F = 3 - P = 3 - 3 = 0$$

Thus, point C is an invariant point (in this case a triple point), and we have no choice in the selection of externally controllable variables in order to define the system.

Development of Microstructure in Iron-Carbon Alloys

10.48 This problem asks that we compute the mass fractions of α ferrite and cementite in pearlite. The lever-rule expression for ferrite is

$$W_{\alpha} = \frac{C_{\text{Fe}_3\text{C}} - C_0}{C_{\text{Fe}_2\text{C}} - C_{\alpha}}$$

and, since $C_{\mathrm{Fe_3C}} = 6.70$ wt% C, $C_0 = 0.76$ wt% C, and $C_{\alpha} = 0.022$ wt% C

$$W_{\alpha} = \frac{6.70 - 0.76}{6.70 - 0.022} = 0.89$$

Similarly, for cementite

$$W_{\text{Fe}_3\text{C}} = \frac{C_0 - C_\alpha}{C_{\text{Fe}_3\text{C}} - C_\alpha} = \frac{0.76 - 0.022}{6.70 - 0.022} = 0.11$$

- 10.49 (a) A "hypoeutectoid" steel has a carbon concentration less than the eutectoid; on the other hand, a "hypereutectoid" steel has a carbon content greater than the eutectoid.
- (b) For a hypoeutectoid steel, the proeutectoid ferrite is a microconstituent that formed above the eutectoid temperature. The eutectoid ferrite is one of the constituents of pearlite that formed at a temperature below the eutectoid. The carbon concentration for both ferrites is 0.022 wt% C.
- 10.50 This problem asks that we compute the carbon concentration of an iron-carbon alloy for which the fraction of total ferrite is 0.94. Application of the lever rule (of the form of Equation 10.12) yields

$$W_{\alpha} = 0.94 = \frac{C_{\text{Fe}_3\text{C}} - C_0'}{C_{\text{Fe}_3\text{C}} - C_{\alpha}} = \frac{6.70 - C_0'}{6.70 - 0.022}$$

and solving for C_0

$$C_0' = 0.42 \text{ wt}\% \text{ C}$$

10.51 In this problem we are given values of W_{α} and $W_{\text{Fe}_3\text{C}}$ (0.86 and 0.14, respectively) for an iron-carbon alloy and then are asked to specify the proeutectoid phase. Employment of the lever rule for total α leads to

$$W_{\alpha} = 0.86 = \frac{C_{\text{Fe}_3\text{C}} - C_0}{C_{\text{Fe}_3\text{C}} - C_{\alpha}} = \frac{6.70 - C_0}{6.70 - 0.022}$$

Now, solving for C_0 , the alloy composition, leads to $C_0 = 0.96$ wt% C. Therefore, the proeutectoid phase is Fe₃C since C_0 is greater than 0.76 wt% C.

- 10.52 This problem asks us to consider various aspects of 1.0 kg of austenite containing 1.15 wt% C that is cooled to below the eutectoid.
- (a) The proeutectoid phase will be Fe_3C since 1.15 wt% C is greater than the eutectoid composition (0.76 wt% C).
- (b) For this portion of the problem, we are asked to determine how much total ferrite and cementite form. Application of the appropriate lever rule expression yields

$$W_{\alpha} = \frac{C_{\text{Fe}_3\text{C}} - C_0}{C_{\text{Fe}_3\text{C}} - C_{\alpha}} = \frac{6.70 - 1.15}{6.70 - 0.022} = 0.83$$

which, when multiplied by the total mass of the alloy (1.0 kg), gives 0.83 kg of total ferrite.

Similarly, for total cementite,

$$W_{\text{Fe}_3\text{C}} = \frac{C_0 - C_\alpha}{C_{\text{Fe}_3\text{C}} - C_\alpha} = \frac{1.15 - 0.022}{6.70 - 0.022} = 0.17$$

And the mass of total cementite that forms is (0.17)(1.0 kg) = 0.17 kg.

(c) Now we are asked to calculate how much pearlite and the proeutectoid phase (cementite) form. Applying Equation 10.22, in which $C_1' = 1.15$ wt% C

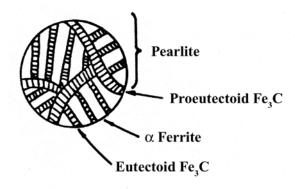
$$W_{\rm p} = \frac{6.70 - C_1}{6.70 - 0.76} = \frac{6.70 - 1.15}{6.70 - 0.76} = 0.93$$

which corresponds to a mass of 0.93 kg. Likewise, from Equation 10.23

$$W_{\text{Fe}_3\text{C'}} = \frac{C_1' - 0.76}{5.94} = \frac{1.15 - 0.76}{5.94} = 0.07$$

which is equivalent to 0.07 kg of the total 1 kg mass.

(d) Schematically, the microstructure would appear as:



- 10.53 We are called upon to consider various aspects of 2.5 kg of austenite containing 0.65 wt% C, that is cooled to below the eutectoid.
 - (a) Ferrite is the proeutectoid phase since 0.65 wt% C is less than 0.76 wt% C.
- (b) For this portion of the problem, we are asked to determine how much total ferrite and cementite form. For ferrite, application of the appropriate lever rule expression yields

$$W_{\alpha} = \frac{C_{\text{Fe}_3\text{C}} - C_0}{C_{\text{Fe}_3\text{C}} - C_{\alpha}} = \frac{6.70 - 0.65}{6.70 - 0.022} = 0.91$$

which corresponds to (0.91)(2.5 kg) = 2.26 kg of total ferrite.

Similarly, for total cementite,

$$W_{\text{Fe}_3\text{C}} = \frac{C_0 - C_\alpha}{C_{\text{Fe}_3\text{C}} - C_\alpha} = \frac{0.65 - 0.022}{6.70 - 0.022} = 0.09$$

Or (0.09)(2.5 kg) = 0.24 kg of total cementite form.

(c) Now consider the amounts of pearlite and proeutectoid ferrite. Using Equation 10.20

$$W_{\rm p} = \frac{C_0' - 0.022}{0.74} = \frac{0.65 - 0.022}{0.74} = 0.85$$

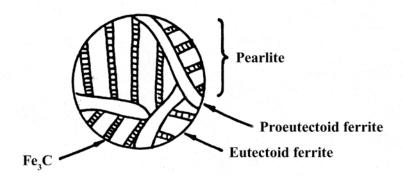
This corresponds to (0.85)(2.5 kg) = 2.12 kg of pearlite.

Also, from Equation 10.21,

$$W_{\alpha'} = \frac{0.76 - 0.65}{0.74} = 0.15$$

Or, there are (0.15)(2.5 kg) = 0.38 kg of proeutectoid ferrite.

(d) Schematically, the microstructure would appear as:



10.54 The mass fractions of proeutectoid ferrite and pearlite that form in a 0.25 wt% C iron-carbon alloy are considered in this problem. From Equation 10.20

$$W_{\rm p} = \frac{C_0' - 0.022}{0.74} = \frac{0.25 - 0.022}{0.74} = 0.31$$

And, from Equation 10.21 (for proeutectoid ferrite)

$$W_{\alpha'} = \frac{0.76 - C_0'}{0.74} = \frac{0.76 - 0.25}{0.74} = 0.69$$

10.55 This problem asks that we determine the carbon concentration in an iron-carbon alloy, given the mass fractions of proeutectoid ferrite and pearlite. From Equation 10.20

$$W_{\rm p} = 0.714 = \frac{C_0' - 0.022}{0.74}$$

which yields $C_0' = 0.55$ wt% C.

10.56 In this problem we are given values of W_{α} and $W_{\text{Fe}_3\text{C}}$ for an iron-carbon alloy (0.91 and 0.09, respectively), and then are asked to specify whether the alloy is hypoeutectoid or hypereutectoid. Employment of the lever rule for total α leads to

$$W_{\alpha} = 0.91 = \frac{C_{\text{Fe}_3\text{C}} - C_0}{C_{\text{Fe}_3\text{C}} - C_{\alpha}} = \frac{6.70 - C_0}{6.70 - 0.022}$$

Now, solving for C_0 , the alloy composition, leads to $C_0 = 0.62$ wt% C. Therefore, the alloy is hypoeutectoid since C_0 is less than 0.76 wt% C.

10.57 We are asked in this problem to determine the concentration of carbon in an alloy for which $W_{\text{Fe}_3\text{C}'} = 0.11$ and $W_p = 0.89$. If we let C_1' equal the carbon concentration in the alloy, employment of the appropriate lever rule expression, Equation 10.22, leads to

$$W_{\rm p} = \frac{6.7 - C_1'}{6.7 - 0.76} = 0.89$$

Solving for C_1 yields $C_1 = 1.41$ wt% C.

- 10.58 In this problem we are asked to consider 2.0 kg of a 99.6 wt% Fe-0.4 wt% C alloy that is cooled to a temperature below the eutectoid.
 - (a) Equation 10.21 must be used in computing the amount of proeutectoid ferrite that forms. Thus,

$$W_{\alpha'} = \frac{0.76 - C_0'}{0.74} = \frac{0.76 - 0.40}{0.74} = 0.49$$

Or, (0.49)(2.0 kg) = 0.99 kg of proeutectoid ferrite forms.

(b) In order to determine the amount of eutectoid ferrite, it first becomes necessary to compute the amount of total ferrite using the lever rule applied entirely across the α + Fe₃C phase field, as

$$W_{\alpha} = \frac{C_{\text{Fe}_{3}\text{C}} - C_{0}'}{C_{\text{Fe}_{2}\text{C}} - C_{\alpha}} = \frac{6.70 - 0.40}{6.70 - 0.022} = 0.94$$

which corresponds to (0.94)(2.0 kg) = 1.89 kg. Now, the amount of eutectoid ferrite is just the difference between total and proeutectoid ferrites, or

$$1.89 \text{ kg} - 0.99 \text{ kg} = 0.90 \text{ kg}$$

(c) With regard to the amount of cementite that forms, again application of the lever rule across the entirety of the α + Fe₃C phase field, leads to

$$W_{\text{Fe}_3\text{C}} = \frac{C_0' - C_\alpha}{C_{\text{Fe}_3\text{C}} - C_\alpha} = \frac{0.40 - 0.022}{6.70 - 0.022} = 0.06$$

which amounts to (0.06)(2 kg) = 0.11 kg cementite in the alloy.

10.59 This problem asks that we compute the maximum mass fraction of proeutectoid cementite possible for a hypereutectoid iron-carbon alloy. This requires that we utilize Equation 10.23 with $C_1' = 2.14$ wt% C, the maximum solubility of carbon in austenite. Thus,

$$W_{\text{Fe}_3\text{C'}} = \frac{C_1 - 0.76}{5.94} = \frac{2.14 - 0.76}{5.94} = 0.232$$

10.60 This problem asks if it is possible to have an iron-carbon alloy for which $W_{\text{Fe}_3\text{C}} = 0.057$ and $W_{\alpha'} = 0.36$. In order to make this determination, it is necessary to set up lever rule expressions for these two mass fractions in terms of the alloy composition, then to solve for the alloy composition of each; if both alloy composition values are equal, then such an alloy is possible. The lever-rule expression for the mass fraction of total cementite is

$$W_{\text{Fe}_3\text{C}} = \frac{C_0 - C_\alpha}{C_{\text{Fe}_2\text{C}} - C_\alpha} = \frac{C_0 - 0.022}{6.70 - 0.022} = 0.057$$

Solving for this C_0 yields $C_0 = 0.40$ wt% C. Now for W_{α} , we utilize Equation 10.21 as

$$W_{\alpha'} = \frac{0.76 - C_0'}{0.74} = 0.36$$

This expression leads to $C_0' = 0.49$ wt% C. And, since C_0 and C_0' are different this alloy is *not* possible.

10.61 This problem asks if it is possible to have an iron-carbon alloy for which $W_{\alpha} = 0.860$ and $W_{p} = 0.969$. In order to make this determination, it is necessary to set up lever rule expressions for these two mass fractions in terms of the alloy composition, then to solve for the alloy composition of each; if both alloy composition values are equal, then such an alloy is possible. The lever-rule expression for the mass fraction of total ferrite is

$$W_{\alpha} = \frac{C_{\text{Fe}_3\text{C}} - C_0}{C_{\text{Fe}_2\text{C}} - C_{\alpha}} = \frac{6.70 - C_0}{6.70 - 0.022} = 0.860$$

Solving for this C_0 yields $C_0 = 0.95$ wt% C. Therefore, this alloy is hypereutectoid since C_0 is greater than the eutectoid composition (0.76 wt%). Thus, it is necessary to use Equation 10.22 for $W_{\rm p}$ as

$$W_{\rm p} = \frac{6.70 - C_1'}{5.94} = 0.969$$

This expression leads to $C_1' = 0.95$ wt% C. Since $C_0 = C_1'$, this alloy is possible.

10.62 This problem asks that we compute the mass fraction of eutectoid cementite in an iron-carbon alloy that contains 1.00 wt% C. In order to solve this problem it is necessary to compute mass fractions of total and proeutectoid cementites, and then to subtract the latter from the former. To calculate the mass fraction of total cementite, it is necessary to use the lever rule and a tie line that extends across the entire $\alpha + \text{Fe}_3\text{C}$ phase field as

$$W_{\text{Fe}_3\text{C}} = \frac{C_0 - C_{\alpha}}{C_{\text{Fe}_2\text{C}} - C_{\alpha}} = \frac{1.00 - 0.022}{6.70 - 0.022} = 0.146$$

Now, for the mass fraction of proeutectoid cementite we use Equation 10.23

$$W_{\text{Fe}_3\text{C'}} = \frac{C_1^{'} - 0.76}{5.94} = \frac{1.00 - 0.76}{5.94} = 0.040$$

And, finally, the mass fraction of eutectoid cementite $W_{\mathrm{Fe_3C''}}$ is just

$$W_{\text{Fe}_3\text{C''}} = W_{\text{Fe}_3\text{C}} - W_{\text{Fe}_3\text{C'}} = 0.146 - 0.040 = 0.106$$

10.63 This problem asks whether or not it is possible to determine the composition of an iron-carbon alloy for which the mass fraction of eutectoid cementite is 0.109; and if so, to calculate the composition. Yes, it is possible to determine the alloy composition; and, in fact, there are two possible answers. For the first, the eutectoid cementite exists in addition to proeutectoid cementite. For this case the mass fraction of eutectoid cementite $(W_{\text{Fe}_3\text{C}"})$ is just the difference between total cementite and proeutectoid cementite mass fractions; that is

$$W_{\text{Fe}_3\text{C''}} = W_{\text{Fe}_3\text{C}} - W_{\text{Fe}_3\text{C'}}$$

Now, it is possible to write expressions for $W_{\text{Fe}_3\text{C}}$ (of the form of Equation 10.12) and $W_{\text{Fe}_3\text{C}'}$ (Equation 10.23) in terms of C_0 , the alloy composition. Thus,

$$W_{\text{Fe}_{3}\text{C"}} = \frac{C_{0} - C_{\alpha}}{C_{\text{Fe}_{3}\text{C}} - C_{\alpha}} - \frac{C_{0} - 0.76}{5.94}$$

$$=\frac{C_0 - 0.022}{6.70 - 0.022} - \frac{C_0 - 0.76}{5.94} = 0.109$$

And, solving for C_0 yields $C_0 = 0.84$ wt% C.

For the second possibility, we have a hypoeutectoid alloy wherein all of the cementite is eutectoid cementite. Thus, it is necessary to set up a lever rule expression wherein the mass fraction of total cementite is 0.109. Therefore,

$$W_{\text{Fe}_3\text{C}} = \frac{C_0 - C_\alpha}{C_{\text{Fe}_2\text{C}} - C_\alpha} = \frac{C_0 - 0.022}{6.70 - 0.022} = 0.109$$

And, solving for C_0 yields $C_0 = 0.75$ wt% C.

10.64 This problem asks whether or not it is possible to determine the composition of an iron-carbon alloy for which the mass fraction of eutectoid ferrite is 0.71; and if so, to calculate the composition. Yes, it is possible to determine the alloy composition; and, in fact, there are two possible answers. For the first, the eutectoid ferrite exists in addition to proeutectoid ferrite (for a hypoeutectoid alloy). For this case the mass fraction of eutectoid ferrite (W_{α}) is just the difference between total ferrite and proeutectoid ferrite mass fractions; that is

$$W_{\alpha''} = W_{\alpha} - W_{\alpha'}$$

Now, it is possible to write expressions for W_{α} (of the form of Equation 10.12) and $W_{\alpha'}$ (Equation 10.21) in terms of C_0 , the alloy composition. Thus,

$$W_{\alpha''} = \frac{C_{\text{Fe}_3\text{C}} - C_0}{C_{\text{Fe}_2\text{C}} - C_\alpha} - \frac{0.76 - C_0}{0.74}$$

$$= \frac{6.70 - C_0}{6.70 - 0.022} - \frac{0.76 - C_0}{0.74} = 0.71$$

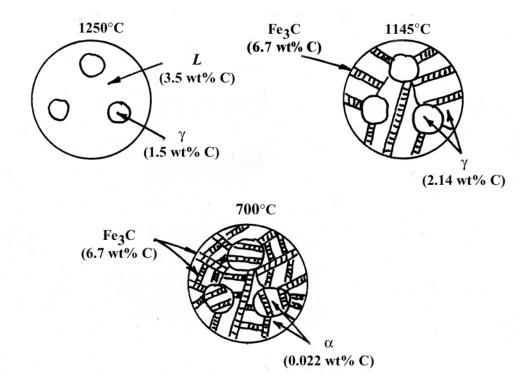
And, solving for C_0 yields $C_0 = 0.61$ wt% C.

For the second possibility, we have a hypereutectoid alloy wherein all of the ferrite is eutectoid ferrite. Thus, it is necessary to set up a lever rule expression wherein the mass fraction of total ferrite is 0.71. Therefore,

$$W_{\alpha} = \frac{C_{\text{Fe}_3\text{C}} - C_0}{C_{\text{Fe}_3\text{C}} - C_{\alpha}} = \frac{6.70 - C_0}{6.70 - 0.022} = 0.71$$

And, solving for C_0 yields $C_0 = 1.96$ wt% C.

10.65 Schematic microstructures for the iron-carbon alloy of composition 3 wt% C-97 wt% Fe and at temperatures of 1250°C, 1145°C, and 700°C are shown below; approximate phase compositions are also indicated.



10.66 This problem asks that we determine the approximate Brinell hardness of a 99.80 wt% Fe-0.20 wt% C alloy. First, we compute the mass fractions of pearlite and proeutectoid ferrite using Equations 10.20 and 10.21, as

$$W_{\rm p} = \frac{C_0' - 0.022}{0.74} = \frac{0.20 - 0.022}{0.74} = 0.24$$

$$W_{\alpha'} = \frac{0.76 - C_0'}{0.74} = \frac{0.76 - 0.20}{0.74} = 0.76$$

Now, we compute the Brinell hardness of the alloy as

$$HB_{alloy} = HB_{\alpha}W_{\alpha'} + HB_{p}W_{p}$$

$$=(80)(0.76) + (280)(0.24) = 128$$

The Influence of Other Alloying Elements

10.67 This problem asks us to consider an alloy of composition 97.5 wt% Fe, 2.0 wt% Mo, and 0.5 wt% C.

- (a) From Figure 10.36, the eutectoid temperature for 2.0 wt% Mo is approximately 850°C.
- (b) From Figure 10.37, the eutectoid composition is approximately 0.22 wt% C.
- (c) Since the carbon concentration of the alloy (0.5 wt%) is greater than the eutectoid (0.22 wt% C), cementite is the proeutectoid phase.

10.68 We are asked to consider a steel alloy of composition 93.8 wt% Fe, 6.0 wt% Ni, and 0.2 wt% C.

- (a) From Figure 10.36, the eutectoid temperature for 6 wt% Ni is approximately 650°C (1200°F).
- (b) From Figure 10.37, the eutectoid composition is approximately 0.62 wt% C. Since the carbon concentration in the alloy (0.2 wt%) is less than the eutectoid (0.62 wt% C), the proeutectoid phase is ferrite.
- (c) Assume that the α -(α + Fe $_3$ C) phase boundary is at a negligible carbon concentration. Modifying Equation 10.21 leads to

$$W_{\alpha'} = \frac{0.62 - C_0'}{0.62 - 0} = \frac{0.62 - 0.20}{0.62} = 0.68$$

Likewise, using a modified Equation 10.20

$$W_p = \frac{C_0' - 0}{0.62 - 0} = \frac{0.20}{0.62} = 0.32$$