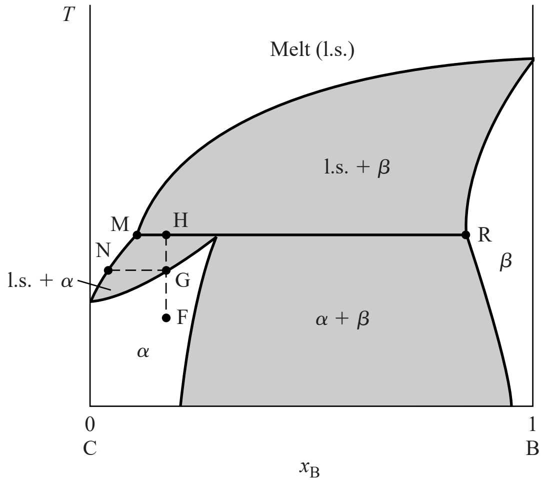

Figure 12.24

A solid–liquid phase diagram with a peritectic temperature.

temperature). Further heating after the transition at H brings us first into a two-phase region of β plus liquid solution and finally into a one-phase region of liquid solution. A *peritectic phase transition* (for example, the transition at H) is one where heating transforms a solid phase to a liquid phase plus a second solid phase: $\text{solid}_1 \rightarrow \text{liquid} + \text{solid}_2$. In contrast, a eutectic phase transition has the pattern on heating: $\text{solid}_1 + \text{solid}_2 \rightarrow \text{liquid}$.

Compound Formation—Liquid-Phase Miscibility and Solid-Phase Immiscibility

Fairly commonly, substances B and C form a solid compound that can exist in equilibrium with the liquid. Figure 12.25 shows the solid–liquid phase diagram for phenol (P) plus aniline (A), which form the compound $C_6H_5OH \cdot C_6H_5NH_2$ (PA). The aniline mole fraction x_A on the abscissa is calculated pretending that only aniline and phenol (and no addition compound) are present. Although the system has $c = 3$ (instead of 2), the number of degrees of freedom is unchanged by compound formation, since we now have the equilibrium restriction $\mu_P + \mu_A = \mu_{PA}$. Thus, $c - r - a = c_{ind}$ in Eq. (7.10) is still 2, and the system is binary.

Figure 12.25 can be understood qualitatively by imagining it to consist of a simple eutectic diagram for phenol–PA adjacent to a simple eutectic diagram for PA–aniline. The liquid solution at the top of the diagram is an equilibrium mixture of P, A, and PA. Depending on the solution's composition, solid phenol, solid PA, or solid aniline will separate out on cooling, until one of the two eutectic temperatures is reached, at which time a second solid also freezes out. If a solution with $x_A = 0.5$ is cooled, only pure solid PA separates out and the solution freezes entirely at one temperature (31°C), the melting point of PA. Although the freezing-point-depression curves for P and for A each start off with nonzero slope, the freezing-point-depression curve of PA has zero slope at the PA melting point (proof of this is given in *Haase and Schönert*, p. 101).

As usual, the composition of each phase present in a two-phase region is given by the endpoints of a tie line drawn across the width of that region. For example, a (horizontal) tie line drawn in one of the l.s. + PA(s) regions of Fig. 12.25 extends from the vertical line at $x(\text{A}) = 0.5$ [corresponding to the phase PA(s)] to the curved boundary line between the l.s. + PA(s) region and the l.s. region.

Some systems exhibit formation of several compounds. If n compounds are formed, the solid–liquid phase diagram can be viewed as consisting of $n + 1$ adjacent simple-eutectic phase diagrams (provided there are no peritectic points—see the next two paragraphs). For an example, see Prob. 12.51.

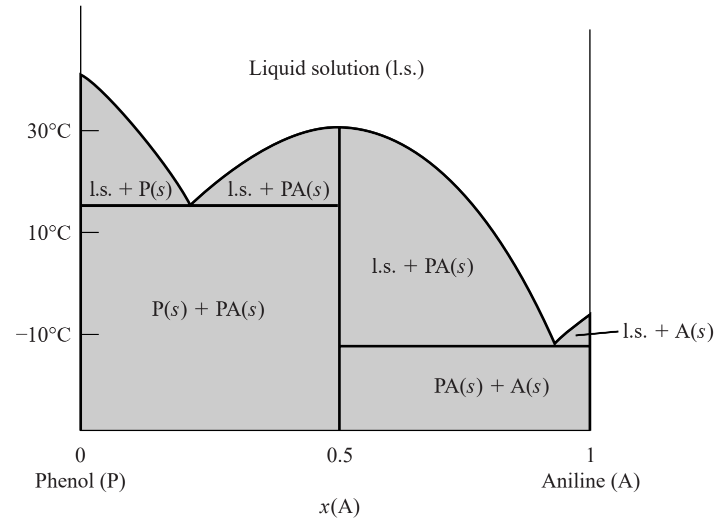

Figure 12.25

Phenol–aniline solid–liquid phase diagram at 1 atm. The symbols P(*s*), PA(*s*), and A(*s*) denote solid phenol, solid addition compound, and solid aniline, respectively.

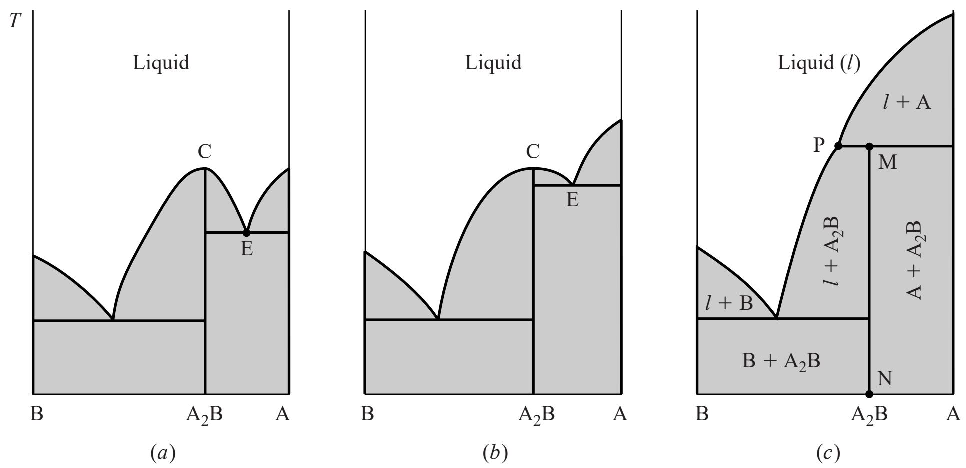

Figure 12.26

Origin of a peritectic point.

Compound Formation with Incongruent Melting—Liquid-Phase Miscibility and Solid-Phase Immiscibility. Figure 12.26*a* shows a phase diagram with formation of the solid compound A_2B. Now let the melting point of A be increased to give Fig. 12.26*b*. A further increase in the A melting point will yield Fig. 12.26*c*. In Fig. 12.26*c*, the freezing-point-depression curve of A no longer intersects the right-hand freezing-point-depression curve of A_2B (curve CE in Fig. 12.26*a* and *b*), so the eutectic point between the compound A_2B and A is eliminated. Instead, the intersection at point *P* produces the phase diagram of Fig. 12.26*c*. (The system K–Na has the phase diagram of Fig. 12.26*c*; the compound formed is Na_2K.)

Line MN is pure solid A_2B. If solid A_2B is heated, it melts sharply at temperature T_P to give a liquid solution (whose composition is given by point P) in equilibrium with pure solid A; $A_2B(s) \rightarrow A(s) +$ solution. Thus, at least some decomposition of the compound occurs on melting. Since the liquid solution formed has a different x_A value than the compound, the compound is said to melt *incongruently*. (The compound in Fig. 12.25 melts *congruently* to give a liquid with the same x_A as the solid compound.) Point P is called a *peritectic point*. When several compounds are formed, there is the possibility of more than one peritectic point. In the system Cu–La, the compounds LaCu and $LaCu_4$ melt incongruently, and the compounds $LaCu_2$ and $LaCu_6$ melt congruently.