15.3 Raoult's Law

Two liquids (A and B) that are miscible and that do not interact form an **ideal solution** and follow Raoult's Law. The law states that the partial vapor pressure of component A in the solution (P_A) equals the vapor pressure of pure A (P_A°) times its mole fraction (N_A) (Equation 1). A similar expression can be written for component B (Equation 2). The mole fractions N_A and N_B were defined in Section 15.2.

$$\text{Partial vapor pressure of A in solution} = P_A = (P_A^\circ)(N_A) \tag{1}$$

$$\text{Partial vapor pressure of B in solution} = P_B = (P_B^\circ)(N_B) \tag{2}$$

P_A° is the vapor pressure of pure A, independent of B. P_B° is the vapor pressure of pure B, independent of A. In a mixture of A and B, the partial vapor pressures are added to give the total vapor pressure above the solution (Equation 3). When the total pressure (sum of the partial pressures) equals the applied pressure, the solution boils.

$$P_{total} = P_A + P_B = P_A^\circ N_A + P_B^\circ N_B \tag{3}$$

The composition of A and B in the vapor produced is given by Equations 4 and 5.

$$N_A\,(\text{vapor}) = \frac{P_A}{P_{total}} \tag{4}$$

$$N_B\,(\text{vapor}) = \frac{P_B}{P_{total}} \tag{5}$$

Several exercises involving applications of Raoult's Law are illustrated in Table 15.1. Note, particularly in the result from Equation 4, that the vapor is richer ($N_A = 0.67$) in the lower-boiling (higher vapor pressure) component A than it was before vaporization ($N_A = 0.50$). This proves mathematically what was described in Section 15.2.

TABLE 15.1 Sample Calculations with Raoult's Law

Consider a solution at 100°C where $N_A = 0.5$ and $N_B = 0.5$.

1. What is the partial vapor pressure of A in the solution if the vapor pressure of pure A at 100°C is 1020 mmHg?
   Answer: $P_A = P_A^\circ N_A = (1020)(0.5) = 510$ mmHg
2. What is the partial vapor pressure of B in the solution if the vapor pressure of pure B at 100°C is 500 mmHg?
   Answer: $P_B = P_B^\circ N_B = (500)(0.5) = 250$ mmHg
3. Would the solution boil at 100°C if the applied pressure were 760 mmHg?
   Answer: Yes. $P_{total} = P_A + P_B = (510 + 250) = 760$ mmHg
4. What is the composition of the vapor at the boiling point?
   Answer: The boiling point is 100°C.

$$N_A(\text{vapor}) = \frac{P_A}{P_{total}} = 510/760 = 0.67$$

$$N_B(\text{vapor}) = \frac{P_B}{P_{total}} = 250/760 = 0.33$$