12.6: Liquid-Liquid Equilibria

12.6.1 Miscibility in binary liquid systems

When two different pure liquids are unable to mix in all proportions, they are said to be *partially miscible*. When these liquids are placed in contact with one another and allowed to come to thermal, mechanical, and transfer equilibrium, the result is two coexisting liquid mixtures of different compositions.

Liquids are never actually completely *immiscible*. To take an extreme case, liquid mercury, when equilibrated with water, has some H_2O dissolved in it, and some mercury dissolves in the water, although the amounts may be too small to measure.

The Gibbs phase rule for a multicomponent system to be described in Sec. 13.1 shows that a two-component, two-phase system at equilibrium has only two independent intensive variables. Thus at a given temperature and pressure, the mole fraction compositions of both phases are fixed; the compositions depend only on the identity of the substances and the temperature and pressure.

Figure 13.5 shows a phase diagram for a typical binary liquid mixture that spontaneously separates into two phases when the temperature is lowered. The thermodynamic conditions for phase separation of this kind were discussed in Sec. 11.1.6. The phase separation is usually the result of positive deviations from Raoult's law. Typically, when phase separation occurs, one of the substances is polar and the other nonpolar.

12.6.2 Solubility of one liquid in another

Suppose substances A and B are both liquids when pure. In discussing the solubility of liquid B in liquid A, we can treat B as either a solute or as a constituent of a liquid mixture. The difference lies in the choice of the standard state or reference state of B.

We can define the solubility of B in A as the maximum amount of B that can dissolve without phase separation in a given amount of A at the given temperature and pressure. Treating B as a solute, we can express its solubility as the mole fraction of B in the phase at the point of phase separation. The addition of any more B to the system will result in two coexisting liquid phases of fixed composition, one of which will have mole fraction x_B equal to its solubility.

Experimentally, the solubility of B in A can be determined from the *cloud point*, the point during titration of A with B at which persistent turbidity is observed.

Consider a system with two coexisting liquid phases α and β containing components A and B. Let α be the A-rich phase and β be the B-rich phase. For example, A could be water and B could be benzene, a hydrophobic substance. Phase α would then be an aqueous phase polluted with a low concentration of dissolved benzene, and phase β would be wet benzene. x_B^α would be the solubility of the benzene in water, expressed as a mole fraction.

Below, relations are derived for this kind of system using both choices of standard state or reference state.

Solute standard state

Assume that the two components have low mutual solubilities, so that B has a low mole fraction in phase α and a mole fraction close to 1 in phase β. It is then appropriate to treat B as a solute in phase α and as a constituent of a liquid mixture in phase β. The value of x_B^α is the solubility of liquid B in liquid A.

The equilibrium when two liquid phases are present is $B(\beta) \rightleftharpoons B(\alpha)$, and the expression for the thermodynamic equilibrium constant, with the solute standard state based on mole fraction, is

$$K = \frac{a_{x,B}^\alpha}{a_B^\beta} = \frac{\Gamma_{x,B}^\alpha \gamma_{x,B}^\alpha x_B^\alpha}{\Gamma_B^\beta \gamma_B^\beta x_B^\beta} \tag{12.6.1}$$

The solubility of B is then given by

$$x_B^\alpha = \frac{\Gamma_B^\beta \gamma_B^\beta x_B^\beta}{\Gamma_{x,B}^\alpha \gamma_{x,B}^\alpha} K \tag{12.6.2}$$

The values of the pressure factors and activity coefficients are all close to 1, so that the solubility of B in A is given by $x_B^\alpha \approx K$. The temperature dependence of the solubility is given by

$$\frac{\mathrm{d}\ln x_{\mathrm{B}}^{\alpha}}{\mathrm{d}T} \approx \frac{\mathrm{d}\ln K}{\mathrm{d}T} = \frac{\Delta_{\mathrm{sol,B}}H^{\circ}}{RT^2} \qquad (12.6.3)$$

where $\Delta_{\mathrm{sol,B}}H^{\circ}$ is the molar enthalpy change for the transfer at pressure p° of pure liquid solute to the solution at infinite dilution.

H_2O and *n*-butylbenzene are two liquids with very small mutual solubilities. Figure 12.8 shows that the solubility of *n*-butylbenzene in water exhibits a minimum at about $12\,^{\circ}C$. Equation 12.6.3 allows us to deduce from this behavior that $\Delta_{\mathrm{sol,B}}H^{\circ}$ is negative below this temperature, and positive above.

Pure-liquid reference state

The condition for transfer equilibrium of component B is $\mu_{\mathrm{B}}^{\alpha} = \mu_{\mathrm{B}}^{\beta}$. If we use a pure-liquid reference state for B in both phases, this condition becomes

$$\mu_{\mathrm{B}}^{*} + RT\ln(\gamma_{\mathrm{B}}^{\alpha}x_{\mathrm{B}}^{\alpha}) = \mu_{\mathrm{B}}^{*} + RT\ln(\gamma_{\mathrm{B}}^{\beta}x_{\mathrm{B}}^{\beta}) \qquad (12.6.4)$$

This results in the following relation between the compositions and activity coefficients:

$$\gamma_{\mathrm{B}}^{\alpha}x_{\mathrm{B}}^{\alpha} = \gamma_{\mathrm{B}}^{\beta}x_{\mathrm{B}}^{\beta} \qquad (12.6.5)$$

As before, we assume the two components have low mutual solubilities, so that the B-rich phase is almost pure liquid B. Then x_{B}^{β} is only slightly less than 1, $\gamma_{\mathrm{B}}^{\beta}$ is close to 1, and Eq. 12.6.5 becomes $x_{\mathrm{B}}^{\alpha} \approx 1/\gamma_{\mathrm{B}}^{\alpha}$. Since x_{B}^{α} is much less than 1, $\gamma_{\mathrm{B}}^{\alpha}$ must be much greater than 1.

In environmental chemistry it is common to use a pure-liquid reference state for a nonpolar liquid solute that has very low solubility in water, so that the aqueous solution is essentially at infinite dilution. Let the nonpolar solute be component B, and let the aqueous phase that is equilibrated with liquid B be phase α. The activity coefficient $\gamma_{\mathrm{B}}^{\alpha}$ is then a *limiting activity coefficient* or *activity coefficient at infinite dilution*. As explained above, the aqueous solubility of B in this case is given by $x_{\mathrm{B}}^{\alpha} \approx 1/\gamma_{\mathrm{B}}^{\alpha}$, and $\gamma_{\mathrm{B}}^{\alpha}$ is much greater than 1.

We can also relate the solubility of B to its Henry's law constant $k_{\mathrm{H,B}}^{\alpha}$. Suppose the two liquid phases are equilibrated not only with one another but also with a gas phase. Since B is equilibrated between phase α and the gas, we have $\gamma_{x,\mathrm{B}}^{\alpha} = f_{\mathrm{B}}/k_{\mathrm{H,B}}^{\alpha}x_{\mathrm{B}}^{\alpha}$ (Table 9.4). From the equilibration of B between phase β and the gas, we also have $\gamma_{\mathrm{B}}^{\beta} = f_{\mathrm{B}}/x_{\mathrm{B}}^{\beta}f_{\mathrm{B}}^{*}$. By eliminating the fugacity f_{B} from these relations, we obtain the general relation

$$x_{\mathrm{B}}^{\alpha} = \frac{\gamma_{\mathrm{B}}^{\beta}x_{\mathrm{B}}^{\beta}f_{\mathrm{B}}^{*}}{\gamma_{x,\mathrm{B}}^{\alpha}k_{\mathrm{H,B}}^{\alpha}} \qquad (12.6.6)$$

If we assume as before that the activity coefficients and x_{B}^{β} are close to 1, and that the gas phase behaves ideally, the solubility of B is given by $x_{\mathrm{B}}^{\alpha} \approx p_{\mathrm{B}}^{*}/k_{\mathrm{H,B}}^{\alpha}$, where p_{B}^{*} is the vapor pressure of the pure solute.

12.6.3 Solute distribution between two partially-miscible solvents

Consider a two-component system of two equilibrated liquid phases, α and β. If we add a small quantity of a third component, C, it will distribute itself between the two phases. It is appropriate to treat C as a solute in *both* phases. The thermodynamic equilibrium constant for the equilibrium $C(\beta) \rightleftharpoons C(\alpha)$, with solute standard states based on mole fraction, is

$$K = \frac{a_{x,\mathrm{C}}^{\alpha}}{a_{x,\mathrm{C}}^{\beta}} = \frac{\Gamma_{x,\mathrm{C}}^{\alpha}\gamma_{x,\mathrm{C}}^{\alpha}x_{\mathrm{C}}^{\alpha}}{\Gamma_{x,\mathrm{C}}^{\beta}\gamma_{x,\mathrm{C}}^{\beta}x_{\mathrm{C}}^{\beta}} \qquad (12.6.7)$$

We define K' as the ratio of the mole fractions of C in the two phases at equilibrium:

$$K' \stackrel{\mathrm{def}}{=} \frac{x_{\mathrm{C}}^{\alpha}}{x_{\mathrm{C}}^{\beta}} = \frac{\Gamma_{x,\mathrm{C}}^{\beta}\gamma_{x,\mathrm{C}}^{\beta}}{\Gamma_{x,\mathrm{C}}^{\alpha}\gamma_{x,\mathrm{C}}^{\alpha}}K \qquad (12.6.8)$$

At a fixed T and p, the pressure factors and equilibrium constant are constants. If x_{C} is low enough in both phases for $\gamma_{x,\mathrm{C}}^{\alpha}$ and $\gamma_{x,\mathrm{C}}^{\beta}$ to be close to unity, K' becomes a constant for the given T and p. The constancy of K' over a range of dilute composition is the **Nernst distribution law**.

Since solute molality and concentration are proportional to mole fraction in dilute solutions, the ratios m_C^α/m_C^β and c_C^α/c_C^β also approach constant values at a given T and p. The ratio of concentrations is called the **partition coefficient** or **distribution coefficient**.

In the limit of infinite dilution of C, the two phases have the compositions that exist when only components A and B are present. As C is added and x_C^α and x_C^β increase beyond the region of dilute solution behavior, the ratios x_B^α/x_A^α and x_B^β/x_A^β may change. Continued addition of C may increase the mutual solubilities of A and B, resulting, when enough C has been added, in a single liquid phase containing all three components. It is easier to understand this behavior with the help of a ternary phase diagram such as Fig. 13.17.