IDEAL SOLUTIONS

THEORY

Entropy, which is a measure of disorder, is the driving force for mixing solutes and solvents to form solutions because there is an increase in the randomness of the molecules of both the solvent and the solute when they mix to form a solution. If the process is somewhat endothermic, a chemical will not readily dissolve if the available increase in the entropy contribution to the change in free energy does not exceed the enthalpy increase. The expression describing the ideal entropy of mixing for a binary system of a single liquid solute in a solvent, ΔS_{mix}, in terms of mole fractions in the solution, X, is:

$$\Delta S_{\text{mix}} = -R\left(n_1 \ln X_1^i + n_2 \ln X_2^i\right) \tag{2.1}$$

where the subscript convention is 1 for the solvent and 2 for the solute, the superscript i indicates that ideal conditions hold, n is the number of moles, and R is the ideal gas law constant (Lewis and Randall, 1961).

The derivation of this equation is based on the statistical mixing of the two components, and the assumptions of random molecular mixing, essentially equal molecular sizes of solute and solvent, no aggregation of solute molecules in solution, and no solvent penetration into the solute phase, that is, solvent molecules would not be found as components in the solute phase exposed to the solution. If the molar volumes of the solute and solvent are not equal, but there is sufficient thermal agitation to accomplish the maximum entropy of mixing, Equation 2.1 still holds (Hildebrand and Scott, 1950). Since the mole fractions must be less than 1, this change in entropy on mixing the solution is always positive and contributes to the spontaneity of solution formation. An interesting feature of ideal solutions involving liquids is that there is no volume change on mixing, the final solution volume being the sum of the volumes of the liquid components. For an ideal solution consisting of a solid dissolved in a liquid solvent, the final volume would equal the sum of the volume occupied by the solvent plus the volume that would be occupied by the mass of solid that has become solute when it has been supercooled to the solution temperature.

If we consider the partial molal entropy of solution with respect to the solute, Equation 2.1 becomes:

$$\Delta \bar{S}_{\text{mix},2} = -R \ln X_2^i \tag{2.2}$$

In the event that the molar volumes of solute and solvent are not comparable, and the thermal agitation is not adequate to achieve maximum entropy of mixing, a nonideal entropy of mixing exists (Bustamante et al., 1989). Two equations that account for the nonideal entropy of mixing have been derived by considering the partial molal volume, $\bar{V}$, and the volume fraction, ϕ, occupied by each solution component. The first was developed by Flory and Huggins (Hildebrand, 1949; Kertes, 1965):

$$\Delta \bar{S}_{\text{mix},2} = -R\left[\ln \phi_2 + \phi_1\left(1 - \frac{\bar{V}_2}{\bar{V}_1}\right)\right] \tag{2.3}$$

The second was introduced by Huyskens and Haulait-Pirson (1985):

$$\Delta \bar{S}_{\text{mix},2} = -R\left[\ln \phi_2 + 0.5\phi_1\left(1 - \frac{\bar{V}_2}{\bar{V}_1}\right) - 0.5 \ln\left(\phi_2 + \phi_1 \frac{\bar{V}_2}{\bar{V}_1}\right)\right] \tag{2.4}$$

Either of these expressions can be substituted for the ideal partial molal entropy of mixing, as defined in Equation 2.2. The Flory–Huggins approach, for example, has been used to improve the