where γ is defined as the activity coefficient when solubility is expressed in mole fraction units. Note that the superscript *i* is not present on the mole fraction in Equation 2.30 because this equation applies to nonideal solutions. For a real solution, Equation 2.15 would be:

$$\ln \gamma_2 X_2 = -\frac{\Delta \bar{H}_f}{RT_m}\left(\frac{T_m - T}{T}\right) \tag{2.31}$$

Rearrangement gives:

$$\ln X_2 = -\frac{\Delta \bar{H}_f}{RT_m}\left(\frac{T_m - T}{T}\right) - \ln \gamma_2 \tag{2.32}$$

Regular Solutions

A molecule will most effectively mix with molecules that have the same cohesive energy density. Cohesive energy density is simply the sum of the interactive forces per unit volume; the customary units in regular solution theory are cal/cm^3. If there are substantial differences in the cohesive energy densities of the two species, the molecules with the greater cohesive energy density will prefer to interact with each other, perhaps even to the extent of excluding the molecules with the lower cohesive energy density. Immiscibility of the two species in whole or in part will result.

Hildebrand (1949) designated nonideal solutions as regular solutions if there was sufficient thermal agitation to overcome the segregating effect of unequal cohesive densities between the solute and the solvent. Thus, the maximum randomness in the final solution can still be achieved, and the ideal partial molal entropy of mixing, as defined in Equation 2.2, still holds. Assumptions were compiled and a quantitative relationship was developed to describe the behavior of nonelectrolytes in nonpolar solvents (Hildebrand, 1929; Scatchard, 1931, 1934). By the 1970s, the general equations that related solubility to the differences in cohesive energy densities between the solute and the solvent had been fully developed (Hildebrand and Scott, 1950, 1962; Hildebrand et al., 1970).

Because the cohesive energy density is a gross sum of the different types of forces that do not necessarily interact effectively, a similarity in cohesive energy density does not ensure miscibility. With this in mind, regular solutions have several characteristics caused by differences in cohesive energy density. The most significant difference between a regular solution and an ideal solution is a nonzero partial molal enthalpy of mixing. It is still assumed that the excess volume on mixing is negligible, although formation of a regular solution is usually accompanied by expansion and an increased entropy (Hildebrand, 1949); an essentially ideal entropy of mixing, derived from the statistical mixing of the components, holds; and the molar volumes of the solute and solvent are essentially equal.

When a solute is mixed with the solvent, one can assume that when both a solute–solute and a solvent–solvent interaction are broken there are two opportunities for solute–solvent interactions exist. Therefore, the enthalpy of mixing per mole of solute is assumed to be proportional to the differences in cohesive energy densities in this same 1:1:2 ratio:

$$\Delta \bar{H}_{mix,2} \propto C_{11} + C_{22} - 2C_{12} \tag{2.33}$$

where C_{xx} refers to a cohesive energy density. C_{11} and C_{22}, then, represent the cohesive energy density of the solvent and solute, respectively (Nelson et al., 1970).

The cohesive energy density of the binary mixture, represented by C_{12}, cannot be easily predicted from the physicochemical properties of the solute and solvent. Instead, the cohesive energy density of the mixture is estimated using the geometric mean of the cohesive energy densities of the pure components:

$$C_{12} = \sqrt{C_{11}C_{22}} \tag{2.34}$$