

$$\Delta\bar{S}_f = \frac{\Delta\bar{H}_f}{T_m} \quad (2.25)$$

Substituting this for the molar entropy of fusion in Equation 2.23, and rearranging, gives:

$$\Delta\bar{G}_2^{\text{sc}} = \Delta\bar{H}_f \left(\frac{T_m - T}{T_m} \right) - \Delta\bar{C}_p T \left[\left(\frac{T_m - T}{T} \right) + \ln \left(\frac{T}{T_m} \right) \right] \quad (2.26)$$

Substituting for $\Delta\bar{G}_2^{\text{sc}}$ using Equation 2.12 gives:

$$-RT \ln a_2 = \Delta\bar{H}_f \left(\frac{T_m - T}{T_m} \right) - \Delta\bar{C}_p T \left[\left(\frac{T_m - T}{T} \right) + \ln \left(\frac{T}{T_m} \right) \right] \quad (2.27)$$

Dividing through by $(-RT)$ and substituting the mole fraction solubility for the activity, which is acceptable since this is an ideal solution, one obtains:

$$\ln X_2^i = -\frac{\Delta\bar{H}_f}{RT_m} \left(\frac{T_m - T}{T} \right) + \frac{\Delta\bar{C}_p}{R} \left[\left(\frac{T_m - T}{T} \right) + \ln \left(\frac{T}{T_m} \right) \right] \quad (2.28)$$

which is a more exact expression for the ideal solubility of a crystalline material in a liquid solvent.

To simplify this expression, one of two assumptions is ordinarily made regarding the molar differential heat capacity. The first assumption is that $\Delta\bar{C}_p$ is negligible, and a practical approach is to set it equal to zero, which gives Equation 2.15:

$$\ln X_2^i = -\frac{\Delta\bar{H}_f}{RT_m} \left(\frac{T_m - T}{T} \right) \quad (2.15)$$

The second assumption is that $\Delta\bar{C}_p$ is essentially equal to the molar entropy of fusion, $\Delta\bar{S}_f$, which can be expressed in terms of the melting point and molar enthalpy of fusion, as in Equation 2.23. This second assumption results in the following expression:

$$\ln X_2^i = -\frac{\Delta\bar{H}_f}{RT_m} \ln \left(\frac{T_m}{T} \right) \quad (2.29)$$

The molar differential heat capacity at the melting point has proved to be negligible only for benzene and rigid, polyaromatic hydrocarbons, and a compilation of literature data indicates that $\Delta\bar{C}_p$ on the average is 80% of the molar entropy of fusion (Neau and Flynn, 1990). Although the first assumption has been applied in many studies, the second assumption gained favor in certain publications (Subrahmanyam et al., 1992; Caramonte et al., 1993; Yu et al., 1994).

NONIDEAL SOLUTIONS

It is unlikely that any real solution could possess the stringent qualifications that define the ideal solution. Indeed, the ideal solution exists only when a solute is dissolved in itself as the liquid solvent. The development of a theory for nonideality amounts to quantitatively estimating an activity coefficient for the solute in the nonideal solution. Irrespective of the nature of the nonideal solution,

$$a_2 = \gamma_2 X_2 \quad (2.30)$$