$$\frac{d \ln a_2}{dT} = \frac{\Delta \bar{H}_\text{f}}{RT^2} \tag{2.13}$$

Integration between the melting point, T_m, and the solution temperature, T (Kertes, 1965) gives:

$$\ln a_2 = -\frac{\bar{H}_\text{f}}{RT_\text{m}}\left(\frac{T_\text{m} - T}{T}\right) \tag{2.14}$$

The mole fraction solubility can be substituted for the activity, keeping in mind that this is acceptable with an ideal solution:

$$\ln X_2^i = -\frac{\bar{H}_\text{f}}{RT_\text{m}}\left(\frac{T_\text{m} - T}{T}\right) \tag{2.15}$$

Therefore, the mole fraction ideal solubility of a crystalline solute in a saturated ideal solution is a function of three experimental parameters: the melting point, the molar enthalpy of fusion, and the solution temperature. Equation 2.15 can be expressed as a linear relationship with respect to the inverse of the solution temperature:

$$\ln X_2^i = -\frac{\Delta \bar{H}_\text{f}}{RT} + \frac{\Delta \bar{H}_\text{f}}{RT_\text{m}} \tag{2.16}$$

where $(\Delta \bar{H}_\text{f} / RT_\text{m})$ is assumed to be a constant.

The general rules regarding the influence of the melting point and the molar enthalpy of fusion are the greater the melting point, the lower the ideal solubility, and the greater the molar enthalpy of fusion, the lower the ideal solubility. In the case of a crystalline solute, the molar enthalpy of fusion determines the temperature sensitivity. One of the easiest ways to see this is to plot the mole fraction solubility as a log-linear function of the inverse of the solution temperature (Figure 2.1). This linear relationship is predicted in Equation 2.16. The slope, therefore, can be derived mathematically from the expression:

$$\frac{d \ln X_2^i}{d\left(\frac{1}{T}\right)} = -\frac{\Delta \bar{H}_\text{f}}{R} \tag{2.17}$$

Thus, it can be seen that the greater the molar enthalpy of fusion, the greater the increase in solubility as the solution temperature is increased, and a steeper slope would be evident in a plot such as Figure 2.1. Note that for a real solution, the enthalpy of solution, designated $\Delta \bar{H}_{\text{sol'n}}$, substitutes for the enthalpy of fusion in Equation 2.17. The enthalpy of solution includes the enthalpy of fusion and the enthalpy associated with mixing of the hypothetical supercooled liquid form of the solute mass with the solvent.

Molar Heat Capacity

The molar enthalpy for the transition from a solid to a supercooled liquid is not a constant with respect to temperature. The heat capacity of the solid and of the supercooled liquid forms of the solute at constant pressure influence the magnitude of the molar enthalpy for this transition at temperatures below the melting point. The heat capacity at constant pressure, C_p, is the amount of energy in the form of heat, Δq, required to raise the temperature of a particular material by a particular amount, ΔT (Dave et al., 2014):

$$C_p = \frac{\partial q}{\partial T} \sim \frac{\Delta q}{\Delta T} \tag{2.18}$$