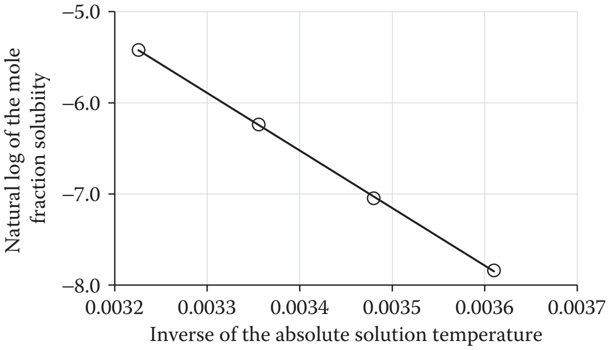

FIGURE 2.1 van't Hoff plot of ideal mole fraction solubility as a function of the inverse solution temperature.

The molar heat capacity at constant pressure, $\bar{C}_p$, would be the heat capacity divided by the amount of that material in moles, n, expressed as follows to show the relevance of the molar enthalpy of fusion:

$$\bar{C}_p = \left[\left(\frac{\partial \bar{H}_{\mathrm{f}}}{\partial T}\right)_p\right] / n \tag{2.19}$$

It is frequently assumed that the heat capacity of the solid at constant pressure, $\bar{C}_{p,s}$, and the molar heat capacity of its liquid form at constant pressure, $\bar{C}_{p,l}$, are nearly constant, or that they change at the same rate with a change in temperature. In either case, the molar differential heat capacity, defined as:

$$\Delta\bar{C}_p = \bar{C}_{p,l} - \bar{C}_{p,s} \tag{2.20}$$

would be a constant. At these temperatures, then, the total enthalpy and entropy changes can be determined by simply acknowledging the contribution of the molar differential heat capacity to each of the solid to supercooled liquid thermodynamic parameters:

$$\Delta\bar{H}_2^{\mathrm{sc}} = \Delta\bar{H}_{\mathrm{f}} - \Delta\bar{C}_p\left(T_{\mathrm{m}} - T\right) \tag{2.21}$$

$$\Delta\bar{S}_2^{\mathrm{sc}} = \Delta\bar{S}_{\mathrm{f}} - \Delta\bar{C}_p \ln\left(\frac{T}{T_{\mathrm{m}}}\right) \tag{2.22}$$

Substitution into Equation 2.6 would then give:

$$\Delta\bar{G}_2^{\mathrm{sc}} = \Delta\bar{H}_{\mathrm{f}} - \Delta\bar{C}_p\left(T_{\mathrm{m}} - T\right) - T\left[\Delta\bar{S}_{\mathrm{f}} - \Delta\bar{C}_p \ln\left(\frac{T}{T_{\mathrm{m}}}\right)\right] \tag{2.23}$$

If we consider the thermodynamic parameters at the melting point, Equation 2.6 becomes:

$$\Delta\bar{G}_{\mathrm{f}} = \Delta\bar{H}_{\mathrm{f}} - T_{\mathrm{m}}\Delta\bar{S}_{\mathrm{f}} \tag{2.24}$$

Fusion can be considered a reversible process at the melting point, and $\Delta\bar{G}_{\mathrm{f}}$ as a result would be zero. Therefore, from rearrangement of Equation 2.24 comes the relationship: