Statistical Molecular Thermodynamics

Christopher J. Cramer

Video 11.4

Colligative Properties — Freezing Point Depression
Consider a solid in equilibrium with a solution where the liquid form of the solid is the solvent (e.g., ice in contact with an aqueous solution). In that case

\[ \mu_{1,\text{sol}}^* (T_{\text{fus}}) = \mu_{1,\text{liq}} (T_{\text{fus}}) = \mu_{1,\text{liq}}^* (T_{\text{fus}}) + RT_{\text{fus}} \ln a_1 \]

where \( T_{\text{fus}} \) is the temperature at which the solid and solution are in equilibrium.

Solving generally for \( \ln a \) as a function of \( T \) yields:

\[ \ln a = \frac{\mu_{1,\text{sol}}^* - \mu_{1,\text{liq}}^*}{RT} \]

Now, differentiating with respect to \( T \)
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\[ \frac{\partial}{\partial T} \left( \ln a \right) = \frac{1}{R} \frac{\partial}{\partial T} \left( \frac{\mu_{1,\text{sol}}^*}{T} - \frac{\mu_{1,\text{liq}}^*}{T} \right) \]

Now, we can make use of the Gibbs-Helmholtz equation (cf. Video 8.7)

\[ \left[ \frac{\partial (\mu / T)}{\partial T} \right]_{P,x_1} = -\frac{\bar{H}}{T^2} \]

to determine:

\[ \frac{\partial}{\partial T} \left( \ln a \right) = \frac{1}{R} \left( \frac{\bar{H}_{1,\text{liq}}^* - \bar{H}_{1,\text{sol}}^*}{T^2} \right) = \frac{\Delta_{\text{fus}} \bar{H}}{RT^2} \]

or, rearranging

\[ d \ln a = \frac{\Delta_{\text{fus}} \bar{H}}{RT^2} dT \]
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\[ d \ln a = \frac{\Delta_{\text{fus}} \bar{H}}{RT^2} \, dT \]

Integrating from the pure liquid \((a = 1, T_{\text{fus}} = T^{*}_{\text{fus}})\) to some other temperature corresponding to a particular solution (so \(a_1 < 1\))

\[ \int_{a=1}^{a=a_1} d \ln a = \int_{T_{\text{fus}}}^{T^{*}_{\text{fus}}} \frac{\Delta_{\text{fus}} \bar{H}}{RT^2} \, dT \]

\[ \ln a_1 = \frac{\Delta_{\text{fus}} \bar{H}}{R} \left( \frac{1}{T^{*}_{\text{fus}}} - \frac{1}{T_{\text{fus}}} \right) \approx \frac{\Delta_{\text{fus}} \bar{H}}{R \left( T^{*}_{\text{fus}} \right)^2} \left( T_{\text{fus}} - T^{*}_{\text{fus}} \right) \]

necessarily negative

necessarily positive

necessarily negative

i.e., \(T_{\text{fus}} < T^{*}_{\text{fus}}\)

Now define \(\Delta T_{\text{fus}} = T^{*}_{\text{fus}} - T_{\text{fus}}\)
Specific Case of Water

\[ \ln a_1 \approx -\frac{\Delta_{\text{fus}} \bar{H}}{R(T_{\text{fus}}^*)^2} \Delta T_{\text{fus}} \]

Now recall for the case of water (cf. Video 11.3):

\[ \ln a_1 \approx \ln x_1 = \ln (1 - x_2) \approx -x_2 \approx -\frac{m}{55.51 \text{ mol kg}^{-1} \text{ water}} \]

and we finally have (for water)

\[ \Delta T_{\text{fus}} \approx \frac{R(T_{\text{fus}}^*)^2}{\Delta_{\text{fus}} \bar{H} \cdot 55.51 \text{ mol kg}^{-1}} m \]

\[ \approx K_f m \]

For water, \( K_f = 1.86 \text{ K kg mol}^{-1} \)
Self-assessment

How much table sugar (sucrose) would you need to add to a liter of water to reduce the freezing point of the sugar solution to about –2 °C?

\[
\Delta T_{\text{fus}} \approx \frac{R (T^*_{\text{fus}})^2}{\Delta_{\text{fus}} \overline{H} \cdot 55.51 \text{ mol kg}^{-1}} m \\
\approx K_f m
\]
Self-assessment Explained

\[ \Delta T_{fus} \approx \frac{R \left( T_{fus}^* \right)^2}{\Delta_{fus} \bar{H} \cdot 55.51 \text{ mol kg}^{-1} m} \]

\[ \approx K_f m \]

For water, \( K_f = 1.86 \text{ K kg mol}^{-1} \)

Given the value of \( K_f \) for water, it would appear that one will need about 1 mol of sucrose (to make a 1 molal solution, given that 1 L of water weighs about 1 kg). So, that’s 342.3 g of sucrose (about \( \frac{3}{4} \) pound) in about one quart of water. Pretty seriously sweetened to only drive down the melting point by a measly 2 degrees C...
**General Observations**

\[
\Delta T_{\text{fus}} \approx \frac{R \left( T^{*}_{\text{fus}} \right)^2}{\Delta_{\text{fus}} \bar{H} \cdot \left( \frac{1000}{MW_1} \right) \text{mol kg}^{-1} \cdot m}
\]

\[
\approx K_f m \quad \text{independent of solute!}
\]

*K_f* increases (solutes *more* able to depress freezing point) for:

- Higher pure substance freezing point
- Weaker intermolecular interactions in pure solid
- Greater molecular weight of solvent
\[ dU = \delta q + \delta w \]

Next: Other Colligative Properties