STATISTICAL MOLECULAR THERMODYNAMICS

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Video 11.4

Colligative Properties — Freezing Point Depression

FREEZING POINT DEPRESSION 1

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_{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

FREEZING POINT DEPRESSION 2

$$\frac{\partial}{\partial T} (\ln a) = \frac{1}{R} \frac{\partial}{\partial T} \left(\frac{\mu_1^{*,\text{sol}}}{T} - \frac{\mu_1^{*,\text{liq}}}{T} \right)$$

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

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

to determine:

$$\frac{\partial}{\partial T} (\ln a) = \frac{1}{R} \left(\frac{\overline{H}_1^{*, \text{liq}} - \overline{H}_1^{*, \text{sol}}}{T^2} \right) = \frac{\Delta_{\text{fus}} \overline{H}}{RT^2}$$

or, rearranging

$$d\ln a = \frac{\Delta_{\rm fus}\bar{H}}{RT^2}dT$$

FREEZING POINT DEPRESSION 3

$$d\ln a = \frac{\Delta_{\rm fus}\overline{H}}{RT^2}dT$$

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

$$\int_{a=1}^{a=a_{1}} d\ln a = \int_{T_{\text{fus}}}^{T_{\text{fus}}} \frac{\Delta_{\text{fus}} \overline{H}}{RT^{2}} dT$$
necessarily positive
$$\ln a_{1} = \frac{\Delta_{\text{fus}} \overline{H}}{R} \left(\frac{1}{T_{\text{fus}}^{*}} - \frac{1}{T_{\text{fus}}} \right) \approx \frac{\Delta_{\text{fus}} \overline{H}}{R \left(T_{\text{fus}}^{*} \right)^{2}} \left(T_{\text{fus}} - T_{\text{fus}}^{*} \right)$$
necessarily negative
necessarily negative
i.e., $T_{\text{fus}} < T_{\text{fus}}^{*}$

Now define
$$\Delta T_{\text{fus}} = T^*_{\text{fus}} - T_{\text{fus}}$$

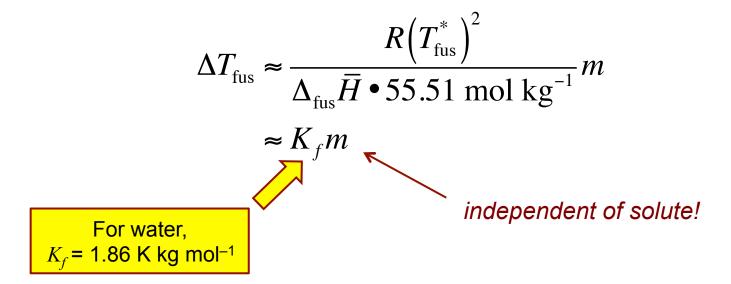
SPECIFIC CASE OF WATER

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

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

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

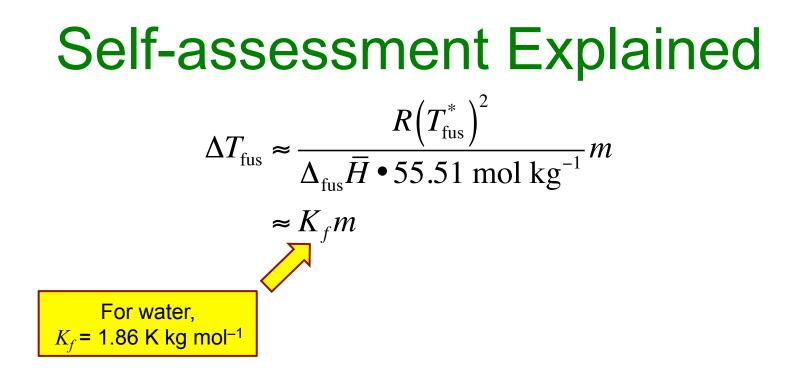
and we finally have (for water)



Self-assessment

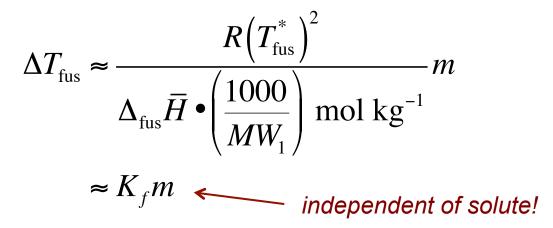
How much table sugar (sucrose) would you need to add to a liter of water to reduce the freezing point of the sugar solution to about –2 °C?

$$\Delta T_{\text{fus}} \approx \frac{R(T_{\text{fus}}^*)^2}{\Delta_{\text{fus}}\overline{H} \bullet 55.51 \text{ mol kg}^{-1}} m$$
$$\approx K_f m$$



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 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



 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



Next: Other Colligative Properties