

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)

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

to determine:

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

or, rearranging

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

FREEZING POINT DEPRESSION 3

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

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

$$\int_{a=1}^{a=a_1} d \ln a = \int_{T_{\text{fus}}^*}^{T_{\text{fus}}} \frac{\Delta_{\text{fus}} \bar{H}}{RT^2} dT$$

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

necessarily positive

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

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

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,
 $K_f = 1.86 \text{ K kg mol}^{-1}$

independent of solute!

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 $-2\text{ }^{\circ}\text{C}$?

$$\begin{aligned}\Delta T_{\text{fus}} &\approx \frac{R(T_{\text{fus}}^*)^2}{\Delta_{\text{fus}}\bar{H} \cdot 55.51 \text{ mol kg}^{-1}} m \\ &\approx K_f m\end{aligned}$$

Self-assessment Explained

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

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

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

$$\Delta T_{\text{fus}} \approx \frac{R(T_{\text{fus}}^*)^2}{\Delta_{\text{fus}} \bar{H} \cdot \left(\frac{1000}{MW_1}\right) \text{ mol kg}^{-1}} m$$
$$\approx K_f m \quad \leftarrow \text{independent of solute!}$$

K_f increases (solute *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