# Freezing point depression

At the freezing point of a solution, solid solvent is in equilibrium with the solvent in solution.   As we have seen, this equilibrium implies that the chemical potential of each phase is equal to the other:

$$\mu_1{}^{solid}\left(T_{fus}\right) = \mu_1{}^{soln}\left(T_{fus}\right)$$

where subscript 1 denotes solvent and $T_{fus}$ is the freezing point of the solution.

$$\mu_1{}^{soln}\left(T_{fus}\right) = \mu_1{}^{*} + RT \ln x_1 = \mu_1{}^{liq} + RT \ln x_1$$

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where subscript 1 denotes solvent and $T_{fus}$ is the freezing point of the solution, so that we can equate $\mu$ for the liquid and solid

$$\mu_1{}^{solid}\left(T_{fus}\right) = \mu_1{}^{liq} + RT \ln x_1$$

Next we can solve for ln $x_1$.

# The phase equilibrium

Solving for $x_1$, we obtain

$$\ln x_1 = \frac{\left(\mu_1{}^{solid} - \mu_1{}^{liq}\right)}{RT} = -\frac{\Delta_{fus}G}{RT}$$

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and when combined with the well known relation

$$\Delta_{fus}G = \Delta_{fus}H - T\Delta_{fus}S$$

we see that

$$\ln x_1 = -\frac{\Delta_{fus}H - T\Delta_{fus}S}{RT} = -\frac{\Delta_{fus}H}{RT} + \frac{\Delta_{fus}S}{R}$$

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For pure solvent $x_1 = 1$ and therefore

$$\ln 1 = 0 = -\frac{\Delta_{fus}H}{RT^*} + \frac{\Delta_{fus}S}{R}$$

# Comparison of phase equilibria

We subtract the equation for $x_1 = 1$ from the equation for $x_1$.

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$$\ln x_1 = -\frac{\Delta_{fus}H}{RT} + \frac{\Delta_{fus}H}{RT^*}$$

For an activity $x_2$ of solute, $\ln x_1 = \ln(1 - x_2) \approx -x_2$

$$-x_2 = -\frac{\Delta_{fus}H}{RT} + \frac{\Delta_{fus}H}{RT^*}$$

We can rearrange this equation so we can clearly see the temperature dependence

$$x_2 = \frac{\Delta_{fus}H}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)$$

# Freezing point depression as an equilibrium shift

In terms of the mole fraction $x_1$ we obtain an expression that looks in a general sense like an application of the van't Hoff Equation

$$\ln x_1 = -\frac{\Delta_{fus}H}{RT}\left(\frac{1}{T} - \frac{1}{T^*}\right)$$

The above expression can be further approximated using

$$\frac{1}{T} - \frac{1}{T^*} = \frac{(T^* - T)}{T^*T} \approx \frac{(T^* - T)}{T^{*2}} = \frac{\Delta T}{T^{*2}}$$

To obtain a compact formula in terms of the temperature shift of the equilibrium,

$$x_2 = \frac{\Delta_{fus}H}{R}\frac{\Delta T}{T^{*2}}$$

# Freezing point depression constant

The above formula can be compared with the formula for freezing point depression

$$\Delta T_{fus} = K_f m$$

For a dilute solution $x_2 \approx M_1 m/1000g \ kg^{-1}$ for small values of m, where m is the molality.  Therefore,

$$K_f = \frac{M_1 \left(\frac{kg}{mol}\right) RT^{*2}}{\Delta_{fus}H}$$

is called the freezing point depression constant.

Justification: ln(1-x) ~ -x

$$f(x) = \sum_{n=1}^{\infty} \left( \frac{d^n f(x)}{dx^n} \right)_{x=x'} \frac{x^n}{n!}$$

The derivative is:

$$\frac{d \ln(1-x)}{dx} = -\frac{1}{1-x} \approx -1$$

and we are expanding about 0 so the first term in the Taylor expansion is:

$$-\frac{1}{1-0}x = -x$$

# Boiling point elevation

We can determine the value of $K_b$ for water.
The phenomenon of boiling point elevation can be derived in a completely analogous fashion. In both cases the physics behind the effect is a lowering of the chemical potential of the solution relative to the pure substance. This can be seen in the diagram below where we plot the chemical potential as a function of the temperature.
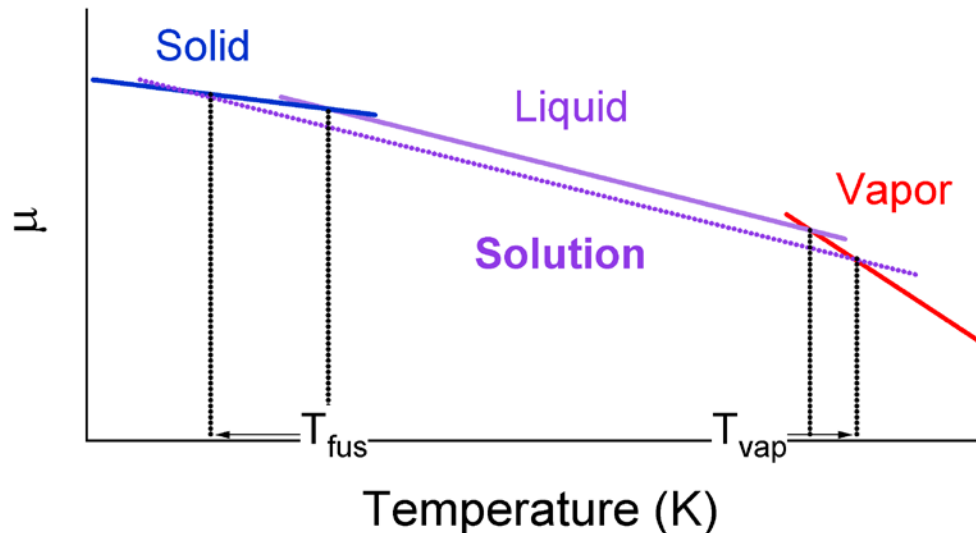
# Boiling point elevation

In this plot notice that the slope increases as the phase changes from solid to liquid and then to vapor. The slope is proportional to - S

$$\left(\frac{\partial \mu}{\partial T}\right)_P = -S$$

The entropy increases in the same order (solid → liquid → gas). Notice that the violet line representing the chemical potential as a function of temperature is shifted down by the addition of solute. Mathematically this is due to

$$\mu_1{}^{soln}\left(T_{vap}\right) = \mu_1{}^* + RT \ln x_1 = \mu_1{}^{liq} + RT \ln x_1$$

Because the chemical potential of the solid and vapor are not shifted by the addition of solute the intersection point (i.e. temperature of phase transition) goes down for fusion, but goes up for vaporization.

# Boiling point elevation

Following precisely the same series of steps as above for the freezing point depression we find that

$$x_2 = -\frac{\Delta_{vap}H}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)$$

The only difference is that the shift is in the opposite direction so there is a minus sign. The boiling point elevation is:

$$\Delta T_{vap} = K_b m$$

Using the same procedure as above we can determine the ebullioscopic constant. Note that $M_1$ is the molar mass of the solvent

$$K_b = \frac{M_1\left(\frac{kg}{mol}\right)RT^{*2}}{\Delta_{vap}H}$$