21.3: The Entropy of a Phase Transition can be Calculated from the Enthalpy of the Phase Transition

Phase transitions (e.g. melting) often occur under equilibrium conditions. We have seen that both the H and the S curves undergo a discontinuity at constant temperature during melting, because there is an enthalpy of fusion to overcome. For a general phase transition at equilibrium at constant T and P, we can say that:

$$\begin{aligned} \Delta_{trs} G &= \Delta_{trs} H - T_{trs} \Delta_{trs} S \\ &= 0 \\ \Delta_{trs} H &= T_{trs} \Delta_{trs} S \\ \frac{\Delta_{trs} H}{T_{trs}} &= \Delta_{trs} S \end{aligned}$$

For melting of a crystalline solid, we now see *why* there is a sudden jump in enthalpy. The reason is that the solid has a much more ordered structure than the crystalline solid. The decrease in order implies a finite $\Delta_{trs} S$. We should stress at this point that we are talking about ***first order*** transitions here. The reason for this terminology is that the discontinuity is in a function like S, that is a first order derivative of G (or A):

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

Second order derivatives (e.g. the heat capacity) will display a singularity (+∞) at the transition point.

Every phase transition will have a change in entropy associated with it. The different types of phase transitions that can occur are:

$l \rightarrow g$	Vaporization / boiling
$g \rightarrow l$	Condensation
$s \rightarrow l$	Fusion / melting
$l \rightarrow s$	Freezing
$s \rightarrow g$	Sublimation
$g \rightarrow s$	Deposition
$s \rightarrow s$	Solid to solid phase transition