

Clausius-Clapeyron equation [tln29]

Consider the variation of the free energy in the two phases I and II along their coexistence line: $dG^I = dG^{II}$.

$$\Rightarrow V^I dp - S^I dT = V^{II} dp - S^{II} dT.$$

Slope of the coexistence line:

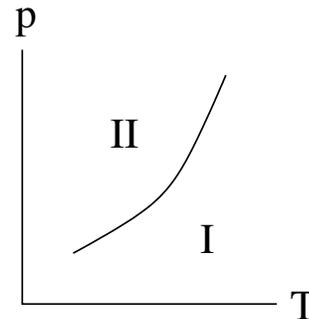
$$\left(\frac{dp}{dT}\right)_{coex} = \frac{S^I - S^{II}}{V^I - V^{II}} = \frac{\Delta S}{\Delta V} = \frac{\Delta E}{T\Delta V} \quad (\text{Clausius-Clapeyron equation}).$$

Latent heat (change in enthalpy): $\Delta E = T\Delta S$

Fact: $\Delta S > 0$ if $dT > 0$.

Consequence: $(dp/dT)_{coex} > 0$ if $\Delta V > 0$.

The case of H_2O : The substance contracts upon melting. Therefore, the fusion curve has negative slope. The highest melting temperature occurs at the triple point. The density maximum at pressures $0.008\text{atm} \lesssim p \lesssim 270\text{atm}$ occurs inside the liquid phase. Ice under pressure tends to melt, which makes skating possible.



(i) **Vaporization curve** (liquid-gas coexistence line):

The equilibrium pressure is then the saturated vapor pressure $p(T)_{coex}$. It can be derived by integrating the Clausius-Clapeyron equation:

$$\begin{aligned} \left(\frac{dp}{dT}\right)_{coex} &= \frac{\Delta E}{T\Delta V} \simeq \frac{\Delta E}{TV_{vap}} \simeq \frac{p}{nRT^2} \Delta E \Rightarrow \ln \frac{p}{p_0} = -\frac{\Delta E}{nR} \left(\frac{1}{T} - \frac{1}{T_0}\right) \\ &\Rightarrow p(T)_{coex} = p(T_0)_{coex} \exp \left[-\frac{\Delta E}{nR} \left(\frac{1}{T} - \frac{1}{T_0}\right) \right]. \end{aligned}$$

(ii) **Fusion curve** (solid-liquid coexistence line):

The fusion curve does not terminate in a critical point. The solid and liquid phases have different symmetries.

(iii) **Sublimation curve** (solid-gas coexistence line):

The sublimation curve ends in the triple point.