

## Derivation of the Clapeyron equation

Consider the phase diagram of a pure substance. The phase boundary between  $\alpha$  and  $\beta$  phases will tell at what temperature-pressure combinations may have an equilibrium between the two phases.

If we take a point on the phase boundary and change both the temperature and pressure slightly but so the resultant phase also sits on the phase boundary we have to recognise that because of the system being in equilibrium before and after the changes in the conditions, the change to the chemical potentials in the different phases must equal;  $d\mu(\alpha) = d\mu(\beta)$  (1).

Because for a pure substance  $dG = Vdp - SdT$  (2), we have seen that  $d\mu = V_m dp - S_m dT$  (3), (from the definition of the chemical potential as the molar Gibbs energy of a pure substance, where  $S_m$  and  $V_m$  are the molar entropy and volume of the pure substance, respectively)

Plug (3) into (1) to get  $-S_m(\alpha)dT + V_m(\alpha)dp = -S_m(\beta)dT + V_m(\beta)dp$ .

Rearrange to  $\{V_m(\beta) - V_m(\alpha)\}dp = \{S_m(\beta) - S_m(\alpha)\}dT$

Recognise that  $\{V_m(\beta) - V_m(\alpha)\}$  and  $\{S_m(\beta) - S_m(\alpha)\}$  are the molar volume ( $\Delta_{\text{trs}}V$ ) and entropy ( $\Delta_{\text{trs}}S$ ) changes, respectively when transitioning from the  $\alpha$  to the  $\beta$  phase to get  $\frac{dp}{dT} = \frac{\Delta_{\text{trs}}S}{\Delta_{\text{trs}}V}$ , the Clapeyron equation.