As we move along any one of the two-phase coexistence curves, \( \mu_\alpha (T, P) = \mu_\beta (T, P) \) at each point on the curve.

- Thus, if we change \( T \) and \( P \) by \( dT \) and \( dP \), staying on curve, \( \mu_\alpha (T, P) + d\mu_\alpha = \mu_\beta (T, P) + d\mu_\beta \), with \( d\mu_\alpha = d\mu_\beta \).

- Then \( d\mu = -S_m \, dT + V_m \, dP \) (can you derive this?) \( \Rightarrow \)

\[-S_m \alpha \, dT + V_m \alpha \, dP = -S_m \beta \, dT + V_m \beta \, dP \]

or \((S_m \beta - S_m \alpha) \, dT = (V_m \beta - V_m \alpha) \, dP\)

or \[
\frac{dP}{dT} = \frac{\Delta S_m}{\Delta V_m} = \text{Clapeyron equation}
\]

Slope of \( P \) vs \( T \) Coexistence Curves
\[
\left( \frac{dP}{dT} \right)_{\text{fusion}} \gg \left( \frac{dP}{dT} \right)_{\text{vap}}
\]

because \[\Delta V_{m}^{\text{fusion}}\] is 2-4 orders of magnitude smaller than \[\Delta V_{m}^{\text{vap}}\] (why?), whereas \[\Delta S_{m}^{\text{fusion}}\] -- while smaller than \[\Delta S_{m}^{\text{vap}}\] (why?) -- is only a few times smaller than \[\Delta S_{m}^{\text{vap}}\] (why?). 

- See Table 8.2, for \[\Delta H_{\text{fusion}}, T_m, \Delta H_{\text{vap}}, T_b\], from which \[\Delta S_{m}^{\text{fusion}} = \frac{\Delta H_{\text{fusion}}}{T_m}\] and \[\Delta S_{m}^{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T_b}\] can be calculated:

\[
(\Delta S_{m}^{\text{fusion}})_{\text{average}} \approx 20 \text{ J/mole K}
\]
and

\[
(\Delta S_{m}^{\text{vap}})_{\text{average}} \approx 90 \text{ J/mole K}
\]

- By contrast, \[\Delta V_{m}^{\text{fusion}} \approx 4 \times 10^{-6} \text{ m}^3/\text{mole}\] 
(Can you estimate this from, say, 10\% change in density upon freezing?) vs

\[\Delta V_{m}^{\text{vap}} \approx \Delta V_{m}^{\text{gas}} \approx 2 \times 10^{-2} \text{ m}^3/\text{mole}\]

- LET'S HAVE SOME FUN (in case we weren't already, before): LET'S ESTIMATE \[\Delta H_{\text{vap}}\].

**KEY OBSERVATION:** \[\Delta H_{m}^{\text{vap}} \approx N \Delta E_a\]

where \(\Delta E_a\) is the attraction energy, \(\Delta E_a\) is the well-depth of the intermolecular potential curve that we considered in estimating the van der Waals a-coefficient: \(a \approx \Delta E_a \cdot b\)
\[ \Delta H_{m} \approx N_{A} E \approx \frac{a}{b} \]

Then, using our \( a \approx 10 \text{ atm mole}^{-2} = 10 \text{ L atm mole}^{-1} \) and \( b \approx 0.05 \text{ mole} \), we have

\[ \Delta H_{m} \approx \frac{10 \text{ L atm}}{0.05 \text{ mole}} = 200 \text{ kJ/mole} \]

(See Table 8.2 values)

→ Dependence of vapor pressure on temperature

- Start with Clapeyron equation for liq.-vapor coexistence curve:

\[ \frac{dP}{dT} = \frac{\Delta S_{m}^{vap}}{\Delta V_{m}^{vap}} = \frac{\Delta H_{m}^{vap}}{T \Delta V_{m}^{vap}} \]

Now use fact that \( \Delta V_{m}^{vap} \approx V_{m}^{gas} \approx \frac{RT}{P} \),

\[ \Rightarrow \frac{dP}{dT} \approx \frac{P \Delta H_{m}^{vap}}{RT} \]

or

\[ \frac{dP}{P} = \frac{\Delta H_{m}^{vap}}{R} \frac{dT}{T^{2}} \]

Neglecting \( T \)-dependence of \( \Delta H_{m}^{vap} \) \( \Rightarrow \)

\[ \int_{P_{1}}^{P_{2}} \frac{dP}{P} = \Delta H_{m}^{vap} \int_{T_{1}}^{T_{2}} \frac{dT}{T^{2}} \]

or

\[ \ln \left( \frac{P_{vap}(T_{2})}{P_{vap}(T_{1})} \right) = - \frac{\Delta H_{m}^{vap}}{R} \left( \frac{1}{T_{2}} - \frac{1}{T_{1}} \right) \]

Clausius-Clapeyron equation
For sol.-vapor coexistence, we can derive an identical equation, but with \( \Delta H_m^{\text{sub}} \) appearing instead of \( \Delta H_m^{\text{vap}} \)

\[ \frac{dP}{dT} = \frac{\Delta S_m}{\Delta V_m^{\text{fus}}} = \frac{\Delta H_m^{\text{fus}}}{T \Delta V_m^{\text{fus}}} \]

\[ \Rightarrow \int_{P_1}^{P_2} dP = \frac{\Delta H_m^{\text{fus}}}{\Delta V_m^{\text{fus}}} \int_{T_1}^{T_2} \frac{dT}{T} \]

or

\[ P(T_2) - P(T_1) = \frac{\Delta H_m^{f}}{\Delta V_m^{f}} \ln \frac{T_2}{T_1} \]

Note: \( T_2 - T_1 = \Delta T \ll T_1 \Rightarrow \)

\[ \ln \frac{T_2}{T_1} = \ln \frac{T_1 + \Delta T}{T_1} = \ln \left(1 + \frac{\Delta T}{T_1}\right) \approx \frac{\Delta T}{T_1}, \]

and hence

\[ \Delta P \approx \frac{\Delta H_m^{f}}{T_1 \Delta V_m^{f}} \Delta T = \frac{\Delta S_m^{f}}{\Delta V_m^{f}} \Delta T, \]

consistent with original Clausius-Clapeyron equation.