

Clausius Clapeyron equation

Condensed phase equilibria

• CLAUSIUS-CLAPERYON EQUATION

We derived the Clapeyron Equation last lecture:

$$\left(\frac{dp}{dT} \right)_{\text{coexist}} = \left[\frac{\bar{S}_\beta - \bar{S}_\alpha}{\bar{V}_\beta - \bar{V}_\alpha} \right] = \left(\frac{\Delta \bar{S}}{\Delta \bar{V}} \right)_{\alpha \rightarrow \beta}$$

This is **exact!**

Let's examine this for equilibrium between solid-liquid and solid-solid phases. For example, fusion:

$$\left(\frac{dp}{dT} \right)_{\text{coexist}} = \frac{\Delta S_{\text{fus}}}{\Delta V_{\text{fus}}} \quad \text{use} \quad \Delta H_{\text{fus}} = T \Delta S_{\text{fus}}$$

We can make some assumptions about these types of phase equilibria.

$$\int_{p_1}^{p_2} dp = \int_{T_m}^{T'_m} \frac{\Delta H_{\text{fus}}}{\Delta V_{\text{fus}}} \cdot \frac{dT}{T} \quad \text{assume } \Delta H_{\text{fus}}, \Delta V_{\text{fus}} \text{ are independent of } p, T$$

$$p_2 - p_1 = \frac{\Delta H_{\text{fus}}}{\Delta V_{\text{fus}}} \ln \left(\frac{T'_m}{T_m} \right) \quad T'_m = \text{melting temp @ } p_2, T_m = \text{melting temp @ } p_1$$

$T'_m - T_m \sim 0$ (expect small change in T_m)

$$\ln \left(\frac{T'_m}{T_m} \right) = \ln \left(\frac{T_m + T'_m - T_m}{T_m} \right) = \ln \left(1 + \frac{T'_m - T_m}{T_m} \right)$$

Since fraction is small, then

$$\ln \left(\frac{T'_m}{T_m} \right) \approx \left(\frac{T'_m - T_m}{T_m} \right) = \frac{\Delta T}{T}$$

Then

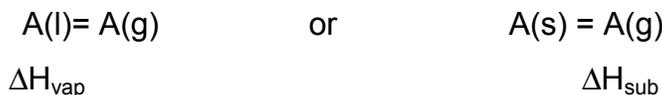
$$\Delta p \cong \frac{\Delta H_{\text{fus}}}{\Delta V_{\text{fus}}} \cdot \frac{\Delta T_m}{T_m}$$

gives you ΔT_m , the melting point increase corresponding to a Δp increase

also says: the coexistence line is approximately **linear**

• **Equilibrium between gas/liquid or gas /solid (gas/condensed phase)**

substance A:



$$\left(\frac{dp}{dT} \right) = \frac{\Delta \bar{S}}{\Delta \bar{V}} = \frac{\Delta \bar{H}}{T(\bar{V}_g - \bar{V}_c)} \quad V_c = V_{\text{solid}} \text{ or } V_{\text{liquid}}$$

a) We can approximate

$$\bar{V}_g - \bar{V}_c \approx \bar{V}_g \quad \text{because } V_g \gg V_c$$

b) We can assume the gas is ideal

$$\bar{V}_g = \frac{RT}{p}$$

Clausius Clapeyron Equation

$$\left(\frac{dp}{dT} \right) \approx \frac{\Delta \bar{H}}{T(\bar{V}_g)} = \frac{\Delta \bar{H} \cdot p}{RT^2}$$

$$\left(\frac{d \ln p}{dT} \right) \approx \frac{\Delta \bar{H}}{RT^2}$$

to get here we made approximations, but very good far from T_c .

Relates the vapor pressure of a liquid to ΔH_{vap} or vapor pressure of a solid to ΔH_{sub} .

c) We can make yet another approximation: assume ΔH independent of T . Then can integrate:

$$\int_{p_0}^p d \ln p = \int_{T_0}^T \frac{\Delta H}{RT^2} dT$$

$$\ln\left(\frac{p}{p_0}\right) \approx -\frac{\Delta\bar{H}}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)$$

This equation allows us to get ΔH_{sub} from p

$$\ln\left(\frac{p}{p_0}\right) \approx -\frac{\Delta\bar{H}}{RT} + \frac{\Delta\bar{H}}{RT_0}$$

