Clausius Clapeyron equation

Condensed phase equilibria

- **CLAUSIUS-CLAPERYON EQUATION**

We derived the Clapeyron Equation last lecture:

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

This is **exact!**

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

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

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

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

$$p_2 - p_1 = \frac{\Delta H_{fus}}{\Delta V_{fus}} \ln\left(\frac{T_m'}{T_m}\right)$$ T_m=melting temp @p_2, T_m =melting temp @ p_1

T_m'-T_m~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:

A(l)= A(g) or A(s) = A(g)

ΔH_{vap} ΔH_{sub}

$$\left(\frac{dp}{dT}\right) = \frac{\Delta \overline{S}}{\Delta \overline{V}} = \frac{\Delta \overline{H}}{T\left(\overline{V}_g - \overline{V}_c\right)}$$

$V_c = V_{solid}$ or V_{liquid}

a) We can approximate

$\overline{V}_g - \overline{V}_c \approx \overline{V}_g$ because $V_g >> V_c$

b) We can assume the gas is ideal

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

Clausius Clapeyron Equation

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

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

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

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:

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

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

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

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