Phase Equilibrium ; Pure Substance

Chemical Potential, $\bar{G}$

pure substance

$$\bar{G}(T,P) = \mu(T,P)$$

$$d\bar{G}(T,P) = d\mu(T,P) = \bar{V}dp - \bar{S}dT$$

pure

Pressure Constant $dp = 0$

$$d\mu(T,P) = -\bar{S}\,dT \quad @\ P = \text{const.}$$

slope $\dfrac{d\mu(T,P)}{dT} = -\bar{S}$

$$\bar{S}_{solid} < \bar{S}_{liquid} < \bar{S}_{gas}$$

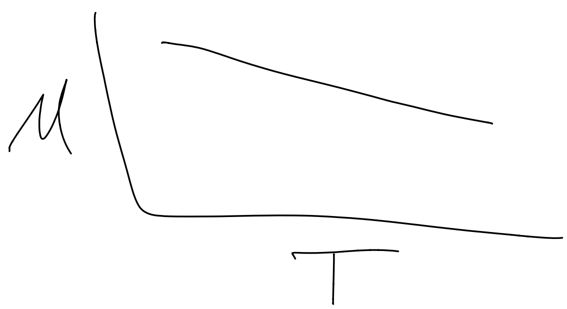
vapor

$$\frac{d\mu_{solid}}{dT} > \frac{d\mu_{liquid}}{dT} > \frac{d\mu_{vapor}}{dT}$$

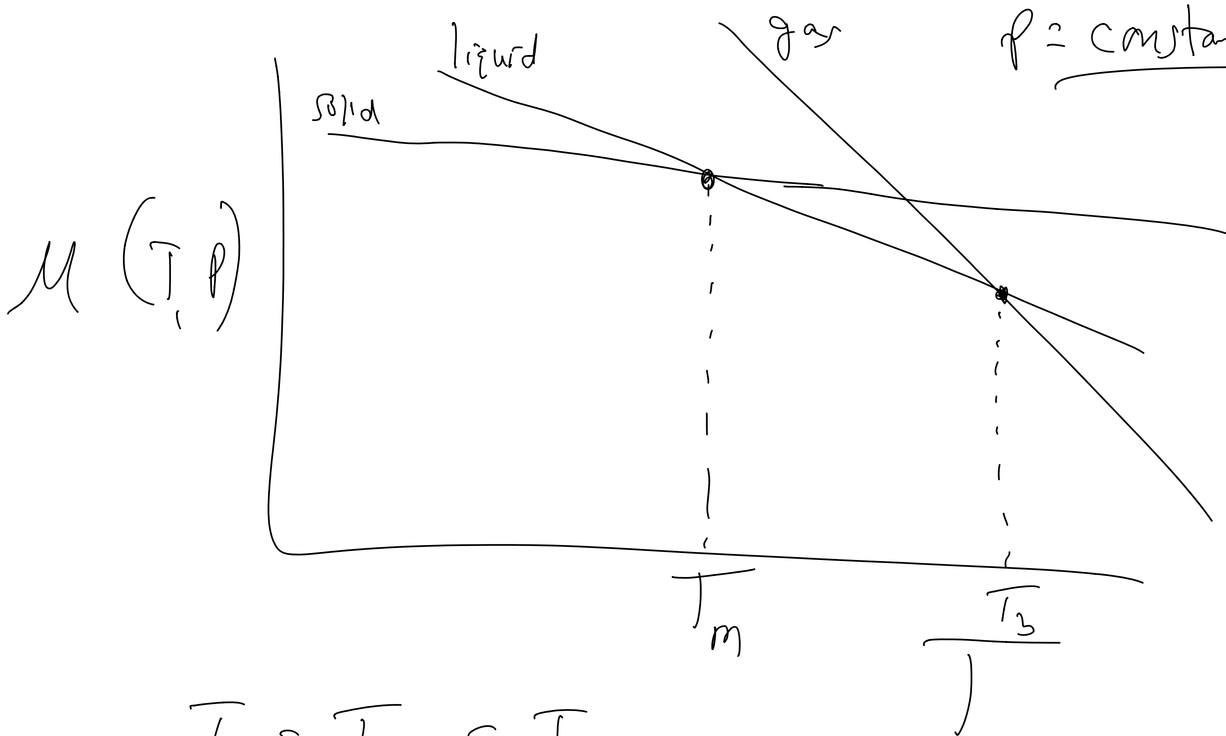
$$\left|\frac{d\mu_{solid}}{dT}\right| < \left|\frac{d\mu_{liquid}}{dT}\right| < \left|\frac{d\mu_{vapor}}{dT}\right|$$

all have positive entropies

all have neg. slopes



so what ——



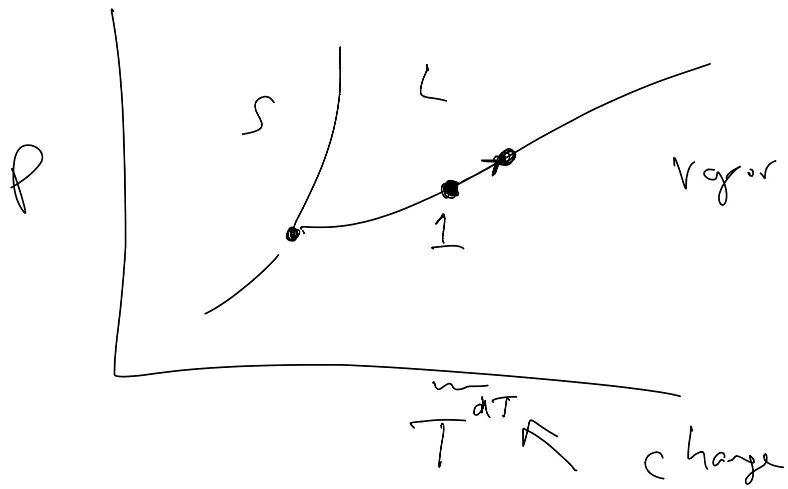
$p = \text{constant}$

$T_{liq} = T_{solid} = T_m$

$p_{liq} = p_{solid} = p_m$

$\mu_{liq} = \mu_{solid}$

So, how do we quantify relationship between $p_{coexistence}$ and $T_{coexistence}$?



change T by dT

$$d\mu_L(T,P) = d\mu_{vapor}(T,P)$$

pure fluid:

$$\bar{V}_L\, dP - \bar{S}_L\, dT = \bar{V}_{vapor}\, dP - \bar{S}_{vapor}\, dT$$

$$\left(\bar{V}_L - \bar{V}_{vapor}\right) dP = \left(\bar{S}_L - \bar{S}_{vapor}\right) dT$$

$$\boxed{\left(\frac{dP}{dT}\right)_{coexistence} = \frac{\left(\bar{S}_L - \bar{S}_{vapor}\right)}{\left(\bar{V}_L - \bar{V}_{vapor}\right)}}$$

At Coexistence:

$$\mu_L(T,P) = \mu_{vapor}(T,P)$$

$$\overline{G}_L(T,P) = \overline{G}_{vapor}(T,P)$$

$$\overline{H}_L(T,P) - T\overline{S}_L(T,P) = \overline{H}_{vapor}(T,P) - T\overline{S}_{vapor}(T,P)$$

$$\overline{H}_L(T,P) - \overline{H}_{vapor}(T,P) = T\overline{S}_L(T,P) - T\overline{S}_{vapor}(T,P)$$

$$\frac{\overline{H}_L(T,P) - \overline{H}_{vapor}(T,P)}{T} = \overline{S}_L(T,P) - \overline{S}_{vapor}(T,P)$$

$$\boxed{\left(\frac{dP}{dT}\right)_{coexistence} = \frac{\overline{H}_L(T,P) - \overline{H}_{vapor}(T,P)}{T\left(\overline{V}_L - \overline{V}_{vapor}\right)}}$$

$$\left(\frac{dP}{dT}\right)_{coexistence} = \frac{-\Delta\overline{H}_{vaporization}}{T\left(\overline{V}_L - \overline{V}_{vapor}\right)}$$

$\bar{V}_{vapor} >>> \bar{V}_{l}$ ~~XXXX~~

$$\boxed{\left(\frac{dP}{dT}\right)_{coexistence} = \frac{\Delta \bar{H}_{vaporization}}{T \bar{V}_{vapor}}}$$

What if we take vapor to be Ideal Gas?

$$\bar{V}_{vapor} = RT/P$$

$$\left(\frac{dP}{dT}\right)_{coex} = \frac{(\Delta \bar{H}_{vaporization}) P}{RT^2}$$

$$\left(\frac{(dP/P)}{dT}\right)_{coex} = \frac{\Delta \bar{H}_{vap}}{RT^2}$$

$$\boxed{\frac{d(\ln P)}{dT} = \frac{\Delta H_{vap}}{RT^2}}$$

$$\int_{P_1}^{P_2} d(\ln P) = \int_{T_1}^{T_2} \frac{\Delta H_{vap}}{RT^2}\, dT$$

$$\boxed{\ln(P_2/P_1) = \frac{\Delta H_{vap}}{R}\left(-\frac{1}{T_2} + \frac{1}{T_1}\right)}$$

Clausius - Clapeyron Eqn.