2-phases in equilibrium

(pure substance)

concept: $\mu_\alpha(T,p) = \mu_\beta(T,p)$

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

$$= -\bar{S}\,dT \quad @\ p = \text{const.}$$

$$\boxed{\begin{aligned} p_\alpha &= p_\beta \\ T_\alpha &= T_\beta \\ \mu_\alpha(T,p) &= \mu_\beta(T,p) \end{aligned}}$$

$$d\mu_\alpha(T,P) = d\mu_\beta(T,P)$$

α, β 2 phases in equilibrium

α, β = liquid, vapor

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

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

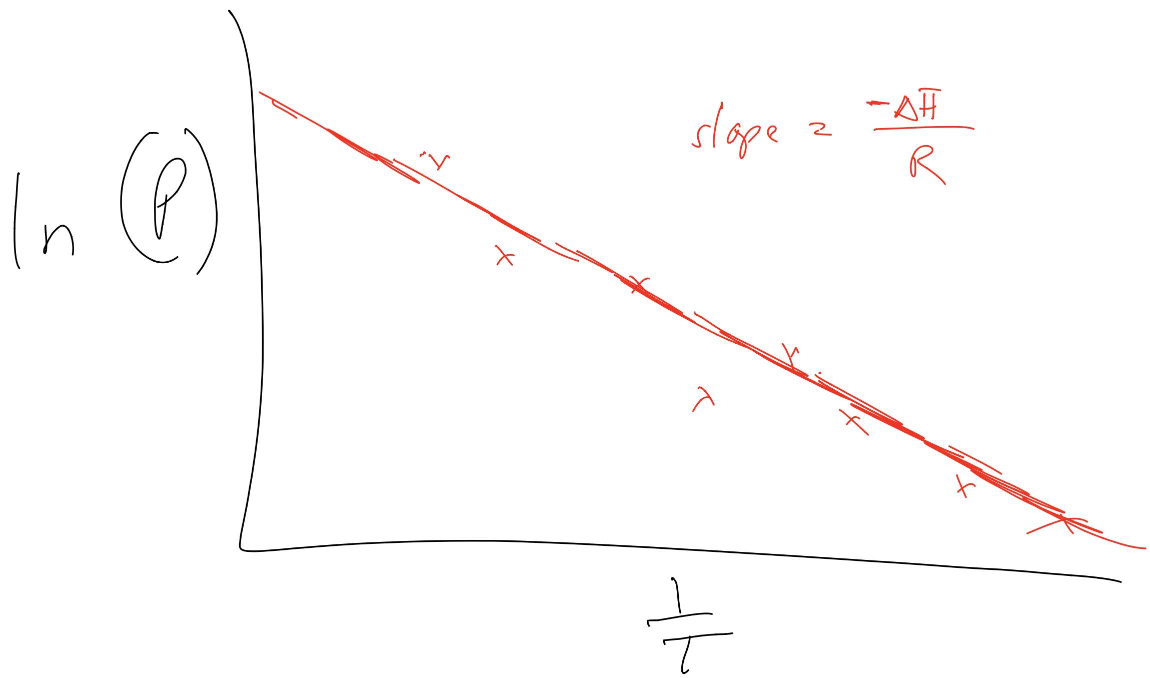
Clausius - Clapeyron Relation

function is a straight line

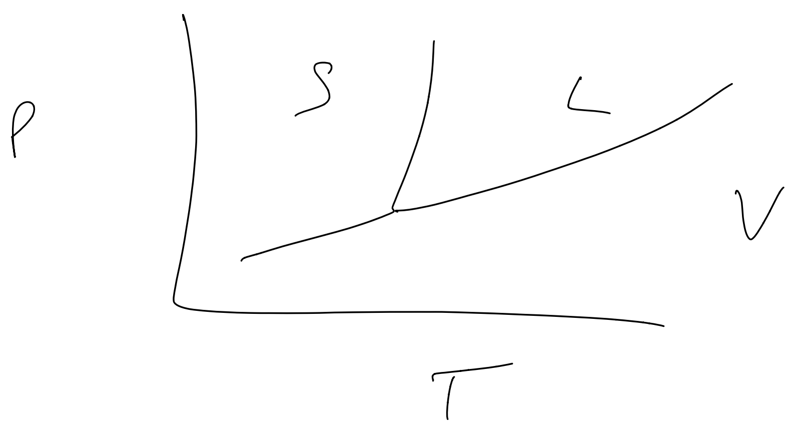
let $y = \ln(P)$

$X = \frac{1}{T}$

slope $= \frac{-\Delta H}{R}$



Degrees of Freedom

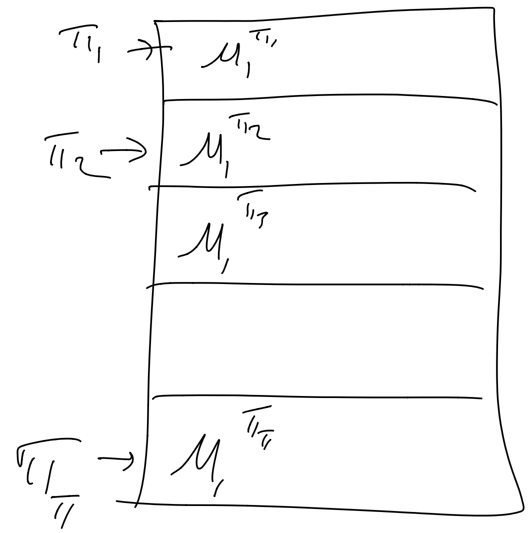


how many independent intensive variables can I control / dial in?

Consider this system.

π ← integer

π phases in equilibrium



C ← # of chemical components

← all of those guys are present in all phases

Specify T for π phases

Specify P " " "

mole fractions of species in each phase.

each phase $(C-1)$ independent mole fractions

$\pi(C-1)$ total mole fractions

Naively: $\quad D.O.F. = \pi + \pi + \pi(C-1)$

$$D.O.F. = 2\pi + \pi C - \pi$$

BUT! $\boxed{\text{Constraints}}$

\# constraints

@ Equilibrium

$$T_1 = T_2 = T_3 = \cdots = T_\pi \qquad \boxed{(\pi - 1)}$$

$$P_1 = P_2 = P_3 = \cdots = P_\pi \qquad \boxed{(\pi - 1)}$$

$$C\left\{ \mu_1^{\pi_1} = \mu_1^{\pi_2} = \mu_1^{\pi_3} = \cdots = \mu_1^{\pi_{\pi}} \right. \qquad \boxed{(\pi - 1)}$$

TOTAL Constraints $= (\pi - 1) + (\pi - 1) + C(\pi - 1)$

$$= 2\pi - 2 + C\pi - C$$

Net D.O.F. = D.O.F. − TOTAL Constraints

$= 2\pi + C\pi - \pi - 2\pi + 2$
$- C\pi + C$

$$\boxed{\text{Net D.O.F} = 2 + C - \pi}$$

Gibbs Phase "Rule"

At Equilibrium

# of Independent, Intensive variables that can be specified

Pure Substance:

1 phase @ Equil.

Net D.o.F. $= 2 + C - \pi$

$= 2 + 1 - 1$

$= \underline{2}$

2 phases @ Equil.

Net D.o.f. $= 2 + C - \pi$

$= 2 + 1 - 2$

$= 1$

3 phases @ Equil.

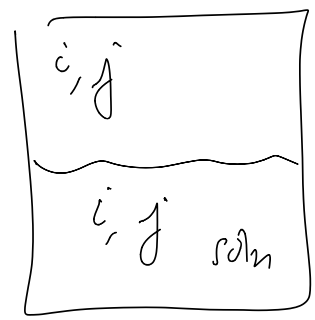
Net. D.O.F $= 2 + C - \pi$

$= 2 + 1 - 3 = 0$!

$C = 2; \quad \pi = 1$

$$D.O.F = 2 + C - \pi$$

$$= 2 + 2 - 1 = 3$$



T, P, x_i

$$D.O.F. = 2 + C - \pi$$

$$= 2 + 2 - 2$$

$$= 2$$

T, P