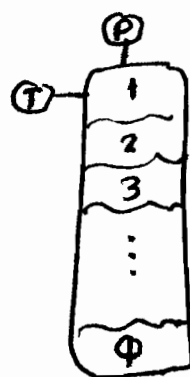


The Gibbs Phase Rule

Coexistence of Φ phases
in an n -component system.

How many intensive variables
are independent?



e.g.
vapor-
liq1-
liq2-
solid1-
solid2-
...

For each phase $n-1$ mole fractions, $T(\text{common})$,
 $P(\text{common})$

$2 + (n-1) \cdot \Phi$ variables

$$\left. \begin{array}{l} \mu_{1,1} = \mu_{1,2} = \dots = \mu_{1,\Phi} \\ \mu_{2,1} = \mu_{2,2} = \dots = \mu_{2,\Phi} \\ \vdots \\ \mu_{n,1} = \mu_{n,2} = \dots = \mu_{n,\Phi} \end{array} \right\} (\Phi-1) \cdot n \text{ equations}$$

"Degrees of Freedom" $\mathcal{F} \equiv$ independent intens. variables

$$\mathcal{F} = 2 + (n-1) \cdot \Phi - (\Phi-1) \cdot n = 2 + n\Phi - \Phi - n\Phi + n$$

$$\Rightarrow \boxed{\mathcal{F} = n - \Phi + 2} \quad \text{Gibbs Phase Rule}$$

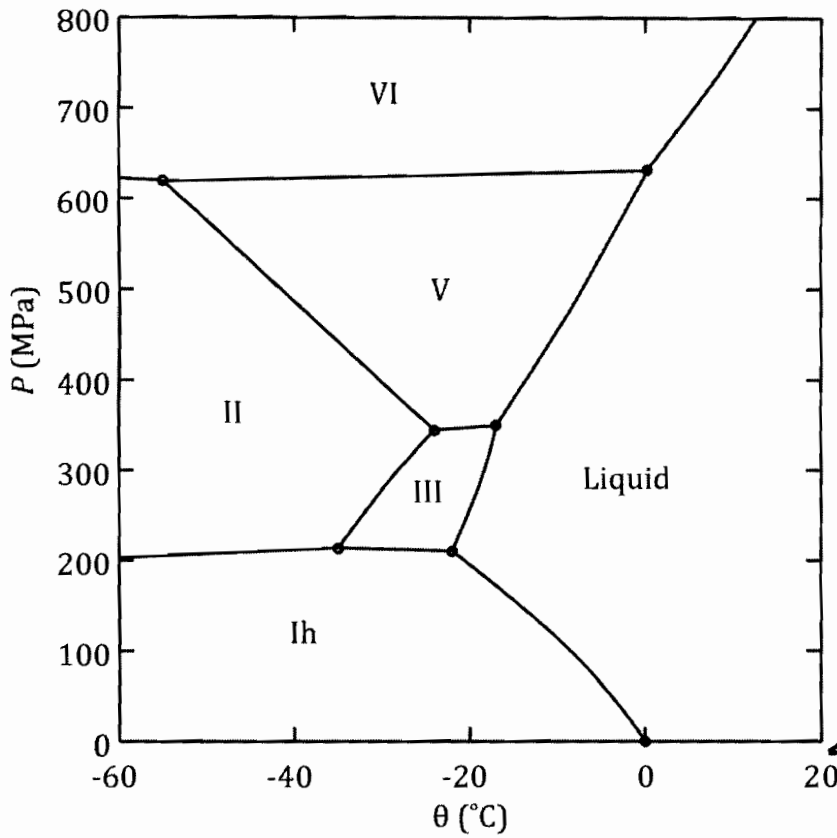
For 1-component systems ($n=1$), $\mathcal{F} = 3 - \Phi$

1 phase \rightarrow 2 degrees of freedom; T, P (2D)

2 phases \rightarrow 1 degree of freedom; T or P (1D)

3 phases \rightarrow no degrees of freedom (0D)

On phase diagrams of 1-component systems
(T versus P) lines are 2-phase coex. meeting
at triple points



E.g. H₂O has many possible solid (ice) phases - "polymorphs"
 * Also problem for pharmaceuticals

← vapor is down here, low pressure (on axis)

Engineers can "read" a phase diagram to extract thermodynamic properties, as follows

Clapeyron Equation

Along a 2-phase coexistence line, 1-comp. system:

$$\mu_I = \mu_{II} \Rightarrow d\bar{G}_I = d\bar{G}_{II} \Rightarrow -\bar{S}_I dT + \bar{V}_I dP = -\bar{S}_{II} dT + \bar{V}_{II} dP \Rightarrow$$

$$\Rightarrow \left. \frac{dP}{dT} \right|_{\text{coexistence of I \& II}} = \frac{\bar{S}_{II} - \bar{S}_I}{\bar{V}_{II} - \bar{V}_I} = \frac{\Delta \bar{S}}{\Delta \bar{V}}$$

From Euler-} $\bar{G} = \bar{u} + P\bar{v} - T\bar{s} = \bar{h} - T\bar{s} \Rightarrow$
 integrated f.e.} $\bar{s} = (\bar{h} - \bar{g}) / T$

$$\Delta \underline{S} = \underline{S}_{II} - \underline{S}_I = \frac{H_{II} - H_I - (G_{II} - G_I) \left. \frac{dP}{dT} \right|_{\text{coex.}}}{T} \Rightarrow \Delta \underline{S} = \frac{\Delta H}{T}$$

$$\therefore \left. \frac{dP}{dT} \right|_{\text{coex.}} = \frac{\Delta H}{T \Delta V} \quad \text{Clapeyron Eq. - exact}$$

no assumptions

For vapor-liquid or vapor-solid equilibria at low temperatures only, we can make two assumptions:

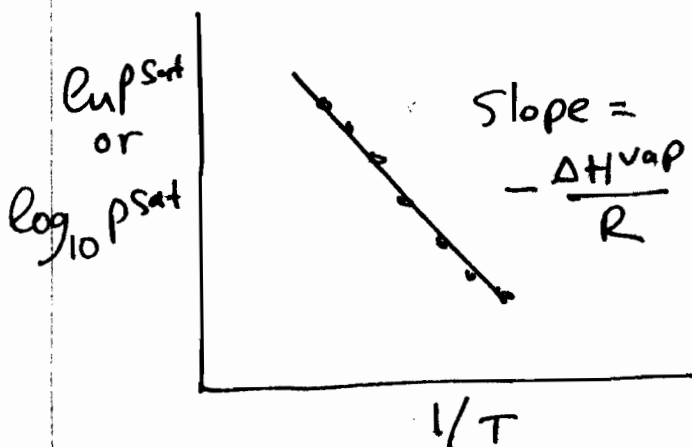
$$\underline{V}_{L \text{ or } S} \ll \underline{V}_V \Rightarrow \Delta \underline{V} = \underline{V}_V$$

and $\underline{V}_V = \frac{RT}{P^{\text{sat}}}$ (vapor ideal, its volume much greater than liq. or solid volume)

$$\text{Then } \left. \frac{dP}{dT} \right|_{\text{VLE or SLE}} = \frac{\Delta H P^{\text{sat}}}{RT^2} \Rightarrow \left. \frac{d \ln P^{\text{sat}}}{d(1/T)} = - \frac{\Delta H}{R} \right.$$

Clausius-Clapeyron Eq.
not exact

useful for interpolation,
mild extrapolations



*Cancellation of errors
gives decent fits
even near T_c !

For accurate fitting of vapor pressures:

Antoine Eq.
(Empirical)

$$\log_{10} P^{\text{sat}} = a - \frac{b}{T+c}$$