# Application of 2nd law of thermodynamics to liquid-gas phase transition

Preliminaries: * systems with variable particle numbers; * chemical potentials; * Gibbs-Duhem equation

$$U = U(S, V, \{N_i\})$$

$$\boxed{dU = TdS - pdV + \sum_i \underbrace{\left(\frac{\partial U}{\partial N_i}\right)_{S,V,N_{j\neq i}}}_{\mu_i} dN_i}$$

$\mu_i$ - chemical potential of species $i$
(- generalized force corresponding to $N_i$; $\mu_i$ - intensive quantity)

- Helmholtz free energy

$$F(T, V, \{N_i\}) = U - TS$$

$$\boxed{dF = -SdT - pdV + \sum_i \mu_i dN_i}$$

$$\Rightarrow \boxed{\mu_i = \left(\frac{\partial F}{\partial N_i}\right)_{T,V,N_{j\neq i}}}$$

- general property when taking derivs over "untouched" variables under Legendre transform

- Gibbs free energy $\quad G(T, p, \{N_i\}) = U - TS + pV$

$$\boxed{dG = -SdT + Vdp + \sum_i \mu_i dN_i}$$

$$\boxed{\mu_i = \left(\frac{\partial G}{\partial N_i}\right)_{T,p,N_{j\neq i}}}$$

- <u>Gibbs – Duhem relation</u>

$\mathcal{U}(S, V, \{N_i\})$ – extensive function of extensive variables $S, V, \{N_i\}$

$$\mathcal{U}(\lambda S, \lambda V, \{\lambda N_i\}) = \lambda \mathcal{U}(S, V, \{N_i\})$$

Differentiate wrt $\lambda$ and set $\lambda = 1$ $\Rightarrow$ Euler's theorem on homogeneous fnctns :

$$\underbrace{\left(\frac{\partial \mathcal{U}}{\partial S}\right)_{V, N_i}}_{T} S + \underbrace{\left(\frac{\partial \mathcal{U}}{\partial V}\right)_{S, N_i}}_{-p} V + \sum_i \underbrace{\left(\frac{\partial \mathcal{U}}{\partial N_i}\right)_{S, V, N_{j \neq i}}}_{\mu_i} N_i = \mathcal{U}$$

$$TS - pV + \sum_i \mu_i N_i = U$$

$$\Rightarrow \boxed{G = U - TS + pV = \sum_i \mu_i N_i}$$

In differential form :

$$dG = -SdT + Vdp + \sum_i \mu_i dN_i \overset{!}{=} \sum_i (\mu_i dN_i + d\mu_i N_i)$$

$$\boxed{SdT - Vdp + \sum_i N_i d\mu_i = 0}$$ – shows that intensive variables $T, p, \{\mu_i\}$ are not all indep.

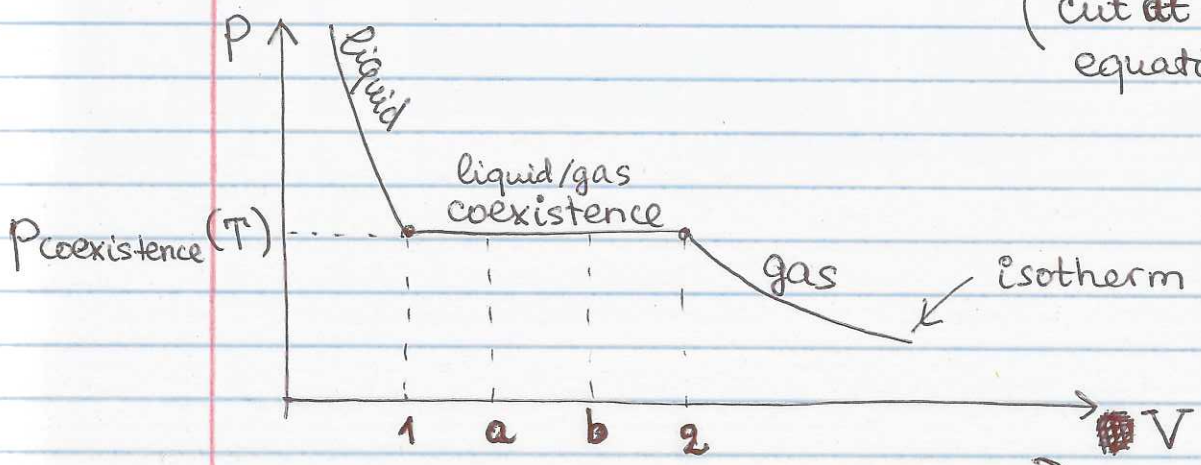
$c$ – component system $(i = 1 \ldots c)$ has $c + 2 - 1 = c + 1$ indep. variables.

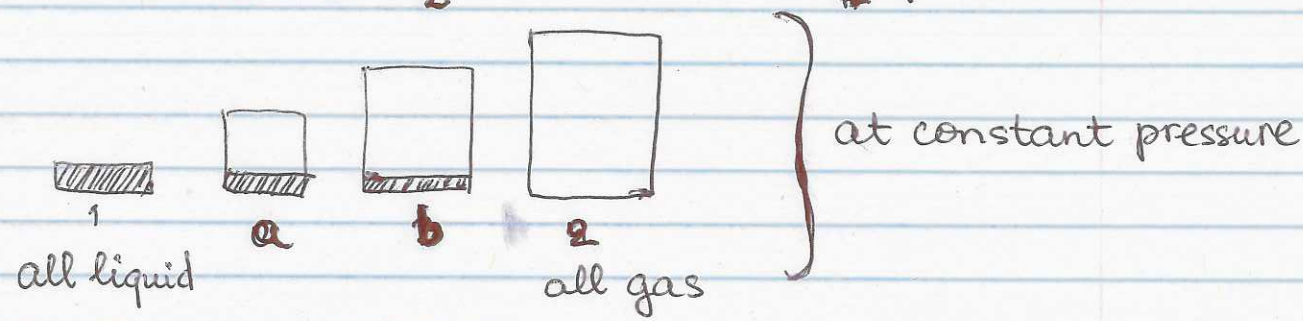
For one – component system

$G = \mu N$, $\mu = \frac{G}{N}$ – chemical potential is Gibbs free energy per particle

## Liquid - gas transition

(cut at fixed T through equation of state



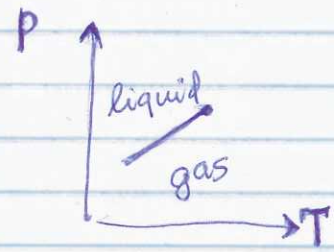

Experimental fact: along the coexistence segment, the liquid remains in the same state as @1 and the gas remains in the same state as @2, only the proportions change.

p and T remain constant - control parameters

$$N_{total} = N_1 + N_2 = N = \text{const}$$

$$G = \mu_1 N_1 + \mu_2 N_2 = \mu_1 N_1 + \mu_2 (N - N_1)$$ - must be minimum $\Rightarrow$ $$\left(\frac{\partial G}{\partial N_1}\right)_{T,p,N} = \mu_1 - \mu_2 = 0$$

$$\boxed{\mu_1 = \mu_2}$$



Using the 2nd law of thermodynamics, can relate the T-dependence of $p_{coexist}(T)$ to measurable quantities like latent heat and change in volume per particle between gas and liquid

Phase 1 (liquid @ 1) : $S_1 dT - V_1 dp + N_1 d\mu_1 = 0$

$$d\mu_1 = \frac{1}{N_1}\left(-S_1 dT + V_1 dp\right) =$$

$$= -\underbrace{s_1}_{\text{entropy per particle}} dT + \underbrace{v_1}_{\text{volume per particle}} dp$$

Phase 2 (gas @ 2) : $d\mu_2 = -s_2 dT + v_2 dp$

Coexistence condition: $d\mu_1 = d\mu_2$

$$-s_1 dT + v_1 dp = -s_2 dT + v_2 dp$$

$$\boxed{\frac{dp}{dT} = \frac{s_2 - s_1}{v_2 - v_1}} = \frac{\ell}{T(v_2 - v_1)} \quad \text{— Clapeyron equation}$$

$p_{coexistence}(T)$

$$\ell = T(s_2 - s_1) \text{ — latent heat per particle}$$

Approximation : $v_{gas} = v_2 = \frac{V}{N} = \frac{k_B T}{p}$ ,

nearly ideal

$$v_1 = v_{liquid} \approx 0$$

$$\Rightarrow \frac{dp_{coex.}}{dT} = \frac{\ell p}{k_B T^2} \qquad \frac{dp}{p} = \frac{\ell}{k_B}\frac{dT}{T^2}$$

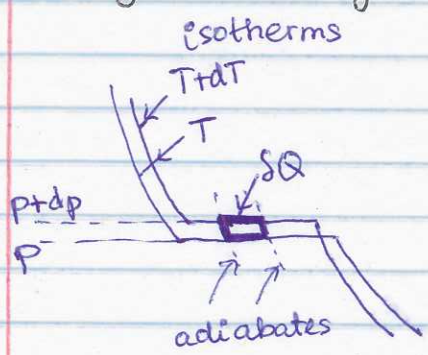
$$\ln\frac{p}{p_0} = \frac{\ell}{k_B}\left(-\frac{1}{T} + \frac{1}{T_0}\right)$$

← Clausius – Clapeyron equation

$$\boxed{p = p_0 \exp\left[-\frac{\ell}{k_B}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right]}$$

Remark: we used thermodynamic potentials (Gibbs potential) to obtain the Clapeyron equation.
The ability to use such potentials is provided by the existence of entropy as state function and ultimately by the 2nd law of thermodynamics.
If the Clapeyron equation were not true, one could trace back our "construction" of thermodynamics and conclude that $\exists$ engine violating second law
(operating here near liquid-gas interface)

- this is often how one "derives" the Clapeyron equation by building a Carnot engine out of liquid-gas system.




$$\delta Q = \ell \cdot dN$$

$$\delta W = dp \cdot dV = dp \cdot dN \cdot (v_2 - v_1)$$

$$\frac{\delta W}{\delta Q} = \frac{(v_2 - v_1)\, dp}{\ell} = \frac{dT}{T}$$

Carnot!