(8) General equilibrium conditions

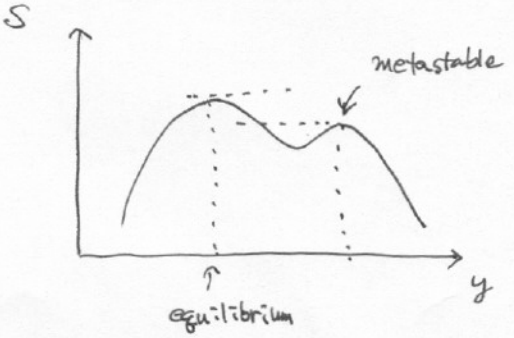
① General equilibrium condition

- isolated system

entropy S

equilibrium $\Rightarrow$ S = maximum

※ Note : metastable



$P(y)$: probability of finding the system with a parameter $y \in [y, y+dy]$

$$P(y) \propto \Omega(y) = e^{S(y)/k}$$

- system ⊕ a reservoir with constant temperature (T_0)

$$A \oplus A' \equiv A^{(0)}$$

$$\Delta S^{(0)} \geq 0$$

$$\Delta S^{(0)} = \Delta S + \Delta S' = \Delta S - \frac{Q}{T_0} = \frac{T_0 \Delta S - (\Delta \bar{E} + W)}{T_0}$$

Remember $F = \bar{E} - TS$, Helmholtz free energy

$$\Rightarrow F_0 \equiv \bar{E} - T_0 S$$

$$\Delta S^{(0)} = \frac{-\Delta F_0 - W}{T_0} \geq 0 \quad \rightarrow (-\Delta F_0) \sim \text{the maximum work by } A.$$

if external parameters are fixed so that $W = 0$,

equilibrium $\Rightarrow$ F_0 = minimum

$$P(y) \propto e^{-\frac{S_0^{(0)}(y)}{k}} \propto e^{-\beta_0 F_0(y)} \qquad \beta_0 = 1/kT_0$$

$$\left(\because S_0^{(0)}(y) = S^{(0)}(y') - \frac{\Delta F_0}{T_0} = S^{(0)}(y') - \frac{F_0(y) - F_0(y')}{T_0} \right)$$

- System ⊕ a reservoir with (constant temperature (T_0) / constant pressure (p_0)

$A \oplus A' = A^{(0)}$

$$\Delta S' = -\frac{Q}{T_0} = -\frac{1}{T_0}\left(\Delta \bar{E} + p_0 \Delta V + \underbrace{W^*}_{\text{other work}}\right)$$

eg. electronic or magnetic work

$$\Rightarrow \Delta S^{(0)} = \Delta S + \Delta S'$$

$$= \frac{T_0 \Delta S - \Delta \bar{E} - p_0 \Delta V - W^*}{T_0}$$

$$= \frac{-\Delta G_0 - W^*}{T_0} \geq 0$$

$$G_0 \equiv \Delta \bar{E} - T_0 S + p_0 V$$

(remember $G = E - TS + pV$, Gibbs free energy)

$(-\Delta G_0)$ ~ the maximum work by A.

$-\Delta G_0 = W^*$ ~ quasi static process ($\because \Delta S^{(0)} = 0$ ↔ equilibrium)

if $W^* = 0$, $\Delta G \leq 0$

⇒ equilibrium ⇒ G_0 = minimum.

$$p(y) \propto e^{-\beta_0 G_0}$$

② Stability

G_0 = minimum , variables: T and V

$$\Rightarrow \text{①} \quad \left(\frac{\partial^2 G_0}{\partial T^2}\right)_V \geq 0 \quad \Rightarrow \quad \left(\frac{\partial \bar{E}}{\partial T}\right)_V \geq 0 \quad \Leftrightarrow \quad \boxed{C_V \geq 0}$$

$$\left(\frac{\partial G_0}{\partial T}\right)_V = 0 \quad \Rightarrow \quad T = T_0$$

(use $\left(\frac{\partial G_0}{\partial T}\right)_V = \left(\frac{\partial \bar{E}}{\partial T}\right)_V - T_0\left(\frac{\partial S}{\partial T}\right)_V$

$T dS = d\bar{E} + p dV \quad \Rightarrow \quad T\left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial \bar{E}}{\partial T}\right)_V$)

$$\text{②} \quad \left(\frac{\partial^2 G_0}{\partial V^2}\right)_T \geq 0 \quad \Rightarrow \quad -\left(\frac{\partial \bar{p}}{\partial V}\right)_T \geq 0 \quad \Leftrightarrow \quad \kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial \bar{p}}\right)_T$$

isothermal compressibility

$$\left(\frac{\partial G_0}{\partial V}\right)_T = 0 \quad \Rightarrow \quad \bar{p} = p_0$$

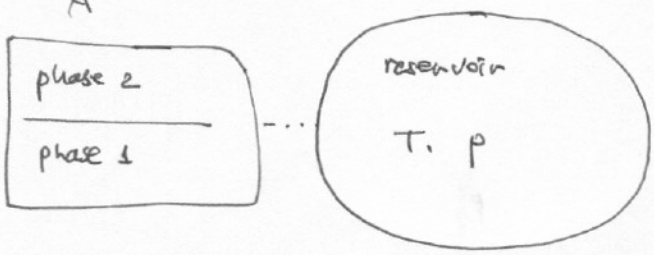
$\boxed{\kappa \geq 0}$

(use $\left(\frac{\partial G_0}{\partial V}\right)_T = \left(\frac{\partial \bar{E}}{\partial V}\right)_T - T_0\left(\frac{\partial S}{\partial V}\right)_T + p_0$

$T\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial \bar{E}}{\partial V}\right)_T + \bar{p}$)

⊙ equilibrium between phases : two equivalent ways

① A $\quad$ A′



$G = E - TS + pV$

~ minimum at equilibrium.

ν_i : # of moles of phase i

g_i : Gibbs free energy per moles of phase i

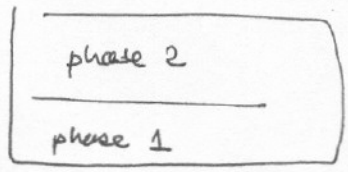
$$\begin{cases} G = \nu_1 g_1 + \nu_2 g_2 \\ \nu = \nu_1 + \nu_2 \end{cases}$$

$dG = 0$

$$\Leftrightarrow \quad g_1 d\nu_1 + g_2 d\nu_2 = (g_1 - g_2) d\nu_1 = 0$$

$$\boxed{g_1 = g_2}$$

② A



A ~ isolated

$$\Rightarrow \begin{cases} E_1 + E_2 = E \\ V_1 + V_2 = V \\ N_1 + N_2 = N \end{cases} \text{ fixed}$$

S ~ maximum at equilibrium

$dS = dS_1 + dS_2 = 0.$

$$\begin{cases} S_1 = S_1(E_1, V_1, N_1) \\ S_2 = S_2(E_2, V_2, N_2) \end{cases}$$

~~T_1 E_1~~

$$dS_i = \left(\frac{\partial S_i}{\partial E_i}\right)_{V_i, N_i} dE_i + \left(\frac{\partial S_i}{\partial V_i}\right)_{E_i, N_i} dV_i + \left(\frac{\partial S_i}{\partial N_i}\right)_{E_i, V_i} dN_i$$

Compare it with $TdS = dE + pdV$

$$\Rightarrow dS_i = \frac{1}{T_i} dE_i + \frac{P_i}{T_i} dV_i - \frac{\mu_i}{T_i} dN_i$$

$$\mu_1 \equiv -T_1 \left(\frac{\partial S_1}{\partial N_1}\right)_{E_1, V_1}.$$

$$\Rightarrow dS = \frac{dE_1}{T_1} + \frac{P_1}{T_1} dV_1 - \frac{\mu_1}{T_1} dN_1 + \frac{dE_2}{T_2} + \frac{P_2}{T_2} dV_2 - \frac{\mu_2}{T_2} dN_2 = 0$$

$$\Leftrightarrow \quad \boxed{T_1 = T_2 \,,\; P_1 = P_2 \,,\; \mu_1 = \mu_2}$$

$\boxed{g_1 = g_2} \equiv \boxed{\mu_1 = \mu_2}$

↑ see the next ~~page~~ page.

※ chemical potential μ.

$$\boxed{dE = TdS - pdV + \sum_{i=1}^{m} \mu_i dN_i}$$ ~ works as a definition

for a system with energy E, volume V, and

m different kinds of molecules

$$\mu_j = \left(\frac{\partial E}{\partial N_j}\right)_{S.V.N} \leftarrow \{N_1 \cdots, N_{j-1}, N_{j+1}, \cdots, N_m\}$$

or $$\mu_j = -T\left(\frac{\partial S}{\partial N_j}\right)_{E.V.N} \qquad S = S(E, V, N_1, N_2, \cdots, N_m)$$

or $$\mu_j = \left(\frac{\partial F}{\partial N_j}\right)_{T.V.N} \qquad F = E - TS$$

or $$\mu_j = \left(\frac{\partial G}{\partial N_j}\right)_{T.p.N} \qquad G = E - TS + pV$$

Remember the grandcanonical ensemble

$$P_r \propto e^{-\beta(E_r - \mu N_r)}$$

$$-\beta\mu = \alpha = \frac{\partial \ln \Omega'}{\partial N'}$$

$$\Leftrightarrow \quad \mu = -T \frac{\partial S'}{\partial N'}$$

⊙ Chemical equilibrium

(eg.) $2H_2 + O_2 \longrightarrow 2H_2O$

$-2H_2 - O_2 + 2H_2O = 0$ → $m = 3$

$\{B_i\} = \{H_2, O_2, H_2O\}$; $i = 1, 2, 3$

$\Rightarrow \sum_{i=1}^{m} b_i B_i = 0$

$b_1 = -2,\ b_2 = -1,\ b_3 = 2$

$S = S(E, V, N_1, \cdots N_m)$

if $E, V \longrightarrow$ constant

$\Rightarrow dS = \sum_{i=1}^{m} \mu_i dN_i = 0$ at equilibrium.

$dN_i \propto b_i$

$\Rightarrow \boxed{\sum_{i=1}^{m} \mu_i b_i = 0}$

Example : ideal gases

m different types of molecules (which can be treated as ideal gases)
in volume V at temperature T.

$\Rightarrow F = F(T, V, N_1, \cdots, N_m)$

at equilibrium, $\delta F = 0 \Rightarrow \delta F = \sum_{i=1}^{m} b_i \mu_i = 0$

$Z = \prod_{i=1}^{m} Z_i$,

$Z_i = \dfrac{\xi_i^{N_i}}{N_i!}$ ξ_i ~ single particle partition function of ith molecule

$$F = -kT \ln Z$$

$$= -kT \sum_i N_i \left(\ln \xi_i - \ln N_i + 1 \right)$$

$$\mu_j = \left(\frac{\partial F}{\partial N_j} \right)_{T,V,N} = -kT \ln \frac{\xi_j}{N_j}$$

$$\Delta F = \sum b_i \mu_i$$

$$= \sum b_i (-kT) \left(\ln \xi_i - \ln N_i \right) = 0 .$$

$$\Delta F_0 \equiv -kT \sum b_i \ln \xi_i$$

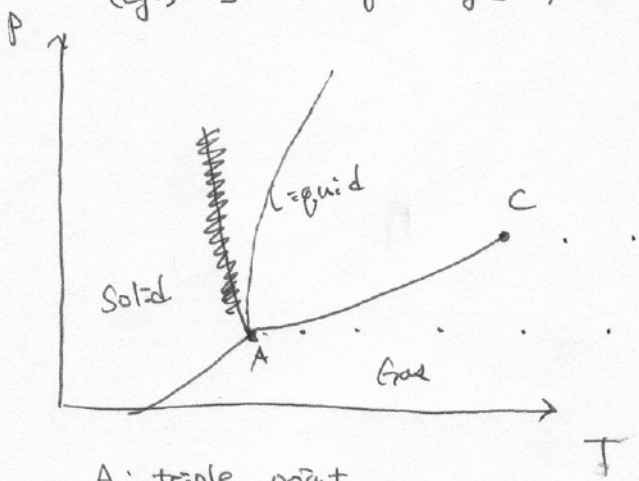
$$\Rightarrow \quad -\frac{\Delta F_0}{kT} = \ln N_1^{b_1} N_2^{b_2} \cdots N_m^{b_m}$$

$$\Rightarrow \quad N_1^{b_1} N_2^{b_2} \cdots N_m^{b_m} = e^{-\frac{\Delta F_0}{kT}}$$

~ law of mass action

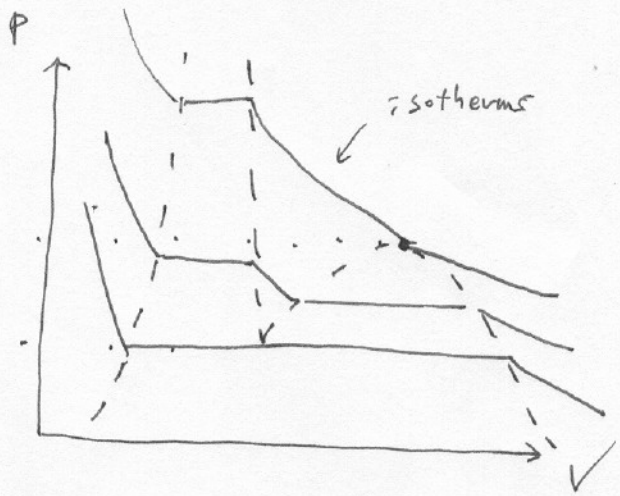
⊙ phase transition

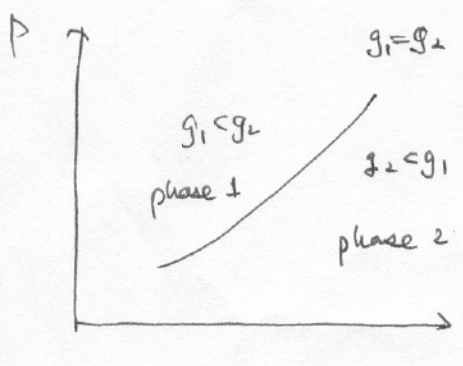
(eg.) solid, liquid, gas phases



A : triple point

C : critical point





$$dg = d(\epsilon - Ts + pV) = -sdT + vdp$$

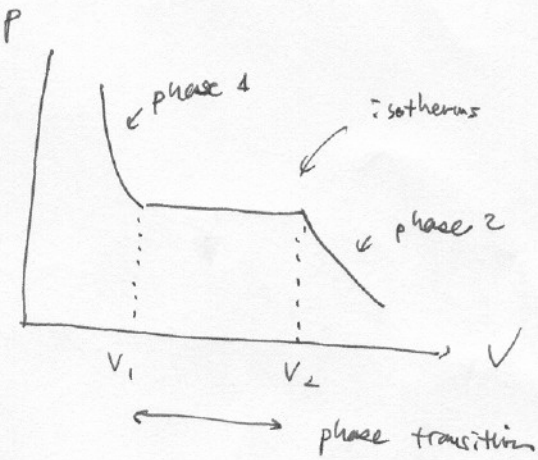
(use $d\epsilon = -Tds + pdV$)

$dg_1 = dg_2$ at equilibrium.

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

$$\Rightarrow \frac{dp}{dT} = \frac{s_2 - s_1}{v_2 - v_1}$$ Clausius-Clapeyron eq.

$$\Delta s = s_2 - s_1 \equiv \frac{L_{12}}{T}$$, L_{12} ~ latent heat



$$V_{tot} = \xi V_2 + (1 - \xi) V_1$$

$\xi : 0 \rightarrow 1$

※ critical point :

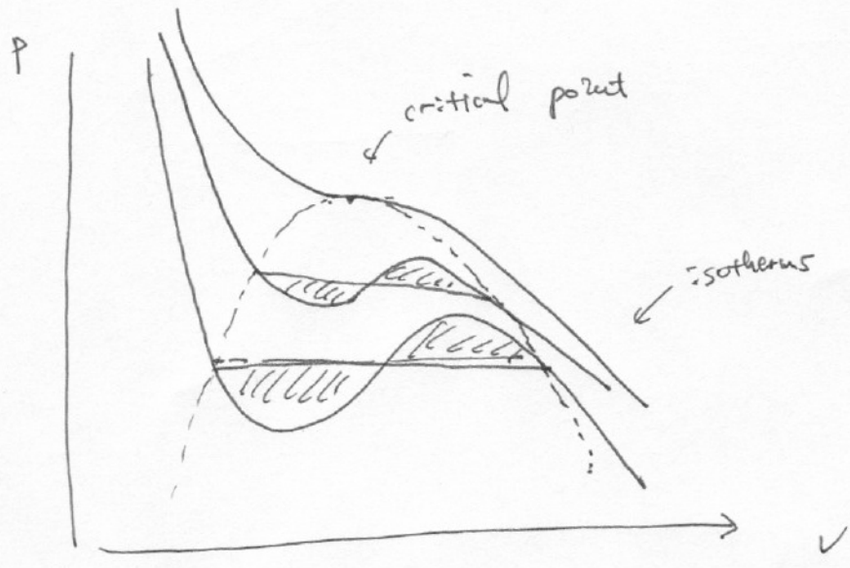
The volume change ΔV between liquid and gas ~~phases~~ is zero.

Above the critical temperature there is no ~~distinction~~ distinction between gas and liquid.

— (Ex) phase transition between gas and liquid

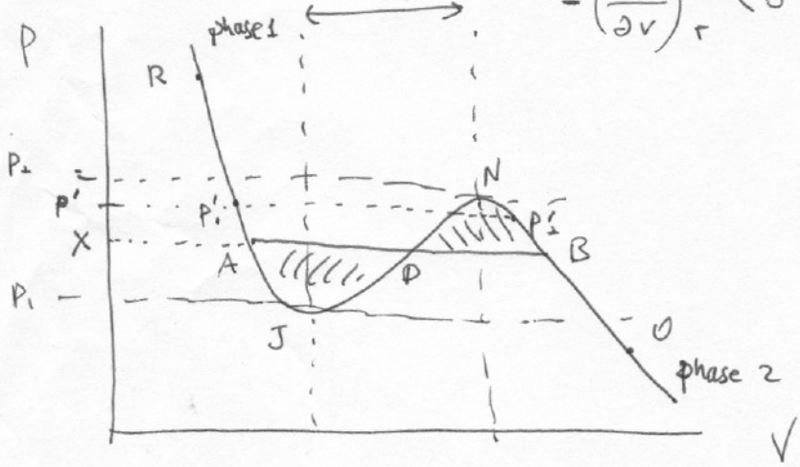
van der Waals eq.

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT.$$



stability condition $\left(\frac{d^2G}{dV^2}\right)_T = -\left(\frac{\partial \bar{P}}{\partial V}\right)_T \geq 0$

$-\left(\frac{\partial \bar{P}}{\partial V}\right)_T < 0$ → unstable



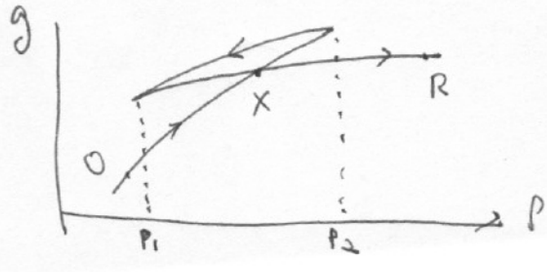
at $p = p'$, which phase is stable ?

$$dg = d(\epsilon - Ts + pV) = -s\,dT + v\,dp \quad \Rightarrow \quad g - g_0 = \int_{p_0}^{p} v\,dp$$

at constant T.

$X: g_A = g_B$

$$\Rightarrow \int_{AJDNB} v\,dp = 0$$



$\Rightarrow$ O → X → R (phase 1) / (phase 2)