

$$\nu_1 A_1 + \nu_2 A_2 + \dots + \nu_n A_n \rightleftharpoons \nu_{n+1} A_{n+1} + \dots + \nu_r A_r$$

$$\downarrow$$
 stoichiometric coefficients.

$$0 \rightleftharpoons \sum_j \nu_j A_j$$



$$\rightarrow 0 \rightleftharpoons -4H_2 - CO_2 + CH_4 + 2H_2O$$

then. $\frac{dN_j}{\nu_j} = d\tilde{N} \rightarrow$ Proportionality factor.

$$\Rightarrow dG = \sum_j \mu_j \cdot dN_j = d\tilde{N} \sum_j \nu_j \mu_j = 0$$

equilibrium condition.

$$* \cdot dG = 0$$

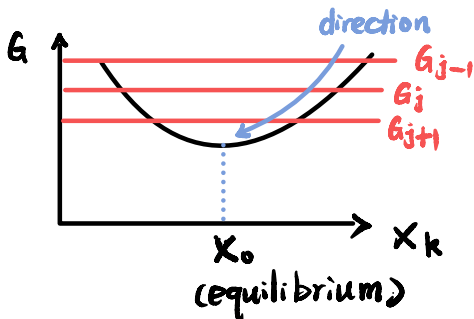
$$\Rightarrow \sum_j \nu_j \mu_j = 0$$

\Rightarrow For evaluation of reaction:

should respect thermo. potential min. principle.

$\int dG = \Delta G_{total}$, if $\Delta G_{total} < 0 \Rightarrow$ reaction proceeds.

G. minimum principle.



$$G_j - G_{j-1} < 0$$

$$G_{j+1} - G_j < 0$$

⇒ How to get ΔG_j (in general)

ΔG_j° → standard formation Gibbs Energy of a species.

↳ 1 bar, 298 K

ΔG_j may not be at the standard condition. → G

↑?
 ΔG_j°

$$\left(\frac{\partial G}{\partial P}\right)_T = V$$

$$\frac{\partial Y_\psi}{\partial P_j} = -X_j \quad \begin{matrix} \text{↖} \\ \text{↘} \end{matrix}$$

↘ V
↖ (-P)

$$dG = V dp \Rightarrow \int dG = \int_{P_0}^{P_f} V dp$$

if assuming ideal gas. $PV = NRT \rightarrow V = \frac{NRT}{P}$

$$\rightarrow \int dG = \int_{P_0}^{P_f} V dp = \int \frac{NRT}{P} dp = NRT \ln \frac{P_f}{P_0}$$

Obj. 9. Maxwell Equations (state - function Nature)

$$Y = Y(x_1, x_2) \Rightarrow \begin{cases} \left[\frac{\partial}{\partial x_2} \left(\frac{\partial Y}{\partial x_1} \right) \right] \\ \left[\frac{\partial}{\partial x_1} \left(\frac{\partial Y}{\partial x_2} \right) \right] \end{cases} \parallel$$

if Y is state function.

e.g., $U = U(S, V, N) \rightarrow$ state function.

$$\rightarrow \left(\frac{\partial}{\partial S} \left(\frac{\partial U}{\partial V} \right)_{S,N} \right)_{V,N} = \left(\frac{\partial}{\partial V} \left(\frac{\partial U}{\partial S} \right)_{V,N} \right)_{S,N}$$

$$\Rightarrow -\left(\frac{\partial P}{\partial S} \right)_{V,N} = \left(\frac{\partial T}{\partial V} \right)_{S,N}$$

$$U \quad dU = Tds - PdV + \mu dN$$

$$1 \Rightarrow S, V : \dots$$

$$2 \Rightarrow S, N : \left(\frac{\partial}{\partial N} \left(\frac{\partial U}{\partial S} \right)_{N,V} \right)_{S,V} = \left(\frac{\partial}{\partial S} \left(\frac{\partial U}{\partial N} \right)_{S,V} \right)_{N,V}$$

$$\Rightarrow \left(\frac{\partial T}{\partial N} \right)_{S,V} = \left(\frac{\partial \mu}{\partial S} \right)_{N,V}$$

$$3 \Rightarrow V, N : \left(\frac{\partial}{\partial V} \left(\frac{\partial U}{\partial N} \right)_{V,S} \right)_{N,S} = \left(\frac{\partial}{\partial N} \left(\frac{\partial U}{\partial V} \right)_{N,S} \right)_{V,S}$$

$$\left(\frac{\partial \mu}{\partial V} \right)_{N,S} = - \left(\frac{\partial P}{\partial N} \right)_{V,S}$$

$$U[T] \equiv F \quad dF = -s dT - P dV + \mu dN.$$

$$1 \Rightarrow T, V ; \quad 2 \Rightarrow T, N ; \quad 3 \Rightarrow V, N.$$

$$U[P] \equiv H \quad dH = T dS + v dP + \mu dN$$

$$1 \Rightarrow S, P ; \quad 2 \Rightarrow S, N ; \quad 3 \Rightarrow P, N$$

$$U[T, P] \equiv G \quad dG = -s dT + v dP + \mu dN$$

$$1 \Rightarrow T, P ; \quad 2 \Rightarrow T, N ; \quad 3 \Rightarrow P, N$$

$$\text{eg. } U[\mu] \quad dU[\mu] = T dS - P dV - N d\mu.$$

$$dY_T = - \sum_0^n X_k dP_k + \sum_{n+1}^t P_k dX_k$$

1) S, V ; 2) S, μ ; 3) V, μ .

$U[S, T], U[S, P]$
 \updownarrow \updownarrow

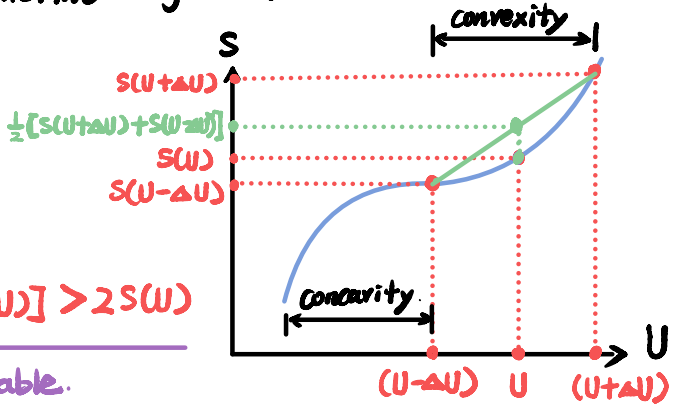
Obj. 10. Thermodynamic Stability.

1) Stability of thermo. sys. (Global, vs. Local)

2) stability conditions. (for different thermo. potentials)

1. Stability of thermo. sys. (Global, vs. Local)

$S = S(U, V, N)$	$S = S(U, \mu)$
↓	↓
$S(U + \Delta U)$	$S(U - \Delta U)$



$$[S(U + \Delta U) + S(U - \Delta U)] > 2S(U)$$

⇒ original state is unstable.

⇒ stability conditions.

$$[S(U + \Delta U) + S(U - \Delta U)] \leq 2S(U) \quad * 1 \Rightarrow$$

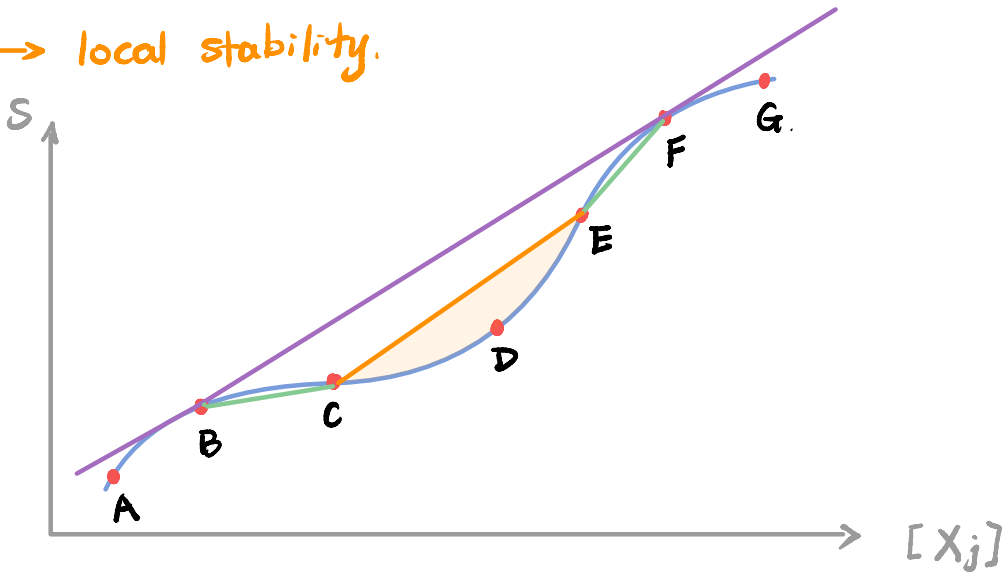
$$\frac{\overbrace{S(U + \Delta U) - S(U)}^{\Delta S_1} - \overbrace{[S(U) - S(U - \Delta U)]}^{\Delta S_2}}{\Delta U^2} \leq 0$$

$$\Rightarrow \lim_{\Delta U \rightarrow 0} \frac{\Delta \Delta S}{\Delta U^2} = \frac{\partial^2 S}{\partial U^2} \leq 0 \quad * 2 \Rightarrow$$

1) is more strict
for defining stability
(v.s. 2))

1) → Global stability.

2) → local stability.



BCDEF: Globally unstable.

BC & EF: Locally stable

CDE: Both globally & locally unstable.