$S, V, N_1, \cdots N_r$, thus, they are also functions of $S, V, N_1 \cdots$

$$\begin{cases} T = T(S, V, N_1 \cdots) \\ P = P(S, V, N_1 \cdots) \\ \mu = \mu(S, V, N_1 \cdots) \end{cases}$$

$(P \cdot V = N \cdot R \cdot T)$

$\left(\frac{P}{T} = \frac{NR}{V}\right)$

E.O.S.: express intensive parameters as functions of extensive parameters.

*. Fundamental equation:

$U = U(S, V, N)$ homogeneous 1^{st}-order.

$\Rightarrow$ EOS homogeneous 0^{th}-order.

$$U(\lambda S, \lambda V, \lambda N) = \lambda U(S, V, N)$$

$$* \; T(\lambda S, \lambda V, \lambda N) = T(S, V, N)$$

*. more general form.

$V, N_1, N_2 \cdots \leftarrow X_1, X_2, X_3$

$\Rightarrow U = U(S, X_1, X_2 \cdots)$

$$\left(\frac{\partial U}{\partial S}\right)_{X_1, X_2 \cdots} = T = T(S, X_1, X_2 \cdots)$$

$$\left(\frac{\partial U}{\partial X_j}\right)_{S, \cdots X_k \cdots}^{k \neq j} = P_j(S, \cdots \overset{\cancel{k \neq j}}{X_k} \cdots)$$

* This condition should be removed for $P_j(S \cdots X_k \cdots)$

$$dU = TdS + \sum_j P_j \, dX_j$$

---

*. if sys is a single component.

$$U = U(S, V, N)$$

write in "per mole" form:

$$s = \frac{S}{N} \qquad v = \frac{V}{N}$$

$$u(s, v) = \frac{1}{N} U(S, V, N) \Rightarrow du(s, v) = \underbrace{\left(\frac{\partial u}{\partial s}\right)_v}_{T} ds + \underbrace{\left(\frac{\partial u}{\partial v}\right)_s}_{-P} dv$$

$$du(s, v) = Tds - Pdv$$

---

*Example. Derive the EOS for the sys:

$$U = \left(\frac{v_0 \theta}{R^2}\right) \frac{S^3}{NV}$$ and prove the sys is 0^{th} order.

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,N} = \underline{3\left(\frac{v_0 \theta}{R^2}\right) \frac{S^2}{NV}}$$

$$P = \left(\frac{\partial U}{\partial V}\right)_{S,N} = -\left(\frac{v_0 \theta}{R^2}\right) \frac{S^3}{NV^2}$$

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V} = -\left(\frac{v_0 \theta}{R^2}\right) \frac{S^3}{N^2 V}$$

$$T(\lambda S, \lambda V, \lambda N) = T(S, V, N) \checkmark$$

$$3\left(\frac{v_0 \theta}{R^2}\right) \frac{(\lambda S)^2}{(\cancel{\lambda} V)(\cancel{\lambda} N)} = 3\left(\frac{v_0 \theta}{R^2}\right) \frac{S^2}{VN}$$

$\Rightarrow$ 0^{th} order.

3. Entropic Intensive Parameter.

$$S = S(U, X_1, X_2 \cdots X_r)$$

$$dU = \underbrace{\left(\frac{\partial U}{\partial S}\right)_{X_j}}_{T} dS + \sum_j \underbrace{P_j}_{\cdots} dX_j \qquad P_j \rightarrow \left(\frac{\partial U}{\partial X_j}\right)$$

$$\left(\frac{\partial U}{\partial X_j}\right) \updownarrow ? \quad \left(\frac{\partial S}{\partial X_j}\right) \Downarrow ?$$

$$dS = \underbrace{\left(\frac{\partial S}{\partial U}\right)_{X_j}}_{\frac{1}{T}} dU + \sum_j \underbrace{F_j}_{?} dX_j \qquad F_j \rightarrow \left(\frac{\partial S}{\partial X_j}\right)$$

cyclic rule : "S", "U", "X_j"

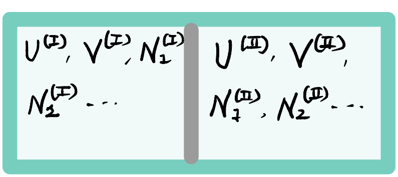
$$\left(\frac{\partial S}{\partial X_j}\right) \cdot \underbrace{\left(\frac{\partial X_j}{\partial U}\right)}_{\frac{1}{P_j}\,=\,\left\{\frac{1}{\left(\frac{\partial U}{\partial X_j}\right)=P_j}\right.} \underbrace{\left(\frac{\partial U}{\partial S}\right)}_{T} = -1$$

$$\Rightarrow \boxed{\left(\frac{\partial S}{\partial X_j}\right) = -\frac{P_j}{T} = F_j}$$

---

4. Conditions of equilibrium.

4-1. Thermal Equilibrium.



→ isolated.

heat flow.

wall : rigid, diathermal.

& No matter flow

* $\rightarrow$ $dS=0$ (maximize S)

$$S = S^{(I)}(U^{(I)}, V^{(I)}, N_1^{(I)} \cdots) + S^{(II)}(U^{(II)}, V^{(II)}, N_1^{(II)} \cdots)$$

$\Rightarrow dS=0$

$$\hookrightarrow = \underline{\left(\frac{\partial S^{I}}{\partial U^{I}}\right)_{V^{I}, N_1^{I} \cdots}} dU^{I} + \left(\frac{\partial S^{II}}{\partial U^{II}}\right)_{V^{II}, N_1^{II} \cdots} dU^{II}$$

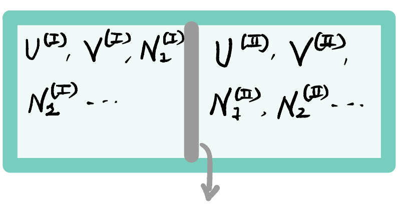
$$= \frac{1}{T^{I}} \underline{dU^{I}} + \frac{1}{T^{II}} \underline{dU^{II}}$$

$dU^{I} + dU^{II} = 0 \Rightarrow dU^{I} = -dU^{II}$ (1^{st} law)

$$\Rightarrow dS = \left(\frac{1}{T^{I}} - \frac{1}{T^{II}}\right) dU^{I} = 0$$

$\Rightarrow \frac{1}{T^{I}} = \frac{1}{T^{II}} \Leftrightarrow$ thermal Equilibrium condition.

4-2. Mechanical Equilibrium



Movable, No matter flow.
diathermal

$dS=0$

$$dS = \left(\frac{\partial S^{I}}{\partial U^{I}}\right)_{V^{I}, N_1^{I} \cdots} dU^{I} + \underline{\left(\frac{\partial S^{I}}{\partial V^{I}}\right)_{U^{I}, N_1^{I} \cdots} dV^{I}}$$

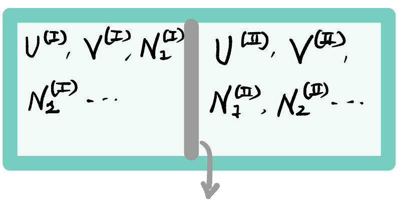
$$\left(\frac{\partial S^{II}}{\partial U^{II}}\right)_{V^{II}, N_1^{II} \cdots} dU^{II} + \underline{\left(\frac{\partial S^{II}}{\partial V^{II}}\right)_{U^{II}, N_1^{II} \cdots} dV^{II}}$$

$\rightarrow dU^{I} = -dU^{II}; \quad dV^{I} = -dV^{II}.$

$$\Rightarrow \underbrace{dS}_{0} = \underbrace{\left(\frac{1}{T^{I}} - \frac{1}{T^{II}}\right)}_{0} dU^{I} + \underbrace{\left(\frac{P^{I}}{T^{I}} - \frac{P^{II}}{T^{II}}\right)}_{0} dV^{I}$$

$$\Rightarrow \frac{1}{T^{I}} = \frac{1}{T^{II}} \Rightarrow \frac{P^{I}}{T^{I}} = \frac{P^{II}}{T^{II}} \Rightarrow P^{I} = P^{II}.$$

4-3 Matter Flow Equilibrium.



rigid, diathermal.

Allows N_1 flow, impermeable to $N_2, \cdots N_r$

$$dS = 0 = \frac{1}{T^{I}} dU^{I} + \underline{\left(\frac{\partial S^{I}}{\partial N_1^{I}}\right)_{U^{I}, V^{I}, N_2^{I} \dots}} dN_1^{I}$$

$\hookrightarrow F_j \equiv -\frac{P_j}{T} = -\frac{\mu_j}{T}$

$$+ \frac{1}{T^{II}} dU^{II} + \left(\frac{\partial S^{II}}{\partial N_1^{II}}\right)_{U^{II}, V^{II}, N_2^{II} \dots} dN_1^{II}$$

$$P_j = \left(\frac{\partial U}{\partial N_j}\right) = \mu_j$$

$$\Rightarrow dS = 0 = \left(\frac{1}{T^{I}} - \frac{1}{T^{II}}\right) dU^{I} - \left(\frac{\mu_1^{I}}{T^{I}} - \frac{\mu_1^{II}}{T^{II}}\right) dN_1^{I}$$

$\Rightarrow \frac{1}{T^{I}} = \frac{1}{T^{II}} \Rightarrow \frac{\mu_1^{I}}{T^{I}} = \frac{\mu_1^{II}}{T^{II}} \Rightarrow \mu_1^{I} = \mu_2^{II}.$ $\quad dN_1^{I} = -dN_1^{II}$

if $dS > 0$; if $\mu_1^{I} > \mu_1^{II}$

$(T^{I} = T^{II} = T)$

$$dS = \Big(\underbrace{\frac{\mu_1^{II}}{T^{II}} - \frac{\mu_1^{I}}{T^{I}}}_{T} \Big) dN_1^{I} = \left(\frac{\mu_1^{II} - \mu_1^{I}}{T} \right) dN_1^{I}$$

*

$\Rightarrow dN_1^{I} < 0 \Rightarrow$ Matter flow from I to II.

$\Rightarrow$ Matter flows from High μ to low μ.