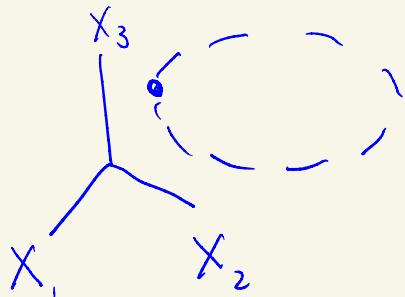


*Recap from L3

Clausius Theorem:



arbitrary (no restriction to quasi-static or reversible) cyclic process

$$\boxed{\oint \frac{dQ(\alpha)}{T(\alpha)} \leq 0}$$

**

Consequences:

$$\textcircled{1} \quad \oint \frac{dQ}{T} = 0$$

entropy

$$\textcircled{2} \quad \int_A^B \frac{dQ}{T} = S(B) - S(A)$$

Reversible processes

$$\Rightarrow dQ = TdS$$

$$\textcircled{3} \quad dE = \sum_{i=1}^n J_i dx_i + TdS$$

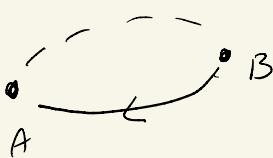
$\Rightarrow n+1$ indep. variables
(free to choose)

e.g. choose $(E, \{x_i\})$

$$dS = \frac{1}{T} dE - \frac{1}{T} \sum_{i=1}^n J_i dx_i$$

$$\left. \frac{\partial S}{\partial E} \right|_X = \frac{1}{T} \quad \left. \frac{\partial S}{\partial x_i} \right|_{E, x_{j \neq i}} = -\frac{J_i}{T}$$

④ Increase of Entropy



$$\int_A^B \frac{dQ}{T} \leq S(B) - S(A)$$

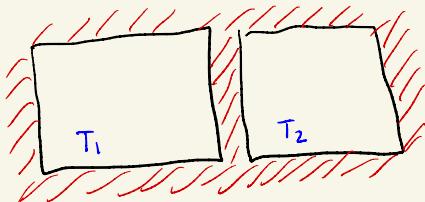
irreversible path

$$\Rightarrow dS \geq \frac{dQ}{T}$$

$$\Rightarrow \boxed{dS \geq 0 \text{ isolated adiabatic system}}$$

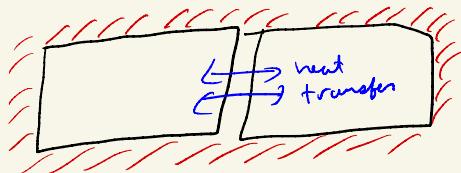
- * when equilibrium is disturbed in an isolated adiabatic system (e.g., by releasing an internal constraint) entropy increases.
- * Entropy is maximized at equilibrium

Ex 1:



$\text{---} = \text{adiabatic walls}$
(e.g., insulation)

Now remove the inner insulation so the 2 boxes can exchange heat \swarrow releasing the constraint of no heat transfer

\Rightarrow 

* Final show entropy increases when we remove the insulation

$$dS = dS_1 + dS_2$$

$$= \left. \frac{\partial S_1}{\partial E_1} \right|_{V_1} dE_1 + \left. \frac{\partial S_2}{\partial E_2} \right|_{V_2} dE_2$$

$$\text{but } dE = 0 = dE_1 + dE_2 \Rightarrow dE_1 = -dE_2$$

$$\therefore dS = dE_1 \left(\left. \frac{\partial S_1}{\partial E_1} \right|_{V_1} - \left. \frac{\partial S_2}{\partial E_2} \right|_{V_2} \right)$$

$$= dE_1 \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\text{Case 1: } T_1 > T_2 \Rightarrow \left(\frac{1}{T_1}, -\frac{1}{T_2} \right) < 0$$

$$dE_1 = dQ_1 < 0 \quad (\text{by 2nd Law})$$

$$\therefore dS > 0$$

$$\text{Case 2: } T_2 > T_1 \Rightarrow \left(\frac{1}{T_1}, -\frac{1}{T_2} \right) > 0$$

$$dE_1 > 0 \quad (\text{by 2nd Law})$$

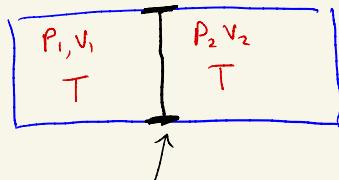
$$\therefore dS > 0$$

* Now show what we infer about the new equilibrium when $dS = 0$

$$\Rightarrow 0 = dS = dE_1 \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\therefore T_1 = T_2 \quad (\text{as expected})$$

Ex 2:



Clamped piston
(so it can't slide)

* Now remove the clamps (internal constraint) so it's free to slide. First let's verify that entropy will increase

$$\begin{aligned} dS &= dS_1 + dS_2 = \left. \frac{\partial S_1}{\partial V_1} \right|_{E_1} dV_1 + \left. \frac{\partial S_2}{\partial V_2} \right|_{E_2} dV_2 \\ &= \left(\frac{P_1}{T} - \frac{P_2}{T} \right) dV_1 \quad (\text{used } dV_1 = -dV_2) \end{aligned}$$

Case 1: $P_1 > P_2 \Rightarrow dV_1 > 0 \Rightarrow dS > 0$

Case 2: $P_2 > P_1 \Rightarrow dV_1 < 0 \Rightarrow dS > 0$

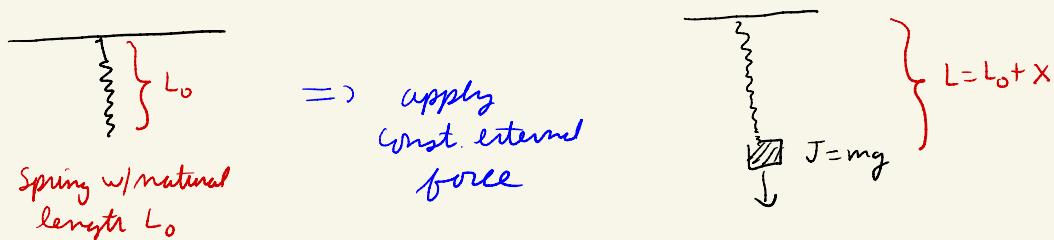
* Condition at the new equilibrium? $dS = 0 \Rightarrow P_1 = P_2$
as expected

Approach to Equilibrium + TD Potentials

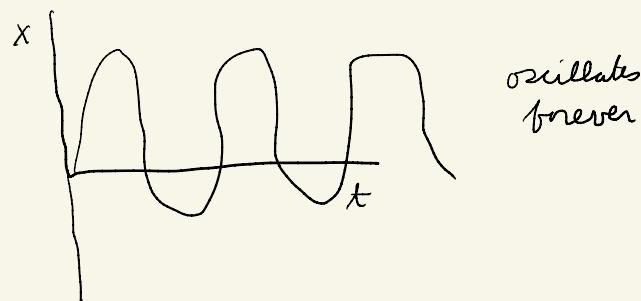
- * What if the system is not adiabatically isolated, and/or is subjected to external work?
- * It is possible to define other TD state functions (TD potentials) that are extremized at equilibrium and that depend on "convenient" choices of independent variables

① Enthalpy (adiabatic transformations w/ constant external force)

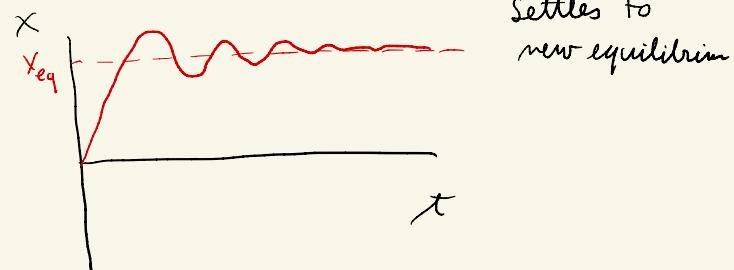
Consider the problem of mechanical equilibrium for:



* without friction



* with friction



* How to find X_{eq} ? Simply minimize PE of spring + external agent

let $H = U_{spring} - Jx$ "enthalpy"

$$\frac{d}{dx} \left(U_{spring} - Jx \right) = 0 \quad \text{say } U_{spring} = \frac{k}{2}x^2$$

$$\Rightarrow kx_{eq} - J = 0$$

$$\Rightarrow x_{eq} = \frac{J}{k}$$

$$\therefore H(x_{eq}) = -\frac{J^2}{2k}$$

* Now let's generalize from this example to some process at constant J and $dQ = 0$

* Due to friction, $dW \leq \vec{J} \cdot d\vec{x}$

$$\therefore dE = \cancel{dQ}^0 + dW \leq \vec{J} \cdot d\vec{x}$$

* Since we consider a process at constant \vec{J} ,

$$d(\vec{J} \cdot \vec{x}) = \cancel{dJ}^0 \cdot \vec{x} + \vec{J} \cdot d\vec{x}$$

$$\therefore \underbrace{d(E - \vec{J} \cdot \vec{x})}_{\text{enthalpy}} \leq 0 \quad \left. \right\} dH \leq 0$$

$$\text{enthalpy } H \equiv E - \vec{J} \cdot \vec{x}$$

(decreases when we disturb adiabatic system by doing work @ constant force)

\therefore enthalpy $H = E - \vec{J} \cdot \vec{x}$ is minimized at equilibrium
for adiabatic systems subjected to external work by constant forces

* Now consider variations of H at equilibrium (no longer restricting to $J = \text{const}$)

$$\begin{aligned} dH &= dE - \vec{J} \cdot d\vec{x} - \vec{x} \cdot d\vec{J} \\ &= TdS + \vec{J} \cdot d\vec{x} - \vec{J} \cdot d\vec{x} - \vec{x} \cdot d\vec{J} \end{aligned}$$

$$\Rightarrow \boxed{\begin{aligned} dH &= TdS - \sum_i x_i dJ_i \\ \left. \frac{\partial H}{\partial S} \right|_{J_i} &= T \\ \left. \frac{\partial H}{\partial J_i} \right|_{S, J_{j \neq i}} &= -x_i \end{aligned}}$$

$H = H(S, \{J_i\})$

② Helmholtz Free Energy (Isothermal processes with no external work)

$$dQ \leq TdS \quad \text{by Clausius}$$

$$\begin{aligned} + \quad dW &= 0 \\ \hline dE &\leq TdS \end{aligned}$$

* at constant T (isothermal) processes, $TdS = d(TS)$

$$\therefore \underbrace{d(E - TS)}_{F} \leq 0 \quad \text{for isothermal processes w/ no external work}$$

$\therefore F = E - TS$ decreases if we disturb a system in equilibrium with some isothermal process w/out any external work

- * F is minimized in equilibrium for mechanically isolated ($dW=0$) systems kept at constant temperature
- * as before with Enthalpy, now let's consider variations in F at equilibrium (no longer requiring constant T)

$$\begin{aligned} dF &= dE - TdS - SdT \\ &= \vec{J} \cdot d\vec{x} + T \cancel{dS} - T \cancel{dS} - SdT \end{aligned}$$

$$\therefore \boxed{\begin{aligned} dF &= \sum_i J_i dx_i - SdT \\ \frac{\partial F}{\partial T} \Big|_{\vec{x}} &= -S \\ \frac{\partial F}{\partial x_i} \Big|_{T, x_{j \neq i}} &= J_i \end{aligned}}$$

$F = F(T, \{x_i\})$

(3) Gibbs Free Energy (Isothermal + constant external force)

$$dW \leq \vec{J} \cdot d\vec{x}$$

$$\vec{J} \cdot d\vec{x} + TdS = d(\vec{J} \cdot \vec{x} + TS)$$

$$\underline{dQ \leq TdS}$$

for isothermal + constant \vec{J}

$$dE \leq \vec{J} \cdot d\vec{x} + TdS$$

$$\therefore \underbrace{d(E - TS - \vec{J} \cdot \vec{x})}_{G} \leq 0$$

$\Rightarrow dG \leq 0$ for isothermal processes
with external work@ constant force

$\Rightarrow G$ is minimized at equilibrium for
constant $T + J$ systems

* arbitrary variations at equilibrium

$$dG = \cancel{dE} - T\cancel{dS} - SdT - \vec{J}/\cancel{dx} - \vec{x} \cdot \cancel{d\vec{J}}$$

↓

$$\boxed{\begin{aligned} dG &= - \sum_i x_i dJ_i - SdT \\ \frac{\partial G}{\partial T} \Big|_{\vec{J}} &= -S \\ \frac{\partial G}{\partial J_i} \Big|_{T, \vec{J}_{j \neq i}} &= -x_i \end{aligned}}$$

$$G = G(T, \{J_i\})$$

Remark: Our manipulations to derive $H = H(S, \{J_i\})$,
 $F = F(T, \{x_i\})$, and $G = G(T, \{J_i\})$ are examples
of Legendre Transformations

(4) Chemical Potential

* We have overlooked one key detail so far. Does $G(T, \{J_i\})$ really completely describe our system?

→ No. There needs to be a variable that indicates how much stuff there is (i.e., $N = \# \text{ of particles}$)

* More generally, we might have a system with multiple species of atoms/molecules that can undergo chemical reactions, so the # of each N_α is variable

* Or, we might have a system with 2 phases of material (e.g., liquid-gas) in equilibrium

||

Chemical Work = change of internal energy due to change in # of particles of a given species

$$\delta W_{\text{chem}} = \sum_{\alpha=1}^{\# \text{ species}} M_\alpha dN_\alpha$$

↑
Chemical Potential = Amt. of work to add additional particle of species α

Revising our previous formulas

$$dE = \sum_i J_i dx_i + T dS + \sum_{\alpha} M_{\alpha} dN_{\alpha}$$

$$\Rightarrow M_{\alpha} = \left. \frac{\partial E}{\partial N_{\alpha}} \right|_{\vec{X}, S, N_{\beta \neq \alpha}}$$

$$\Rightarrow J_i = \left. \frac{\partial E}{\partial X_i} \right|_{S, \vec{N}, X_{j \neq i}}$$

$$\Rightarrow T = \left. \frac{\partial E}{\partial S} \right|_{\vec{N}, \vec{X}}$$

$$dF = \sum_i J_i dx_i - SdT + \sum_{\alpha} M_{\alpha} dN_{\alpha}$$

$$M_{\alpha} = \left. \frac{\partial F}{\partial N_{\alpha}} \right|_{T, \vec{X}, N_{\beta \neq \alpha}} \text{ etc.}$$

$$dG = - \sum_i X_i dJ_i - SdT + \sum_{\alpha} M_{\alpha} dN_{\alpha}$$

etc...

⑤ Grand Potential (processes in chemical equilibrium with no mechanical work)

$$G = E - TS - \vec{M} \cdot \vec{N}$$

$$dG = - SdT + \vec{J} \cdot d\vec{X} - \vec{N} \cdot d\vec{M}$$

$$S = - \left. \frac{\partial G}{\partial T} \right|_{\vec{J}, \vec{M}} \quad J_i = \left. \frac{\partial G}{\partial X_i} \right|_{T, \vec{M}, X_{j \neq i}} \quad N_{\alpha} = - \left. \frac{\partial G}{\partial M_{\alpha}} \right|_{\vec{X}, T, N_{\beta \neq \alpha}}$$

example: N supersaturated steam molecules

@ constant V + T



describe approach to equilibrium

mix of N_w liquid molecules + N_s gas

⇒ appropriate potential to use $F(V, T, N)$



(assume $\sqrt{w} \approx 0$)

$$F(V, T, N, N_w) = F_w(T, N_w) + F_s(V, T, N - N_w)$$

$$dF = \left. \frac{\partial F_w}{\partial N_w} \right|_{T, V} dN_w + \left. \frac{\partial F_s}{\partial N_s} \right|_{T, V} dN_s \quad \text{but } dN = dN_w + dN_s = 0 \\ \therefore dN_s = -dN_w$$

$$= dN_w \left(\left. \frac{\partial F_w}{\partial N_w} \right|_{T, V} - \left. \frac{\partial F_s}{\partial N_s} \right|_{T, V} \right)$$

$$= dN_w (M_w - M_s)$$

∴ equilibrium reached when $M_w = M_s$.

