Lecture 8 Entropy Continued

motivation

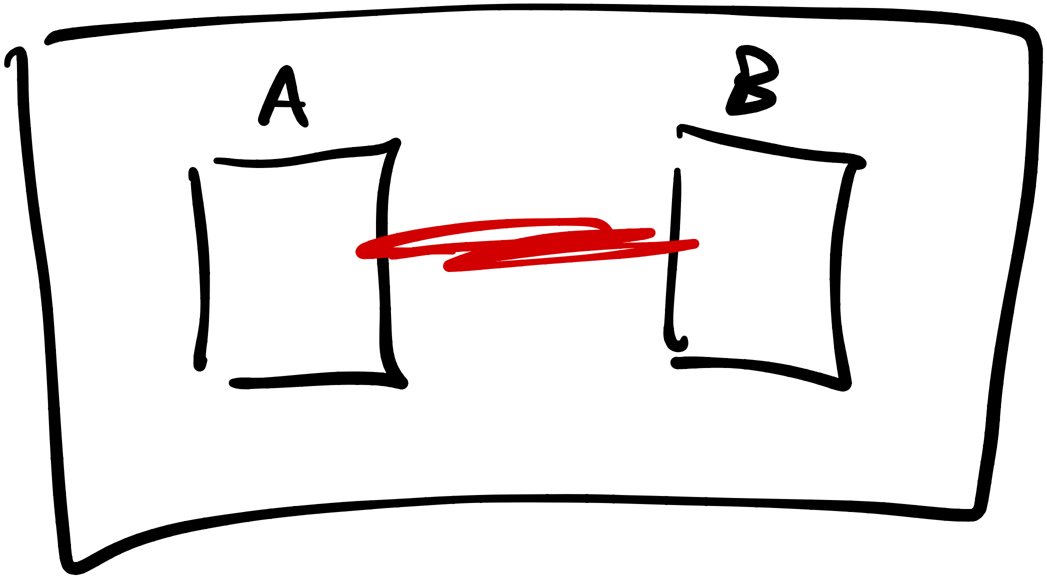
$$\sum_{loop} q_i / T_i = 0$$

motivates idea that $dS \equiv dq^{rev}/T$

$\Delta S_1 = \Delta S_2$

$\Delta E_1 = \Delta E_2$

Imagine



system isolated

$T_A \neq T_B$ at beginning

$$\mathcal{E}_{total} = \mathcal{E}_A + \mathcal{E}_B$$

$$d\mathcal{E}_{total} = d\mathcal{E}_A + d\mathcal{E}_B = 0 \quad \text{(isolated)}$$

1st law: $d\mathcal{E}_A = dq_A + \cancel{dw} \rightarrow 0 \quad (dU = 0)$

$d\mathcal{E}_B = dq_B$

$$dS = dS_A + dS_B$$

$$\left(dS = dq^{rev}/T \right)$$

$$dS = dq_A^{rev}/T_A + dq_B^{rev}/T_B$$

$$= d\varepsilon_A/T_A + d\varepsilon_B/T_B$$

$$= d\varepsilon_A\left(\frac{1}{T_A} - \frac{1}{T_B}\right)$$

$T_A > T_B$, $d\varepsilon < 0$, $\left(\frac{1}{T_A} - \frac{1}{T_B}\right) < 0$

$$dS > 0$$

$dS = 0$ @ equilibrium

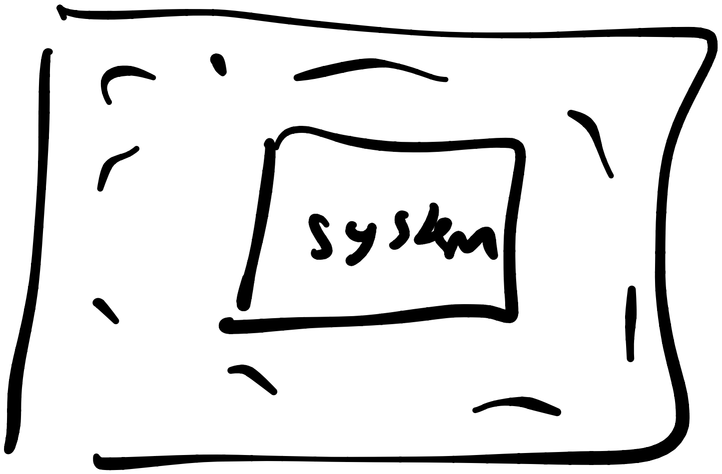
Spontaneous processes occur until entropy is Maximized [isolated system]

$dS > 0$ (spontaneous process, isolated)

$dS = 0$ (reversible process isolated system)

Irreversible process, entropy is produced in a system (isolated)

Not in isolated system



$$dS = dS^{system}_{prod} + dS_{exchange}$$

(q, or $dN \neq 0$)

$$dS = dS_{prod} + \text{đ}q/T$$

if reversible process, $dS = \text{đ}q^{rev}/T$

irreversible process, $dS > \text{đ}q^{irr}/T$

$dS_{prod} > 0$

For any process

$$dS \geq \text{đ}q/T \quad \text{any process}$$

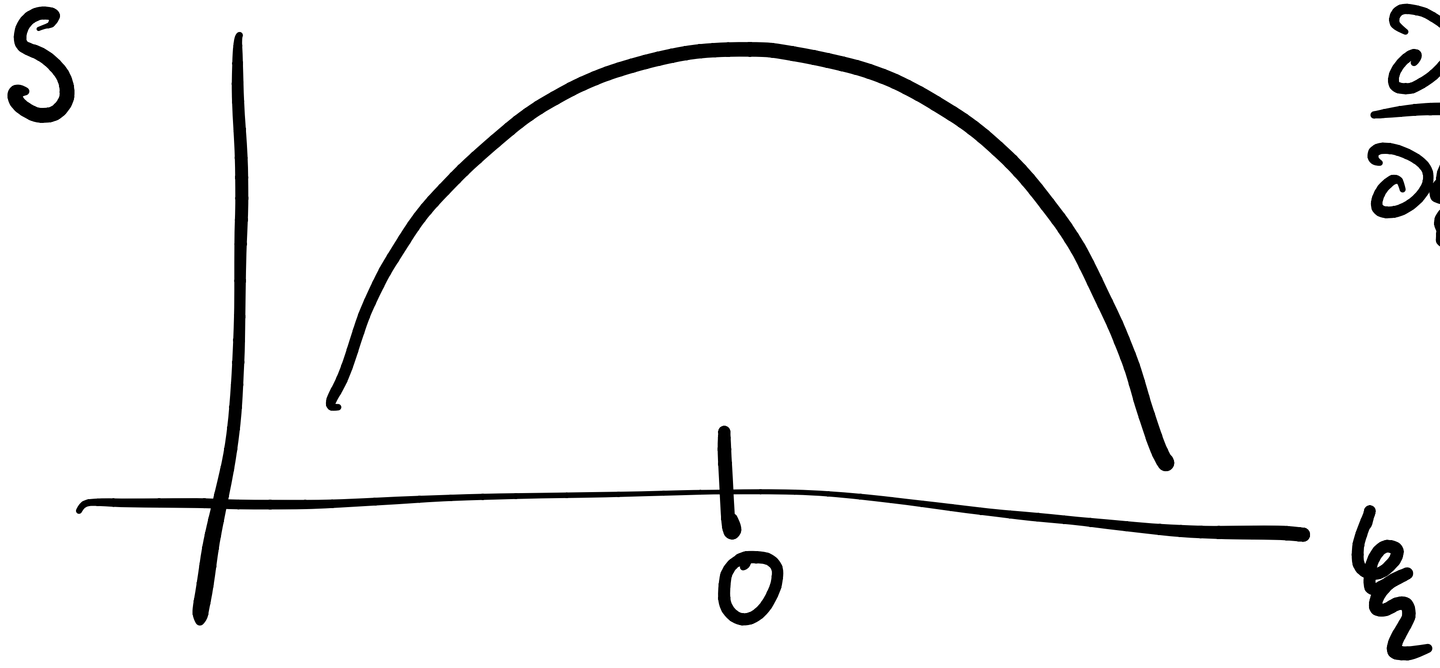
(equal when reversible, $dS = \text{đ}q^{rev}/T$)

$$\Delta S \geq \int_{start}^{finish} \text{đ}q/T \quad \leftarrow \text{2nd law of thermodynamics}$$

For universe, isolated system

$$dS^{universe} \geq 0$$

Entropy is maximized
not at equilibrium, S kind of
acts like a potential



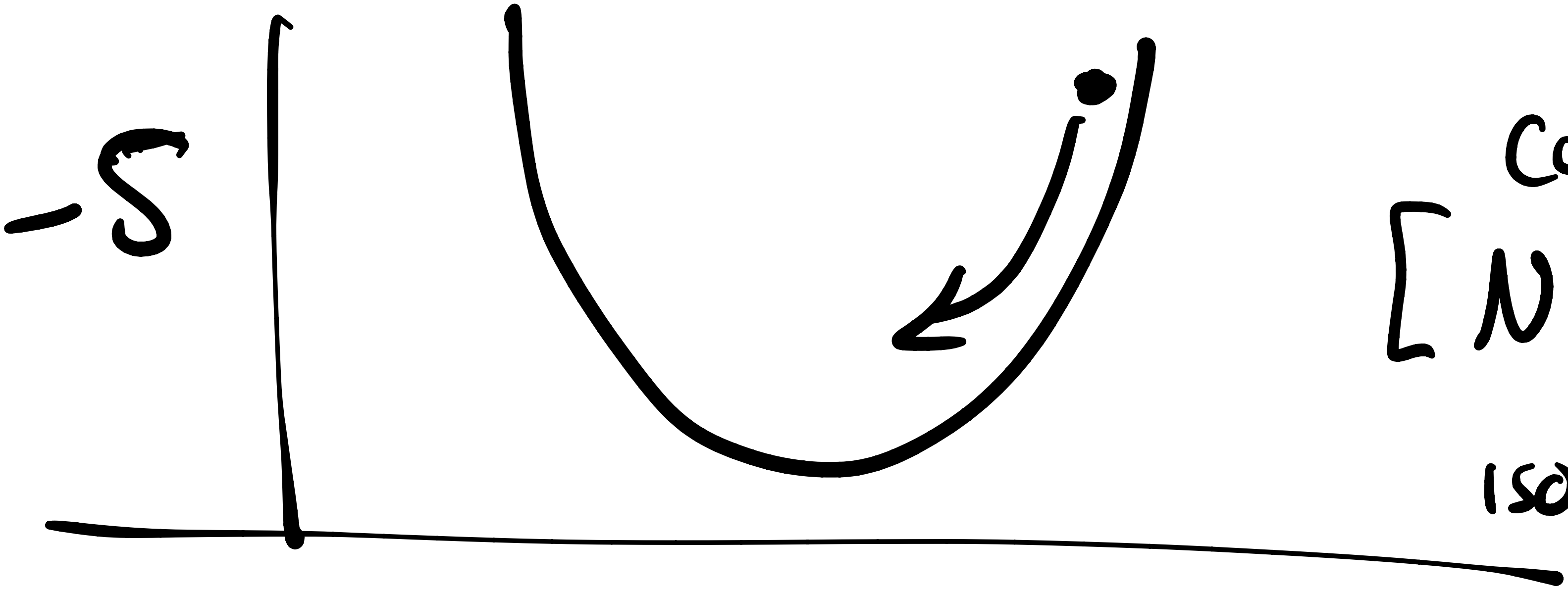
$\frac{\partial S}{\partial \xi} = 0$ @ eq

ξ

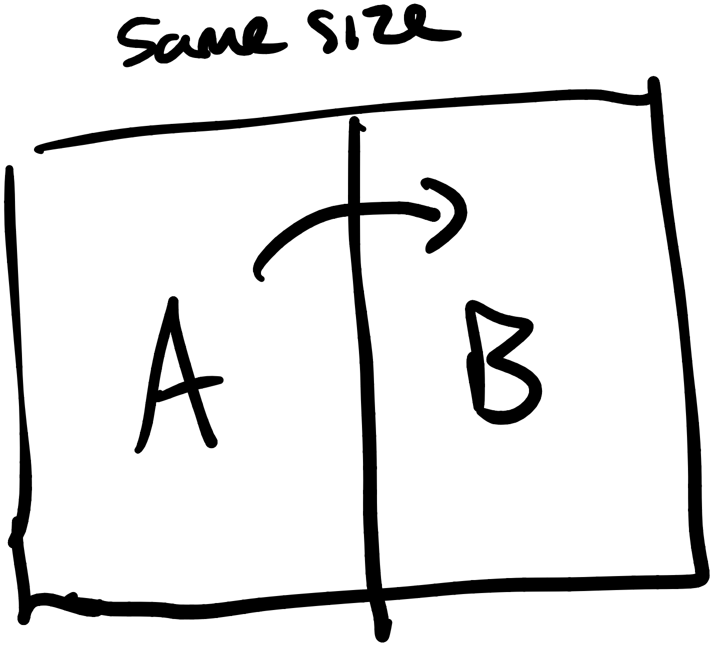
eq $\xi = V - V_{eq}$

$\xi = [A] - [A]_{eq}$

$-S$ is like a potential



const
$[N, V, E]$
isolated system



Argue, $T_f = \frac{T_A + T_B}{2}$

same material

$q = nC\Delta T$

$$\Delta S_A = C_v \ln(T_f/T_A)$$

$$\Delta S_B = C_v \ln(T_f/T_B)$$

$$\Rightarrow \Delta S = C_v \ln\left(\frac{(T_A+T_B)^2}{4T_A T_B}\right)$$

$\Delta S = 0$ only if $T_A = T_B$

$\Delta S > 0$ if $T_A \neq T_B$

Boltzmann Entropy

Origin Entropy ~ disorder

Wanted a function which had properties of macroscopic S

$$S = k_B \ln \Omega$$

↑ # of micro states

[constant energy]

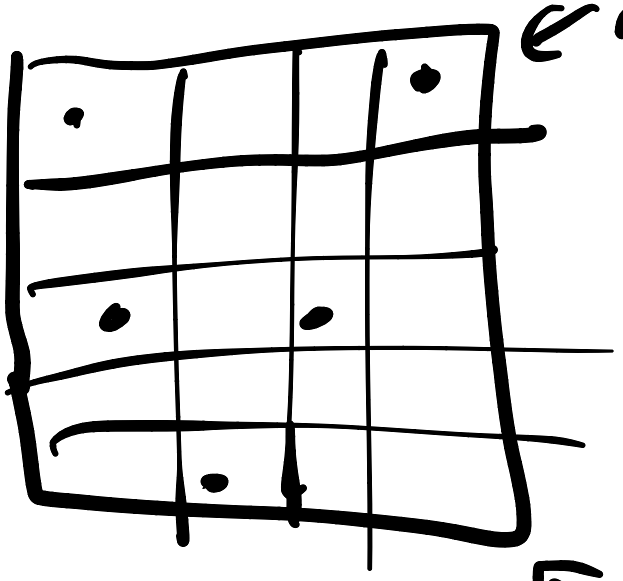
Motivation: S is extensive

$$\boxed{\Omega} \times 2$$

$$k_B = \frac{\overset{8.314\ J/K}{R}}{N_A} \qquad \overline{6\times10^{23}}$$

$$\Omega_{2x} = \Omega \times \Omega$$

$$S_{A+B} = k_B \ln \Omega_A \Omega_B = k_B \ln \Omega_A + k_B \ln \Omega_B$$



$$\Omega = \binom{N_c}{M} = \frac{N_c!}{M!\,(N_c-M)!}$$

[don't care about overlaps
$\Omega = N_c^M$]

$$V = N_c v$$

↖ ℓ^2 in 2d or ℓ^3 in 3d

Molecules $\quad \varepsilon = \begin{cases} 0 & \text{no overlaps} \\ \infty & \text{if overlaps} \end{cases}$

Can show $\Delta S(V_1 \to V_2) = M k_B \ln\left(V_2/V_1\right)$

~~Effective~~ thermo... potentials for equilibrium <u>ch 5</u>

$-dS \le 0$ for a change of state for an isolated system

Claussius Ineq : $dS \ge \text{đ}q/T$

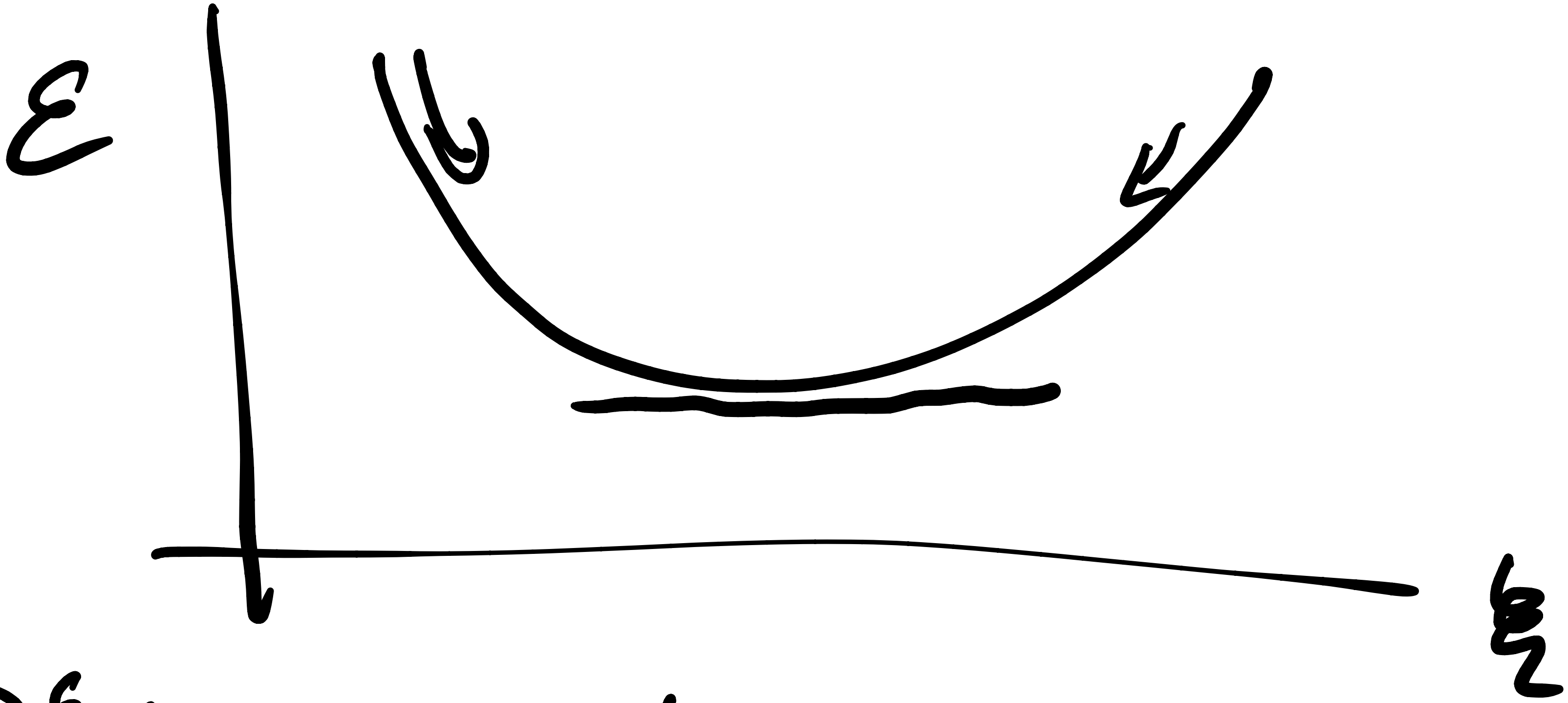
<u>1st law</u>

$$dE = \text{đ}q + \text{đ}w$$

$$= \text{đ}q - PdV \le TdS - PdV$$

<u>If</u> $dS = 0$, $\underline{dU} = 0$ then $dE \le 0$

(1) if S & V constant



$\partial \mathcal{E}/\partial \xi < 0$ if not at ξ_{eq}

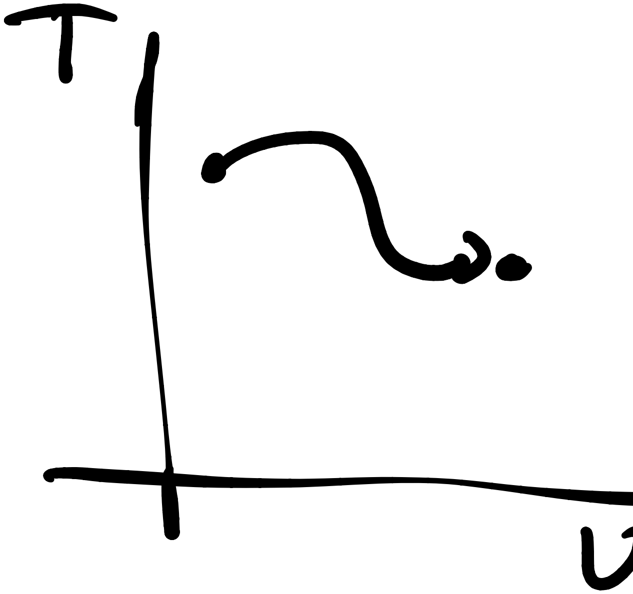
$$\mathcal{E}(S,V) \Rightarrow d\mathcal{E} = \left(\frac{\partial \mathcal{E}}{\partial S}\right)_V dS + \left(\frac{\partial \mathcal{E}}{\partial V}\right)_S dV$$

also $d\mathcal{E} = T\,dS - P\,dV$

$$\Rightarrow T = \left(\partial \mathcal{E}/\partial S\right)_V, \quad P = -\left(\partial \mathcal{E}/\partial V\right)_S$$

$$d\mathcal{E} = \underbrace{\left(\frac{\partial \mathcal{E}}{\partial S}\right)_V}_{T} dS + \underbrace{\left(\frac{\partial \mathcal{E}}{\partial V}\right)_S}_{-P} dV$$

$$dS = \frac{1}{T}\underset{\substack{\uparrow \\ C_V dT}}{d\mathcal{E}} + \frac{P}{T} dV$$



$$dS = \frac{C_V}{T} dT + \frac{P}{T} dV$$

$$= \frac{C_V}{T} dT + \frac{nR}{V} dV \quad \text{(ideal gas)}$$

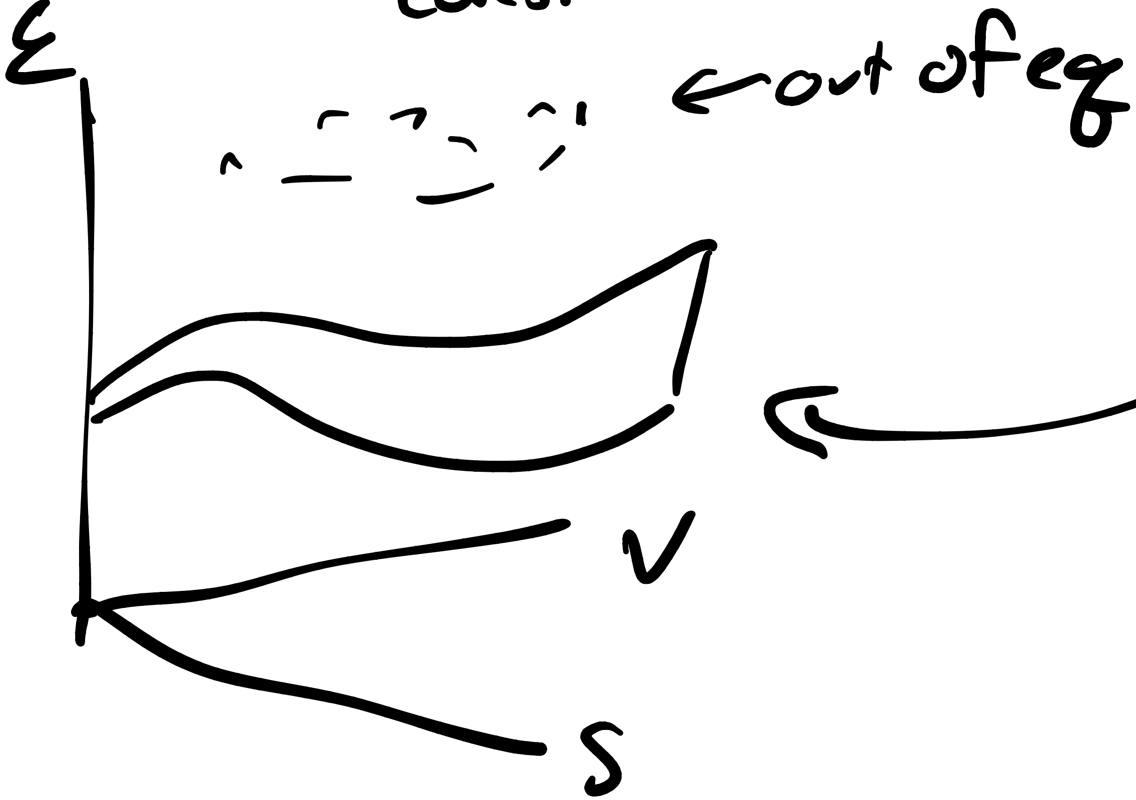
$$\Delta S = C_V \ln\left(T_2/T_1\right) + nR \ln\left(V_2/V_1\right)$$

FYI →

$$\mathcal{E}(\underline{S},\underline{V}) = \frac{3}{2} n R T_{ref}\, e^{(S-S_{ref})/c_V} \left(\frac{V_r}{V}\right)^{2/3}$$

✓ const

typo book



S&V are bad choices

define other potentials

$$H = \mathcal{E} + PV$$

adding PV swapped P&V in our inequality

$$dH = d\mathcal{E} + PdV + VdP$$

$$d\mathcal{E} \le TdS - PdV$$

2nd law

$$\le \underline{TdS} + VdP$$

If S, P are constant, H is a potential for constant S, P

$$G \equiv H - TS$$

$$dG = dH - TdS - SdT$$

$$dH \le TdS + VdP$$

$$dG \le + SdT + VdP$$

(check

@ const T & P, $G\downarrow$

$A = \mathcal{E} - TS$ (helmholz free energy)

$$dA = d\mathcal{E} - TdS - SdT$$

$$\leq (TdS - PdV) - TdS - SdT$$

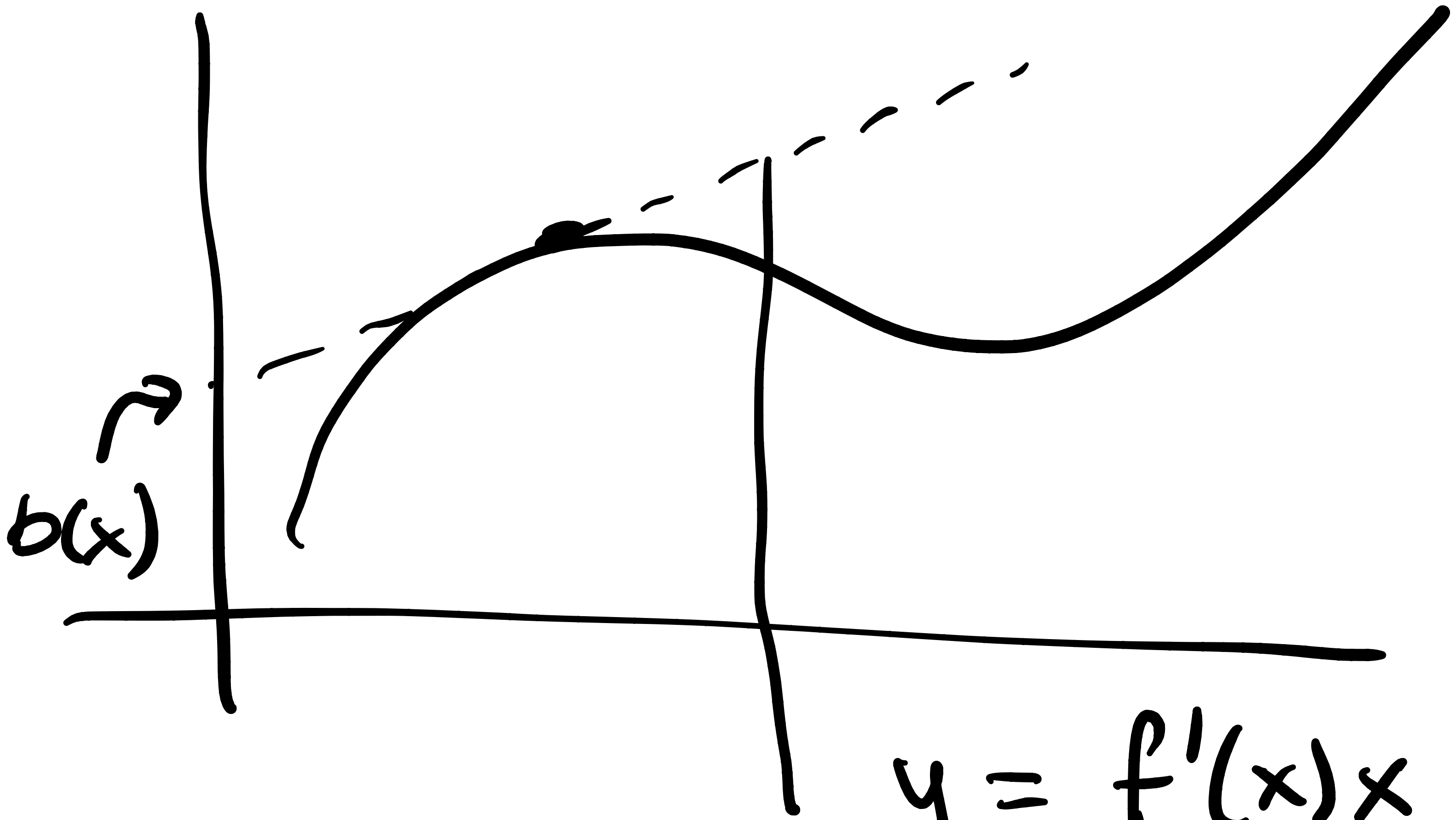
$$\leq -PdV - SdT$$

potential for constant T & V

Pattern

$$\begin{tikzcd}
E \arrow[r, "-TS"] \arrow[d, "+pV"'] & A \arrow[d, "+PV"] \\
H \arrow[r, "-TS"'] & G
\end{tikzcd}$$

Legendre
Transform



$$y = f'(x)x + b(x)$$

$$b(x) = y - f'(x)x$$

$$\mathcal{E}(S,V) \to \quad A = \mathcal{E} - \left(\frac{\partial \mathcal{E}}{\partial S}\right)S \quad - V\left(\frac{\partial A}{\partial V}\right)$$

$$= \mathcal{E} - TS$$