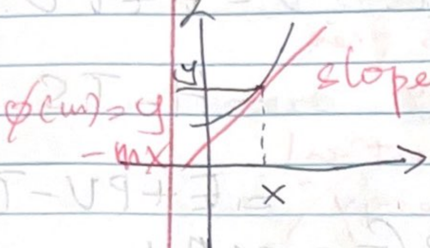
Last Time:
Going from extensive variables like S, V, ...
to intensive variable like T, P, ...



$$E(S, V, \dots) \xrightarrow{T = \frac{\partial E}{\partial S}} F(T, V, \dots) = E - TS$$

$$\Big\downarrow -P = \frac{\partial E}{\partial V} \qquad\qquad \Big\downarrow$$

$$H(S, P, \dots) \longrightarrow G(T, P, \dots)$$

$$= E + PV$$

$$G = H - TS$$
$$= F + PV$$
$$= E - TS + PV$$
$$= \mu n + \dots$$

All these function prepare the full knowledge about the system that recover to postulate I ~~&~~ & 2

Today: ① Heat capacity: equations that lose knowledge can still be useful.

② Using stat mech to derive "laws of nature"

① How much does T have to go up so E and S increase by a certain amount.

$dE = TdS - PdV + \mu dn + \dots$; at constant V and n

Can't get too OK

$\Rightarrow dS = \frac{dE}{T} = \frac{dq_{V,n}}{T}$ at constant V, n.

$dH = TdS + VdP + \mu dn + \dots$ at constant P and n

$\Rightarrow dS = \frac{dH}{T}$ at constant P and n.

Similarly:

$$\left(\frac{\partial E}{\partial T}\right) = \left(\frac{\partial E}{\partial S}\right)\left(\frac{\partial S}{\partial T}\right) = T\boxed{\left(\frac{\partial S}{\partial T}\right)_{V,n}} \leftarrow C_V$$

$\Rightarrow dE = C_V dT$ & $dS = \frac{C_V dT}{T}$ at constant V, n

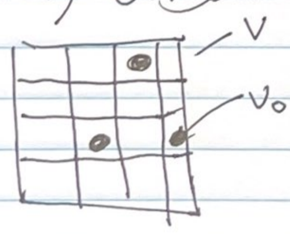
$\Rightarrow dH = C_p dT$ & $dS = \frac{C_p dT}{T}$ P, n

② Let's derive "a law" using stat mech.

i) Find a formula for your specific system

ii) Find a formula that's always true according to P1 & P2.

iii) Combine.

ex 

$\Rightarrow M = \frac{V}{V_0}$

N molecules

$\Rightarrow W = \left(\frac{M}{N}\right)^N = \left(\frac{V}{V_0 N}\right)^N$

$\Rightarrow S = R \ln W. \Rightarrow S = nR\ln\left(\frac{V}{N}\right) - nR\ln(V_0)$

density of gas.

$$\Rightarrow \left(\frac{\partial S}{\partial V}\right) = nR \frac{1}{\left(\frac{V}{N}\right)} \cdot \frac{1}{N} = \frac{n}{V} \cdot R = \rho \cdot R$$

iii) A formula for S & V that's always true!

$$dE = TdS - PdV + \mu dn + \ldots$$

$$\Rightarrow dS = \frac{1}{T} dE + \frac{P}{T} dV + \frac{\mu}{T} dn + \ldots$$

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

iii) $\left(\frac{\partial S}{\partial V}\right) = \frac{P}{T} \stackrel{\&}{=} \frac{n}{V} \cdot R$

(ii)

$$\Rightarrow PV = nRT.$$