Last Time:

Postulate I: Isolated sym specified by extensive variable E, v, n, ...

Postulate 2: Macrostate with bigger w (more microstate) is more likely $W(E, V, n, \dots)$ ←

$S(E, V, n, \dots) \xleftrightarrow[\text{tonic}]{\text{mono-}} E(S, V, n, \dots)$

Derivative:

$$dE = \underset{\parallel}{\left(\frac{\partial E}{\partial S}\right)} dS + \left(\frac{\partial E}{\partial V}\right) dV + \left(\frac{\partial E}{\partial n}\right) dn + \dots$$

$$= T\,dS - P\,dV + \mu\,dn + \dots$$

T is equated with E change

P is equated with V change

μ is equated with n change

Also E has a very simple formula: (See p. 5.12)

$$E = TS - PV + \mu N$$

Next few ~~This~~ Lecture: How to work with T, P, ... instead of S, V, ...

Today: E, F, G, H, I, J, K ...

E(S, V, ...) is not very predicted because we don't have an "S" known in Lab!

But we do have a "T" known.

So why not just:

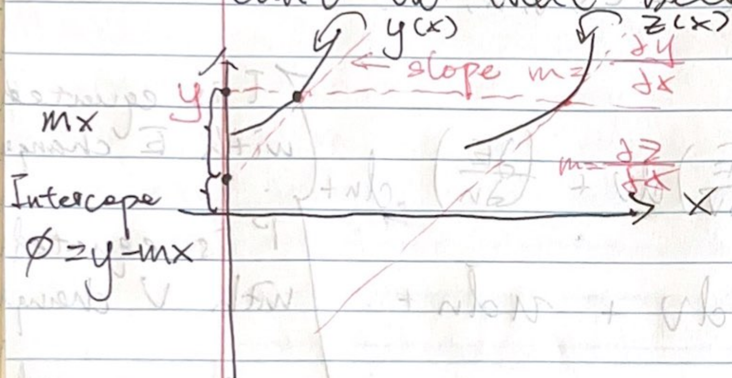
- Calc $T(S) = \left(\frac{\partial E}{\partial S}\right)_{V,N}$

- Solve for $S(T)$.

- Insert $E(S(T), \dots) \stackrel{?}{=} E(T)$?

Cannot go back to P1 and P2

Can't do that because info is lost.



$y(m) = z(m)$

Can't tell y and z apart if they are functions of slope m.

ex. HWK S3.3 $\quad y = x^2 \qquad z = (x-5)^2$

$$\frac{dy}{dx} = 2x = m \qquad \frac{dz}{dx} = 2(x-5) = m$$

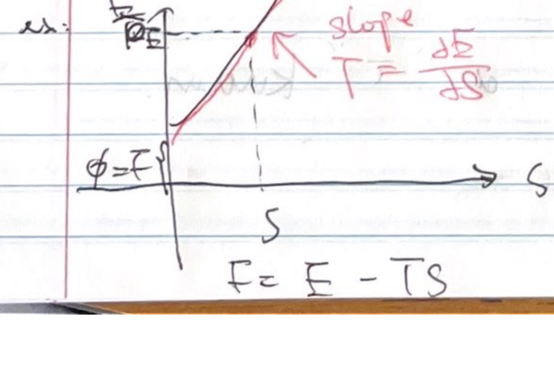
$$x = \frac{m}{2} \implies \frac{m^2}{4} = y \ ; \quad x - 5 = \frac{m}{2}$$

$$z = \frac{m^2}{4}$$

How to solve problem: want $f(T) \Leftrightarrow E(S)$

Fix: $\phi(m)$ allows you to recover $y(x)$

ex:



$E(S, V, \dots)$

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

$= E - TS$

Helmholtz Free Energy

$$E(S, V, \dots) \xrightarrow{P = -\frac{\partial E}{\partial V}} H(S, P, \dots) = E + PV$$

enthalpy

$$F(T, V, \dots) \xrightarrow{P = -\frac{\partial F}{\partial V}} G(T, P, \dots) = F + PV$$

"Gibb's free energy"

$$= H - TS$$

chemical potential

"molar free energy"

$$= E + PV - TS$$

$$\Rightarrow G = \mu n + \dots$$

So, if you know how to do an expt at constant T and P. use $G(T, P) \Leftrightarrow E(S, V)$

What about derivative?

$$\boxed{dy = \frac{\partial y}{\partial x} dx}$$

ex $dG = d(E + PV - TS)$

$$= \cancel{TdS} - \cancel{PdV} + \mu dn + \cancel{PdV} + VdP - \cancel{TdS} - SdT + \dots$$

$$= \underbrace{V}_{\frac{\partial G}{\partial P}} dP - \underbrace{S}_{\frac{\partial G}{\partial T}} dT + \underbrace{\mu}_{\frac{\partial G}{\partial n}} dn + \dots$$