

Lecture 22

Last time: The more microstates (larger W)

the more likely the system will go there,

$$W(E, V, n, \dots) \Leftrightarrow S(E, V, n, \dots) \Leftrightarrow E(S, V, n, \dots)$$

because they are all monotonically increasing functions of one another.

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

$$= \underbrace{T dS}_{\text{"heat"}} - \underbrace{p dV}_{\text{"work"}} + \underbrace{\mu dn}_{\text{"free energy"}} + \dots$$

\Rightarrow

- T is what is equalized if energy is allowed to flow ("heat flows")
- P is what is equalized if volume is allowed to change ("work is done")
- μ is what is equalized if particles are allowed to flow ("free energy flows")

Today: The Alphabet E, F, G, H, \dots

Using $E(S, V, n, \dots)$ is not very practical in lab - we don't have an S adjusting knob, V is usually not constant, etc.

\rightarrow But we do have a " T " knob!

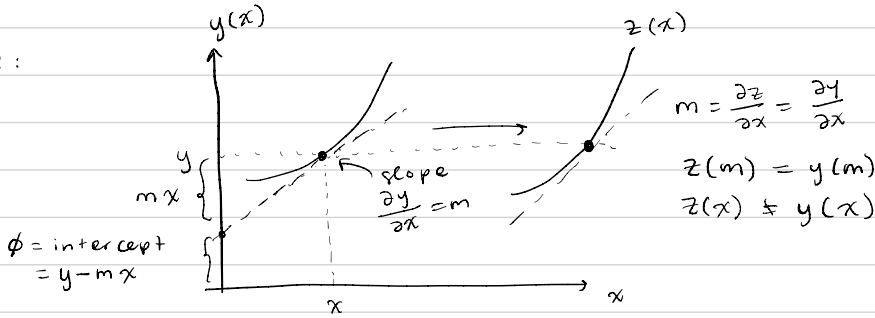
So why not just do the following = get $E(T)$
- calc $T(S) = \frac{\partial E(S)}{\partial S}$

- solve for S as a function of T

- insert into $E(S) \rightarrow E(S(T)) \rightarrow E(T)$?

NO! you are losing information and can't go back to W !

ex:



The fix: calculate the intercept as a function of slope, $\phi(m)$. This is unique again.

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

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

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

$$H(S, P) = E + PV \xrightarrow{S \rightarrow T = \frac{\partial E}{\partial S}} G(T, P) = E - TS + PV = F + PV = H - TS$$

So, if you know how to do an experiment as a function of T, P , then use $G(T, P, \dots)$ instead of $E(S, V, \dots)$

Changes in $F, H, G \dots$

$$\text{ex: } dG = d(E + PV - TS)$$

$$= dE + PdV + VdP - TdS - SdT$$

$$= TdS - PdV + \mu dn + PdV + VdP - TdS - SdT$$

$$dG = -SdT + VdP + \mu dn$$

Things to note:

- now, G is a function of T and P , just like E is a function of S and V

- at constant temp. and pressure $\Rightarrow dG = \mu dn$

partial molar quantities:

if there is more than one substance $i=1, 2, 3, \dots$
then:

$$dG = \sum_{i=1} \mu_i dn_i \quad (\text{at const } T, P)$$

$$\frac{\partial G}{\partial P} = V = \sum \underbrace{\frac{\partial \mu_i}{\partial P}}_{\text{molar volume } \nu_i} n_i$$

Thought experiment: can $\nu_i < 0$?

