

L22: review

Extensivity $\Rightarrow E(S, V, \dots) = TS - PV + \mu n + \dots$

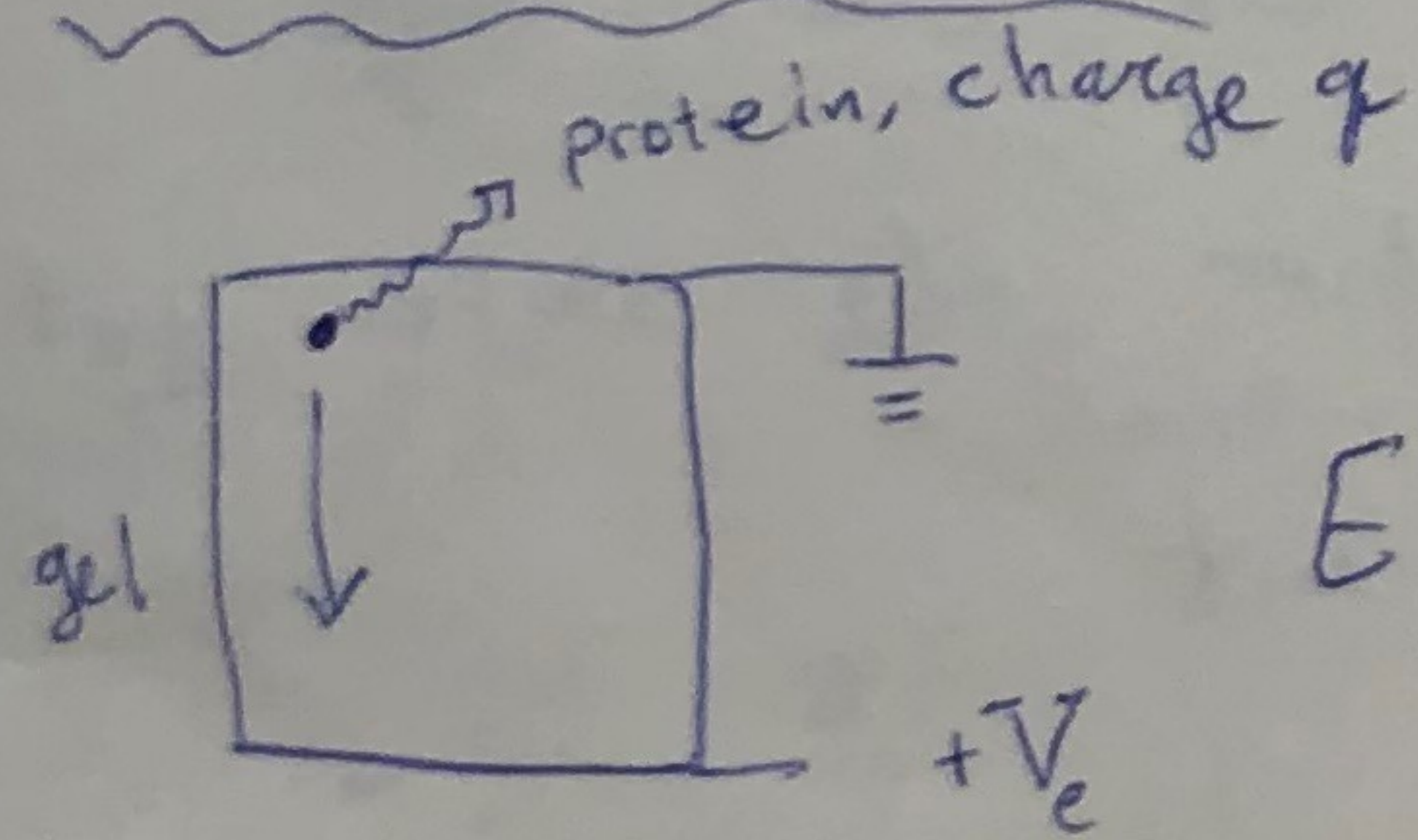
$T \equiv \frac{\partial E}{\partial S}$ is "the quantity equal on both sides when heat stops flowing"

$P \equiv \frac{\partial E}{\partial V}$ is "the quantity equal on both sides when volume stops changing"

$\mu \equiv \frac{\partial E}{\partial n}$ is "the quantity equal on both sides when particles stop flowing"

* other variables are possible. ex:

gel electrophoresis



$$E = TS - PV + \mu n + \underbrace{V_e \cdot q}_{\text{electric energy}}$$

electric energy

Today: "thermodynamic potentials, E, F, G, H that are equivalent to W & S"

$$P1: \begin{cases} A = \sum_{j=1}^W p_j A_j \\ p_j = \frac{1}{W} \\ S \equiv k_B \ln(W) \\ \hookrightarrow \text{extensive} \end{cases}$$

$E(W)$ increases with $W \Rightarrow E(S)$ is monotonically increasing with $S \xRightarrow{\text{invert}}$

$S(E),$

BUT $E(S, V, n, \dots)$ is not a

convenient form of energy because

S is not a practical variable to control.

So, wouldn't it be nice (just to switch from $E(S)$ to $E(t)$,

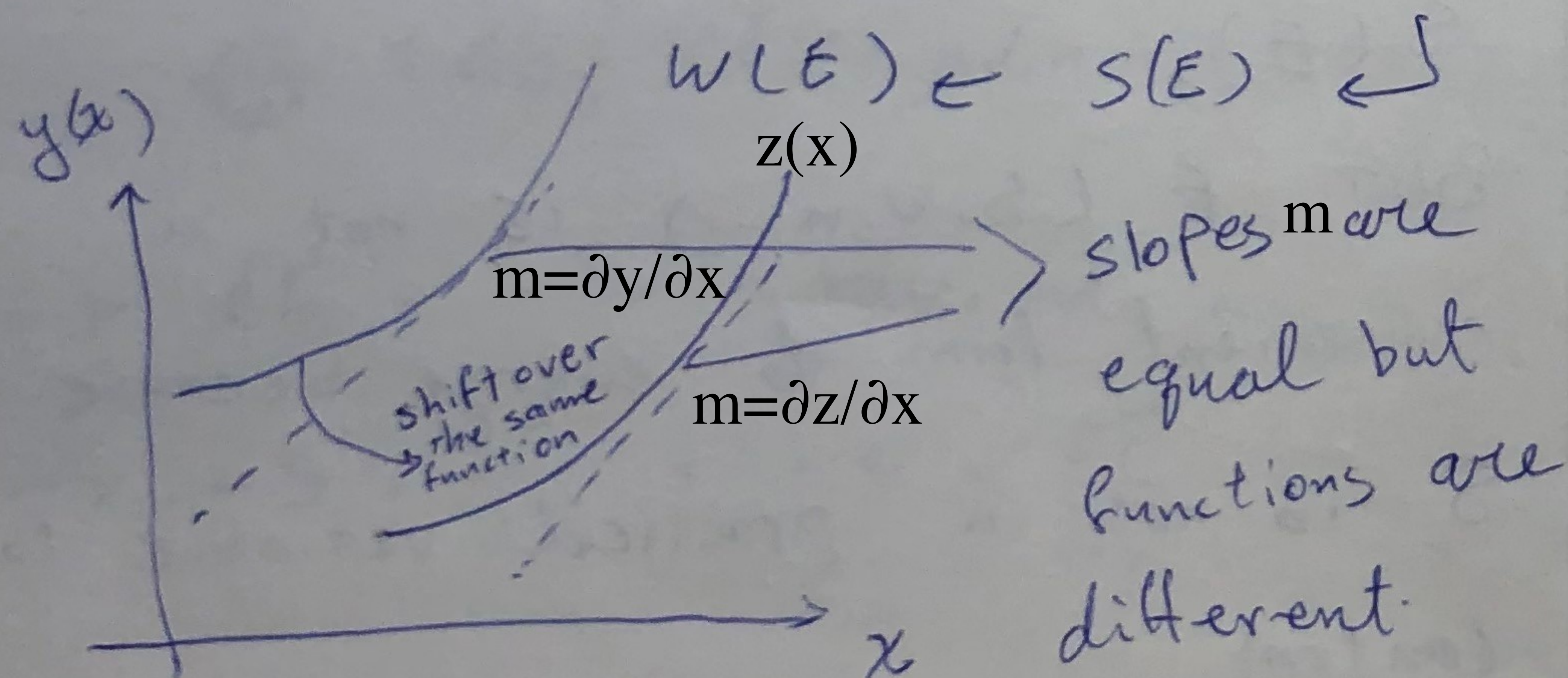
Since $T \equiv \frac{\partial E}{\partial S}$?

$\hookrightarrow E(S) \xrightarrow[\text{derivative}]{\text{calculate}} T \equiv \frac{\partial E}{\partial S} = T(S)$

$E = TS \dots$
 $= T \cdot S(T) \dots$
 $= E(t)$

$\xleftarrow[\text{in}]{\text{plug}}$ $S(T)$ $\xleftarrow{\text{invert}}$

\Rightarrow NO! Information is lost with this manipulation, can't go back to $E(S)$



* By knowing the slope, $m = \frac{\partial y}{\partial x}$, one can solve $y(m)$ but info. is lost. To illustrate this point read the example below:

HW 5.3.3

$$y(x) = x^2 \Rightarrow m = \frac{\partial y}{\partial x} = 2x \Rightarrow$$

$$x = \frac{m}{2} \Rightarrow y(m) = \frac{m^2}{4}$$

$$z(x) = (x-5)^2 \Rightarrow m = \frac{\partial z}{\partial x} = 2(x-5) \Rightarrow$$

$$x-5 = \frac{m}{2} \Rightarrow z = \frac{m^2}{4} = z(m)$$

although z and y have the same form as a function of slope, yet they are different.

So replacing $y(x)$ by $y(m)$ does not work; we can't just go from $E(S)$ to $E(T)$,

* How to do the $S \rightarrow T$ (or $x \rightarrow m$) variable change correctly, so no info is lost:
 Instead of $y(m)$, calculate $\phi(m)$, the intercept of y as a function of slope:

Calculate $y(x) \rightarrow \phi(m) = y(x) - m \cdot x$
 \uparrow
 "Legendre transform" of $y(x)$

ex: I want a function of T , not S :

$$F(T, V, n, \dots) = E - TS \quad \text{"Free Energy"}$$

$$dF = dE - Tds - d(TS)$$

$$dE = (\text{derived before spring break}) = \left. \begin{aligned} & Tds - PdV + \mu dn + \dots \end{aligned} \right\}$$

$$\rightarrow dF = -SdT - PdV + \mu dn + \dots$$

$$\Rightarrow -S = \frac{\partial F}{\partial T}, \quad -P = \frac{\partial F}{\partial V}$$

Instead of $\partial E(S)/\partial S = T$, we now have
 $\partial F(T)/\partial T = -S$

Chain of changing variables

$$E(S, V, \dots) \xrightarrow[T]{S \text{ to}} F(T, V) \xrightarrow[P]{V \text{ to}} G(T, P)$$

$$H(S, P) \xleftarrow[S]{T \text{ to}}$$

$G(T, P)$ is the most common form as temperature and pressure are usually the controllable parameters in the lab. $G(T, P)$ is called the Gibbs free energy.

$$E(S, V) \rightarrow F(T, V) = E - TS$$

$$F(T, V) \rightarrow G(T, P) = F + PV =$$

$$E - TS + PV = \mu n + \dots =$$

$$\sum_i \mu_i \cdot n_i$$

$$H(S, P) = G + TS \Rightarrow G = H - TS$$

partial molar quantities:

$$\frac{\partial G}{\partial p} = V \Rightarrow \frac{\partial}{\partial p} \sum_{i=1} \mu_i \cdot n_i = \sum_{i=1} \frac{\partial \mu_i}{\partial p} \cdot n_i$$

$$= \sum_{i=1} \underbrace{v_i}_{\text{molar volume}} n_i$$

thought experiment: Adding magnesium salt

to water reduces the total volume of

the solution $\Rightarrow v_{\text{Mg}^{2+}} < 0$. The reason
is the strong solvation of Mg^{2+} ions

shrinks the space between water
molecules to bring water molecules
close to Mg^{2+} ions.