Lecture 21

Last Time: Isolated system goes to macrostate
w/ largest N (or $S = k_B \ln W$) because
it is the most probable (most microstates)
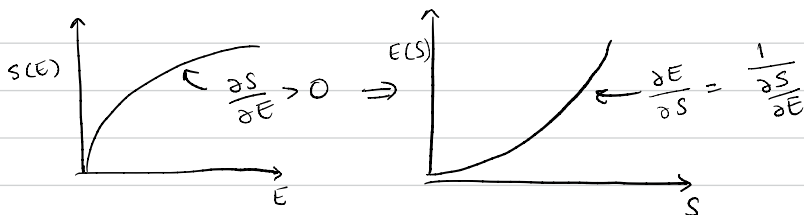- $E = $ const. 1st law
- $S(t>0) \geq S(t=0)$ or $\Delta S \geq 0$ 2nd law
- $\lim\limits_{E \to min} S = 0$ $(W=1)$ 3rd law

Ex: gas $S = nR \ln\left(\dfrac{V}{N}\right) - nR \ln(V_0)$
                        ↑
                   extensive

k_b and $R = $ conversion factors from Kelvin
to Joules or Joules per mole

Today: What is temperature T?
E increases $\Rightarrow$ $W(E)$ increases $\Rightarrow$ $S(E)$ increases

So, $S(W)$, $S(E)$, $E(S)$ are monotonically
increasing functions and they contain
equivalent information.
$\Rightarrow$ S is also a state function $S(E, V, N \dots)$
$E(S, V, n, \dots) \Rightarrow$ $dE = \dfrac{\partial E}{\partial S} dS + \dfrac{\partial E}{\partial V} dV + \dfrac{\partial E}{\partial n} dn + \dots$

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

$$dE = TdS - PdV + \mu\, dn + \dots \qquad \text{change } E \text{ by}$$

$$\underbrace{}_{\text{heat}} \quad \underbrace{}_{\text{work}} \quad \underbrace{}_{\substack{\text{free} \\ \text{energy}}} \qquad \text{changing } S, V, n, \text{ etc.}$$

or solve for S:

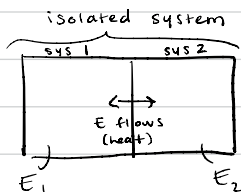$$dS = \frac{1}{T} dE + \frac{P}{T} dV - \frac{\mu}{T} dn + \dots$$

what is the meaning of the derivatives

$$T = \frac{\partial E}{\partial S}, \quad -P = \frac{\partial E}{\partial V}, \quad \mu = \frac{\partial E}{\partial n}?$$
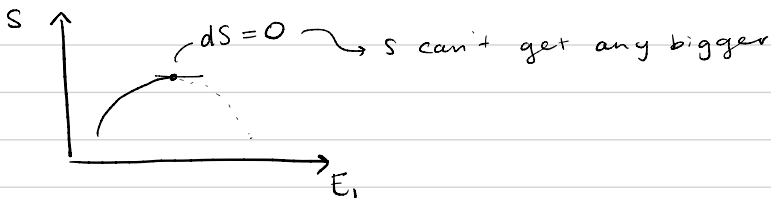
ex: temperature

$$S(E) = \text{monotonic function}$$

$$T = \frac{\partial E}{\partial S} \geq 0, \qquad \text{what does it mean?}$$

isolated system

we allow energy = "heat" to flow b/t sys 1 & 2

sys 1 + sys 2 are isolated

$$dE = dE_1 + dE_2 = 0$$

$dS = 0 \rightsquigarrow$ S can't get any bigger

$$\Rightarrow \quad dS = 0 = \left(\frac{\partial S_1}{\partial E_1}\right) dE_1 + \left(\frac{\partial S_2}{\partial E_2}\right) dE_2$$

equilibrium

$$= \frac{1}{T_1} dE_1 + \frac{1}{T_2} dE_2 \qquad dE_1 = -dE_2$$

$$= \frac{1}{T_1} dE_1 - \frac{1}{T_2} dE_1$$

$$= \left(\frac{1}{T_1} - \frac{1}{T_2}\right) dE_1 = 0$$

$\frac{\partial S}{\partial E_1} = 0$ at eq. $\quad \Rightarrow \quad \frac{1}{T_1} = \frac{1}{T_2} \quad \Rightarrow \quad T_1 = T_2$

"Temperature is the thing that's equal on both sides when heat is allowed to flow."

On Hwk: "pressure is the thing that's equal on both sides when volume is allowed to change."

"Chemical potential is the thing that's equal on both sides when particles are allowed to flow."