Lecture 27

Last Time: const E v. const T

$$S = R \ln W \iff -\frac{F}{T} = R \ln Z$$

F → macro world

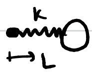
Ex: gas $E_j = \frac{h^2 j^2}{8 m L^2}$ $Z = \sum W_j e^{-E_j/RT}$

$$\Downarrow$$

$$Z(T) = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} \cdot V$$

$$\Downarrow$$

$$E = \frac{3}{2} nRT \quad \text{or} \quad \frac{E}{3n} = \frac{1}{2} RT$$ } energy per degree of freedom or "equipartition"

Ex: spring  $F = kL$

$$\rightarrow L^2 = \frac{-F}{k} = \frac{+RT}{k} \ln Z$$ { broadens X-ray of proteins

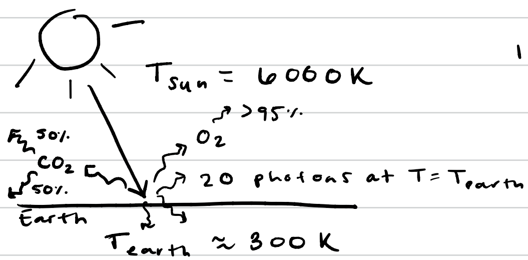
today: reactions, ΔG, and mass action law (Part 1)

We saw $S_{tot}(t>0) \geq S_{tot}(t=0)$ or $dS_{tot} \geq 0$ when E, V = constant.

What happens when T = constant? (and P = const)

Ex: heat trapping by earth's atmosphere (HWK S5.1)

1ν (6000 K $\sim \lambda = 500$ nm) $\rightarrow$ 20ν (300K $\sim \lambda \approx$ IR)



1 solar photon $\longrightarrow$ $N = \frac{6000}{300}$

$= 20$ IR photons

HW 5.2 : Photons are like gas particles in a box.

Use $E = mc^2 \Rightarrow Z(T) = \left(\frac{kT}{ch}\right)^3 V$

So for 1 solar photon:

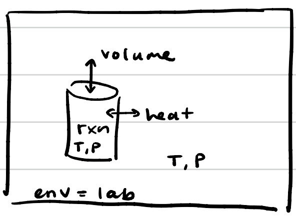
$$\underset{\text{per } m^3}{Z(T)} = 8\pi \left(\frac{k_B \cdot 6000K}{ch}\right)^3 \simeq 2 \times 10^{18}$$ microstates per cubic meter

So for 20 earth photons:

$$\underset{\text{per } m^3}{Z(T)} = \left[8\pi \left(\frac{k_B \cdot 300K}{ch}\right)^3\right]^{20} \frac{1}{20!} = 10^{288}$$ microstates per cubic meter

Making thermal photons (thermal energy) out of solar photons is a very spontaneous process.

Let's formulate this in terms of an extensive (additive) quantity.



S is additive

$S_{TOT} = S_{rxn} + S_{env}$

$dS_{TOT} = dS_{rxn} + dS_{env} \geq 0$ spontaneous process / equilibrium

$$\underbrace{dS_{env} = \frac{dH_{env}}{T}}_{E \text{ conservation}} = -\frac{dH_{rxn}}{T}$$

$$\Rightarrow dS_{TOT} = dS_{rxn} - \frac{dH_{rxn}}{T} \geq 0$$

$$-T\,dS_{TOT} = dH_{rxn} - T\,dS_{rxn} \leq 0$$ (at const T, P)

$$= dG_{rxn} \leq 0$$