Last time: more "laws" at const T

Gas: $-\frac{F}{RT} = \ln Z + E_n = \frac{h^2 n^2}{8mL^2}$ "degree of freedom" x, y, z

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

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

One more example:
Diatomic molecule: how much does it "jiggle" at a given temperature T?

$\begin{cases} E_n = h \cdot \nu \cdot n \text{ (referencing } E_0 = 0) \\ E = TS - fL \quad \left\{ \Rightarrow Z = \sum e^{-E_n/kT} \right. \end{cases}$

$F = k \cdot L$ force constant

$\frac{\partial E}{\partial S}$ $\frac{\partial E}{\partial L}$

$= \sum e^{-h\nu/RT \cdot n}$

Also $F = E - TS \Rightarrow F = -fL = -kL^2 = \frac{1}{1 - e^{-h\nu/RT}}$

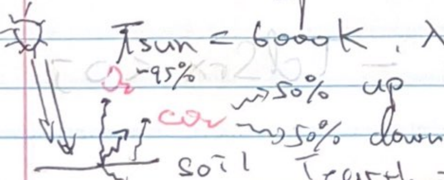
$\Rightarrow L^2 = -F/k = \frac{RT}{k} \ln Z$ For a isolated spectroscopy process (E, V = constant)

Today: $Z(T)$ vs $G(T)$; mass-action law, part I

we see $S_{tot}(t>0) > S_{tot}(t=0)$ or $dS_{tot} > 0$

let's see what happen when T, P = constant

ex: HWK 5.5.1 - heat trapping in the atmosphere



$T_{sun} = 6000K$, $\lambda_{sun} \approx 500$ nm, 1 solar photon ≈ 20 thermal photons

$T_{earth} = 300K$

HWK 5.5.2: photone are just like particle in a box.

$$Z(T) = 8\pi \left(\frac{k_B T}{ch}\right)^3 \cdot V$$

is the number of microstate of photon at temperature T in volumn V per unit volume.

So for 1 photon at 6000 K per unit volume.

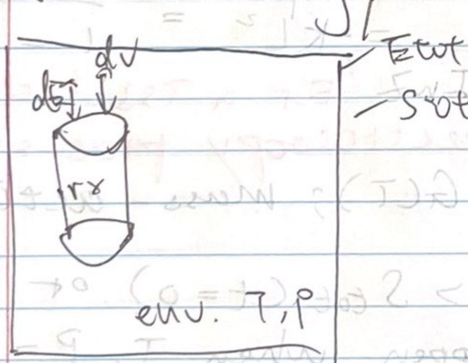
$$Z(T) = 8\pi \left(\frac{k_B \cdot 6000k}{ch}\right)^3 \simeq 2 \cdot 10^{18}\ m^{-3}$$

For 20 thermal photon.

$$Z(T) = \left[8\pi \left(\frac{k_B \cdot 300k}{ch}\right)^3\right]^{20} \Big/ 20! \simeq 10^{288}\ m^{-3}$$

⇒ making 20 thermal photons out of 1 solar photon is very sponteneous!

Let's formulate this in terms of Free energy:



$$dS_{tot} = \underbrace{dS_{rx}}_{>0} + dS_{env}$$

$$dS_{env} = \frac{dH_{env}}{T}$$ at constant P.

$$= -\frac{dH_{rx}}{T}$$ (E conservation

$$\Rightarrow dS_{tot} = dS_{rx} - \frac{dH_{rx}}{T} > 0;$$

multiply by $(-T)$

$$\Rightarrow -T\,dS_{tot} = dH_{rx} - T\,dS_{rx} < 0;$$

at const. T

$\Rightarrow -T\,dS_{tot} = dG_{rx} < 0$ for a ~~sponeneous~~ sponteneous rx.