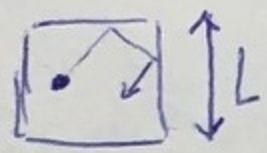


L27: review

(Exam: 31.5 ± 7.5 out of 40)

* Deriving properties of sys. using quantum instead of classical equations

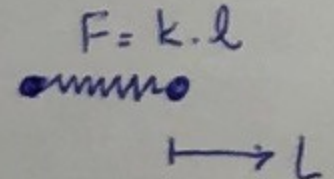
$$* Z = \sum_j w_j e^{-E_j/RT}$$

1) particle in box: 

$$E_{j_x, j_y, j_z} = \frac{h^2}{8mL^2} (n_x^2 + n_y^2 + n_z^2) \Rightarrow Z = \left(\frac{2\pi mk_B T}{h^2} \right)^{3/2} \cdot V$$

$\Rightarrow E = \frac{3}{2} nRT$ for n moles of particles;

(Equipartition: $\frac{1}{2} k_B T$ of energy per active degree of freedom)

2) Spring : $E_n = \hbar \omega n$ (subtracting off zero point energy)

$$\Rightarrow Z = \frac{1}{1 - e^{-\frac{\hbar \omega}{k_B T}}} \Rightarrow L_{rms} = \sqrt{\frac{k_B T}{k}} \cdot Z$$

k is force constant, L_{rms} is "root mean square or random displacement"

note that for both systems as $T \rightarrow \infty$, $Z \rightarrow \infty$ and as $T \rightarrow 0$, $Z \rightarrow 1$.

Today: $S_{tot}(t > 0) > S_{tot}(t = 0)$ for

spontaneous process (P1)

or

$dS_{tot} > 0$ (E, V, \dots constant)

Question: what is the equivalent of

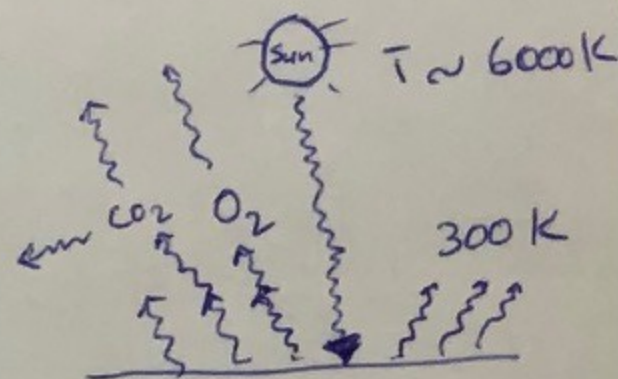
$dS_{tot} > 0$ for a system at const. T, P ?

HWK 5.1 & 5.2:

As light energy of sun is being absorbed it is either

stored as chemical form (bond energy) or dissipated off as radiation. For example,

the earth surface with $T = 300K$ emits IR photons that have energy of $\frac{1}{20}$ of photons from sun.



$$Z_{\text{photon}} \sim \left(\frac{k_B T}{c h} \right)^3$$

↓
per unit volume

In-class problem: how spontaneous?

$$Z_{\text{photon}} = 8\pi \left(\frac{k_B T}{hc} \right)^3$$

$$1) T = 6000\text{K}, N = 1 \Rightarrow Z_1 \sim 10^{18} \quad 20$$

$$2) T = 300\text{K}, N = 20 \Rightarrow Z_2 = \frac{Z_{\text{one photon}}}{20!} \approx 10^{270}$$

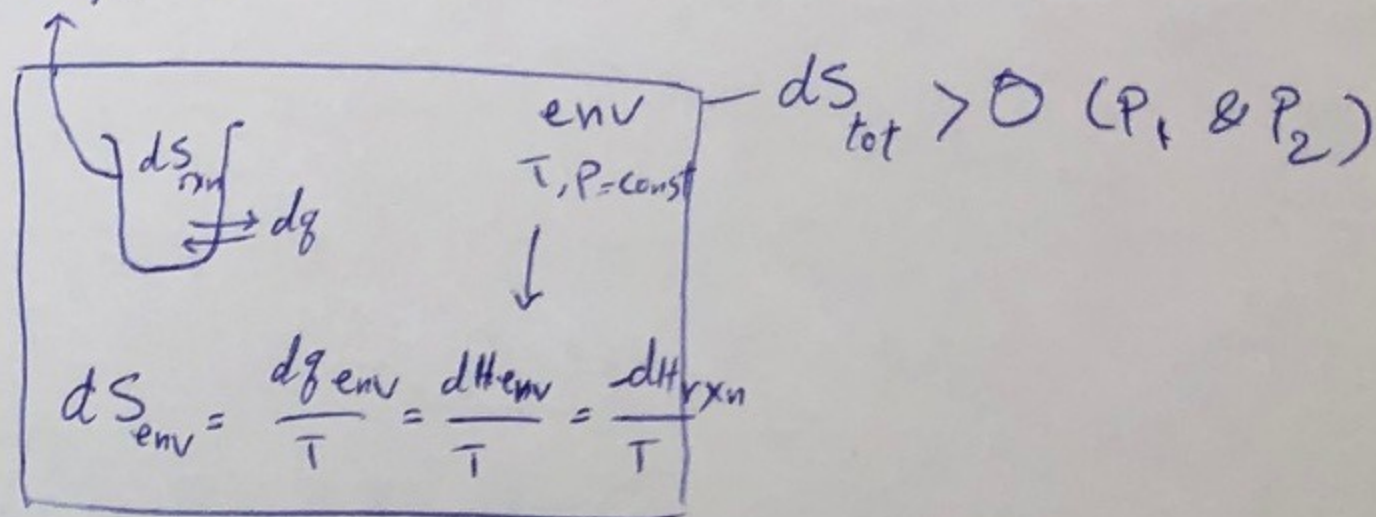
$\Rightarrow \frac{Z_2}{Z_1} \approx 10^{252} \Rightarrow 20$ IR photons have a much higher entropy than 1 visible/UV photon from sun.

O_2 and CO_2 in the atmosphere:

oxygen does not interact with IR photons so Z remains unchanged but CO_2 absorbs IR and re-emits photons with lower energies so Z increases.

Now getting back to the question mentioned on page 2...

Sys:



$$ds_{\text{tot}} = ds_{\text{rxn}} + ds_{\text{env}} > 0 \quad (\text{spontaneous process})$$

$$= ds_{\text{rxn}} - \frac{dH_{\text{rxn}}}{T} > 0$$

In the second line, ds_{tot} is written only as functions of system variable s (i.e. S_{rxn} and H_{rxn}).

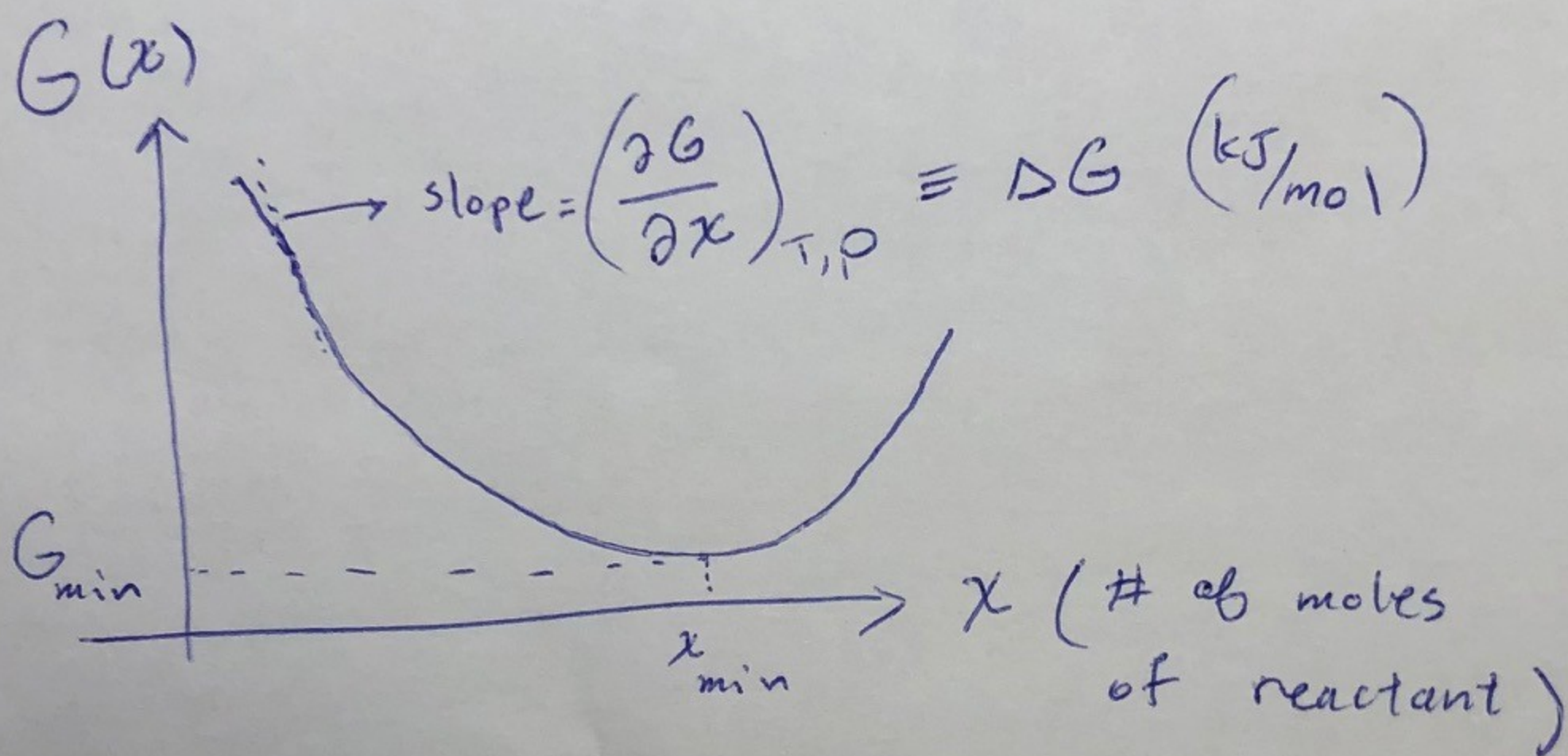
multiply by T \Rightarrow

$$-T ds_{\text{tot}} = dH_{\text{rxn}} - T ds_{\text{rxn}}$$

also: ~~$G = H - TS$~~ $G = H - TS \Rightarrow dG = dH - T ds$ \Rightarrow next page

$$-TdS_{\text{tot}} = dG_{\text{rxn}} < 0$$

Const
T & P: Thus, instead of maximizing S_{tot} we can minimize G_{rxn} . The advantage of G_{rxn} over S_{tot} is that G_{rxn} only depends on system variables.



note that ΔG of a chemical reaction is simply the slope of $G-x$ plot at a given x .

