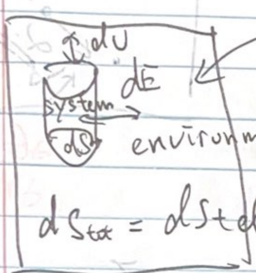
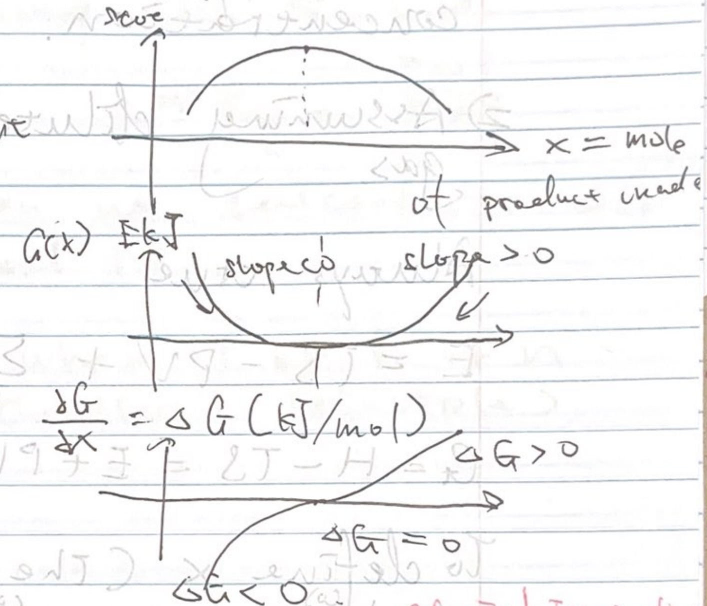
(See Youtube "Carl Sagan ~~G Ferry~~ green House")

Last Time: | $\gamma_{solar} \rightarrow 20\ \gamma_{thermal}$ | ↗ up, ↘ down

what is G & & ΔG — system or reaction.

$dS_{tot} > 0 \overset{\text{constant } T, P}{\Longrightarrow} -T\,dS_{tot} = dG < 0$





stoichiometric coefficient

Today: the mass action law $\Delta G(x) = ?$

consider the reaction $\nu_A A + \nu_B B + \dots \rightleftharpoons \nu_C C + \nu_D D$

or $\sum_i \nu_i X_i = 0$

$\begin{cases} \nu_i > 0 & \text{for product} \\ \nu_i < 0 & \text{for reactant} \end{cases}$

what we know from stat mech:

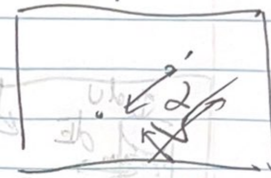
① Our molecules move randomly in the reaction container.

$S_i = S_i^{(0)} + R \ln \frac{V}{n_i}$ (one mole).

$= S_i^{(0)} - R \ln c_i$ ← n_i / V.

② Enthalpy is independent of concentration.

⇒ Assuming dilute or gas.



$\frac{\partial G_i}{\partial n_i}$

Always true

$E = TS - PV + \sum_i u_i n_i + \ldots$

$G = H - TS = E + PV - TS$

} $G = \sum_i u_i n_i$; $u_i = h_i - Ts_i$

To define x (the "reaction progress")
$n_i = n_i^{(0)} + x \cdot \nu_i$; $n_i^{(0)}$ is the number of moles of X_i at the start of the rx.

$\Rightarrow G(x) = \sum_i u_i (n_i^{(0)} + \nu_i x)$.

$\Rightarrow \frac{\partial G}{\partial x} = \Delta G \left(\frac{kJ}{mol}\right) = \sum_i u_i \nu_i$.

$\Rightarrow \Delta G = \sum_i (h_i - Ts_i) \nu_i$; inserting our info ① & ②

$\approx \sum_i (h_i^{(0)} - Ts_i^{(0)} + RT \ln c_i) \cdot \nu_i$

$= \sum_i (h_i^{(0)} - Ts_i^{(0)}) \nu_i + RT \ln c_i^{\nu_i}$ ← $a \ln x = \ln x^a$; $\prod c_i^{\nu_i}$

$\Delta G = \Delta G_0 + RT \ln Q$

Thus $\Delta G = \frac{\partial G}{\partial x} \geq 0$ if

$$\Delta G^{(0)} = -RT\ln Q \Rightarrow Q = e^{-\frac{\Delta G^{(0)}}{RT}} = K_{eq}$$

$$= \frac{[C]^{\nu_C}[D]^{\nu_D}}{[A]^{\nu_A}[B]^{\nu_B}}.$$

ex: protein folding $1 \cdot F \rightleftharpoons 1 \cdot U$

$$\Rightarrow K_{eq} = \frac{[U]}{[F]}$$

Next ~~Time~~ time: can we calculate $\Delta G^{(0)}$ using QM P1 and P2.

What happened when T or P or n change. (Le Chetelier's principle).