L28: review

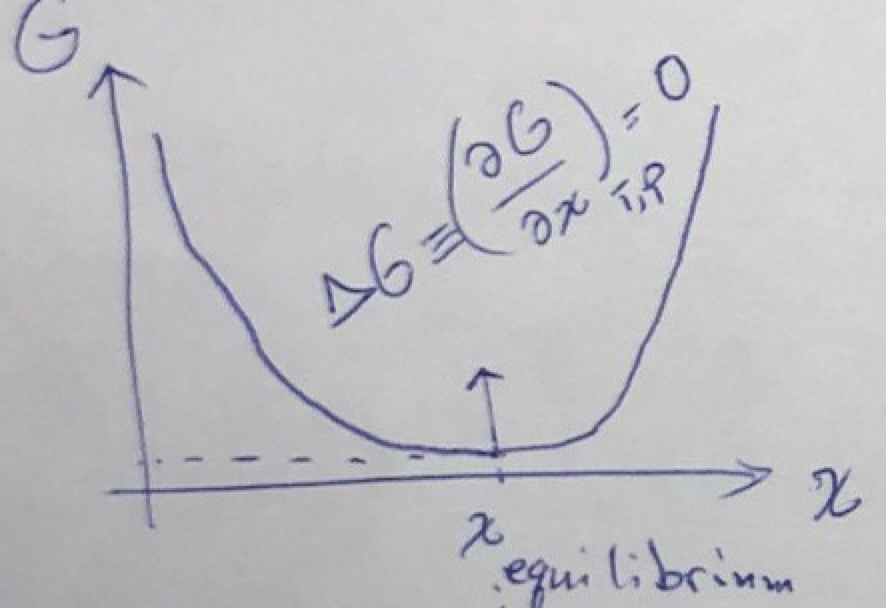
$S_{tot}(t>0) > S_{tot}(t=0)$

OR

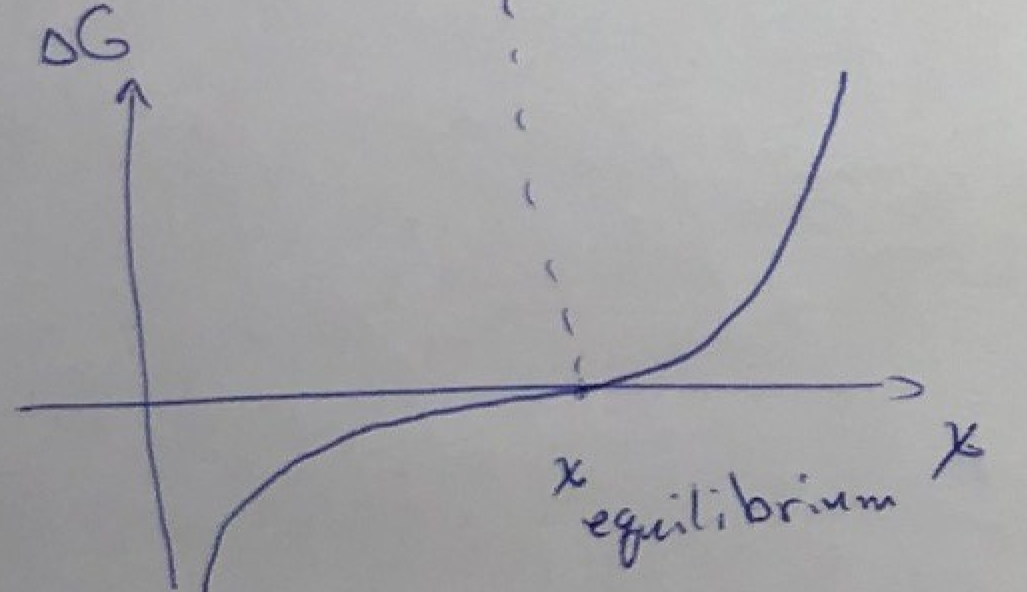
$dS_{tot} > 0$

At const. T & P: $dS_{tot} = -dG_{rxn} > 0$

At const. T & V: $dS_{tot} = -dF_{rxn} > 0$



ΔG: kJ/mol



$\Delta G < 0$: spontaneous rxn

$\Delta G = 0$: equilibrium

$\Delta G > 0$: reverse rxn

Today: concentration dependence of ΔG

general rxn:

$$\nu_A A + \nu_B B + \cdots \rightleftharpoons \nu_C C + \nu_D D + \cdots$$

OR

$$\sum_i \nu_i X_i = 0 \; ; \quad \nu_i \text{ is negative for reactants. } \nu_i \text{ positive for products}$$

~~reaction turnover~~
~~For example, x = 1 mol if ν_A mol of A is consumed and ν_C mol of C is produced~~

Assumptions:

① $S = S^\circ + R \ln V = S^\circ - R \ln c$

② $h = h^\circ$

$E = TS - PV + n\mu$

$G = E - TS + PV$

$G_{rxn} = \sum_i n_i \mu_i$

$n_i = n_i^\circ + \nu_i x$

$\Rightarrow G_{rxn} = \sum_i (n_i^\circ + \nu_i x)\mu_i$

reaction progress (moles)

$\Rightarrow \Delta G_{rxn} = \left(\frac{\partial G_{rxn}}{\partial x}\right)_{T,P} = \sum_i \nu_i \mu_i \; ; \; \mu_i = h_i - Ts_i$

$$\Rightarrow \Delta G_{rxn} = \sum_i \nu_i (h_i - Ts_i) = \sum_i \nu_i h_i - T\sum_i \nu_i s_i$$

$$s = s^\circ - R \ln c \, ; \quad h = h^\circ$$

$$\Delta G_{rxn} = \sum_i \nu_i h_i^\circ - T \sum_i \nu_i (s^\circ - R \ln c)$$

$$= \sum_i \nu_i \mu_i^\circ + RT \sum_i \nu_i \ln c_i$$

where $\mu_i^\circ = h_i^\circ - T s_i^\circ$

$$\boxed{\Delta G_{rxn} = \Delta G_{rxn}^\circ + RT \ln Q}$$

"Mass action law"

where $Q \equiv \prod_i c_i^{\nu_i} = \dfrac{c_C^{C} \cdot c_D^{D} \cdots}{c_A^{A} \cdot c_B^{B} \cdots}$

mass action

* the "o" in ΔG_{rxn}° denotes standard conditions. The standard conditions are defined as: $T^\circ \equiv 298\,K$

$P^\circ \equiv 1\,atm$

$c^\circ \equiv 1\,M$ (ideal solution)

At equilibrium: $\Delta G = 0$

$$\Rightarrow 0 = \Delta G_{rxn}^\circ + RT \ln Q_{eq}$$

$$K_{eq} \equiv Q_{eq} = e^{-\frac{\Delta G_{rxn}^\circ}{RT}}$$

$\downarrow$

equilibrium constant