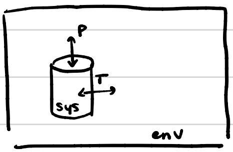
Lecture 28

Last Time: $S_{TOT} \rightarrow G$

$$G = H - TS \Rightarrow dG = dH - TdS - S\cancel{dT}$$

(0 at const T)



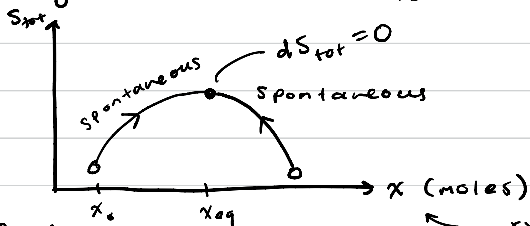
$$dS_{tot} = dS_{env} + dS_{sys} \geq 0$$

$dS_{env} \rightarrow \frac{dH_{env}}{T}$ (at const P) $\rightarrow \frac{-dH_{sys}}{T}$ (energy conservation)

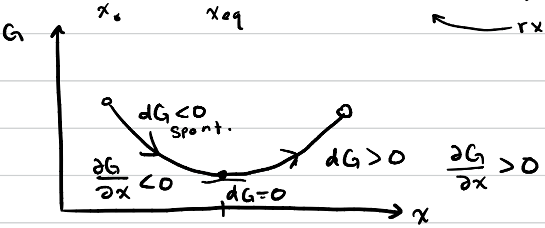
$$\Rightarrow dS_{tot} = -\frac{1}{T} dH + dS \geq 0$$ (dropping "sys" subscript)

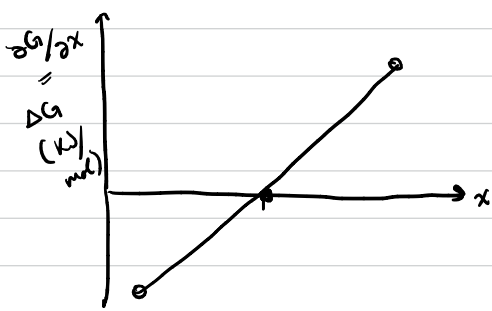
$$\Rightarrow T\,dS_{tot} = dH - TdS = dG \leq 0$$ at const T, P

Today: mass action law: what is ΔG (kJ/mol K)



← rxn progress in moles of reactant used





If the forward rxn is not spontaneous, then the backward rxn. is.

Formula for $\Delta G = \frac{\partial G}{\partial x}$ (kJ/mol)

1) the rxn:

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

$$0 \rightleftharpoons -\nu_A A - \nu_B B + \nu_C C + \nu_D D + \ldots$$

$$\Rightarrow \sum_i \nu_i A_i \quad \begin{cases} \nu_i < 0 & \text{if } A_i \text{ is reactant} \\ \nu_i > 0 & \text{if } A_i \text{ is product} \end{cases}$$

$$n_i = n_i^{(0)} + x\,\nu_i$$

(n_i: # of mols of A_i; $n_i^{(0)}$: at start of rxn; x: reaction progress in mols; ν_i: stoich. coeff.)

2) The free energy:

$$E = TS - PV + \sum_i \mu_i n_i \; ; \quad G = H - TS = E + PV - TS$$

$$\Rightarrow G = \sum \mu_i n_i$$

(μ_i: chemical potential = molar free energy)

$$= \sum_i \mu_i \left(n_i^{(0)} + \nu_i x\right)$$

$$\Rightarrow \Delta G = \sum_i \mu_i \nu_i \quad \text{(kJ/mol)}$$

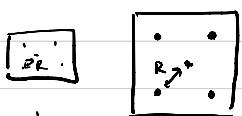
3) The molar free energy of substance A_i

$$G = H - TS \Rightarrow \mu_i = h_i - T s_i$$

(h_i: molar enthalpy; s_i: molar entropy)

Let's think about the concentration dependence of h_i and s_i:

h: $h_i \approx h_i^{(0)}$ (approx const.)



dilute gas or solution, then R is on average large enough that h_i does not depend on concentration

s: $$S = n_i R \ln\left(\frac{V}{n_i}\right) + \text{const.}$$

$$= -n_i R \ln(c_i) + \text{const.} \quad \left(\text{bc } c_i = \frac{n_i}{V}\right)$$

$$s_i = \frac{S}{n_i} = -R \ln(c_i) + \text{const.}$$

$$= -R \ln(c_i) + s_i^{(0)}$$

4) Combine into mass action law:

$$\Rightarrow \Delta G = \sum_i \mu_i \nu_i$$

$$\approx \sum_i \left(h_i^{(0)} - T s_i^{(0)} + RT \ln(c_i)\right) \nu_i$$

$$= \underbrace{\sum_i \left(h_i^{(0)} - T s_i^{(0)}\right)\nu_i} + RT \sum_i \nu_i \ln c_i$$

$$= \Delta G^{(0)} + RT \ln Q \qquad \text{w/ } Q = \prod_i c_i^{\nu_i}$$

$(a \ln b + c \ln d = \ln b^a + \ln d^c = \ln(b^a d^c))$

Mass action law:

$$\Delta G = \Delta G^{\circ} + RT \ln Q$$

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

Rxn stops when $\frac{\partial G}{\partial x} = \Delta G = 0$

$$0 = \Delta G^{(0)} + RT \ln Q$$

at eq: $Q = e^{-\Delta G^{(0)}/RT} = K_{eq}$