

Connecting Chemical Equilibrium to Stat. Mech

①

Review of the basics: Consider the reaction



← equilibrium concentrations

$$K_{eq} = \frac{[C]}{[A][B]^2}$$

We know from general chemistry that K_{eq} is related to ΔG one of the thermodynamic free energies.

$G(T, P, N_A, N_B, N_C)$ = Gibbs free energy, fixed T & P

$A(T, V, N_A, N_B, N_C)$ = Helmholtz free energy, fixed T & V

$$dA = \left(\frac{\partial A}{\partial T}\right) dT + \left(\frac{\partial A}{\partial V}\right) dV + \left(\frac{\partial A}{\partial N_A}\right) dN_A + \left(\frac{\partial A}{\partial N_B}\right) dN_B + \left(\frac{\partial A}{\partial N_C}\right) dN_C$$

↑ exact differential ↑ all the things A can depend on

$$dA = -SdT - p dV + \mu_A dN_A + \mu_B dN_B + \mu_C dN_C$$

If we hold the reaction volume & temperature fixed
(which should be the case at equilibrium), $dV = dT = 0$

$$\therefore dA = \mu_A dN_A + \mu_B dN_B + \mu_C dN_C$$

Now, in a reaction, the number of particles is tied together

$$dN_A = -dN_C \quad \leftarrow \text{everytime we lose an A, we gain a C}$$

$$dN_B = -2dN_C \quad \leftarrow \text{everytime we lose 2 B's we gain a C}$$

$$\begin{aligned} \therefore dA &= \mu_A dN_A + \mu_B dN_B + \mu_C dN_C \\ &= (-\mu_A - 2\mu_B + \mu_C) dN_C \end{aligned}$$

(2)

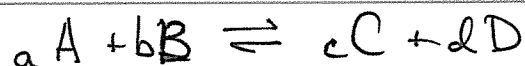
At equilibrium, the free energy is minimized with respect to the number of particles; so $\left(\frac{\partial A}{\partial N_i}\right) = 0$

$$\therefore \mu_A + 2\mu_B = \mu_C$$

(A similar treatment works with G if we fix T & P .)

What this tells us is that the thermodynamic variable that predicts equilibrium is the chemical potential.

A more general reaction:



or

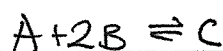
one-sided reaction:

$$0 = cC + dD - aA - bB$$

$$0 = \sum_i \nu_i \mu_i$$

ν_i symbol for compound.
 ν_i stoichiometric coefficient for compound i

example:



$$0 = C - A - 2B$$

$$\nu_A = -1$$

$$\nu_B = -2$$

$$\nu_C = +1$$

We can also define a variable for the extent of reaction

$$dN_i = \nu_i d\lambda$$

λ extent of reaction

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Some can express dA in terms of the extent variable:

$$\begin{aligned} dA &= \sum_i \left(\frac{\partial A}{\partial N_i} \right) dN_i \\ &= \sum_i \mu_i dN_i \\ &= \sum_i \mu_i \nu_i d\lambda = \left(\sum_i \mu_i \nu_i \right) d\lambda \end{aligned}$$

Generally, at equilibrium A is minimized with respect to the extent of the reaction: $\left(\frac{\partial A}{\partial \lambda} \right) = 0$
So we have:

$$\boxed{\sum_i \mu_i \nu_i = 0}$$

Now, to connect this up with Stat. Mech., let's consider a mixture of our reactants & products $A+B+C+D$

$$\begin{aligned} Q &= Q_A Q_B Q_C Q_D \\ &= \frac{q_A^{N_A}}{N_A!} \cdot \frac{q_B^{N_B}}{N_B!} \cdot \frac{q_C^{N_C}}{N_C!} \cdot \frac{q_D^{N_D}}{N_D!} \end{aligned}$$

Also:

$$A = -k_B T \ln Q$$

And

$$\mu_i = \left(\frac{\partial A}{\partial N_i} \right)_{V,T}$$

So: $\mu_A = \left(\frac{\partial A}{\partial N_A} \right) = -k_B T \left(\frac{\partial \ln Q}{\partial N_A} \right) = -k_B T \frac{\partial}{\partial N_A} [N_A \ln q_A - \ln N_A!]$

We can show that:

$$\mu_A = -k_B T \ln \frac{q_A}{N_A}$$

Relating this to our equilibrium condition:

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$$\sum_i \mu_i \nu_i = 0$$

$$\nu_c \ln \left(\frac{q_c}{N_c} \right) + \nu_d \ln \left(\frac{q_d}{N_d} \right) + \cancel{\nu_a} \ln \left(\frac{q_a}{N_a} \right) + \nu_b \ln \left(\frac{q_b}{N_b} \right) = 0$$

these are positive

because C & D are products

these are negative because

A & B are reactants

If we bring back $a = -\nu_a$ $b = -\nu_b$ $c = +\nu_c$ $d = +\nu_d$

We can rearrange this expression

$$\frac{q_c^c q_d^d}{q_a^a q_b^b} = \frac{N_c^c N_d^d}{N_a^a N_b^b}$$

If we divide every quantity above by the volume,
density = concentration = $\frac{N}{V}$

We get:

$$K_c = \frac{\left(\frac{N_c}{V}\right)^c \left(\frac{N_d}{V}\right)^d}{\left(\frac{N_a}{V}\right)^a \left(\frac{N_b}{V}\right)^b} = \frac{\left(\frac{q_c}{V}\right)^c \left(\frac{q_d}{V}\right)^d}{\left(\frac{q_a}{V}\right)^a \left(\frac{q_b}{V}\right)^b}$$
$$\rightleftharpoons \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

So the equilibrium constant is derivable from
the partition functions of reactants & products

Let's do one example:

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$$K_c(T) = \frac{(q_{\text{HI}}/V)^2}{(q_{\text{H}_2}/V)(q_{\text{I}_2}/V)} = \frac{q_{\text{HI}}^2}{q_{\text{H}_2} q_{\text{I}_2}}$$

Remember:

$$q = q_{\text{trans}} q_{\text{vib}} q_{\text{rot}} q_{\text{elect}}$$

$$= \left(\left(\frac{2\pi M k_B T}{h^2} \right)^{3/2} V \frac{1}{\sigma \Theta_{\text{rot}}} \frac{e^{-\Theta_{\text{vib}}/2T}}{1 - e^{-\Theta_{\text{vib}}/T}} g_{\text{el}} e^{D_e/k_B T} \right)$$

M = total mass of the diatomic

If we put it all together we get.

$$K_c(T) = \left(\frac{m_{\text{HI}}^2}{m_{\text{H}_2} m_{\text{I}_2}} \right)^{3/2} \left(\frac{4 \Theta_{\text{rot}}^{\text{H}_2} \Theta_{\text{rot}}^{\text{I}_2}}{(\Theta_{\text{rot}}^{\text{HI}})^2} \right) \frac{(1 - e^{-\Theta_{\text{vib}}^{\text{H}_2}/T})(1 - e^{-\Theta_{\text{vib}}^{\text{I}_2}/T})}{(1 - e^{-\Theta_{\text{vib}}^{\text{HI}}/T})^2}$$

$$\times \frac{e^{-\Theta_{\text{vib}}^{\text{HI}}/2T}}{(e^{-\Theta_{\text{vib}}^{\text{H}_2}/2T})(e^{-\Theta_{\text{vib}}^{\text{I}_2}/2T})} \times e^{2D_0^{\text{HI}} - D_0^{\text{H}_2} - D_0^{\text{I}_2}/k_B T}$$

What do we need to predict K_c ?

$$\underbrace{m, M}_{\text{easy}}, \underbrace{r_0, k, D_0}_{\text{all come from gas phase spectroscopy}}$$

all come from gas phase spectroscopy