Connecting Chemical Equilibrium to Stat. Mech

Review of the basics: Consider the reaction

$$A + 2B \rightleftharpoons C$$

← 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

$$dA = -S\,dT - p\,dV + \mu_A\,dN_A + \mu_B\,dN_B + \mu_C\,dN_C$$

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

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

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

$dN_A = -dN_C$ ← everytime we lose an A, we gain a C

$dN_B = -2\,dN_C$ ← everytime we lose 2 B's we gain a C

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

$$= (-\mu_A - 2\mu_B + \mu_C)\,dN_C$$

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

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

(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:

$$aA + bB \rightleftharpoons cC + dD$$

or

One-sided reaction:

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

$$0 = \sum_i \nu_i M_i$$

ν_i: stoichiometric coefficient for compound i

M_i: symbol for compound

example:

$A + 2B \rightleftharpoons C$

$0 = C - A - 2B$

$\nu_A = -1$

$\nu_B = -2$

$\nu_C = +1$

We can also define a variable for the extent of reaction

$$dN_i = \nu_i \, d\lambda$$

λ: extent of reaction

Some can express dA in terms of the extent variable:

$$dA = \sum_i \left(\frac{\partial A}{\partial N_i}\right) dN_i$$

$$= \sum_i \mu_i \, dN_i$$

$$= \sum_i \mu_i \nu_i \, d\lambda \quad = \left(\sum_i \mu_i \nu_i\right) d\lambda$$

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 $A + B + C + D$

$$Q = Q_A Q_B Q_C Q_D$$

$$= \frac{q_A^{N_A}}{N_A!} \cdot \frac{q_B^{N_B}}{N_B!} \cdot \frac{q_C^{N_C}}{N_C!} \cdot \frac{q_D^{N_D}}{N_D!}$$

Also:

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

And

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

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

We can show that:

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

Relating this to our equilibrium condition:

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

$$\nu_c \ln\left(\frac{q_c}{N_c}\right) + \nu_D \ln\left(\frac{q_D}{N_D}\right) + \nu_A \ln\left(\frac{q_A}{N_A}\right) + \nu_B \ln\left(\frac{q_B}{N_B}\right) = 0$$

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:

$$K_c = \frac{\left(\frac{N_c}{V}\right)^c \left(\frac{N_D}{V}\right)^d}{\left(\frac{N_A}{V}\right)^a \left(\frac{N_B}{V}\right)^b} = \frac{\left(\frac{q_c}{V}\right)^c \left(\frac{q_D}{V}\right)^d}{\left(\frac{q_A}{V}\right)^a \left(\frac{q_B}{V}\right)^b}$$

$$\Sigma \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

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

Let's do one example:

$$H_2 + I_2 \rightleftharpoons 2\,HI$$

$$K_c(T) = \frac{(q_{HI}/V)^2}{(q_{H_2}/V)(q_{I_2}/V)} = \frac{q_{HI}^2}{q_{H_2}\, q_{I_2}}$$

Remember:

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

$$= \left(\left(\frac{2\pi M k_B T}{h^2} \right)^{3/2} V \frac{T}{\sigma \Theta_{rot}} \frac{e^{-\Theta_{vib}/2T}}{1 - e^{-\Theta_{vib}/T}}\, g_{e_1}\, e^{D_e/k_B T} \right)$$

M = total mass of the diatomic

If we put it all together we get:

$$K_c(T) = \left(\frac{M_{HI}^2}{m_{H_2}\, m_{I_2}} \right)^{3/2} \left(\frac{4\,\Theta_{rot}^{H_2}\,\Theta_{rot}^{I_2}}{\left(\Theta_{rot}^{HI}\right)^2} \right) \frac{\left(1 - e^{-\Theta_{vib}^{H_2}/T}\right)\left(1 - e^{-\Theta_{vib}^{I_2}/T}\right)}{\left(1 - e^{-\Theta_{vib}^{HI}/T}\right)^2}$$

$$\times \frac{e^{-\Theta_{vib}^{HI}/2T}}{\left(e^{-\Theta_{vib}^{H_2}/2T}\right)\left(e^{-\Theta_{vib}^{I_2}/2T}\right)} \times e^{2D_0^{HI} - D_0^{H_2} - D_0^{I_2}/kT}$$

What do we <u>need</u> to predict K_c?

$\underbrace{m, M}$, $\underbrace{r_0, k, D_0}$

easy — all come from gas phase spectroscopy