**Chemical Equilibrium. I.**

\[ aA + bB \rightleftharpoons cC + dD \]

**GOAL:** to calculate \( K_p \) from microscopic properties

\[ \Delta G^0 = -RT \ln K_p = cG_C^0 + dG_D^0 - aG_A^0 - bG_B^0 \]

**NEED:** \( G^0 \) for each reactant and product

\[ G = A + PV = -kT \ln Q + PV \]

\[ Q = \left( \frac{q_{\text{trans}}^N}{N!} \right) \] \( q_{\text{int}}^N \)

\[ \ln Q = \ln q_{\text{trans}}^N - \ln N! + \ln q_{\text{int}}^N \]

Stirling’s approximation: \( \ln N! \approx N \ln N - N \) (for large \( N \))

\[ \ln Q = N \ln q_{\text{trans}} - N \ln N + N + N \ln q_{\text{int}}^* e^{-\theta_{\text{vib}}/2T} \]

where \( q_{\text{int}} = q_{\text{int}}^* e^{-\theta_{\text{vib}}/2T} = q_{\text{el}} q_{\text{rot}} q_{\text{vib}}^* e^{-\theta_{\text{vib}}/2T} \)

(factor the zero-point vibrational energy out of \( q_{\text{int}} \). Shifts zero of vibrational energy to \( v=0 \))

\[ \ln Q = N \ln q_{\text{trans}} - N \ln N + N + N \ln q_{\text{int}}^* - N \theta_{\text{vib}} / 2T \]

\[ G = -NkT \ln q_{\text{trans}} + NkT \ln N - NkT - NkT \ln q_{\text{int}}^* + \frac{NkT \theta_{\text{vib}}}{2T} + PV \]

Since \( NkT = PV \) and \( \frac{Nk}{2} \theta_{\text{vib}} = E_0 \)

\[ G = -NkT \ln q_{\text{trans}} + NkT \ln N - NkT \ln q_{\text{int}}^* + \frac{Nk}{2} \theta_{\text{vib}} \]

\[ G = -NkT \ln \left( \frac{q_{\text{trans}} q_{\text{int}}^*}{N} \right) + E_0 \]
Therefore
\[ G_C^0 = -NkT \ln \left( \frac{q_C^*}{N} \right) + E_{0,C} \text{ where } q_C^* = q_{\text{trans},C} q_{\text{int},C} \]

\[ G^0 \] is G for 1 bar pressure and \( N=N_a \)

Need: \( \Delta G^0 \)
\[ \Delta G^0 = -cNkT \ln \left( \frac{q_C^*}{N} \right) + cE_{0,C} - dNkT \ln \left( \frac{q_D^*}{N} \right) + dE_{0,D} + aNkT \ln \left( \frac{q_A^*}{N} \right) \]
\[ -aE_{0,A} + bNkT \ln \left( \frac{q_B^*}{N} \right) + bE_{0,B} \]
\[ \Delta G^0 = [cE_{0,C} + dE_{0,D} - aE_{0,A} - bE_{0,B}] - RT \ln \left\{ \frac{(q_C^* / N)^c (q_D^* / N)^d}{(q_A^* / N)^a (q_B^* / N)^b} \right\} \]

Before plugging \( \Delta G^0 \) into \( \Delta G^0 = RT \ln K_p \), a word about \( E_0 \)’s...
\[ cE_{0,C} + dE_{0,D} - aE_{0,A} - bE_{0,B} = \sum_{\text{products}} pE_{0,p} - \sum_{\text{reactants}} rE_{0,R} \]

difference between sum of zero point energies of products and sum of zero point energies of reactants, where \( p,r \) are stoichiometric #’s

Since the separated atoms are the same for products as reactants...
But convention is to use dissociation energies, $D_0$, where $D_0$ is energy required to dissociate molecules into atoms, where the “zero” of energy is set at the energy of all atoms separated. So...

$$
\sum_{\text{products}} p(E_0 + \varepsilon_0) - \sum_{\text{reactants}} r(E_0 + \varepsilon_0) = \sum_{\text{products}} p(-D_0) - \sum_{\text{reactants}} r(-D_0) = -\Delta D_0
$$

So...

$$
\Delta G^0 = -\Delta D_0^0 - RT \ln \left[ \frac{(q_C^* / N)^c (q_D^* / N)^d}{(q_A^* / N)^a (q_B^* / N)^b} \right] = -RT \ln K_p
$$

($\Delta D_0^0$ means difference in dissociation energies relative to zero point energies computed at standard state.)

$$
K_p = e^{+\Delta D_0^0 / RT} \frac{(q_C^* / N)^c (q_D^* / N)^d}{(q_A^* / N)^a (q_B^* / N)^b} 
$$

where $q^*/N = (q_{\text{trans}}/N)q_{\text{int}}^*$

$$
\frac{q_{\text{trans}}}{N} = \frac{(2\pi mkT)^{3/2}}{h^3} V = \frac{(2\pi mkT)^{3/2}}{h^3} \frac{kT}{P}
$$

(specification of standard state enters here and nowhere else)

For $P = 1$ bar = $10^5$ Pa, $\Delta G^0$ (and $K_p$) will be in standard state. Standard state (i.e., specification of pressure) only appears in $q_{\text{trans}}$.

$$
q_{\text{int}}^* = \sum_i q_{\text{elec}}^{(i)} q_{\text{vib}}^{(i)} q_{\text{rot}}^{(i)}
$$

$q_{\text{vib}}^* = 1$ for atoms

For molecules,
\[ q_{vib}^* = \prod_{i=1}^{m} (1 - e^{-\theta_{vib}/T})^{-1} \] (linear: m=3n-5, non-linear: m=3n-6)
\[ q_{rot} = 1 \] for atoms

For molecules,
\[ q_{rot} = \frac{T}{\sigma \theta_{rot}} \] (diatoms, linear polyatomics)
\[ q_{rot} = \frac{\pi^{1/2} T^{3/2}}{\sigma \theta_a^{1/2} \theta_b^{1/2} \theta_c^{1/2}} \] (non-linear polyatomics)

**EXAMPLES OF CHEMICAL EQUILIBRIA**

(1) Isomerization of a non-linear molecule

\[ A \rightarrow B \] (i.e. cis-A \rightarrow trans-A)

\[ K_P = \frac{(q_B^*/N)^b}{(q_A^*/N)^a} e^{+\Delta D_0^0 / RT} = \left(\frac{q_{trans,B}^*/N}{q_{trans,A}^*/N}\right) q_{int,B}^* e^{+\Delta D_0^0 / RT} \]

Since \((q_{trans,A}^*/N) = (q_{trans,B}^*/N)\) for an isomer

\[ K_P = \frac{q_{int,B}^*}{q_{int,A}^*} e^{+\Delta D_0^0 / RT} = \frac{g_{0,B} q_{vib,B}^* q_{rot,B}^*}{g_{0,A} q_{vib,A}^* q_{rot,A}^*} e^{+\Delta D_0^0 / RT} \]

Let’s try to arrive at a “physical” understanding for what drives a reaction – for what determines \(K_P\).

Suppose \(q_{int,A}^* \approx q_{int,B}^*\) but A has a lower ground state

<table>
<thead>
<tr>
<th>reactant A</th>
<th>product B</th>
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<tbody>
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At low T, reaction will be on side of lower energy molecule. That is, almost all A because $K_p \approx 0$. As T increases, $K_p \to 1$ because $e^{+\Delta D_0^0/RT} \to 1$. So there will be equal amounts of A and B.
Suppose \( q_{\text{int}, B}^* > q_{\text{int}, A}^* \)

\[
\Delta D_0^0
\]

**STATES OF A**

**STATES OF B**

\[
K_P = \frac{q_{\text{int}, B}^*}{q_{\text{int}, A}^*} e^{+\Delta D_0^0/RT}
\]

At low T, \( e^{+\Delta D_0^0/RT} \ll 1 \) so \( K_P \ll 1 \). Equilibrium mixture consists of almost all A. As T increases \( e^{+\Delta D_0^0/RT} \rightarrow 1 \) again, but now \( K_P > 1 \) because \( q_{\text{int}, B}^* > q_{\text{int}, A}^* \). So at equilibrium at high T, there is more B than A.