5.62 Physical Chemistry II
Spring 2008

5.62 Lecture #16: Chemical Equilibrium. I.

Readings:	Hill, pp. 177-182 Maczek, pp. 77-83 Metiu, pp. 179-191

Following the treatment of equilibrium in 5.60.

$$aA + bB = cC + dD \qquad \text{A,B,C,D are all ideal gases}$$
$$\mu_i(T,p_i) = \mu_i^\circ(T) + RT\ln p_i$$

° means standard state, usually p° = 1 bar.

at equilibrium,

$$c\mu_C + d\mu_D - a\mu_A - b\mu_B = 0$$

plug in equations for each $\mu_i(T,p_i)$

$$0 = \left[c\mu_C^\circ(T) + d\mu_D^\circ(T) - a\mu_A^\circ(T) - b\mu_B^\circ(T)\right] + RT\ln\frac{p_C^c p_D^d}{p_A^a p_B^b}$$

term in [ ] is ΔG°(T).

In 5.60 we can look up values for $\Delta G_f^\circ(T)$ for each substance. In 5.62 we will use Statistical Mechanics to compute each $\mu_i^\circ(T)$.

$$0 = \Delta G^\circ(T) + RT\ln K_p(T)$$
$$K_p(T) = e^{-\Delta G^\circ(T)/RT}$$

$\mu_i^\circ(T)$ is chemical potential in units of J/mole of i. $N = N_a$. What is μ_i?

$$\left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_{j\neq i}} = \underbrace{\left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_{j\neq i}}}_{\text{more convenient in Statistical Mechanics}}$$

Both definitions of μ will give the same result. You should verify this.

Need $\mu_i^o(T)$ for i = A, B, C, D

$$A = -kT\ln Q$$

$$\mu_i = \left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_{j\neq i}} = -kT\left(\frac{\partial \ln Q}{\partial n_i}\right)_{T,V}$$

$$Q_i = \left(q_{trans,i}^{N_i}/N_i!\right)q_{int,i}^{N}$$

$$\ln Q_i = N_i \ln q_{trans,i} - N_i \ln N_i + N_i + N_i \ln q_{int,i}$$

$$\frac{\partial \ln Q_i}{\partial n_i} = \frac{\partial \ln Q}{\partial N_i}\underbrace{\frac{\partial N_i}{\partial n_i}}_{N_a} = N_a\left[\ln q_{trans,i} - \ln N_i - 1 + 1 + \ln q_{int,i}\right]$$

$$= N_a\left[\ln\left(q_{trans,i}/N_i\right) + \ln\left(q_{int}^{*}e^{-\theta_{vib,i}/2T}\right)\right]$$

$$\mu_i^o = -kTN_a\left[\ln\left(q_{trans,i}/N_a\right) + \ln q_{int,i}^{*} - \frac{\theta_{vib,i}}{2T}\right]$$

Look at the last term in the previous equation:

$$\left(-kTN_a\right)\left(-\frac{\theta_{vib,i}}{2T}\right) = +kN_a\frac{hc\omega_i}{2k} = +N_a\frac{hc\omega_i}{2} = E_{0,i}$$

$$kTN_a = RT$$

$$\mu_i^o(T) = -RT\ln\left(q_i^{*}/N_a\right) + E_{0,i}$$

We will soon need to worry about putting all chemical species into a common energy scale. This will be to set the zero of energy at all separated gas phase atoms.

Putting everything together to get ΔG°(T):

$$\Delta G^\circ(T) = \left[cE_{0,C} + dE_{0,D} - aE_{0,A} - bE_{0,B}\right] - RT\ln\left\{\frac{\left(q_C^{*}/N_a\right)^c\left(q_D^{*}/N_a\right)^d}{\left(q_A^{*}/N_a\right)^a\left(q_B^{*}/N_a\right)^b}\right\}$$

The $E_{0,i}$ in the above equation should be reinterpreted as the energy of v = 0 of species i on an energy scale shared by all of the chemical species. This is the scale where the zero of energy is set at the energy of all separated gas phase atoms.

When we do all of the bookkeeping carefully, we have

$$K_p(T) = e^{+D_0^0/RT}\left[\frac{\left(q_C^{*}/N_a\right)^c\left(q_D^{*}/N_a\right)^d}{\left(q_A^{*}/N_a\right)^a\left(q_B^{*}/N_a\right)^b}\right]$$

$$\Delta D_0^0 = cD_{0,C} + dD_{0,D} - aD_{0,A} - bD_{0,B}$$

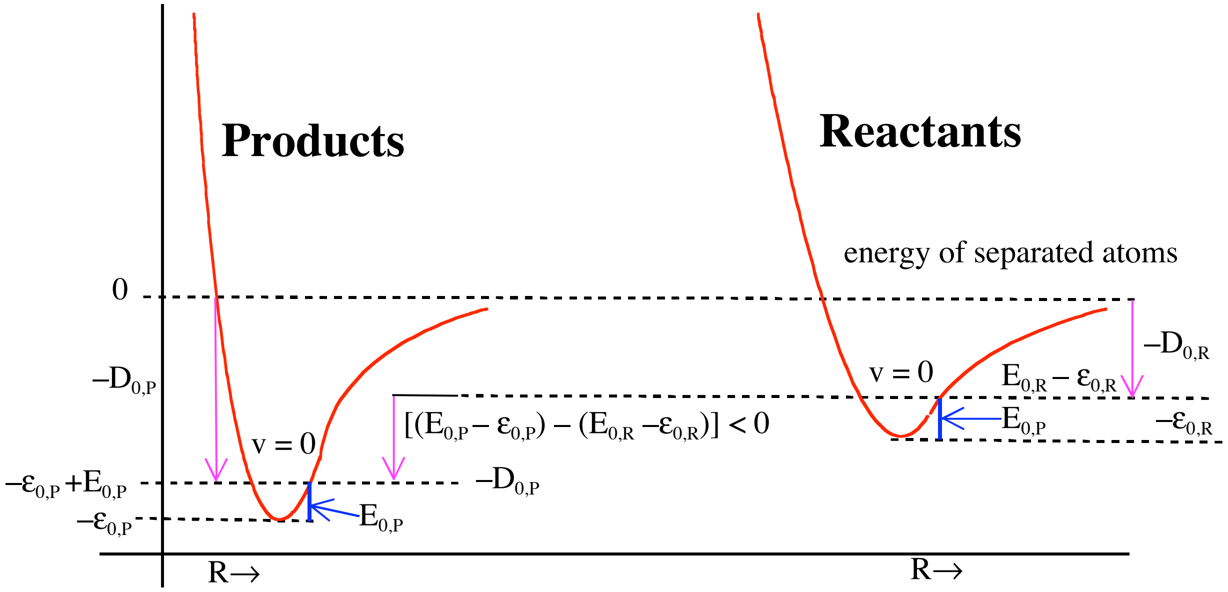
$D_{0,i}$ is the energy required to go from the v = 0 level of species i to all separated atoms.

If $\Delta D_0^0 > 0$, it means that the products have a larger total bonding energy than the reactants.

Here ° means at 0K.

If $\Delta D_0^0 > 0$ the products are more stable than reactants and the $e^{+\Delta D_0^0/RT}$ factor makes $K_p(T)$ large.

We need to put all of the zero point energies of the various products and reactants onto a common energy scale. This will be made clear by the following energy level diagram.



As drawn here, $\Delta D_0 = D_{0,P} - D_{0,R} > 0$

But convention is to use *dissociation energies*, D_0, where D_0 is energy required to dissociate a molecule into atoms, where the "zero" of energy is set at the energy of **all atoms separated**. $-\varepsilon_0$ is the energy of the minimum of the potential curve (surface) below its separated atom asymptote.

Zero of $\bar{E}$ is defined here to be at separated atoms because the same set of separated atoms is common to both $\sum$ (reactants) and $\sum$ (products). We put products and reactants onto a common $\bar{E}$ scale.

The minimum of each potential energy curve (or surface) is at $-\varepsilon_0$. Thus the zero-point ($v = 0$) level is at $-\varepsilon_0 + E_0$ (the 0 refers to the lowest electronic state). We use zero-point energies for each molecule so that we can use q_{vib}^{*} rather than q_{vib} for each molecule.

The dissociation energy, D_0, is the energy that must be added to the system to convert the molecule in its zero-point level into separated atoms ($D_0 > 0$).

$-D_0 = -\varepsilon_0 + E_0$ (The energy of the molecule in its zero-point level relative to the zero-of-energy defined at separated atoms)

For several reactants, use shorthand (r and p are stoichiometric coefficients)

$$\sum_{\text{reactants}} r\left(-\varepsilon_{0,R} + E_{0,R}\right) = \sum_{\text{reactants}} r\left(-D_{0,R}\right)$$

and for products

$$\sum_{\text{products}} p\left(-\varepsilon_{0,P} + E_{0,P}\right) = \sum_{\text{products}} p\left(-D_{0,P}\right)$$

Thus the energy difference between products and reactants in their zero-pont levels is

$$\sum_{\text{products}} p\left(-\varepsilon_{0,P} + E_{0,P}\right) - \sum_{\text{reactants}} r\left(-\varepsilon_{0,R} + E_{0,R}\right)$$

$$\sum_{\text{products}} p\left(-D_{0,P}\right) - \sum_{\text{reactants}} r\left(-D_{0,R}\right) = -\Delta D_0$$

If $\Delta D_0 > 0$, then {products} are more stable than {reactants}, as shown on the figure above. BE REALLY CAREFUL ABOUT THIS!

$$-\Delta D_0 = c\bar{E}_{0,C} + d\bar{E}_{0,D} - a\bar{E}_{0,A} - b\bar{E}_{0,B}$$

Thus

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

(ΔD_0^0 means difference in dissociation energies relative to zero point energies computed at zero Kelvin. This is usually a non-trivial quantity, thus it is essential to get its sign correct.) Divide above equation by $-RT$ and exponentiate:

$$K_p = e^{+\Delta D_0^0/RT}\left[\frac{\left(q_C^*/N\right)^c\left(q_D^*/N\right)^d}{\left(q_A^*/N\right)^a\left(q_B^*/N\right)^b}\right] \qquad \left[\text{note } +\Delta D_0^0!\right]$$

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

$$\frac{q_{trans}}{N} = \frac{(2\pi mkT)^{3/2}}{h^3}\frac{V}{N} = \frac{(2\pi mkT)^{3/2}}{h^3}\frac{kT}{\underset{\uparrow}{p}} = \frac{(2\pi m)^{3/2}}{h^3}(kT)^{5/2}\frac{1}{p}$$

specification of standard state
enters here and nowhere else.

For $p = p^0 = 1$ bar $= 10^5$ Pa, ΔG^0 (and K_p) will be in standard state. The partial pressures that appear in the equilibrium expression are in units of bar. Standard state (i.e., specification of pressure) only appears in q_{trans}. Note also, p here is the standard pressure in SI units (10^5 Pa), not the partial pressure at equilibrium of a specific chemical species.

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

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

For molecules,

$$q_{vib}^* = \prod_{\substack{j=1 \\ \text{vibrational modes}}}^{m} \left(1 - e^{-\theta_{vib}/T}\right)^{-1} \qquad \begin{matrix} m = 3n - 5 \text{ linear} \\ m = 3n - 6 \text{ non linear}\end{matrix}$$

$q_{rot} = 1$ for atoms

For molecules,

$q_{rot} = T/\sigma\,\theta_{rot}$ diatomics, linear polyatomics

$$q_{rot} = \frac{\pi^{1/2}}{\sigma}\frac{T^{3/2}}{\theta_a^{1/2}\theta_b^{1/2}\theta_c^{1/2}}$$

non-linear polyatomics (one factor of $\frac{T^{1/2}}{\theta_i^{1/2}}$ for each principal axis of rotation)

EXAMPLES OF CHEMICAL EQUILIBRIA

$\boxed{1.}$ isomerization
$\boxed{2.}$ dissociation (next time)
$\boxed{3.}$ isotope exchange (next time)

$\boxed{1}$ Isomerization of a non-linear molecule

$$A \rightarrow B \qquad \text{i.e., … cis–A} \rightarrow \text{trans–B}$$

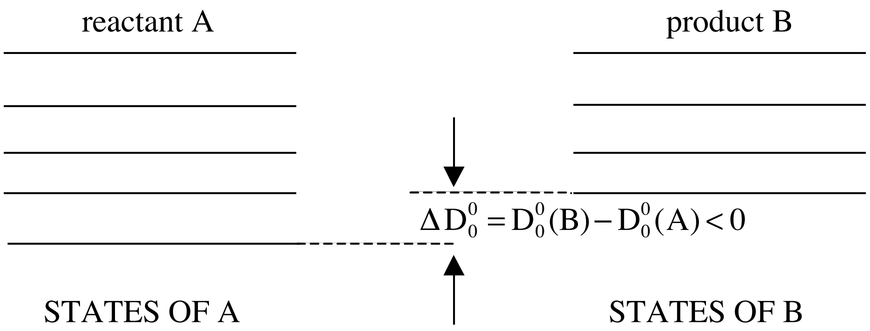
$$K_p = \frac{\left(q_B^*/N\right)^b}{\left(q_A^*/N\right)^a} e^{+\Delta D_0^0/RT} = \frac{\left(q_{trans,B}/N\right) q_{int,B}^*}{\left(q_{trans,A}/N\right) q_{int,A}^*} e^{+\Delta D_0^0/RT}$$

Since $\left(q_{trans,A}/N\right) = \left(q_{trans,B}/N\right)$ for two isomers of the same molecule (because they have same mass),

$$K_p = \frac{q_{int,B}^*}{q_{int,A}^*} e^{+\Delta D_0^0/RT} = \frac{g_{0,B} q_{vib,B}^* q_{rot,B}}{g_{0,A} q_{vib,A}^* q_{rot,A}} e^{+\Delta D_0^0/RT}.$$

Let's try to arrive at a "physical" understanding for what drives a reaction — i.e. what determines K_p.

- Suppose $q_{int,A}^* \approx q_{int,B}^*$ but A has lower energy ground state (larger dissociation energy).



$$K_p \approx e^{+\Delta D_0^0/RT}$$

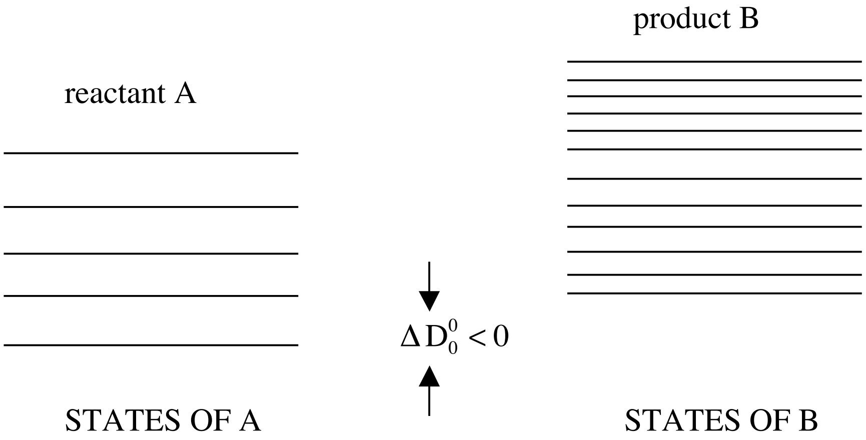
$$\Delta D_0^0 = D_{0,P}^0 - D_{0,R}^0 < 0 \qquad \text{(as drawn)}$$

$\boxed{\text{Remember this figure and definition of } \Delta D_0^0}$

At low T, equilibrium will lie toward the lower energy molecule. That is, the reaction mixture is almost all A because $K_p < 1$. As T increases, $K_p \rightarrow 1$ because $e^{+\Delta D_0^0/RT} \rightarrow 1$.

So, there will be equal amounts of A and B at $RT \gg \left|\Delta D_0^0\right|$.

- Suppose $q^*_{\text{int,B}} > q^*_{\text{int,A}}$ (and $\Delta D^0_0 < 0$, as before)



$$K_p = \frac{q^*_{\text{int,B}}}{q^*_{\text{int,A}}} e^{+\Delta D^0_0/RT}$$

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 $e^{+\Delta D^0_0/RT} \to 1$ again, but now $K_p > 1$ because $q^*_{\text{int,B}} > q^*_{\text{int,A}}$. So, at equilibrium at high T, the reaction mixture is more B than A.

Next time: dissociation, isotope exchange.

Keep in mind that K_p involves an enormous number of microscopic quantities. But many cancel, either exactly or approximately. ΔD^0_0 *is almost always the most important factor in determining* K_p.