Lecture 23  Chapter 12 Sections 1-6
Announce:
• Exam will be 3:00 – 5:00 Monday 4 November. Two people will take Tuesday so when the exam is easy, keep it to yourself.
• Seminar today. Sign up for lunch if you are interested.

Outline:

Reaction equilibrium
Extent of reaction
\(\Delta_{\text{rxn}} G\) at non-standard state
G and \(\xi\) and K and p

Review

**Gibbs phase rule**

\[ F = C - P + 2 \]

![Diagram showing phase behavior of a liquid-vapor system](image)

The vapor above an acetone water mixture is enriched in? acetone

Azeotropes demonstrate deviation from ideality.

OK, on to new stuff – back to MacQuarrie & Simon

In the past couple weeks, we have used thermodynamics to predict the direction of spontaneous change for a number of **physical processes** - phase transitions, expansion of gases, etc.
Of course, we would really like to be able to predict spontaneous change for chemical processes. So, we are going to take a close look at chemical equilibria in order to predict the quantitative conversion of reactants to products for any general chemical process.

Remember that spontaneity doesn’t say anything about rate. That we leave for kinetics, which will be our topic for much of the rest of the semester (after exam 2)

Let’s define the simplest possible reaction:
\[ \nu_A \text{A} \rightarrow \nu_B \text{B} \]

If we started with \( n_{A0} \) and \( n_{B0} \) moles of A and B then let’s define the amounts of A and B at any time…
\[
\begin{align*}
\text{n}_A &= n_{A0} - \nu_A \xi \\
\text{n}_B &= n_{B0} + \nu_B \xi
\end{align*}
\]

\( \xi \) (xi or squiggle) is the extent of reaction. It measures the progress of the reaction and has units of moles. Subtraction is because A is a reactant.

For instance: \( \text{H}_2 + \frac{1}{2}\text{O}_2 \leftrightarrow \text{H}_2\text{O} \)

At start: \( n_{\text{H}_2} \quad n_{\text{O}_2} \quad n_{\text{H}_2\text{O}} \)
Later: \( n_{\text{H}_2} - \xi \quad n_{\text{O}_2} - \frac{1}{2}\xi \quad n_{\text{H}_2\text{O}} + \xi \)

Of course, we are really interested in the change in the amount of the substances:
\[
dn_J = \nu_J d\xi \quad \text{(negative if reactant)}
\]

We can substitute this expression into our result from long ago relating the Gibbs energy to the chemical potential:
\[
dG = \sum_j \mu_j dn_j \quad \text{(jog anyone's memory? Gibbs-Duhem)}
\]

this gives:
\[
dG = \sum_j \mu_j v_j d\xi
\]

(approximately – take negative/positive signs in with coefficients)

This can be rewritten as:
\[
\left( \frac{\partial G}{\partial \xi} \right)_{p,T} = \sum_j v_j \mu_j (\xi) = \Delta_r G
\]

where \( \Delta_r G \) is the reaction Gibbs energy. This is defined for a balanced chemical equation and the reactants and products at their standard states. (add products, subtract reactants)
Let’s look at a simple case:

**Isomerization Reaction:** 11-cis retinal $\leftrightarrow$ all trans retinal

**Everyone know what this does?** vision

\[
\left( \frac{\partial G}{\partial \xi} \right)_{p,T} = \mu_{\text{trans}} - \mu_{\text{cis}}
\]

Both of these chemical potentials change as the rxn proceeds, so this differential depends on the extent of reaction.

When $\mu_A > \mu_B$, or \( \left( \frac{\partial G}{\partial \xi} \right)_{p,T} < 0 \) the reaction $A \rightarrow B$ is spontaneous ($\xi$ must increase to minimize $G$)

When $\mu_A < \mu_B$, or \( \left( \frac{\partial G}{\partial \xi} \right)_{p,T} > 0 \) the reaction $B \rightarrow A$ is spontaneous ($\xi$ must decrease to minimize $G$)

The minimum in \( \left( \frac{\partial G}{\partial \xi} \right)_{p,T} \) occurs when its value is zero, or $\mu_A = \mu_B$. This is when the reaction is at equilibrium! The reaction “stops.”

The **standard molar** reaction Gibbs energy is different than the reaction Gibbs energy because for the standard energy, the composition of reactants and products are fixed at their standards states (1 M or 1 atm), rather than an arbitrary composition:

\[
\Delta_r G^0 = v_B \mu_B^0 - v_A \mu_A^0
\]
Exergonic and endergonic reactions

$\Delta_r G < 0$: reaction is spontaneous and exergonic (work-producing); could drive other processes. e.g. ATP → ADP or glucose combustion

$\Delta_r G > 0$: reaction is not spontaneous; it is endergonic (work-consuming) e.g. ADP → ATP or electron transfer

Calculating the composition of reactions at equilibrium (what is the yield?)

If A and B are assumed to be perfect gases, we can calculate $\Delta_r G$ just as we have done before:

$\Delta_r G = v_B \mu_B - v_A \mu_A$

$\Delta_r G = v_B \mu_B^0 + RT \ln \left( \frac{p_B}{p^0} \right) - v_A \mu_A^0 + RT v_B \ln \left( \frac{p_B}{p^0} \right) - RT v_A \ln \left( \frac{p_A}{p^0} \right)$

$\Delta_r G = \left( \Delta_r G^0 + RT \ln \left( \frac{p_B}{p_A} \right) \right)$ where $\Delta_r G^0 = v_B \mu_B^0 - v_A \mu_A^0$

We will find it convenient (for more complicated reactions) to denote the argument of the logarithm as the reaction quotient, $Q$

(Terrible notation of course. $Q$ is not the partition function.)

$\Delta_r G = \left( \Delta_r G^0 + RT \ln Q \right)$

At equilibrium $\Delta_r G = 0$ and $Q$ is equal to the equilibrium constant $K$ (by definition):

$\Delta_r G^0 = -RT \ln K$

This is one of the most useful equations in chemical thermodynamics because it provides a direct relationship between all that thermodynamic data and information on how actual chemical reactions proceed.

Obviously, when $K < 1$ (the reactant is favored), $\Delta_r G > 0$ and the reaction is not spontaneous and when $K > 1$ (the product is favored), $\Delta_r G < 0$ and the reaction is spontaneous in the direction $A \rightarrow B$. 
Discussion of the general form of $G$ vs. $\xi$

If $\Delta G^0$ for a reaction is negative, the products are more thermodynamically stable than the reactants. Everyone agree? Do most reactions go all the way to products, or stop somewhere in equilibrium? Most stop short of 100 % yield. Why?

The standard molar reaction Gibbs energy ($\Delta r G^0$) does not account for the additional entropy introduced when substances are mixed together. In other words, $\Delta r G^0$ does not include contributions from $\Delta_{\text{mix}} G$.

$$\Delta_{\text{mix}} G = nRT(X_A \ln X_A + X_B \ln X_B)$$  (ignoring enthalpy contributions)

So, the minimum in $\Delta_{\text{mix}} G$ occurs when? our $A \rightarrow B$ reaction is 50 % complete. After that point, our devious friend entropy ‘fights’ the continued conversion of reactants to products.

Depending on the relative magnitudes of $\Delta r G^0$ and $\Delta_{\text{mix}} G$, the extent of reaction can vary dramatically.
Now that we have a relationship between equilibrium constants and thermodynamic data, we can calculate the extent of reactions ($\xi$) for real systems.

Use this format:

<table>
<thead>
<tr>
<th></th>
<th>$N_2O_4$ (g) $\leftrightarrow$</th>
<th>2 $NO_2$ (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial amounts</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>Equilibrium amounts</td>
<td>1 - $\xi$</td>
<td>2$\xi$</td>
</tr>
<tr>
<td>Equilibrium mole fractions</td>
<td>($1 - \xi$)/($1 + \xi$)</td>
<td>2$\xi$/($1 + \xi$)</td>
</tr>
</tbody>
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Total amount = 1 + $\xi$

(Note that in this case $\xi$ must be between 0 and 1 because of how we have set up our initial conditions in relation to the stoichiometry.)

Using Dalton’s law and neglecting non-ideal effects:

$$K_p = \frac{\text{products}}{\text{reactants}} = \frac{(P_{NO_2})^2}{(P_{N2O4})} = \frac{(X_{NO_2}P_{Tot})^2}{X_{N2O4}P_{Tot}} = \frac{[2\xi/(1 + \xi)] \times P}{[(1 - \xi)/(1 + \xi)] \times P} = \frac{4\xi^2 P}{1 - \xi^2}$$

K clearly is constant. So if p changes, $\xi$ must change to compensate!

Solving for $\xi$

$$\xi = \frac{1}{[1 + (4/K)P]^2}$$

This is an interesting result. The equilibrium constant does not depend on total pressure, but the extent of the reaction does. We will discuss this further later.

For the above reaction mixture at 1 bar total pressure and 298 K and using the equilibrium expression: $\Delta G^0 = -RT \ln K$ to calculate K ($\Delta G^0 = 4.73$ kJ mol$^{-1}$):

$$K = 0.148$$

$$\xi = 0.191$$

So at room temperature and one atmosphere pressure, only about 20% to the product gets used up. Perhaps the surprise is that any NO$_2$ gets consumed at all since $\Delta G^0$ is positive.