Lecture 22  Chapter 13 & 14 – Extent of reaction and equilibrium

Remember next exam is 1 week from Friday. Today will be last quiz before exam. GRE practice today

Outline:

- van’t Hoff
- partition function
- phase diagrams

Review

\[ \Delta_{\text{mix}} G = nRT(X_A \ln X_A + X_B \ln X_B) \]

Recall we looked at \( \text{N}_2\text{O}_4 \rightarrow 2\text{NO}_2 \)

<table>
<thead>
<tr>
<th></th>
<th>( \text{N}_2\text{O}_4 \text{ (g)} ) ( \leftrightarrow ) 2 ( \text{NO}_2 \text{ (g)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial amounts</td>
<td>1</td>
</tr>
<tr>
<td>Equilibrium amounts</td>
<td>1 - ( \xi )</td>
</tr>
<tr>
<td>Equilibrium mole fractions</td>
<td>( (1 - \xi)/(1 + \xi) )</td>
</tr>
</tbody>
</table>

\[ \text{Total amount} = 1 + \xi \]

\[ K_p = \frac{\text{products}}{\text{reactants}} = \frac{(P_{\text{NO}_2})^2}{(P_{\text{N}_2\text{O}_4})} = \frac{(X_{\text{NO}_2} P_{\text{Tot}})^2}{X_{\text{N}_2\text{O}_4} P_{\text{Tot}}} = \frac{[2\xi/(1+\xi)] \times P}{[(1-\xi)/(1+\xi)] \times P} = \frac{4\xi^2 P}{1 - \xi^2} \]

Solving for \( \xi \)

\[ \xi = \frac{1}{\left[1 + (4/K)P\right]^{1/2}} \]
OK then to clarify from last time:
The equilibrium constant is constant ONLY with respect to concentration. In the case above we are using pressure to measure concentration so \( K \) is constant \( w.r.t. \) pressure, but not Temperature.

So, when we see \( \Delta_r G^0 = -RT \ln K \) the \( \Delta_r G^0 \) must be constant; T and K both move to balance each other.

**Response of equilibria to temperature**

We can use Le Chatelier’s principle to guide what to expect for temperature dependence.

Exothermic reactions generate heat \( \rightarrow \) heat is one of the products. **So if we increase the temperature?** The equilibrium will shift to make less heat (less products).

Endothermic reactions absorb heat \( \rightarrow \) heat is a reactant. If we increase T, we can expect that the equilibrium will shift to absorb more heat (more products).

OK, so now we are going to do a little derivation in that direction. (FAST)
Recall that \( \Delta_r G^0 = -RT \ln K \)
so \( \frac{\Delta_r G^0}{T} = -R \ln K \)

Recall also that \( \Delta G = \Delta H - T \Delta S \) or \( \Delta G^0/T = \Delta H^0/T - \Delta S^0 \)
If we take a derivative wrt T:
\[
\frac{\partial}{\partial T} \left( \frac{\Delta_r G^0}{T} \right) = - \frac{\Delta_r H^0}{T^2} \quad (H^0 \text{ and } S^0 \text{ do not depend on } T)
\]
substitute for \( G^0 \).
\[
\frac{d}{dT} \left( R \ln K \right) = \frac{\Delta_r H^0}{T^2}
\]
A little cleanup gives us the **van’t Hoff** (a Dutch guy) equation:

\[
\frac{d \ln K}{dT} = \frac{\Delta_r H^0}{RT^2} \quad \text{or in a different form that is sometimes more convenient:}
\]

\[
\frac{d \ln K}{d(1/T)} = - \frac{\Delta_r H^0}{R}
\]

We can see from the first form of the van’t Hoff equation that if a reaction is exothermic (\( \Delta H < 0 \)), \( d \ln K/dT \) will be negative. Therefore as the temperature rises, K will become smaller. Similarly, if the reaction is endothermic (\( \Delta H > 0 \)), K will increase as the temperature is raised.
In fact, $\Delta H^\circ$ is often **determined** by measuring the equilibrium constant as a function of temperature.

To help these experimentalists, we need to recast the van’t Hoff equation in a way to get a linear dependence of some function of $K$ on some function of $T$.

**How do we integrate the second form of the van’t Hoff?** rearrange to get common variables on the same side of the equation and do definite integration:

\[
\int_{K_1}^{K_2} \frac{d \ln K}{R} = -\frac{1}{T} \int_{1/T_1}^{1/T_2} \Delta_r H^\circ \left( \frac{1}{T} \right)
\]

**What assumption should we make?** $\Delta_r H^\circ$ does not vary significantly with $T$.

\[
\ln K_2 - \ln K_1 = -\frac{\Delta_r H^0}{R} \times \left( \frac{1}{T_2} - \frac{1}{T_1} \right)
\]

\[
\ln K_2 = -\frac{\Delta_r H^0}{R} \frac{1}{T_2} + \left( \ln K_1 - \frac{1}{T_1} \right)
\]

Therefore, a plot of $\ln K$ vs. $1/T$ gives a slope with $-\Delta_r H^\circ/R$.

Recall that $K \rightarrow \Delta_R G$ through $\Delta_R G = -RT \ln K$.

**Therefore, we also can get what?** $\Delta S = (\Delta H - \Delta G)/T$.

So, measuring $K$ as a function of $T$ gives us all the important thermodynamic quantities!

<PAUSE>

Okay, finally, the moment you all have been waiting for... let's relate our equilibrium constant to the partition function. Let's go back and make our general reaction look slightly more complicated

\[aA + bB \rightarrow yY + zZ\]

**What should our equilibrium constant look like in terms of concentration?**

\[K_c(T) = \frac{c_Y^y c_Z^z}{c_A^a c_B^b}\]

We’ll get back to this in a minute. First, Dill showed back in chapter 11 that

\[\mu_i = -RT \ln \frac{q_i}{N_i}\]

$q$ is, of course, the molecular partition function.

Putting this together with Gibbs-Duhem and $dG = 0$ gives

\[
\frac{N_Y^y N_Z^z}{N_A^a N_B^b} = \frac{q_Y^y q_Z^z}{q_A^a q_B^b}
\]
Stop for a second and think about what this means… Draw version of Figure 13.1
Population will distribute itself among all energy states of the system according to Boltzmann, irrespective of the molecular identities.

Okay, then let’s get back to $K$. Recognizing that concentration is $N/V$

$$K_c(T) = \left( \frac{q_T}{V} \right)^y \left( \frac{q_z}{V} \right)^z \left( \frac{q_x}{V} \right)^a \left( \frac{q_y}{V} \right)^b$$

Of course $q_i = q_{\text{trans}} q_{\text{rot}} q_{\text{vib}} q_{\text{elec}}$ for each species $i$ in the chemical reaction

For the $\text{H}_2 + I_2 \rightarrow 2 \text{HI}$ reaction we have

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

the expression is (similar to example 13.2 in Dill)

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

translational rotational vibrational electronic

Where is our T dependence? Only in the vibrational and electronic parts of the expression, and the biggest contributor is vibrational part again! (With our usual approximation that $T >> \Theta_{\text{Rot}}$)

Let’s look at how $K$ changes as temp changes.
As $T$ increases, the exponential term goes toward 1 and $(1 - \text{exponential})$ goes toward zero. A big $\Theta_{\text{vib}}$ means that the $(1-\text{exp})$ term decreases more slowly. So, if reactant $\Theta_{\text{vib}} >$ product $\Theta_{\text{vib}}$ then numerator (reactant) decreases more slowly than denominator (product):

therefore, $K$ increases as $T$ increases.

Because

$$\Theta_{\text{vib}} = \hbar \nu / k_B \text{ and } \nu = 1/2\pi (k/\mu)^{1/2}$$

$\Theta_{\text{vib}}$ is proportional to $k$ (force constant)
So, if product has weaker bonds than reactant, than indeed:
\[ \Theta_{\text{vib}}^\text{reactant} > \Theta_{\text{vib}}^\text{product} \]
and K increases with temp – just like endothermic reaction – makes sense if product bonds are weak! Stronger bonds are more stable than weaker ones – weak bonds are higher in energy than strong ones.

The reverse (K decreases with increasing T) is the case for the \( \text{H}_2 + \text{I}_2 \rightarrow 2\text{HI} \) reaction, since the HI bond is modest but the I\(_2\) bond is very weak. Note that the weak I\(_2\) bond offsets the relatively strong H\(_2\) bond.

![Vibrational contributions to equilibrium constant](image)

Note that the book example uses H\(_2\) and D\(_2\) going to 2HD, so bond strengths are basically identical. The important thing then is the factor of 4 coming from rotational symmetries.

Okay then next time we’ll move into chapter 14, where we get into phase equilibria. I will not be describing his liquids lattice model today, but we will be using it in the future. So, please please please read through it carefully. It is a little long, but he explains things thoroughly I think.