Lecture 20  Chapt 13 – end.

Outline:

- K and ξ as fctn of p
- K and ξ as fctn of T
- Van’t Hoff Equation
- Statistical K

Review

ξ (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:
- \( n_{\text{H}_2} \)
- \( n_{\text{O}_2} \)
- \( n_{\text{H}_2\text{O}} \)

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

And at the end of class, we derived:

\[ \Delta_r G^0 = -RT \ln K \]

Exergonic and endergonic reactions

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

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

Discussion of the general form of \( G \) vs. \( \xi \)

If \( \Delta_r G^0 \) 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 \( \Delta_{\text{mix}} G \).
\[ \Delta_{\text{mix}} G = nRT (X_A \ln X_A + X_B \ln X_B) \]  
(sort of from Jill’s chapt 6 homework) 
(X is mole fraction, ignore enthalpy)

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.

\[ \begin{align*}
\Delta G_{\text{react}} & \quad \Delta G_{\text{Mix}} \\
\Delta G_{\text{Rxn}} & \quad \Delta G_{\text{Tot}}
\end{align*} \]

\[ \xi \]

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:

|                    | \( \text{N}_2\text{O}_4 \) (g) \| \( \text{NO}_2 \) (g) |
|--------------------|-----------------|-----------------|
| **Initial amounts**| 1               | 0               |
| **Equilibrium amounts** | \( 1 - \xi \) | \( 2\xi \) |
| **Equilibrium mole fractions** | \( (1 - \xi)/(1 + \xi) \) | \( 2\xi/(1 + \xi) \) |

(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.)

What should the equilibrium constant look like in terms of pressures?
\[ K_p = \frac{\text{products}}{\text{reactants}} = \frac{(P_{\text{NO}_2})^2}{(P_{\text{H}_2\text{O}})} \]

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

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

\( K \) should be constant (though this isn’t strictly true in all cases). So if \( p \) changes, \( \xi \) must change to compensate. **Who told us this in GenChem?** (Le Chatelier)!

Solving for \( \xi \)

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

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 \( K \) (\( \Delta G^0 = 4.73 \text{ kJ mol}^{-1} \)):

\[ K = 0.148 \]

\[ \xi = 0.191 \]

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

**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).

Recall that \( \Delta G^0 = -RT \ln K \)

so \( \frac{\Delta G^0}{T} = -R \ln K \)

Recall also that \( \Delta G = \Delta H - T\Delta S \) or \( \frac{\Delta G^0}{T} = \frac{\Delta H^0}{T} - \Delta S^0 \)
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:

$$\frac{d\ln K}{dT} = \left( \frac{\Delta_r H^0}{RT^2} \right) \text{ or in a different form that is sometimes more convenient:}$$

$$\frac{d\ln K}{d(1/T)} = -\left( \frac{\Delta_r H^0}{R} \right)$$

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, $\Delta_r H^0$ 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:

$$\int_{K_1}^{K_2} d\ln K = -\frac{1}{R} \int_{1/T_1}^{1/T_2} \Delta_r H^0 d\left( \frac{1}{T} \right)$$

**What assumption should we make?** $\Delta_r H^0$ 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 $-\Delta_r H^0/R$.
Recall that \( K \to \Delta_R G \) through \( \Delta_R G = -RT \ln K \)
\[ K(T) \to \Delta H \]

**Therefore, we also can get what?** \( \Delta S = (\Delta H - \Delta G)/T \)
So, measuring \( K \) as a functn 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

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

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

\[
K_c(T) = \frac{c_y^a c_z^b}{c_A^a c_B^b}
\]

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

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

\((q \text{ is, of course, the molecular partition functn)}\)

Putting this together with Gibbs-Duhem and \( dG = 0 \) gives

\[
\frac{N_y^a N_z^b}{N_A^a N_B^b} = \frac{q_y^a q_z^b}{q_A^a q_B^b}
\]

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 \( N/V \)

\[
K_c(T) = \left( \frac{q_y^a}{V} \right)^y \left( \frac{q_z^b}{V} \right)^z \left( \frac{q_A^a}{V} \right)^a \left( \frac{q_B^b}{V} \right)^b
\]

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 \( H_2 + I_2 \to 2 \text{ HI} \) reaction we have
\[ K_e(T) = \left( \frac{q_{HH}}{V} \right)^2 = q_{HH}^2 \]

the expression is (similar to example 13.2 in Dill)

\[ K_e(T) = \left( \frac{m_{HH}^2}{m_{H_2} m_{I_2}} \right)^{3/2} \left( \frac{4 \Theta_{rot}^H \Theta_{rot}^{I_2}}{(\Theta_{rot}^H)^2} \right) \left(1 - e^{-\Theta_{vib}^{I_2}/T}\right)(1 - e^{-\Theta_{vib}^{I_2}/T}) e^{\frac{2D_{I_2}^2 - D_{I_2}^H}{RT}} \]

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- exponential) goes toward zero. A big \( \Theta_{vib} \) means that the (1-exp) term decreases more slowly. So, if reactant \( \Theta_{vib} \) > product \( \Theta_{vib} \) then numerator (reactant) decreases more slowly than denominator (product):

therefore, K increases as T increases.

Because

\[ \Theta_{vib} = h\nu/k_B \quad \text{and} \quad \nu = 1/2\pi (k/\mu)^{1/2} \]

-> \( \Theta_{vib} \) is proportional to \( k \) (force constant)

So, if product has weaker bonds than reactant, than indeed:

reactant \( \Theta_{vib} \) > product \( \Theta_{vib} \)

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 H\(_2\) + I\(_2\) -> 2HI 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.

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.