Lecture 14 – Chapter 16, Sections 3-4
Equilibrium

• Nifty $K_{eq}$ math
  • $Q$ and $K_{eq}$
• Connection with $\Delta G$
  • Le Chatelier
Remember...

- In general for a reaction like

\[ aA + bB \leftrightarrow dD + eE \]

\[ K_{eq} = \frac{[D]_eq^d [E]_eq^e}{[A]_eq^a [B]_eq^b} \]
**K_{eq}s can be combined**

• Suppose we have a 2-step reaction

  step 1: \[2\text{NO}_2 \rightarrow \text{NO}_3 + \text{NO}\]

  step 2: \[
  \text{NO}_3 \rightarrow \text{O}_2 + \text{NO}
  \]

  Overall: \[2\text{NO}_2 \rightarrow 2\text{NO} + \text{O}_2\]

• Add reactions to get overall reaction… multiply K_{eq}s

  \[
  K_{eq1} = \frac{p_{NO_3} p_{NO}}{(p_{NO_2})^2}
  \]

  \[
  K_{eq2} = \frac{p_{O_2} p_{NO}}{p_{NO_3}}
  \]

  \[
  K_{eq,tot} = \frac{p_{NO_3} p_{NO}}{(p_{NO_2})^2} \cdot \frac{p_{O_2} p_{NO}}{p_{NO_3}} = \frac{p_{O_2} (p_{NO})^2}{(p_{NO_2})^2}
  \]
Compare Q and K

• Q and K are constructed the same way
  – Q is true at all concentrations/pressures
  – At equilibrium, Q is equal to the value of K

• Comparing Q and K tells us which direction a rxn will go
  – If Q < K (numerator too small) make products
  – If Q = K (just right) equilibrium
  – If Q > K (numerator too big) make reactants
So if $Q > K_{eq}$, can we say anything about $\Delta G_{rxn}$ at these conditions?

| 25% | 1. Yes, $\Delta G_{rxn}$ must be $< 0$ |
| 25% | 2. Yes, $\Delta G_{rxn}$ must be $= 0$ |
| 25% | 3. Yes, $\Delta G_{rxn}$ must be $> 0$ |
| 25% | 4. No, don’t talk to me about $\Delta G_{rxn}$ |
$K_{eq}$ and $\Delta G$ are connected

- Recall from Chapter 14

\[
\Delta G_{rxn} = \Delta G^\circ_{rxn} + RT \ln Q
\]

- If we are equilibrium, then…

\[
\Delta G_{rxn} = 0
\]

\[
Q = K_{eq}
\]

\[
0 = \Delta G^\circ_{rxn} + RT \ln K_{eq}
\]

\[
\Delta G^\circ_{rxn} = -RT \ln K_{eq}
\]

Since you know how to calculate $\Delta G^\circ_{rxn}$, you can calculate $K_{eq}$!
What is $K_{eq}$ for making ATP?

$$ADP + H_2PO_4 \rightarrow ATP + H_2O$$

$$\Delta G^\circ_{\text{rxn}} = +30.6 \text{ kJ/mol}$$

<table>
<thead>
<tr>
<th>25%</th>
<th>1. 0</th>
</tr>
</thead>
<tbody>
<tr>
<td>25%</td>
<td>2. $1.41 \times 10^{-6}$</td>
</tr>
<tr>
<td>25%</td>
<td>3. $4.36 \times 10^{-6}$</td>
</tr>
<tr>
<td>25%</td>
<td>4. 0.988</td>
</tr>
</tbody>
</table>
What about H and S?

- Of course, if $K_{eq}$ is related to $\Delta G$, it is also related to $\Delta H$ and $\Delta S$.

$$
\Delta G^\circ_{rxn} = -RT \ln K_{eq}
$$

$$
\Delta H^\circ_{rxn} - T\Delta S^\circ_{rxn} = -RT \ln K_{eq}
$$

$$
\ln K_{eq} = -\frac{\Delta H^\circ_{rxn}}{RT} + \frac{\Delta S^\circ_{rxn}}{R}
$$

or

$$
K_{eq} = e^{-\frac{\Delta H^\circ_{rxn}}{RT}} e^{\frac{\Delta S^\circ_{rxn}}{R}}
$$

So, if you had $\Delta H^\circ$ and $\Delta S^\circ$, you could calc $K_{eq}$ at many temps
Disturbances in Equilibrium

- Let’s say we are making rocket fuel
  \[ \text{CH}_4(g) + \text{H}_2\text{O}(g) \rightarrow \text{CO}(g) + 3\text{H}_2(g) \]

- What happens if we are at equilibrium, then introduce more steam?
  - Q instantly becomes smaller
  - Now Q < K, so we form more products

- Introducing reactant, pushed reaction toward products
  - We shifted the equilibrium
Equilibrium is Dynamic

\[ \text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{CO}(\text{g}) + 3\text{H}_2(\text{g}) \]
Le Chatelier’s Principle

- Response of a system at equilibrium to outside influence is described by Le Chatelier’s principle
- System at equilibrium responds to reduce the change

- We introduced extra H$_2$O, system tried to reduce H$_2$O by using some up, which make more product.

- True for all products and reactants
  - Chemicals
  - Heat
  - Pressure/Volume (for gas-phase reactants/products)
Le Chatelier Example

\[ \text{CaCl}_2(s) \rightarrow \text{Ca}^{2+}(aq) + 2\text{Cl}^-(aq) \]

• If this reaction is endothermic (\(\Delta H = +585 \text{ kJ} \)) will heat push left or right?

• Endothermic means that heat is like a reactant

• So, adding heat pushes toward products – more salt dissolves
Le Chatelier example 2
What happens to the following equilibrium if we reduce the volume of the container?
\[ \text{CaCO}_3 (s) \rightarrow \text{CaO} (s) + \text{CO}_2 (g) \]

| 33% | 1. It shifts left toward reactants |
| 33% | 2. If shifts right toward products |
| 33% | 3. No change |

1 2 3 4 5
Effect of Catalyst

- Catalyst changes $E_A$
- Catalyst does not effect products or reactants, so it does not effect $\Delta G_{rxn}$
- Therefore catalyst has no effect on $K_{eq}$
  - Though it does help system reach equilibrium more quickly
<table>
<thead>
<tr>
<th>Change</th>
<th>What Occurs</th>
<th>Effect on Equilibrium</th>
<th>Effect on K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Addition of Reactant</td>
<td>Added reactant consumed</td>
<td>Shift to right</td>
<td>No Change</td>
</tr>
<tr>
<td>Addition of Product</td>
<td>Added product consumed</td>
<td>Shift to left</td>
<td>No Change</td>
</tr>
<tr>
<td>Decrease V, Increase P</td>
<td>Pressure Decreases</td>
<td>Shift to fewer gas molecules</td>
<td>No Change</td>
</tr>
<tr>
<td>Increase V, Decrease P</td>
<td>Pressure Decreases</td>
<td>Shift to more gas molecules</td>
<td>No Change</td>
</tr>
<tr>
<td>Increase T</td>
<td>Heat is consumed</td>
<td>Shift in endo direction</td>
<td>Change</td>
</tr>
<tr>
<td>Decrease T</td>
<td>Heat is generated</td>
<td>Shift in exo direction</td>
<td>Change</td>
</tr>
</tbody>
</table>
Equil. from Initial Conditions

- Often given initial concentrations/pressures and asked to find concentrations at equilibrium

\[ \text{ADP} + \text{H}_2\text{PO}_4 \rightarrow \text{ATP} + \text{H}_2\text{O} \]

Initially: \([\text{ADP}] = 0.10 \text{ M} \hspace{1cm} [\text{ATP}] = 0 \text{ M} \]
\([\text{H}_2\text{PO}_4] = 0.24 \text{ M} \]

\[ K_{eq} = 4.36 \times 10^{-6} \]

What are concentrations at equilibrium?
**Equil. from Initial Conditions**

\[
\text{ADP} + \text{H}_2\text{PO}_4 \rightarrow \text{ATP} + \text{H}_2\text{O}
\]

<table>
<thead>
<tr>
<th></th>
<th>[ADP]</th>
<th>[H\textsubscript{2}PO\textsubscript{4}]</th>
<th>[ATP]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.10</td>
<td>0.24</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>(-x)</td>
<td>(-x)</td>
<td>(+x)</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.10(-x)</td>
<td>0.24(-x)</td>
<td>(+x)</td>
</tr>
</tbody>
</table>

\[
4.36 \times 10^{-6} = K_{eq} = \frac{[ATP]}{[ADP][H_2PO_4]} = \frac{x}{(0.10-x)(0.24-x)}
\]

\[
4.36 \times 10^{-6} \left(0.024-0.34x+x^2\right) = x
\]

\[
4.36 \times 10^{-6} x^2 - 1.00x + 1.046 \times 10^{-7} = 0
\]
Tricks

\[4.36 \times 10^{-6} x^2 - 1.00x + 1.046 \times 10^{-7} = 0\]

YUCK, how do we solve that?

- Quadratic equation
- Polynomial solver in calculator (or excel)
- In this case we know \( x \) is small
  - Because \( K_{EQ} \) is much less than initial concentrations
  - So, \( x^2 \) is way, way smaller than \( x \) – negligible
    \[-1.00x + 1.046 \times 10^{-7} = 0\]
    \[x = 1.046408 \times 10^{-7}\]

Solving exactly gives \( x = 1.046398 \times 10^{-7} \)
Today

• Go to Neckers lecture 4:00 VDW102

Monday

• Work on $K_{eq}$ worksheet (except part C)
• Finish CAPA #8