Chapters 17 & 20-1 to 20-3

Chemical Equilibria
Chemical Equilibrium: It is the condition of a chemical reaction in which the rate of formation of products (from reactants) equals the rate of formation of the reactants (from products).

\[
\text{rate}_1 \quad A + B \xrightarrow{\text{rate}_1} \quad C + D
\]

Equilibrium occurs when \( \text{rate}_1 = \text{rate}_{-1} \).

Although chemists usually want reactions to go completely to products (and ideally only to a single product), many do not. Theoretically all reactions are in equilibrium.

A reaction will not generally reach equilibrium if:

1) The rxn is very exothermic (exoergic)
2) One (or more) of the products (or reactants) is removed from the rxn
3) One of the products (or reactants) is insoluble
Consider the very important industrial reaction (the Haber process) of nitrogen and hydrogen to produce ammonia, which is used as a fertilizer:

$$\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g)$$

This is a very difficult reaction (large activation barrier) that requires high temperatures, pressures and a catalyst. At the high temperatures required to make the reaction proceed at a reasonable rate, the thermodynamics favors the $\text{N}_2 + \text{H}_2$ reactants producing the following behavior:

Note that the rxn does not go to completion, rather the forward and backward rxns reach a state of chemical equilibrium.
Equilibrium is a *dynamic* process. This means that when a reaction has reached a state of equilibrium, the forward and backward reactions making up the overall reaction *have not stopped*!! The equilibrium definition states that equilibrium is reached when the forward and backward reaction rates become equal!

For example consider a *saturated solution* of NaCl (no additional salt will dissolve):

\[
\text{NaCl}(s) \rightleftharpoons \text{Na}^+(aq) + \text{Cl}^-(aq)
\]

If we add 5 g more NaCl(s) to this solution, the amount of solid NaCl in the container will increase by 5 g (that is, no additional solid NaCl will dissolve into solution). This does not mean, however that some of the new NaCl that we just added won't dissolve at all. Some of it will dissolve, while some \(\text{Na}^+(aq) + \text{Cl}^-(aq)\) in solution elsewhere will precipitate out! We could follow this by adding radioactive \(^{24}\text{Na}^{38}\text{Cl}\) to the container:
Demonstration:

\[ \text{Hg}^{2+} + 2\text{I}^- \rightarrow \text{HgI}_2 \]

Yellow form
Kinetic Product

Orange form
Thermodynamic Product

\[ \text{Hg}^{2+} + 2\text{I}^- \rightarrow \text{HgI}_2 \]
Law of Mass Action

One can set up a general mathematical expression to describe the following chemical equilibria:

$$K_{eq} = \frac{[C]^y[D]^z}{[A]^w[B]^x}$$

$K_{eq}$ is called the equilibrium constant.

The equilibrium expression for the Haber process reaction would be written as:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

$$K_{eq} = \frac{[NH_3]^2}{[N_2][H_2]^3}$$
Consider, for example, the equilibrium between \( \text{N}_2\text{O}_4(g) \) and \( \text{NO}_2(g) \):

\[
\text{N}_2\text{O}_4(g) \quad \rightleftharpoons \quad 2\text{NO}_2(g)
\]

\[
K_{eq} = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}
\]

Listed below is experimental data giving initial concentrations for \( \text{N}_2\text{O}_4(g) \) and \( \text{NO}_2(g) \). After some time the reaction reaches equilibrium and the concentrations listed.

<table>
<thead>
<tr>
<th>Initial</th>
<th>@ Equilibrium</th>
<th>( K_{eq} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{N}_2\text{O}_4 )</td>
<td>( \text{NO}_2 )</td>
<td>( \text{N}_2\text{O}_4 )</td>
</tr>
<tr>
<td>0.00</td>
<td>0.02</td>
<td>0.0014</td>
</tr>
<tr>
<td>0.00</td>
<td>0.03</td>
<td>0.0028</td>
</tr>
<tr>
<td>0.00</td>
<td>0.04</td>
<td>0.0045</td>
</tr>
<tr>
<td>0.02</td>
<td>0.00</td>
<td>0.0045</td>
</tr>
</tbody>
</table>

Note how \( K_{eq} \) is the same regardless of the initial concentrations. This is why it is called the equilibrium constant.
Some Features of Equilibrium Constants

✓ $K_{eq}$ usually depends on temperature

✓ If one reverses the way a reaction is written the new $K_{eq}$ is the inverse of the original value:

$$K_{eq} = \frac{[H_2O]}{[H_2][O_2]^{\frac{1}{2}}} = 10 \text{ (@ high temp)}$$

Reversing the above rxn we now write:

$$K^*_eq = \frac{[H_2][O_2]^{\frac{1}{2}}}{[H_2O]} = 0.1 = \frac{1}{K_{eq}}$$

✓ Multiplying a reaction by a constant factor results in raising $K_{eq}$ to that power:

$$K_{eq}^\# = \frac{[H_2O]^2}{[H_2]^2[O_2]} = 100 \text{ (@ high temp)}$$
**Equilibrium constants** have a number of very important functions:

1) whether a rxn will be **spontaneous** under a given set of conditions (equilibrium constants are directly related to \( \Delta G \) – Gibbs Free Energy, see end of this chapter)

2) in which **direction** a reaction is going to proceed to reach equilibrium

3) allow us to calculate the **concentrations** of products and reactants at equilibrium

Qualitatively, the **magnitude** of \( K_{eq} \) should immediately tell you in what **direction** a reaction is going to proceed and **how far it will go** before reaching equilibrium. For example:

\[
K_{eq} \gg 1 \quad \text{reaction will go mainly to products}
\]

\[
K_{eq} \sim 1 \quad \text{reaction will produce roughly equal amounts of product and reactant}
\]

\[
K_{eq} \ll 1 \quad \text{reaction will go mainly to reactants}
\]
**Problem:** Will the following equilibria proceed mainly to **products**, **reactants** or produce an approximately equal amount of both?

a) \( \text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g) \quad K_{eq} = 0.001 \)

b) \( 2\text{SO}_3(g) \rightleftharpoons 2\text{SO}_2(g) + \text{O}_2(g) \quad K_{eq} = 2 \)

c) \( 2\text{HBr}(g) + \text{Cl}_2(g) \rightleftharpoons 2\text{HCl}(g) + \text{Br}_2(g) \quad K_{eq} = 10^4 \)

d) \( 2\text{H}_2\text{O}(g) \rightleftharpoons 2\text{H}_2(g) + \text{O}_2(g) \quad K_{eq} = 10^{-28} \)

e) \( \text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g) \quad K_{eq} = 1 \)

f) \( \text{H}_2(g) + \text{Cl}_2(g) \rightleftharpoons 2\text{HCl}(g) \quad K_{eq} = 10^{44} \)

g) \( \text{PCl}_3(sol) + \text{Cl}_2(sol) \rightleftharpoons \text{PCl}_5(sol) \quad K_{eq} = 0.1 \)

h) \( 2\text{HCl}(g) + \text{Br}_2(g) \rightleftharpoons 2\text{HBr}(g) + \text{Cl}_2(g) \quad K_{eq} = 10^{-4} \)
Units on $K_{eq}$

There are typically no units on equilibrium constants. This is because one is formally supposed to use the activities of compounds instead of their concentrations. The activity of a compound in an ideal mixture is the ratio of its concentration (or partial pressure) to a standard concentration (or pressure). Since the activity is defined as a ratio, the units cancel out.

Despite the fact that we should use dimensionless activities, most chemists still refer to equilibrium concentrations in terms of $M$ or pressure units (atm).

One does need to watch out when one is working with gases. An equilibrium constant calculated with gas pressures (atm is the standard unit for gases) will not have the same numerical value as one calculated using molarity values if there are different # of gas molecules on each side of the equilibrium. This is because of the relationship between pressure and molarity as defined by the ideal gas law.

Chemists use various subscripts on the equilibrium constant $K$ to indicate different types of equilibria: $K_p =$ gases (pressure), $K_c =$ solutions (molarity), $K_a =$ acids, $K_b =$ bases, $K_{sp} =$ solubility product (slightly soluble solids).
Equilibrium 12

**Reaction Quotient**

If a reaction is at equilibrium, then the equilibrium relationship will hold true:

\[ \frac{[C]^y [D]^z}{[A]^w [B]^x} \]

But, what if one is *NOT* at equilibrium? Then we find that the equilibrium expression is redefined as the reaction quotient, \( Q \):

\[ K_{eq} \neq \frac{[C]^y [D]^z}{[A]^w [B]^x} = Q \]

when this occurs, the equilibrium expression is defined as being equal to \( Q \), the Reaction Quotient.
By comparing $Q$ to $K_{eq}$, one can tell in which direction a reaction will go to reach a state of equilibrium:

$$wA + xB \rightleftharpoons yC + zD$$

$$K_{eq} = \frac{[C]^y [D]^z}{[A]^w [B]^x} = Q$$

- $Q > K_{eq}$: reverse reaction will be spontaneous
- $Q = K_{eq}$: reaction @ equilibrium
- $Q < K_{eq}$: forward reaction will be spontaneous
**EXAMPLES:**

\[
\text{CO}_2(g) + \text{H}_2(g) \rightleftharpoons \text{CO}(g) + \text{H}_2\text{O}(g)
\]

\[
\frac{[\text{CO}][\text{H}_2\text{O}]}{[\text{CO}_2][\text{H}_2]} = K_{eq} = 4.4
\]

If the initial concentrations of all species are 1 M, which way will the reaction proceed to reach equilibrium?

\[
\frac{[\text{CO}][\text{H}_2\text{O}]}{[\text{CO}_2][\text{H}_2]} = \frac{(1)(1)}{(1)(1)} = 1 = Q
\]

\[
K_{eq} = 4.4
\]

\[
Q = 1
\]

\[Q < K_{eq} \} \text{ therefore, the rxn will go } \text{FORWARD} \text{ to reach equilibrium}\]
What if we increase the [CO] concentration to 10 M?

\[
\frac{[\text{CO}] \cdot [\text{H}_2\text{O}]}{[\text{CO}_2] \cdot [\text{H}_2]} = \frac{(10)(1)}{(1)(1)} = 10 = Q
\]

\[K_{eq} = 4.4\]

\[Q = 10\]

\[Q > K_{eq}\] therefore, the rxn will go BACKWARD to reach equilibrium

If you are ever given a problem where the product and reactant concentrations are all non-zero, you **MUST** calculate \(Q\) and compare it to \(K_{eq}\) in order to figure out which way the reaction has to go to reach equilibrium.

**DANGER!!**

*Common mistake!!*
Problem: Are the following rxns @ equilibrium? If not, which way must they proceed to reach a state of equilibrium?

a) \[
\text{CO(g)} + 2\text{H}_2(g) \rightleftharpoons \text{CH}_3\text{OH(g)} \quad K_{eq} = 1
\]
\[\begin{array}{c}
5\text{M} \\
1\text{M} \\
5\text{M}
\end{array}\]

b) \[
\text{CO}_2(g) + \text{H}_2(g) \rightleftharpoons \text{H}_2\text{O(g)} + \text{CO(g)} \quad K_{eq} = 4
\]
\[\begin{array}{c}
1\text{M} \\
2\text{M} \\
2\text{M} \\
3\text{M}
\end{array}\]

c) \[
\text{Br}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{BrI(g)} \quad K_{eq} = 1 \times 10^{-4}
\]
\[\begin{array}{c}
0.2\text{ M} \\
0.2\text{ M} \\
0.1\text{ M}
\end{array}\]

d) \[
\text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{NO(g)} \quad K_{eq} = 9
\]
\[\begin{array}{c}
2\text{ M} \\
0.0001\text{ M} \\
2\text{ M}
\end{array}\]
EXAMPLE: Consider the following rxn. The initial concentrations are $[I_2] = [H_2] = 2\text{M}$, $[HI] = 0\text{M}$, and $K_{eq} = 16$. What will be the various concentrations when the reaction reaches equilibrium?

$$I_2(g) + H_2(g) \rightleftharpoons 2HI(g)$$

**Step 1:** Write out your initial and @ equilibrium conditions:

Initial cond: $[I_2] = [H_2] = 2\text{M}$

$[HI] = 0\text{M}$

Note that since $[HI] = 0\text{M}$, the reaction must proceed to the right to make more product. Thus, for this example, we will lose reactants and gain product. What we don't know is how much. Therefore, we will setup an algebraic expression to solve for $x$, the amount of product being produced and the amounts of reactant that we are losing. **It is CRITICAL to remember to multiply $x$ by the appropriate coefficient from the balanced chemical equation.**

@ Equilibrium:

$[I_2] = [H_2] = (\text{initial conc.}) - (\text{coefficient})(x)$

$= 2 - x$

$[HI] = (\text{initial conc.}) + (\text{coefficient})(x)$

$= 0 + 2x$

$= 2x$

**DANGER!! Common mistake!!**
**Step 2:** Write out your equilibrium expression:

\[
K_{eq} = \frac{[HI]^2}{[H_2][I_2]} = 16
\]

now substitute in the equilibrium conditions:

\[
\frac{[HI]^2}{[H_2][I_2]} = \frac{(2x)^2}{(2-x)(2-x)} = 16
\]

now solve for \(x\):

\[
\frac{(2x)^2}{(2-x)^2} = 16
\]

**DANGER!!**

**Common mistake!!**

_make sure that you don't miss common algebraic simplifications!!_

take the square root of each side:

\[
\sqrt{\frac{(2x)^2}{(2-x)^2}} = \sqrt{16} \quad \rightarrow \quad \frac{(2x)}{(2-x)} = 4
\]

\[
2x = (4)(2-x) \quad \rightarrow \quad 2x = 8 - 4x
\]

\[
6x = 8 \quad \rightarrow \quad x = \frac{8}{6} \quad x = 1.33
\]
**Step 3:** Substitute the value for x that you solved back into the equilibrium conditions that you wrote out in Step 1 above:

@ Equilibrium: \([I_2] = [H_2] = 2 - x = 2 - 1.33 = 0.66 \text{ M}\)
\([HI] = 2x = 2.66 \text{ M}\)

\([I_2] = [H_2] = 0.66 \text{ M}\)
\([HI] = 2.66 \text{ M}\)

**Step 4:** Substitute the equilibrium concentrations you just found back into the equilibrium expression to see if you calculate the correct value for \(K_{eq}\):

\[
K_{eq} = \frac{[HI]^2}{[H_2][I_2]} = 16
\]

substitute in the calculated equilibrium concentrations and see if you get \(K_{eq}\)

\[
\frac{[HI]^2}{[H_2][I_2]} = \frac{(2.66)^2}{(0.66)(0.66)} = 16
\]

**Step 5:** Carefully read the question and make sure that you are picking the right answer. Note that what you solve for x may not be the answer (make sure you do Step 3)!!

**DANGER!!**
**Common mistake!!**
Problem:

Starting with \([\text{CO}_2] = 2 \text{ M}\), \([\text{H}_2] = 2 \text{ M}\), \([\text{CO}] = 0 \text{ M}\) and \([\text{H}_2\text{O}] = 0 \text{ M}\), what will be the various concentrations @ equilibrium. \(K_{eq} = 9\).

\[
\text{CO}_2(g) + \text{H}_2(g) \rightleftharpoons \text{CO}(g) + \text{H}_2\text{O}(g)
\]
More Difficult EXAMPLE: Calculate $K_{eq}$ for the following reaction. Initial concentrations are: $[\text{SO}_2] = 4 \text{ M}$, $[\text{O}_2] = 4 \text{ M}$, $[\text{SO}_3] = 6 \text{ M}$. At equilibrium $[\text{SO}_2] = 3 \text{ M}$.

$$2\text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{SO}_3(g)$$

Solution:

This is really just a stoichiometry problem. Given the initial concentrations and a single equilibrium concentration (along with some algebra) one can solve for the other equilibrium concentrations. Once you have obtained all the equilibrium concentrations, one can put them into the equilibrium expression to solve for $K_{eq}$.

First one must figure out which way the reaction is going to go in order to reach equilibrium. We can't use the Reaction Quotient, $Q$, because we don't know $K_{eq}$. We do, however, have our initial and one final equilibrium condition to tell us which way the reaction will shift: initial $[\text{SO}_2] = 4 \text{ M}$, @ equilib $[\text{SO}_2] = 3 \text{ M}$. So we are losing $[\text{SO}_2]$, therefore, the reaction will go to make more product and to lose reactant.

Now we can setup and solve for the other equilib values:
\[ \text{initial:} \quad \begin{array}{ccc} \text{SO}_2 & \text{O}_2 & \text{SO}_3 \\ 4 & 4 & 6 \end{array} \]

\[ \text{2SO}_2(g) + \text{O}_2(g) \quad \rightleftharpoons \quad 2\text{SO}_3(g) \]

\[ \text{@ equilib:} \quad \begin{array}{ccc} \text{SO}_2 & \text{O}_2 & \text{SO}_3 \\ 4-2x & 4-x & 6+2x \end{array} \]

Normally we would substitute our \( x \) values into the equilibrium expression and solve for \( x \). Here, however, we actually know one of the equilibrium values:

\[ \text{@ equilib:} \quad \begin{array}{ccc} \text{SO}_2 & \text{O}_2 & \text{SO}_3 \\ 3 & ? & ? \end{array} \]

So we can let \( 4-2x = 3 \) and solve for \( x \):

\[
4-2x = 3 \quad \Rightarrow \quad 2x = 1 \quad \Rightarrow \quad x = 0.5
\]

Now, substitute \( x \) into our \( @ \) equilibrium formulas:

\[ \text{@ equilib:} \quad \begin{array}{ccc} \text{SO}_2 & \text{O}_2 & \text{SO}_3 \\ 4-2x & 4-x & 6+2x \\ 3 \text{ M} & 3.5 \text{ M} & 7 \text{ M} \end{array} \]

Finally, substitute the final values into the equilibrium expression to solve for \( K_{eq} \):

\[
K_{eq} = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]} = \frac{(7)^2}{(3)^2(3.5)} = 1.6
\]
Problem:

Consider the following reaction:

\[ \text{CO}(g) + 2\text{H}_2(g) \rightleftharpoons \text{CH}_3\text{OH}(g) \]

Initially we start with [CO] = 10 M and [H\textsubscript{2}] = 11 M. When the reaction reaches equilibrium there is 5 M [CH\textsubscript{3}OH]. Calculate \( K_{eq} \) for this reaction.
As Tough as We Get **EXAMPLE**: Calculate equilibrium concentrations for the following reaction. Initial values are: \([\text{CO}_2] = 1 \text{ M}, [\text{H}_2] = 2 \text{ M}, [\text{CO}] = 6 \text{ M}, \text{ and } [\text{H}_2\text{O}] = 6 \text{ M.} \)  
\(K_{eq} = 2\).

\[
\text{CO}_2(\text{g}) + \text{H}_2(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g})
\]

**Solution:**
First we need to determine in which direction the reaction will shift to reach equilibrium because none of the concentrations are zero. To do this we use the *Reaction Quotient, \(Q\)*, and the initial concentrations:

\[
\frac{[\text{CO}] [\text{H}_2\text{O}]}{[\text{CO}_2] [\text{H}_2]} = \frac{(6)(6)}{(1)(2)} = 18 = Q
\]

\(K_{eq} = 2\)

\(Q = 18\)

\(Q > K_{eq} \} \quad \text{therefore, the rxn will go BACKWARDS to reach equilibrium}\)

Now we can write out our initial and (most importantly) @ equilibrium values using x's:

**Initial cond:**  
\[
[\text{CO}_2] = 1 \text{ M} \quad [\text{H}_2] = 2 \text{ M} \\
[\text{CO}] = 6 \text{ M} \quad [\text{H}_2\text{O}] = 6 \text{ M}
\]

**@ Equilibrium:**  
\[
[\text{CO}_2] = 1 + x \quad [\text{H}_2] = 2 + x \\
[\text{CO}] = 6 - x \quad [\text{H}_2\text{O}] = 6 - x
\]
\[ K_{eq} = \frac{[\text{CO}] \times [\text{H}_2\text{O}]}{[\text{CO}_2] \times [\text{H}_2]} = \frac{(6-x) \times (6-x)}{(1+x) \times (2+x)} = 2 \]

\[ \frac{x^2 - 12x + 36}{x^2 + 3x + 2} = 2 \]

\[ x^2 - 12x + 36 = 2x^2 + 6x + 4 \]

\[ x^2 + 18x - 32 = 0 \]

\[ x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \]

\[ x = \frac{-18 \pm \sqrt{(18)^2 - 4(-32)}}{2} = \frac{-18 \pm \sqrt{324 + 128}}{2} \]

\[ x = \frac{-18 \pm \sqrt{452}}{2} = \frac{-18 \pm 21.3}{2} = 1.7 \text{ or } -19.7 \]

Physically impossible

Note that x is NOT OUR ANSWER!!!!

DANGER!!
Common mistake!!
@ Equilibrium: \([\text{CO}_2] = 1 + x\) \quad [\text{H}_2] = 2 + x
\[\text{[CO]} = 6 - x\] \quad [\text{H}_2\text{O}] = 6 - x

Substituting in \(x = 1.7\) we can get the equilibrium values:

@ Equilibrium: \([\text{CO}_2] = 2.7 \text{ M}\) \quad [\text{H}_2] = 3.7 \text{ M}
\[\text{[CO]} = 4.3 \text{ M}\] \quad [\text{H}_2\text{O}] = 4.3 \text{ M}

**Double-check** that these numbers are correct by recalculating \(K_{eq}\) and comparing to the value given to you in the problem:

\[
\frac{[\text{CO}][\text{H}_2\text{O}]}{[\text{CO}_2][\text{H}_2]} = \frac{(4.3)(4.3)}{(2.7)(3.7)} \approx 1.85 \approx 2
\]

You don’t get exactly 2.0 due to round-off error (I only carried one decimal point in my calculation)
A Simple EXAMPLE (but looks really hard if you don’t think): If 2 moles of H₂O are placed into a 5L container, what will be the equilibrium concentration of H₂, O₂ and H₂O?

\[2 \text{H}_2\text{O(g)} \rightleftharpoons 2 \text{H}_2(g) + \text{O}_2(g) \quad K_c = 6.0 \times 10^{-28}\]

\[K_c = \frac{[\text{H}_2]^2[\text{O}_2]}{[\text{H}_2\text{O}]^2} = 6.0 \times 10^{-28}\]

initial cond: \[\text{[H}_2\text{O}] = 2.0 \text{ moles/5 L} = 0.40 \text{ M}\]
\[\text{[H}_2] = \text{[O}_2] = 0 \text{ M}\]

@ equilibrium: \[\text{[H}_2] = 2x\]
\[\text{[O}_2] = x\]
\[\text{[H}_2\text{O}] = 0.40 - 2x\]

substituting into our equilibrium expression we get:

\[\frac{[2x]^2[x]}{[0.4 - 2x]^2} = 6.0 \times 10^{-28}\]
\[4x^3 - 24.0 \times 10^{-28}x^2 + 9.6 \times 10^{-28}x - 0.96 \times 10^{-28} = 0\]

But this is a cubic equation!!! Almost impossible for you to solve!!!

**OH MY GOD, WHAT DO I DO NOW!!**

What is this idiot Professor doing to me!!
HOWEVER, consider the physical reality of the situation. \( K_c = 6.0 \times 10^{-28} \) is extremely small, this means that very little H_{2}O will decompose to form H_{2} or O_{2}!! That means that the amount of H_{2} or O_{2} forming will be very, very small. That means that \( x \) will be very, very small. Small enough that we can ignore it in the \([H_{2}O] = 0.40 - 2x \) expression. This considerably simplifies the math:

\[
\frac{[2x]^2[x]}{[0.4]^2} = 6.0 \times 10^{-28}
\]

\[
\frac{4x^3}{0.16} = 6.0 \times 10^{-28}
\]

\[x^3 = 0.24 \times 10^{-28}\]

\[x = 2.9 \times 10^{-10} M\]

Since \( x \) is indeed much, much smaller than 0.40, the approximation was a very good one. So our concentrations at equilibrium are:

@ equilibrium:  
[H_{2}] = 5.8 \times 10^{-10} M  
[O_{2}] = 2.9 \times 10^{-10} M  
[H_{2}O] = 0.40 M

Actually, one didn't have to do any calculations for this problem! Because \( K_c \) is so very small, you should know that virtually no products will be produced. Therefore:

@ equilibrium:  
[H_{2}] = [O_{2}] = 0 M  
[H_{2}O] = 0.40 M

For this course and this kind of problem, there isn't much difference between 5.8 \times 10^{-10} M and 0 M!!
Heterogeneous Equilibria

So far all the equilibrium examples we have used have involved gases or solutions. What happens if we have other states of matter present -- such as solids or pure liquids?? How do they affect the equilibrium??

It turns out that as long as some solid or liquid is present, the equilibrium will be independent of the amount of that solid or liquid that is present!

**EXAMPLE:**

\[ \text{Br}_2(l) \rightleftharpoons \text{Br}_2(g) \]

\[ K_{eq} = \frac{[\text{Br}_2(g)]}{[\text{Br}_2(l)]} \]

What is the concentration of \([\text{Br}_2(l)]\)?

\[ M = \frac{\text{moles of } \text{Br}_2(l)}{\text{volume}} \]

The density of \(\text{Br}_2(l)\) is 3.12 g/mL, so the # of moles is:

\[# \text{ moles} = (3.12 \text{ g/mL}) / (159.8 \text{ g/mol})\]

\[# \text{ moles} = 0.0195\]
The M can now be calculated for liquid bromine:

\[ M = \frac{\text{moles of } \text{Br}_2(l)}{\text{volume}} = \frac{0.0195 \text{ moles of } \text{Br}_2(l)}{0.001 \text{ L}} \]

\[ M = 19.5 \text{ mol/L} \]

Now we can look at our equilibrium expression:

\[ K_{eq} = \frac{[\text{Br}_2(g)]}{[\text{Br}_2(l)]} = \frac{[\text{Br}_2(g)]}{19.5 \text{ M}} \]

**note that this is a constant concentration -- it is independent of the amount of liquid bromine present, as long as some is there!!**

Because the \([\text{Br}_2(l)]\) concentration is a constant value we can multiply the equilibrium expression by that amount and incorporate it into \(K_{eq}:\)

\[ (K_{eq})(19.5 \text{ M}) = [\text{Br}_2(g)] \]

\[ K_{eq}^* = [\text{Br}_2(g)] \]

**DANGER!! VERY Common mistake!!**

Therefore, one should **NOT** include **solids** or **pure liquids** in equilibrium expressions!!

A more technical, but simpler explanation is that we are actually using activities instead of concentrations (see section on units), and the activity of a solid or pure liquid is defined as being = 1. Thus it factors out of the equilibrium expression.
**Problem:** Write out equilibrium expressions for the following reactions:

a) \( \text{CaO}(s) + \text{CO}_2(g) \rightleftharpoons \text{CaCO}_3(s) \)

b) \( \text{Ag}^+(aq) + \text{Cl}^-(aq) \rightleftharpoons \text{AgCl}(s) \)

c) \( \text{Br}_2(l) + \text{Ni(CO)}_4(l) \rightleftharpoons \text{NiBr}_2(s) + 4\text{CO}(g) \)

d) \( \text{H}_2\text{CO}_3(aq) \rightleftharpoons \text{H}_2\text{O}(l) + \text{CO}_2(g) \)

e) \( \text{HCl}(g) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}^+(aq) + \text{Cl}^-(aq) \)
**Numerical Example:** What is the equilibrium concentration for $[\text{Ag}^+]$ in the following reaction:

$$\text{Ag}_2(\text{SO}_4) \ (s) \rightleftharpoons 2\text{Ag}^+(aq) + \text{SO}_4^{2-}(aq) \quad K_{sp} = 4 \times 10^{-9}$$

**Answer:** $K_{sp}$ refers to equilibria involving *solubility products*, that is, solids that are slightly soluble in water (or other solvents). Note that the reactant in this problem is a solid and, as such, will NOT appear in the final equilibrium expression. We also usually do NOT give the amount of the solid and assume that there is excess present, since only a little bit will dissolve in solution. Otherwise, set it up and solve just like a regular equilibrium problem:

<table>
<thead>
<tr>
<th>Initial:</th>
<th>excess solid</th>
<th>0M</th>
<th>0M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag$_2$(SO$_4$) (s)</td>
<td>$2\text{Ag}^+(aq) + \text{SO}_4^{2-}(aq)$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

@Equilib: less excess solid $\rightarrow 2x \quad x$

The equilibrium expression for this rxn is:

$$K_{sp} = [\text{Ag}^+]^2[\text{SO}_4^{2-}]$$

(the solid Ag$_2$SO$_4$ doesn’t appear in the equilibrium expression because it is a solid!). Plug in the @equilb values and solve for x:

$$[2x]^2[x] = 4 \times 10^{-9}$$

$$4x^3 = 4 \times 10^{-9}$$

$$x^3 = 1 \times 10^{-9}$$

$$x = 1 \times 10^{-3}$$

**BUT, watch out, x is NOT our answer!!**

$$[\text{Ag}^+] = 2x, \quad [\text{Ag}^+] = 2 \times 10^{-3} \text{ M.}$$
Problems:

a) What is the equilibrium concentration for OH$^-$ in the following reaction:

$$\text{Ca(OH)}_2(s) \rightleftharpoons \text{Ca}^{2+}(aq) + 2\text{OH}^-(aq) \quad K_{sp} = 4 \times 10^{-6}$$

b) What is the equilibrium concentration for Ag$^+$ for the following system:

$$\text{Ag}_3(\text{AsO}_4)(s) \rightleftharpoons 3\text{Ag}^+(aq) + \text{AsO}_4^{3-}(aq) \quad K_{sp} = 1 \times 10^{-22}$$
**$K_p - K_c$ Relationship**

When the number of equivalents of gas phase reactants and products is *not* equal the following relationship relates $K_c$ (concentration in $M$) and $K_p$ (concentration in *pressures - atm*). This is true even if we technically use dimensionless *activities* due to the relationship between molarity and pressure (even when units are factored out).

$$K_p = K_c(RT)^\Delta n$$

$$K_c = K_p(RT)^{-\Delta n} \quad \text{-or-} \quad K_c = \frac{K_p}{(RT)^{\Delta n}}$$

$$\Delta n = (n_{\text{gas prod}}) - (n_{\text{gas react}})$$

No gas molecules? Then $\Delta n = 0$.

Equal number of gas molecules on reactant & product side? Then $\Delta n = 0$.

Pressures must be expressed in atmospheres (atm).
**Le Chatelier's Principle**

When a system in a state of equilibrium is acted upon by some outside stress, the system will, if possible, shift to a new equilibrium position to oppose the effect of the stress.

What do we mean by "stress"? **Stress** means that we are *disturbing* the reaction by: adding or removing reactants or products; increasing or decreasing the temperature; and increasing or decreasing the pressure (if gases are involved). Once we do one of these things, the reaction will (usually) no longer be in equilibrium and will have to shift to make more reactants or products to reattain a state of chemical equilibrium.

\[
\text{A} + \text{B} \rightleftharpoons \text{C} + \text{D} + \text{C}
\]

The reaction has to shift backwards to consume some of the products and make more reactants!

original rxn in equilibrium

but now we have added more product C and there is too much product
Concept Demonstration:

Chemical Demonstration:

\[ \text{CoCl}_4^{2-} \text{(sol)} + x\text{H}_2\text{O} \rightleftharpoons \text{Co(H}_2\text{O)}_6^{2+} \text{(sol)} + 4\text{Cl}^- \text{(sol)} \]
Listed below are how various "disturbances" affect equilibria:

1) Adding *products* (unless one of the products is a solid!) to a reaction will cause the equilibrium to shift back to produce more *reactants*.

2) Adding *reactants* (unless one of the reactants is a solid!) to a reaction will cause the equilibrium to shift forward to produce more *products*.

3) Removing *reactants* (unless one of the reactants is a solid and as long as there is some left) will cause the equilibrium to shift back to produce more *reactants*.

4) Removing *products* (unless one of the products is a solid and as long as there is some left) will cause the equilibrium to shift forward to produce more *products*.
5) The effect of **temperature** on a reaction is dependent on whether the reaction is **exothermic** ($\Delta H_{rxn} = \text{negative}$) or **endothermic** ($\Delta H_{rxn} = \text{positive}$):

**Exothermic rxn:**

\[ A + B \rightleftharpoons C + \text{heat} \quad \text{heat is one of the products} \]

a) increasing the temperature (adding heat) will cause the equilibrium to shift back to make more reactants

b) decreasing the temperature (removing heat) will cause the equilibrium to shift forward to make more products

**Endothermic rxn:**

heat is one of the reactants

\[ A + B + \text{heat} \rightleftharpoons C \]

a) increasing the temperature (adding heat) will cause the equilibrium to shift forward to make more products

b) decreasing the temperature (removing heat) will cause the equilibrium to shift back to make more reactants
6) The effect of changing pressure depends on the number of gasous reactants and products present:

- a) if there are NO gas phase species present then pressure will have NO effect on the equilibrium (actually, there is an effect at very high pressures -- but we won't worry about this).

- b) if there are gas phase species present, but there are the same number of gaseous molecules on each side of the reaction, pressure will have NO effect on the equilibrium.

- c) if there are different numbers of gas phase species present on the reactant and product sides of the equilibrium, then:
  
  i) increasing the pressure will favor the side of the equilibrium with the smaller number of gas phase molecules.

  ii) decreasing the pressure will favor the side of the equilibrium with the larger number of gas phase molecules.
Qualitative EXAMPLE:

Consider the following equilibrium:

\[ \text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g) \]

Note how the \( \text{N}_2\text{O}_4 \) molecules have dissociated in order to produce more \( \text{NO}_2 \) molecules. These more efficiently fill up the "empty" space present in this system.

Note how the \( \text{NO}_2 \) molecules have combined in order to produce fewer \( \text{N}_2\text{O}_4 \) molecules. These more efficiently save space, which is in short supply in this compressed system.
**Mathematical EXAMPLE:** Effect of doubling the pressure (halving the volume) on $\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g)$

\[
\begin{align*}
\text{original equilib} & \quad \begin{cases} \text{N}_2\text{O}_4 & \rightleftharpoons 2\text{NO}_2 \\ 0.0045 \text{ M} & \quad 0.031 \text{ M} \end{cases} \\
\text{compress} & \\
\text{new equilib} & \quad \begin{cases} \text{N}_2\text{O}_4 & \rightleftharpoons 2\text{NO}_2 \\ 0.009 \text{ M} & \quad 0.062 \text{ M} \end{cases} 
\end{align*}
\]

is this in equilibrium?

Calculate $Q$, the reaction quotient, to determine the direction of the reaction to reach equilibrium:

\[
Q = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = \frac{(0.062)^2}{(0.009)} = 0.427
\]

since $Q > K_{eq}$ the reaction has to go backwards to reach equilibrium. That means that some of the $\text{NO}_2$ has to disappear.

\@ equilibrium: \quad [\text{N}_2\text{O}_4] = 0.009 + x \quad \text{we are gaining N}_2\text{O}_4
\quad [\text{NO}_2] = 0.062 - 2x \quad \text{we are losing NO}_2

substituting $[\text{N}_2\text{O}_4] = 0.009 + x$ and $[\text{NO}_2] = 0.062 - 2x$ into our equilibrium expression we can solve for $x$:
\[
\frac{(0.062 - 2x)^2}{0.009 + x} = 0.21
\]
\[
4x^2 - 0.458x + 0.0019 = 0
\]
[solve using quadratic equation]
\[
x = 0.004, 0.106
\]

\[x = 0.106 \text{ M is } \text{physically unreasonable} \text{ (that would give us a negative concentration, which is impossible)},\text{ we can forget it.}\]

So \[x = 0.004 \text{ M}.\] Substituting this back into our equilibrium conditions we can find the final equilibrium concentrations:

\[
\text{[N}_2\text{O}_4\text{]} = 0.009 + x = 0.013 \text{ M} \\
\text{[NO}_2\text{]} = 0.062 - 2x = 0.054 \text{ M}
\]

So the \text{N}_2\text{O}_4\text{ concentration has increased} and the \text{NO}_2\text{ concentration has decreased: exactly what one would qualitatively predict from Le Chatilier's principle!!}
**Problem:** What are the various things that one can do to the following reactions to shift the equilibria to a) favor the reactants; b) favor the products? (you can add or remove products and reactants; change the temperature; change the pressure)

a) \( \text{CaO}(s) + \text{CO}_2(g) \rightleftharpoons \text{CaCO}_3(s) \)  
\[ \Delta H_{rxn} = -179 \text{ kJ/mol} \]

b) \( \text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g) \)

c) \( \text{Ca}^{+2}(aq) + 2\text{Cl}^-(aq) \rightleftharpoons \text{CaCl}_2(s) \)  
\[ \Delta H_{rxn} = +95 \text{ kJ/mol} \]

d) \( \text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI}(g) \)

e) \( \text{Br}_2(l) + \text{Ni(CO)}_4(l) \rightleftharpoons \text{NiBr}_2(s) + 4\text{CO}(g) \)

f) \( \text{H}_2\text{CO}_3(aq) \rightleftharpoons \text{H}_2\text{O}(l) + \text{CO}_2(g) \)

g) \( \text{Ag}^+(aq) + \text{Cl}^-(aq) \rightleftharpoons \text{AgCl}(s) \)
The **common ion effect** is Le Chatelier’s principle – just under a different name. You will see another variant of this at the end of the Acid/Base chapter when we discuss Buffer solutions.

Consider the following equilibrium:

$$\text{AgCl}(s) \rightleftharpoons \text{Ag}^+(aq) + \text{Cl}^-(aq)$$

$$K_{sp} = 1.8 \times 10^{-10}$$

What happens to the $\text{Ag}^+(aq)$ concentration if we add enough NaCl to raise the $\text{Cl}^-(aq)$ concentration to 0.1 M?

Qualitatively, of course, from Le Chatelier’s principle, adding **product** ($\text{Cl}^-$) to the solution will push the equilibrium **backwards** to produce more **reactant** ($\text{AgCl}(s)$). This will decrease the free $\text{Ag}^+(aq)$ concentration in solution. The $\text{Na}^+$ cations will not have any effect, so we can pretty much ignore them (**spectator ions**).

In this case the $\text{Cl}^-$ anion is the **Common Ion** between the NaCl and AgCl.
Let’s set this up and mathematically solve for the concentration of Ag\(^+\) after adding \(0.1\, M\) Cl\(^-\).

**Initial:**

<table>
<thead>
<tr>
<th></th>
<th>solid</th>
<th>0</th>
<th>0.1</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th></th>
<th>AgCl(s)</th>
<th>Ag(^+)(aq) + Cl(^-)(aq)</th>
</tr>
</thead>
</table>

@ equilib: less solid (-x) \(x\) 0.1 + \(x\)

\[
K_{sp} = [Ag^+][Cl^-] = 1.8 \times 10^{-10}
\]

\[
(x)(x + 0.1) = 1.8 \times 10^{-10}
\]

\[
x^2 + 0.1x - 1.8 \times 10^{-10} = 0
\]

solve via the *quadratic equation* to get:

\[
x = 1.8 \times 10^{-9} \quad -- \ or \ -- \quad -0.10000000003
\]

\[
x = [Ag^+] = 1.8 \times 10^{-9} \, M
\]

Physically impossible!!
But, there is a simple approximation we can use to make our math a lot easier. Before we add any extra Cl\(^-\), let's show that the concentrations of [Ag\(^+\)] and [Cl\(^-\)] present are very small:

<table>
<thead>
<tr>
<th>Initial:</th>
<th>solid</th>
<th>0</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgCl(s)</td>
<td>⇌</td>
<td>Ag(^+)(aq) + Cl(^-)(aq)</td>
<td></td>
</tr>
</tbody>
</table>

@ equilib: less solid (-x) | x | x |

\[
K_{sp} = [Ag^+] [Cl^-] = 1.8 \times 10^{-10}
\]

\[
(x)(x) = 1.8 \times 10^{-10}
\]

\[
x^2 = 1.8 \times 10^{-10}
\]

\[
x = [Ag^+] = [Cl^-] = 1.3 \times 10^{-5} \text{ M}
\]

So the Ag\(^+\) and Cl\(^-\) concentrations in solution from AgCl(s) are 1.3 x 10\(^{-5}\) M. Le Chatelier’s principle tells us that adding more Cl\(^-\) will decrease the Ag\(^+\) and Cl\(^-\) (x values) from the AgCl(s) dissociation even further. Small enough that we can make the approximation that 0.1 + x in the original problem is essentially 0.1. This will reduce our quadratic expression down to a very simple algebra problem:
<table>
<thead>
<tr>
<th>Initial:</th>
<th>solid</th>
<th>0</th>
<th>0.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgCl(s)</td>
<td>⇌</td>
<td>Ag⁺(aq) + Cl⁻(aq)</td>
<td></td>
</tr>
</tbody>
</table>

@ equilib: less solid (-x) x 0.1 + x

\[ K_{sp} = [Ag^+][Cl^-] = 1.8 \times 10^{-10} \]
\[ (x)(0.1) = 1.8 \times 10^{-10} \]

Approximation!

divide through by 0.1

\[ x = [Ag^+] = 1.8 \times 10^{-9} \text{ M} \]

Note that this is the same as what we calculated from the quadratic equation \([Ag^+] = 1.8 \times 10^{-9} \text{ M}\). And it is a LOT quicker and easier to calculate!

So using this approximation, when appropriate, will save you a lot of time. Typically it is OK to drop \(x\) in a \((# + x)\) or \((# - x)\) algebraic expression when \(x\) is going to be more than an order of magnitude smaller than the \# it is being added or subtracted to AND it will simplify the algebra.

You will see similar approximations a lot in Acids & Bases for weak acid and base equilibrium calculations.
**Problem:** What is the concentration of Ag\(^+\) in a 0.01 \( M \) \( K_2SO_4 \) solution to which excess \( Ag_2(SO_4) \) is added. \( K_{sp} (Ag_2(SO_4)) = 4 \times 10^{-9} \)

**Initial:**

\[
\begin{array}{ccc}
Ag_2(SO_4) (s) & \rightleftharpoons & 2Ag^+(aq) + SO_4^{2-}(aq)
\end{array}
\]

@Equilib:
**Problem:** What is the concentration of $\text{H}^+$ in a 0.1 $M$ acetic acid (HOAc) solution to which 0.1 $M$ Na$^+$OAc$^-$ is added. $K_{eq}$ (HOAc) = $2 \times 10^{-5}$

<table>
<thead>
<tr>
<th>Initial:</th>
<th>0.1</th>
<th>0</th>
<th>0.1</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HOAc(aq)</td>
<td>H$^+$(aq) + OAc$^-$ (aq)</td>
<td></td>
</tr>
<tr>
<td>@Equilib:</td>
<td>0.1 $- x$</td>
<td>$x$</td>
<td>0.1 $+ x$</td>
</tr>
</tbody>
</table>

**Note:** This is called a *Buffer Solution* (see *Acids/Bases*)
As I’ve mentioned during the first part of this chapter, the equilibrium constant is directly related to the Gibbs Free Energy, $\Delta G$.

- $\Delta G^\circ$ = negative $\rightarrow$ $K_{eq} > 1$ (spontaneous)
- $\Delta G^\circ$ = zero $\rightarrow$ $K_{eq} = 1$ (rare)
- $\Delta G^\circ$ = positive $\rightarrow$ $K_{eq} < 1$ (non-spontaneous)

The mathematical relationship for calculating $\Delta G^\circ$, given $K_{eq}$ is:

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

$R = 8.314$ $J/K$ (gas constant) $T = \text{Temp in } ^\circ \text{K}$

Given the value of $\Delta G^\circ$, we can rearrange the above equation to solve for $K_{eq}$:

$$K_{eq} = e^{-(\Delta G^\circ / RT)}$$

Thus, given $\Delta G^\circ$ (or $\Delta H^\circ$ and $\Delta S^\circ$) we can calculate $K_{eq}$ at a given temperature. Similarly, given $K_{eq}$, we can calculate $\Delta G^\circ$. 
\[ \Delta G^o \text{ vs. } \Delta G: \text{ Standard vs. Non-Standard Conditions} \]

Remember that the \(^o\) ("not") on \(\Delta G^o\) indicates that the numerical value of \(\Delta G^o\) is based on the reaction at standard conditions (1 M solution concentration, 1 atm gas pressure). Temperature is NOT part of standard conditions!

As soon as one has a concentration different than 1 M or 1 atm pressure, the \(^o\) "not" goes away and one has \(\Delta G\).

Consider the reaction:

Initial: \hspace{1cm} 1 atm \hspace{1cm} 1 atm \hspace{1cm} 1 atm

\[ 2\text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{SO}_3(g) \]

\[ \Delta G^o_{rxn} = -142 \text{ kJ/mol} \]

The \(\Delta G^o_{rxn}\) of \(-142 \text{ kJ/mol}\) is for when each gas is present with a concentration of 1 atm. This indicates that the reaction under these conditions will proceed to make products (spontaneous).

As the reactants start reacting, however, their concentrations decrease (\(\text{SO}_2\) twice as fast as \(\text{O}_2\)) and \(\Delta G^o\) turns into \(\Delta G\) and becomes less negative.

When \(\Delta G = 0\) the reaction has reached equilibrium.
Example: A reaction has a $\Delta G^o$ value of $-40$ KJ/mol at 25ºC. What is the $K_{eq}$ for this reaction?

First convert the temperature from ºC to K:

Temp (K) = 25ºC + 273 = 298 K

Now we can use the formula for calculating $K_{eq}$:

$$K_{eq} = e^{-\left(\frac{\Delta G^o}{RT}\right)}$$

$$K_{eq} = e^{-\left(\frac{-40000 \text{ J/mol}}{8.314 \text{ J/mol K}(298\text{K})}\right)}$$

*Important Note:* R the gas constant has units of J/molK, while we usually express $\Delta G^o$ in KJ/mol. The units must match!!! The easiest thing is to multiply the $\Delta G^o$ value in KJ/mol by 1000 to give J/mol.

$$K_{eq} = e^{16.14}$$

$$K_{eq} = 1.02 \times 10^7$$

The negative $\Delta G^o$ represents a *spontaneous reaction*. See how this converts over to a large positive $K_{eq}$ value, indicating that the reaction goes mainly to *products*. Note also how there are no units when you calculate $K_{eq}$ this way.
Example: A reaction has a $K_{eq}$ value of 0.01 at 25ºC. What is $\Delta G^\circ$ for this reaction?

First convert the temperature from ºC to K:

$$\text{Temp (K)} = 25^\circ + 273 = 298 \text{ K}$$

Now we can use the formula for calculating $\Delta G^\circ$:

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

$$\Delta G^\circ = -(8.314 \text{ J/mol K})(298 \text{ K}) \ln(0.01)$$

$$\Delta G^\circ = -(2477 \text{ J/mol})(-4.6)$$

$$\Delta G^\circ = +11,394 \text{ J/mol} \quad \text{or} \quad +11.4 \text{ KJ/mol}$$

Don’t forget to convert J/mol to KJ/mol for the $\Delta G^\circ$ value!!
**Problem:** A reaction has a $K_{eq}$ value of 10 at 25ºC. What is $\Delta G^o$ for this reaction?
Catalysts

**Catalyst**: a material that speeds up the *RATE* of a reaction without being consumed in the reaction.

A catalyst will *NOT* change an equilibrium, only the speed (rate) at which equilibrium is reached!

Remember that equilibrium is directly related to **thermodynamics**. Catalysts never affect the thermodynamics of a reaction. They only lower the *energy of activation* (kinetics) of a reaction.
Chemical Demonstration:
Oscillating Iodine Reaction

$\text{H}_2\text{O}_2 \rightarrow \text{IO}_3^- \xrightarrow{\text{Mn}^{2+} \text{ to Mn}^{3+}} \text{HOI} \xrightarrow{\text{HO} \text{C} \text{C} \text{O}} \text{HO} \text{C} \text{C} \text{OH} \xrightarrow{\text{Mn}^{3+} \text{ to Mn}^{2+}} \text{I}^- \\
\text{I}_2 \xrightarrow{\text{H}_2\text{O}_2} \text{I}_3^- \xrightarrow{\text{I}^-} \text{H}_2\text{O}_2 \xrightarrow{\text{2CO}_2 \text{ HCOOH}} \text{I}^- \\
\text{HO} \text{C} \text{C} \text{O} \text{H}$