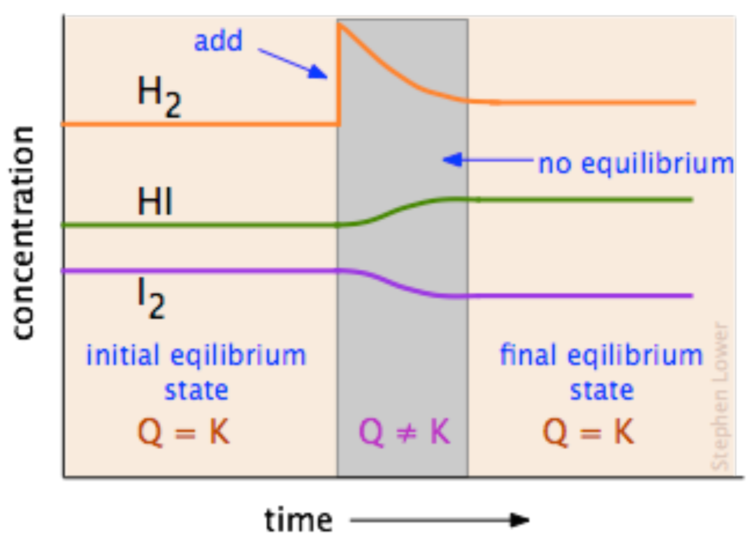
EQUILIBRIUM PART 2

Brief Outline:

1. **LCP predictions**
2. **LCP labs**
3. **LCP graphs**
4. **Common Ion Effect**
5. **Precipitates**



Introduction to Le Chatelier's Principle

It is important to know the factors that will affect or control the position of equilibrium. The Le Chatelier's principle will allow us to study those factors which control the equilibrium position of a system.

Henri Louis Le Chatelier (1850 - 1936) was a French chemist and a mining engineer. In 1884 Le Chatelier proposed the Law of Mobile Equilibrium, more commonly called **Le Chatelier's Principle**. The principle states:

When a system at equilibrium is subjected to a stress, the system will adjust so as to relieve the stress.

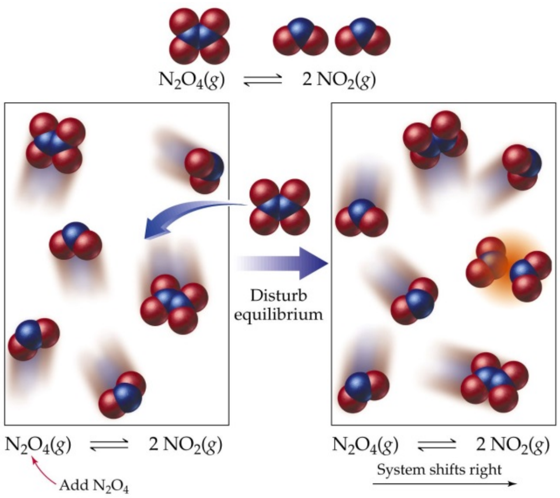
Le Chatelier's Principle is considered to be the chemistry version of Newton's Third Law of Motion. According to Newton's 3rd Law, for every action force there is an equal but opposite reaction force. In chemistry, Le Chatelier's Principle says that whatever change is made to a system at equilibrium, the system responds to reverse that change. That is, whatever is added is reacted, whatever is removed is replaced, etc.

We are going to look at several different stresses including:

- Concentration
- Pressure
- Temperature
- Catalysts

What you always need to think is:

1. What did I change?
2. What is the opposite?
3. How will the system achieve that? Shift ___________
4. What will that do to concentrations?



Challenge:
If this is an exothermic reaction, what four different things (five if we really want to push it) could we do to make this reaction shift forward?

Concentration Changes

In a system at equilibrium, a change in the concentration of products or reactants present at equilibrium, constitutes a stress. Adding more reactant upsets the established equilibrium.

Let's look at this imaginary equilibrium system where the size of the symbol represents the concentration of that reactant or product.

$$A + B \rightleftharpoons C + D$$

In this system the product concentrations are larger than the reactants. As a result the value of K should be larger than 1. If we add some reactant A to the system, the system will initially appear as

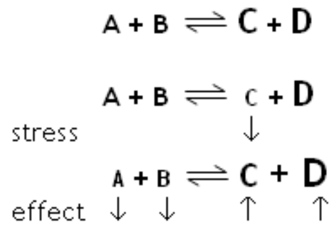
$$\underset{\text{stress}\ \uparrow}{A} + B \rightleftharpoons C + D$$

The value of K would no longer be the same. If you recall from the Kinetics unit, adding reactant increases the rate of a reaction. By adding more A the forward rate increases until a new equilibrium position is reached, where the value of K is re-established.

$$\underset{\text{effect}\ \downarrow}{A} + \underset{\downarrow}{B} \rightleftharpoons \underset{\uparrow}{C} + \underset{\uparrow}{D}$$

According to Le Chatelier's principle, the stress is relieved by using up some of the added reactant and forming more product. In the process the concentration of reactant B also decreases. Note that all of the added A is NOT consumed, only enough so that the ratio of product to reactant concentrations equals K. If reactant is added or product is removed, we say that the equilibrium position "shifts to the right".

Removing product results in a similar shift to the right.



Removing product is a stress on a system at equilibrium. Lowering the concentration of a product causes the reverse reaction rate to decrease.

Since the forward rate is now larger than the reverse rate the amount of product begins to increase and the reactant concentration decreases.

Similarly, according to Le Chatelier's adding more product causes the position of equilibrium to shift towards the left, or reactants. The reverse rate is favoured until the product to reactant ratio is equal to K once again.

Iron-Thiocyanate Equilibrium

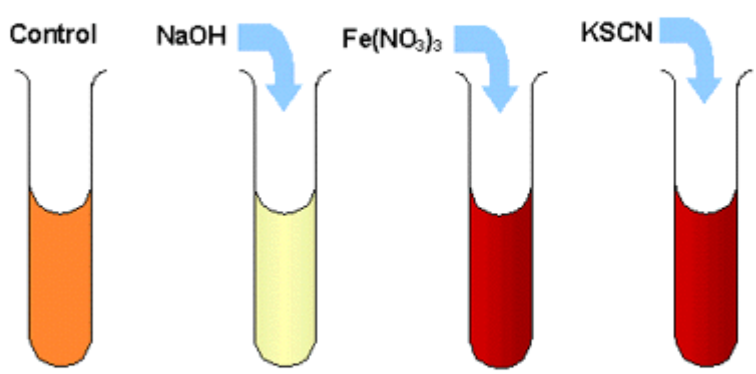
A standard laboratory example for demonstrating the effect of changing concentrations on equilibrium is shown below:

$$Fe^{3+}(aq) + SCN^{-}(aq) \leftrightarrow FeSCN^{2+}(aq)$$

pale yellow red

The position of equilibrium can be determined from the colour of the solution. If the equilibrium lies to the right more $FeSCN^{2+}$ is present and the solution is a darker red. If the equilibrium lies to the left the solution is lighter in colour.

Consider the experiment below:



If salts containing either Fe^{3+}, SCN^{-} or both, area added to the equilibrium system the colour of the solution becomes a deeper red. This suggests a shift in the equilibrium to the right. The concentration of $FeSCN^{2+}$ increases, establishing a new equilibrium position. The system uses up some of the added reactant to counteract the change.

When NaOH is added to the system the solution turns to a pale yellow. If NaOH is added to the system, the hydroxide ions combine with the iron (III) ions to produce an insoluble complex of iron (III) hydroxide. Thus reducing the number of free iron ions and a shift to the left to create more Fe3+ is favoured as is indicated by the colour change.

<u>The practice questions start on page 9 try these Questions:</u>
#2 (e), #3 (a), #4 (c), #5 (a) and (b), and
All of the Questions 1-3 on page 10

Pressure Changes

Changing the pressure of a system only affects those equilibrium with gaseous reactants and/or products.

According to Le Chatelier's Principle, increasing the pressure on a system at equilibrium causes the system to shift to reduce its pressure. The only way a system can reduce the pressure is by reducing the number of particles in the system. The system accomplishes this by favouring the side of the equation that has the fewest gaseous molecules. That is, the equilibrium position shifts to the side with fewer molecules.

Conversely, decreasing the pressure on a system causes the system to shift to increase the pressure by increasing the number of particles in the container. The equilibrium position shifts to the side with more molecules.

Pressure Change Example

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

a) What is the effect on the equilibrium if the size of the container is cut in half, but the number of particles and temperature remain unchanged?

Reducing the size of the container, increases the pressure of the system.
According to Le Chatelier's Principle, the system will adjust to reduce pressure. The system reduces pressure by reducing the number of molecules in the container.

There are four moles of gaseous reactants on the left ($1\ N_2 + 3\ H_2 = 4$ molecules) and only two ($2\ NH_3$) on the right. The rate of the forward reaction will increase as the reaction shifts to the side with fewer molecules, thus increasing the concentration of NH_3 and reducing the concentration of N_2 and H_2.

b) What is the effect on equilibrium if the reaction chamber is increased in volume, while keeping temperature and total number of particles constant?

Increasing volume, while keeping other factors constant, decreases pressure.

According to Le Chatelier's Principle, the system will adjust to increase pressure. The system does this by increasing the number of molecules in the container.

The system increases the number of molecules in the container by shifting the equilibrium to the left, increasing the concentration of reactants.

Hydrogen Iodide Equilibrium

For the following reaction pressure changes would have **NO** effect on the equilibrium position.

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

Each side of the reaction has two moles of molecules. There is no way to either increase or reduce the number of particles. Therefore, in response to pressure changes, the equilibrium position remains **unchanged**.

The practice questions start on page 9 try these Questions:
1(a) and (d), 2 (c) and (d), 3 (b), 4(b), and 6(a)

Picture explanation tomorrow…..

$$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(g)}$$

Temperature Changes

Recall from Kinetics that increasing temperature always increases the rate of a reaction. However, increasing temperature always increases the rate of an endothermic reaction more than the rate of an exothermic reaction.

According to Le Chatelier's Principle, a change in temperature causes a stress on a system at equilibrium. The system attempts to relieve the stress by either replacing lost heat or consuming added heat.

To solve equilibrium problems involving heat changes you can consider heat to be a product (exothermic reactions – heat is released) or a reactant (endothermic reactions – heat is absorbed) and predict the change in equilibrium position as you would with concentration changes.

Nitrogen Dioxide Equilibrium

The conversion of dinitrogen tetroxide to nitrogen dioxide is reversible and temperature dependent:

$$N_2O_4(g) \leftrightarrow 2\ NO_2(g) \qquad \Delta H = +58\ kJ$$

colourless brown

or

$$N_2O_4(g) + heat \leftrightarrow 2\ NO_2(g)$$

The ΔH is positive, so the forward reaction is endothermic (we can consider heat to be a reactant in this reaction). According to Le Chatelier's Principle, adding heat is a stress on a system at equilibrium. The system attempts to remove added heat by using it up in the forward reaction (endothermic reaction). The equilibrium position shifts towards the right (products). The concentration of NO_2 increases and the concentration of N_2O_4 decreases.

We can also think of adding heat can as increasing one of the reactants. According to Le Chatelier's Principle, increasing a reactant causes the equilibrium position to shift right to consume some of the added reactant (heat).

If a container holding an N_2O_4-NO_2 mixture is cooled, according to Le Chatelier's Principle, the system replaces lost heat by favouring the reaction where heat is produced. The equilibrium position shifts towards the left. This increases the concentration of N_2O_4 and reduces the concentration of NO_2.

Temperature and K

The equilibrium constant is temperature dependent.

In the example on the previous page, increasing temperature caused a shift in the equilibrium to the right, favouring products. This would cause an increase in product concentration and a reduction in reactant concentration. This would result in an increase in the value of K.

A decrease in temperature causes a shift to the left, reducing product concentration and increasing reactant concentration. This would result in a decrease in the value of K.

Temperature is the only factor which will change the value of K.

<u>The practice questions start on page 9 try these Questions:</u>
Questions: 1(c), 2 (a) and (b), 3 (c), 4 (a), 5 (c), 6 (b)

Effect of a Catalyst

We saw in kinetics that adding a catalyst to a system decreases the activation energy of a reaction. This will cause the rate of a reaction to increase. However, a catalyst lowers the activation energy of BOTH forward and reverse reactions equally.

Therefore, adding a catalyst to a system at equilibrium will NOT affect the equilibrium position. However, if a catalyst is added to a system which is not at equilibrium, the system will reach equilibrium much quicker since forward and reverse reaction rates are increased.

Now you can do all of the practice questions. Go back and finish any you missed including the catalyst ones.

Le Chatelier's Principle: http://www.mhhe.com/physsci/chemistry/essentialchemistry/flash/lechv17.swf

Show what you can do……Exercises

1. For the reaction predict the effect on equilibrium that results from:

   $PCl_3(g) + Cl_2(g) \quad PCl_5(g)$ $\Delta H = -92.5$ kJ

   a) increasing the total pressure by decreasing volume.
   b) injecting more Cl_2 gas without changing the volume.
   c) increasing the temperature.
   d) increasing the volume of the container.
   e) adding a catalyst.

2. For the reaction predict the effect on equilibrium that results from:

   $CH_4(g) + H_2O(g) + 49.3$ kJ $\quad CO(g) + 3\ H_2(g)$

   a) increasing temperature.
   b) decreasing temperature.
   c) decreasing the pressure.
   d) decreasing the volume of the container.
   e) adding a solid drying agent such as $CaCl_2$ which reacts with $H_2O(g)$.

3. For the reaction

   9.4 kJ + $2\ HI(g) \quad H_2(g) + I_2(g)$

   a) What is the effect on [HI] if a small amount of H_2 is added?
   b) What is the effect on [HI] if the pressure of the system is increased?
   c) What is the effect on [HI] if the temperature is increased?
   d) What is the effect on [HI] if a catalyst is added?

4. For the reaction
   $CO(g) + 2\ H_2(g) \quad CH_3OH(g)$ + energy
   predict the effect of the following changes on the equilibrium concentration of $CH_3OH(g)$

   a) a decrease in temperature.
   b) an increase in pressure.
   c) addition of $H_2(g)$.
   d) addition of a catalyst.

5. In the equilibrium reaction

   $2\ NO(g) + O_2(g) \qquad 2\ NO_2(g) + 114.6\ kJ$

   What will be the change in the equilibrium $[NO_2]$ under each of the following conditions?

   a) O_2 is added.
   b) NO is removed.
   c) energy is added.

6. For the following reaction $\Delta H = +58.9\ kJ$

   $N_2O_4(g) \qquad 2\ NO_2(g)$

   how will the equilibrium $[NO_2]$ be affected by the following?

   a) an increase in pressure.
   b) an increase in temperature.
   c) the addition of a catalyst.

LCP – changing concentration

1. For the following system at equilibrium:

   $H_{2\,(g)} + I_{2\,(g)} \leftrightarrow 2\ HI_{\,(g)}$

   a. Predict the shift in equilibrium when more $HI_{(g)}$ is added to the system.

   b. How will the concentration of I_2 change?

2. For the reaction below, predict the direction the equilibrium will shift given the following changes. Temperature and volume are held constant.

   $2\ NO_{2\,(g)} + 7\ H_{2\,(g)} \leftrightarrow 2\ NH_{3\,(g)} + 4\ H_2O_{(g)}$

   a. addition of ammonia

   b. removal of nitrogen dioxide

   c. removal of water vapour

   d. addition of hydrogen

3. At a particular temperature, the following reaction has an equilibrium constant, K_{eq} of 0.18

   $PCl_{3\,(g)} + Cl_{2\,(g)} \leftrightarrow PCl_{5\,(g)}$

   More PCl_3 is added to the system. Will the value of K_{eq} increase or decrease?

More practice for when you have time.

1. The pressure on each of the following systems is increased by decreasing the volume of the container. Explain whether each system would shift in the forward direction, the reverse direction, or stay the same.

   a. $2\ SO_{2\ (g)} + O_{2\ (g)} \rightarrow 2\ SO_{3\ (g)}$

   b. $H_{2\ (g)} + I_{2\ (g)} \rightarrow 2\ HI_{(g)}$

   c. $CaCO_{3\ (s)} \rightarrow CaO_{(s)} + CO_{2\ (g)}$

   d. $AgCl_{(s)} \rightarrow Ag^{1+}_{(aq)} + Cl^{1-}_{(aq)}$

2. List three ways that the following equilibrium reaction could be forced to shift to the right:

   $2\ NO_{2\ (g)} \rightarrow 2\ NO_{(g)} + O_{2\ (g)}$

3. Given the following equilibrium reaction:

   $2\ C_{(s)} + O_{2\ (g)} \rightarrow 2\ CO_{(g)}$

   What will be the effect of the following disturbances to the system:

   a. adding CO (at constant volume and temperature)

   b. addition of O_2 (at constant volume and temperature)

   c. addition of solid carbon (at constant temperature)

   d. decreasing the volume of the container

Le Chatelier's Principle Multiple Choice Questions

1. The reaction: $3\ O_2(g) \rightarrow 2\ O_3(g) + 288.7\ kJ$ is aided by
   a. higher temperature and higher pressure;
   b. higher temperature and lower pressure;
   c. lower temperature and higher pressure;
   d. lower temperature and lower pressure.

2. What is the effect of a catalyst on the reaction $N_2(g) + 3\ H_2(g) \rightleftarrows 2\ NH_3(g)$?
   a. It produces more product.
   b. It changes the time needed to reach equilibrium.

3. When at equilibrium, which reaction shifts to the right if pressure is increased?

   a. $2\ H_2(g) + O_2(g) \rightleftarrows 2\ H_2O(g)$
   b. $2\ SO_3(g) \rightleftarrows 2\ SO_2(g) + O_2(g)$
   c. $2\ NH_3(g) \rightleftarrows N_2(g) + 3\ H_2(g)$
   d. $2\ NO(g) \rightleftarrows N_2(g) + O_2(g)$

4. The reaction in which increased pressure has no affect on the equilibrium reaction is

   a. $N_2(g) + 3\ H_2(g) \rightleftarrows 2\ NH_3(g)$.
   b. $2\ H_2(g) + CO(g) \rightleftarrows CH_3OH(l)$.
   c. $CaCO_3(s) \rightleftarrows CaO(s) + CO_2(g)$.
   d. $CO(g) + H_2O(g) \rightleftarrows CO_2(g) + H_2(g)$.

5. How does an increase in pressure at constant temperature affect this equilibrium?
   $N_2(g) + 3\ H_2(g) \rightleftarrows 2\ NH_3(g) + \text{heat}$.

   a. produces no noticeable affect
   b. shifts the equilibrium to the left
   c. increases the concentration of N_2
   d. causes the reaction to become endothermic
   e. increases the concentration of NH_3

6. Given the equation AgC1(s) $\rightleftarrows Ag^+(aq) + Cl^-(aq)$. As NaC1(s) dissolves in the solution, temperature remaining constant, the $Ag^+(aq)$ concentration will

   a. decrease as the amount of AgC1(s) decreases.
   b. decrease as the amount of AgC1(s) increases.
   c. increase as the amount of AgCl(s) decreases.
   d. increase as the amount of AgCl(s) increases.

7. In the reaction represented by the equation, $H_2F_2(g) + \text{energy} \rightleftarrows 2\ HF(g)$, which set of conditions favors the formation of HF?

   a. low temperature and high pressure
   b. high temperature and high pressure
   c. low temperature and low pressure
   d. high temperature and low pressure

8. In which reaction does high pressure favor the formation of the products?

a. $2\ H_2O(g) \rightleftarrows 2\ H_2(g) + O_2(g)$

b. $CaCO\ (s) \rightleftarrows CaO(s) + CO_2(g)$

c. $N_2(g) + 3\ H_2(g) \rightleftarrows 2\ NH_3(g)$

d. $CO(g) + H_2O(g) \rightleftarrows CO_2(g) + H_2(g)$

9. Consider the equation**:** $CO + 2\ H_2 \rightleftarrows CH_3OH$ + heat. **All** substances are **gaseous**. How will lowering the temperature affect this equilibrium system?

a. increase the concentration of H_2
b. increase the concentration of CH_3OH
c. increase the concentration of CO
d. increase the concentration of CO and H_2

10. When a stress is applied to a system at equilibrium

a. the reaction is driven to the left;
b. a new product forms;
c. the reaction is driven to the right;
d. equilibrium is altered to relieve the stress;
e. none of these.

11. When at equilibrium, which reaction will shift to the right if the pressure is increased and the temperature is kept constant?

a. $2\ H_2(g) + O_2(g) \rightleftarrows 2\ H_2O(g)$

b. $2\ NO(g) \rightleftarrows N_2(g) + O_2(g)$

c. $2\ SO_3(g) \rightleftarrows 2\ SO_2(g) + O_2(g)$

d. $2\ CO_2(g) \rightleftarrows 2\ CO(g) + O_2(g)$

12. If heat is added to the system $C_2H_4 + H_2 \rightleftarrows C_2H_6$ + heat,

a. the concentration of C_2H_4 will decrease;
b. the concentration of H_2 will decrease;
c. the concentration of C_2H_6 will decrease;
d. no change will occur;
e. none of these.

13. A decrease in pressure will shift the equilibrium $3\ O_2(g) \rightleftarrows 2\ O_3(g)$

a. to the right;
b. to the left;
c. to the right, then left;
d. to the left, then right;
e. there will be no change.

14. Which change favors high concentration of $CO_2(g)$ at equilibrium?

$$2\,CO(g) + O_2(g) \rightleftarrows 2\,CO_2(g) + 566.1\text{ kJ}$$

a. lowering the pressure
b. lowering the $O_2(g)$ concentration
c. raising the temperature
d. raising the CO(g) concentration

15. Consider the system in equilibrium: $2\,SO_2(g) + O_2(g) \rightleftarrows 2\,SO_3(g)$ + heat.
What might be done to increase the quantity of SO_3?

a. introduce a catalyst
b. decrease the concentration of $SO_2(g)$
c. increase the pressure on the system
d. increase the temperature of the system
e. decrease the concentration of $O_2(g)$

Effects of Disturbances on Equilibrium and K_{eq}

Disturbance	Change That Occurs as System Returns to Equilibrium	Effect on Equilibrium	Effect on K_{eq}
Addition of reactant	Some added reactant is consumed	Right	No change
Addition of product	Some added product is consumed	Left	No change
Decrease in volume Increase in pressure	Pressure decreases	Shifts toward fewer gas molecules	No change
Increase in volume Decrease in pressure	Pressure increases	Shifts toward more gas molecules	No change
Rise in temperature	Energy will be consumed	Shifts toward endothermic reaction	K will increase if products are formed
Drop in temperature	Energy will be produced	Shifts toward exothermic reaction	K will decrease if reactants are formed

Practice Problems

$$N_{2(g)} + 3\,H_{2(g)} \leftrightarrows 2\,NH_{3(g)} \qquad \Delta H = -22 \text{ kcal}$$

1. Does equilibrium shift to the left or the right when extra H_2 is added? When extra NH_3 is added?

2. What is the effect on the position of equilibrium when the volume of the system is increased? Does the equilibrium shift to the left or to the right, or is the system unchanged?

3. List all the stresses that can be imposed on this system to maximize the production of NH_3.

Le Chatelier's Principle Worksheet

Complete the following chart by writing left, right, or none for equilibrium shift, and decreases, increases, or remains the same for the concentrations of reactants and products, and for the value of K_{eq}.

$$N_{2(g)} + 3\ H_{2(g)} \leftrightarrows 2\ NH_{3(g)} + 22\ \text{kcal}$$

Stress	Equilibrium Shift	$[N_2]$	$[H_2]$	$[NH_3]$	K_{eq}
1. Add N_2	right	--------	decreases	increases	remains the same
2. Add H_2	→	↓	--------	↑	↓
3. Add NH_3	←	↑	↑	--------	
4. Remove N_2	←	--------	↑	↓	
5. Remove H_2	←	↑	--------	↓	
6. Remove NH_3	→	↓	↓	--------	
7. Increase Temperature	←	↑	↑	↓	smaller
8. Decrease Temperature	→	↓	↓	↑	larger
9. Increase Pressure	→	↓	↓	↑	no change
10. Decrease Pressure	←	↑	↑	↓	no change

Le Chatelier's Principle Worksheet cont.

$$12.6\ \text{kcal} + H_{2(g)} + I_{2(g)} \leftrightarrow 2\ HI_{(g)}$$

<table>
<tr><th>Stress</th><th>Equilibrium Shift</th><th>[H₂]</th><th>[I₂]</th><th>[HI]</th><th>K_{eq}</th></tr>
<tr><td>1. Add H_2</td><td>right</td><td>--------</td><td>decreases</td><td>increases</td><td rowspan="6">remains the same ↓</td></tr>
<tr><td>2. Add I_2</td><td>→</td><td>↓</td><td>--------</td><td>↑</td></tr>
<tr><td>3. Add HI</td><td>←</td><td>↑</td><td>↑</td><td>--------</td></tr>
<tr><td>4. Remove H_2</td><td>←</td><td>--------</td><td>↑</td><td>↓</td></tr>
<tr><td>5. Remove I_2</td><td>←</td><td>↑</td><td>--------</td><td>↓</td></tr>
<tr><td>6. Remove HI</td><td>→</td><td>↓</td><td>↓</td><td>--------</td></tr>
<tr><td>7. Increase Temperature</td><td>→</td><td>↓</td><td>↓</td><td>↑</td><td>↑</td></tr>
<tr><td>8. Decrease Temperature</td><td>←</td><td>↑</td><td>↑</td><td>↓</td><td>↓</td></tr>
<tr><td>9. Increase Pressure</td><td colspan="5" rowspan="2">NO CHANGE</td></tr>
<tr><td>10. Decrease Pressure</td></tr>
</table>

Le Chatelier's Principle Worksheet cont.

$$NaOH_{(s)} \leftrightarrow Na^{+}_{(aq)} + OH^{-}_{(aq)} + 10.6\ kcal$$

*remember that pure solids and liquids do not affect equilibrium values

Stress	Equilibrium Shift	Amount $NaOH_{(s)}$	$[Na^{+}]$	$[OH^{-}]$	K_{eq}
1. Add $NaOH_{(s)}$		--------			
2. Add NaCl (adds Na^{+})	←	↑	--------	↓	remain the same
3. Add KOH (adds OH^{-})	←	↑	↓	--------	
4. Add H^{+} (removes OH^{-})	→	↓	↑	--------	
5. Increase Temperature	←	↑	↓	↓	↓
6. Decrease Temperature	→	↓	↑	↑	↑
7. Increase Pressure	NO CHANGE				
8. Decrease Pressure					

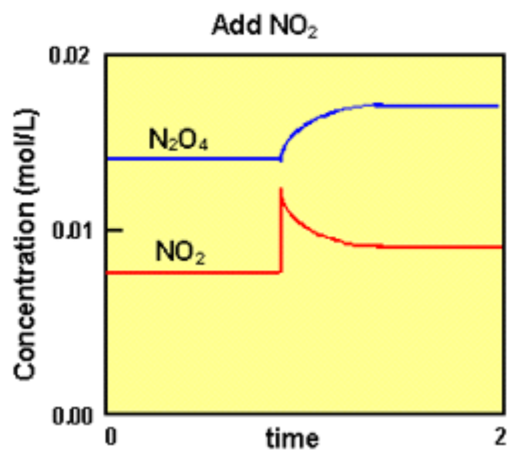
LCP & Graphing

Concentration vs Time Graphs for Changing Reactant Concentrations

The sketches below illustrate concentration changes in the NO_2-N_2O_4 equilibrium system.

$$2\ NO_2(g) \leftrightarrow N_2O_4(g)\ \Delta H = -58.0\ kJ/mol\ N_2O_4$$

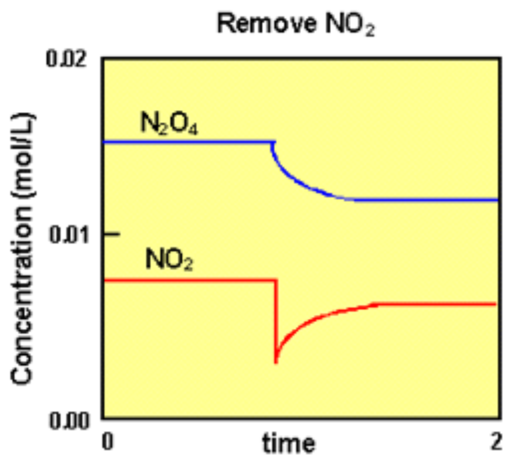
The first graph shows the results of the addition of NO_2.



What's happening?

The system is at equilibrium at the beginning because the concentrations of NO_2 and N_2O_4 remain stable. NO_2 is added to the system, so the $[NO_2]$ immediately increases which is a stressor. In order to decrease the stress on the system, $[NO_2]$ needs to decrease to offset this change. The forward reaction will be favoured to use up some of the $[NO_2]$ and increase the $[N_2O_4]$ until a new equilibrium is reached and the concentrations are no longer changing.

The next graph shows the removal of NO_2.



What's happening?

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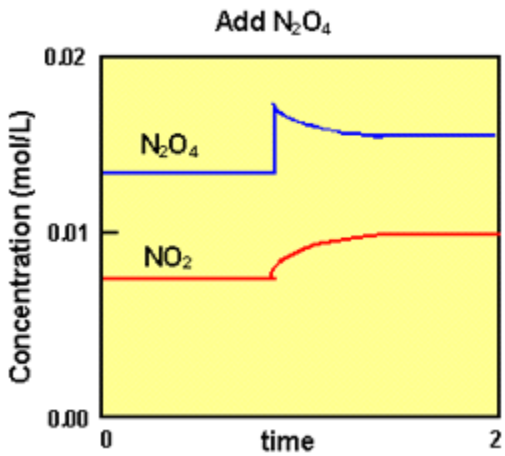
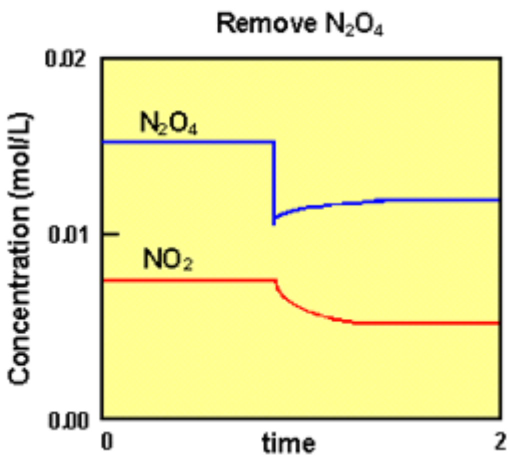
<u>Concentration vs Time</u> Graphs for Changing Product Concentrations

We will first examine the effect of adding more product.



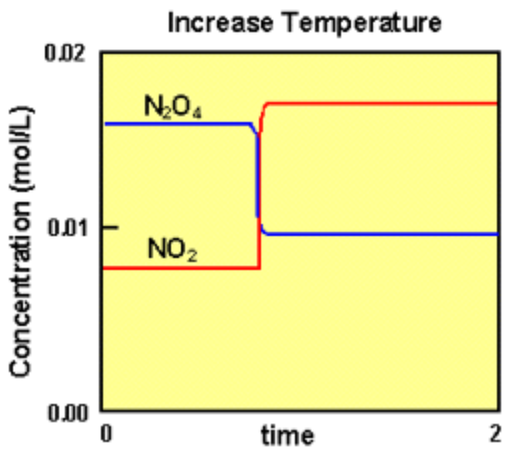
What's happening?



What's happening?

Concentration vs Time Graphs for Temperature Changes

We will now look at the graphs which illustrate the effect of changing temperature on reactant and product concentrations. Remember that the forward reaction is exothermic.



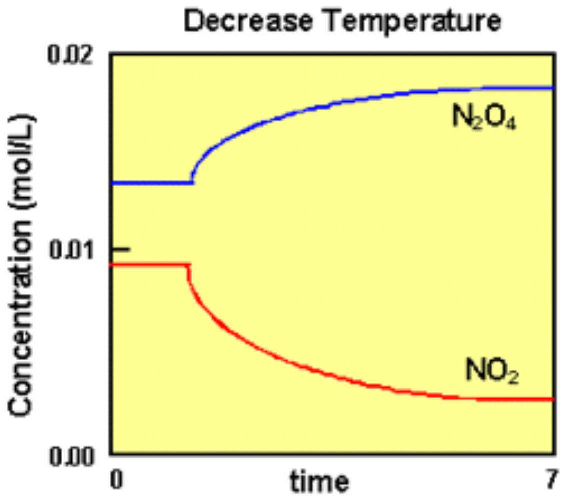
If we increased the temperature which way would the reaction shift? Left

When the temperature is increased the concentration of the reactant increases rapidly. The system adjusts to use up added heat. If you recall from the rate vs. time graph, both forward and reverse rates increase, but the endothermic reaction increases more to use up the heat. This results in a net increase in reactant.

If you enter the concentration data into the mass action expression, you will find that the value of K has changed.

How it will change? The value of K should decrease.

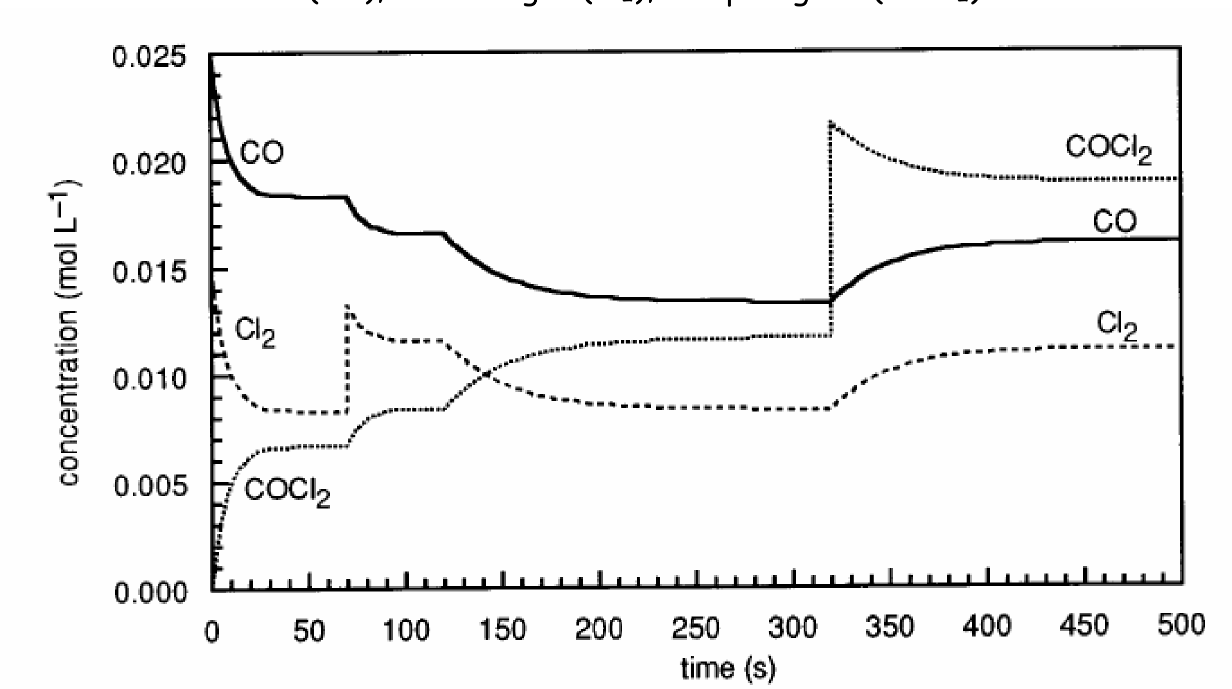
Why? ___K will decrease because the reactant increased which is the denominator in the mass action expression



When the temperature is decreased, according to Le Chatelier's Principle (and the graph), the exothermic reaction (forward) is favoured. The system adjusts to replace lost heat, resulting in an increased product concentration and a decreased reactant concentration, and an increased K value because the forward reaction is favoured.

Interpreting Graphs Worksheet

1. The graph below shows concentration versus time for a system containing carbon monoxide (CO), chlorine gas (Cl_2), and phosgene ($COCl_2$).



a. Write a balanced equation to represent the reaction studied.

b. How much time was required for the system to reach equilibrium?

c. Calculate the approximate value for the equilibrium constant, K_{eq}, using the concentrations at 60 s.

d. Explain the changes 70 s after the initiation of the reaction.

e. What changes in conditions might have been imposed on the system 120 s after the initiation of the reaction?

Interpreting Graphs Worksheet Cont.

f. Are any events taking place at 320 s?

g. What differences would you have noticed if a catalyst had been present during the entire course of this reaction?

h. List the changes you might impose on this system if you wanted to produce a maximum amount of phosgene?

i. How could you account for the differences in the value calculated for the equilibrium constant, K_{eq}, from the concentrations at different time points on the graph?

2. $2\ SO_{2(g)} + O_{2(g)} \leftrightarrows 2\ SO_{3(g)} + 180\ kJ$

a. List 4 ways in which you could increase the amount of SO_3 produced.

b. What affect does temperature have on this reaction.

Interpreting Graphs Worksheet Cont.

3. Consider the reaction: Heat + $2\ NOCl_{(g)} \leftrightarrows 2\ NO_{(g)} + Cl_{2(g)}$
At 462°C, the reaction has a K_{eq} of 8.0×10^{-2}. What is the K_{eq} at 462°C for the following reaction: $2\ NO_{(g)} + Cl_{2(g)} \leftrightarrows 2\ NOCl_{(g)}$ + Heat

4. With reference to the first equation given in question 3 answer the following (**True or False**). **Explain** your answer.

a. The reaction is exothermic.

b. After equilibrium is established, increasing the concentration of NO causes an increase in $[Cl_2]$.

c. After equilibrium is established, decreasing the volume favours the formation of NOCl.

d. Increasing the temperature favours the formation of NO and Cl_2.

e. Decreasing the $[Cl_2]$ causes the equilibrium to shift to the left.

f. Adding argon gas to the equilibrium system will cause an increase in the yield of products.

g. Adding a catalyst decreases the time required for the reaction to reach equilibrium.

h. Adding more NOCl to the system, causes an increase in K_{eq}.

i. Adding a catalyst causes a change in K_{eq}.

j. Increasing temperature, increases the rate of the forward reaction.

k. Increasing temperature, increases the rate of the reverse reaction.

l. At a given temperature, only one set of product and reactant concentrations satisfies K_{eq}.

Practical Applications of LCP

Blood pH

Blood contains dissolved carbonic acid in equilibrium with carbon dioxide and water.

$$H_2CO_{3(aq)} \leftrightarrows CO_{2(aq)} + H_2O_{(l)}$$

To keep carbonic acid at safe concentrations in the blood, the CO_2 product is exhaled. The removal of a product causes the forward reaction to be favoured, reducing the amount of carbonic acid to keep blood pH within a safe range.

Haemoglobin Production and Altitude

In the body haemoglobin in readily used to transport oxygen to tissues.

$$Hb_{(aq)} + O_{2(g)} \leftrightarrows HbO_{2(aq)}$$

In a place such as Mexico City, where the elevation is 2.3 km, atmospheric pressure and oxygen concentration are low. To offset the stress equilibrium favours the reverse direction. This results in hypoxia, which can cause headache, nausea, and extreme fatigue. In serious cases, if a victim is not treated quickly, they may slip into a coma and die. Individuals living at high altitudes for extended periods of time adapt to reduced oxygen concentrations by producing more haemoglobin. This shifts equilibrium to the right once more so that the symptoms of hypoxia disappear. Studies have shown that the Sherpas, long-time residents of the mountains, have adapted to high altitude conditions by maintaining high levels of haemoglobin in their blood, sometimes as much as 50% more than individuals living at sea level.

Carbonated Beverages

Soft drinks are carbonated under high pressure to create the following equilibrium system:

$$CO_{2(g)} \leftrightarrows CO_{2(aq)} + \text{heat}$$

When a bottle of soda is opened, the pressure above the carbon dioxide decreases. The system shifts to the left, the solubility of the carbon dioxide drops, and carbon dioxide bubbles out of solution. If the bottle is left open for long periods of time, the pop will go "flat" due to the reduced pressure. Shaking a pop bottle will increase the pressure on the system, which will shift to relieve the stress by favouring the forward reaction. Increasing the temperature of a pop bottle (i.e. leaving it in a warm car on a summer's day) will cause equilibrium to shift in the reverse direction, creating more carbon dioxide gas. This generates a pressure that could potentially cause the pop bottle to burst.

Practical Applications of Le Chatelier's Principle

In your own words describe how equilibrium and LCP effect the following situations.

Blood pH	
Haemoglobin production	
Carbonated Drinks	

Le Chatelier Review – Multiple Choice

1. In the reaction (all gas phase) $N_2 + 3H_2 \rightleftarrows 2NH_3$ an increase in pressure forces the reaction to the right because
a) hydrogen diffuses more rapidly than nitrogen.
b) there are fewer molecules in the products than in the reactants.
c) ammonia is a gas.
d) ammonia is very soluble in water.
e) the product weighs more than either reactant.

2. How does an increase in pressure at constant temperature affect this equilibrium?
$N_{2(g)} + 3H_{2(g)} \Leftrightarrow 2NH_{3(g)} + \text{heat}$

a) produces no noticeable effect
b) increases the concentration of N_2
c) increases the concentration of NH_3
d) shifts the equilibrium to the left
e) causes the reaction to become endothermic

3. Consider the system in equilibrium, $2SO_{2(g)} + O_{2(g)} \Leftrightarrow 2SO_{3(g)}$ + heat. What might be done to increase the quantity of $SO_{3(g)}$?
a) Introduce a catalyst
b) Increase the pressure on the system
c) Decrease the concentration of $O_{2(g)}$
d) Decrease the concentration of $SO_{2(g)}$
e) Increase the temperature of the system

4. $N_{2(g)} + 3H_{2(g)} \Leftrightarrow 2NH_{3(g)} + 100kJ$
Which change will increase the equilibrium concentration of ammonia, NH_3?
a) a decrease in the total pressure
b) a decrease in the concentration of $H_{2(g)}$
c) an increase in the volume of the reaction chamber
d) a decrease in the temperature of the reaction chamber

5. What is the result of increasing the concentration of acetic acid, CH_3COOH, in this equilibrium system? (all gaseous at constant temperature)
$CH_3COOC_2H_5 + H_2O \Leftrightarrow C_2H_5OH + CH_3COOH$
a) a change in the equilibrium constant
b) a decreased concentration of H_2O
c) a decreased concentration of C_2H_5OH
d) a decreased concentration of $CH_3COOC_2H_5$

6. Which change favors high concentration of $CO_{2(g)}$ at equilibrium?
$2CO_{(g)} + O_{2(g)} \Leftrightarrow 2CO_{2(g)}$ $\Delta H = -566kJ$
a) lowering the pressure
b) raising the temperature
c) lowering the $O_{2(g)}$ concentration
d) raising the $CO_{(g)}$ concentration

7. In this equation: $N_{2(g)} + 3H_{2(g)} \Leftrightarrow 2NH_{3(g)}$
increasing the pressure on the total system causes the equilibrium to shift to produce
a) more $NH_{3(g)}$
b) more $N_{2(g)}$
c) more $N_{2(g)}$ and $H_{2(g)}$
d) no change in either reactants or products

8. How can the concentration of substance AB be increased in this equilibrium system?
$A_{2(g)} + B_{2(g)} + heat \Leftrightarrow 2AB_{(g)}$
a) increase the pressure
b) decrease the pressure
c) increase the temperature
d) decrease the temperature

9. Which change increases the amount of $H_2O_{(g)}$ in the equilibrium system described by the equation?
$H_{2(g)} + CO_{2(g)} \Leftrightarrow H_2O_{(g)} + CO_{(g)}$
a) addition of $H_{2(g)}$
b) addition of $CO_{(g)}$
c) increase in volume
d) increase in pressure

10. $2NO_{(g)} + O_{2(g)} \Leftrightarrow 2NO_{2(g)}$ $\Delta H = -113kJ/mol$
increasing the temperature of this system at equilibrium will result in
a) increased concentrations of NO and NO_2
b) increased concentration of NO and O_2
c) decreased concentration of NO
d) decreased concentration of O_2

11. Which change to this system at equilibrium will increase the concentration of $Br_{2(g)}$?
$4HBr_{(g)} + O_{2(g)} \Leftrightarrow 2H_2O_{(g)} + 2Br_{2(g)}$ $\Delta H = -276kJ$
a) an increase in pressure
b) an increase in temperature
c) the removal of oxygen, O_2

d) the addition of water vapor, $H_2O_{(g)}$

12. In which reaction does high pressure favor the formation of the products?

a) $2H_2O_{(g)} \Leftrightarrow 2H_{2(g)} + O_{2(g)}$
b) $N_{2(g)} + 3H_{(g)} \Leftrightarrow 2NH_{3(g)}$
c) $CaCO_{3(s)} \Leftrightarrow CaO_{(s)} + CO_{2(g)}$
d) $CO_{(g)} + H_2O_{(g)} \Leftrightarrow CO_2 + H_{2(g)}$

13. Consider the equation: $CO + 2H_2 \Leftrightarrow CH_3OH + \text{heat}$

All substances are gaseous. How will lowering the temperature affect this equilibrium system?

a) increase the concentration of H_2
b) increase the concentration of CO
c) increase the concentration of CH_3OH
d) increase the concentrations of CO and H_2
e) increase the concentrations of all components.

QUESTIONS 14 to 17 relate to the following all gas phase system at 400 ˚ C:

$$CO_{(g)} + H_2O_{(g)} \Leftrightarrow CO_{2(g)} + H_{2(g)}$$

Suppose you began examining this system when it was already at equilibrium. Now, you decide to dump in some more $CO_{(g)}$. The system responds to the disturbance and a new equilibrium position is attained. Relative to the original equilibrium concentration, the new equilibrium concentration of …

14. CO is

a) greater
b) smaller
c) the same

15. H_2O is

a) greater
b) smaller
c) the same

16. CO_2 is

a) greater
b) smaller
c) the same

17. H_2 is

a) greater
b) smaller
c) the same

Solubility Equilibrium

Soluble: all of the substance dissolves in water.

Partially Soluble: dissolves to a great extent in water (some precipitate left).

Insoluble: will dissolve in water, but the amount that dissolves is extremely small, almost ALL the substance precipitates.

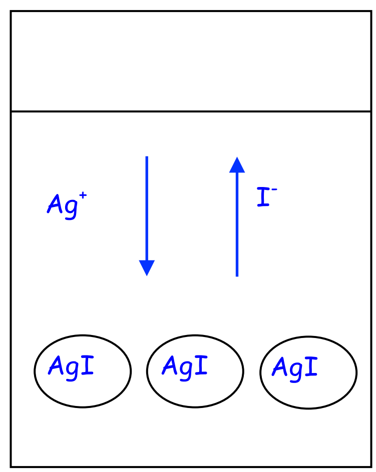
**Solubility Equilibrium looks at the partially or almost insoluble solids in equilibrium with their ions.*

Solubility Equilibrium: When the rate of dissolving is equal to the rate of precipitation.

Example:

Draw the solubility equilibrium of $AgI_{(s)}$.

Dissociation Equation: $AgI_{(s)} \rightarrow Ag^{+}_{(aq)} + I^{-}_{(aq)}$



Explain what is occurring at equilibrium.

Rate of dissolving = rate of precipitation

Using your equation, write the equilibrium constant expression for it.

$K_{eq}=[Ag^{+}][I^{-}]$

Whenever you write a chemical equation for the dissolving of a solid ionic substance, you always obtain an equilibrium expression in which there is no denominator. Why?

Because reactants are always solid.

Solubility Equilibrium

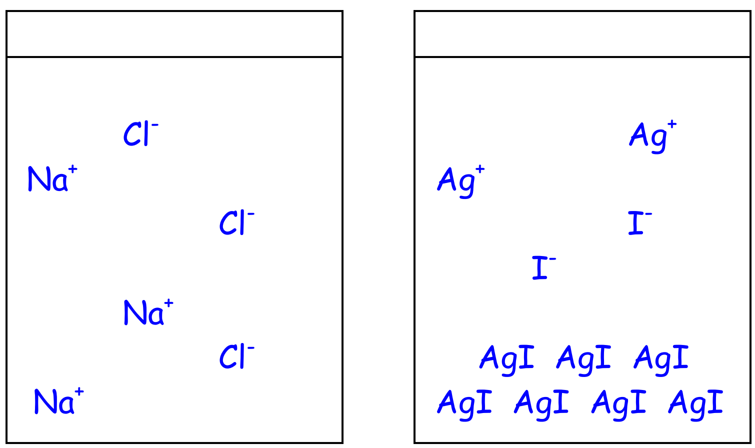
When reactions involve solubilities, the equilibrium constants for these reactions is called a solubility product constant referred to as K_{sp}.

Solubility product constant: The constant value obtained at standard temperature when the concentration of the ions in a saturated solution are multiplied together and raised to their coefficients.

Why K_{sp} is useful:

- K_{sp} tells you the relative solubilities of **slightly** soluble electrolytes.
- Smaller K_{sp}'s are less soluble than larger K_{sp}'s.

Compare NaCl (very soluble) to AgI (insoluble) using a picture.



Solubility Equilibrium

Example:
The solubility of calcium sulphate, $CaSO_4$, is $4.9 x 10^{-3}$ mol/L. Calculate the K_{sp} for $CaSO_4$.

Step 1: Write the dissociation equation for $CaSO_4$.

$CaSO_{4(s)} \rightarrow Ca^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)}$

Step 2: Write the K_{sp} expression for $CaSO_4$.

$K_{sp}=[Ca^{2+}][SO_4^{2-}]$

Step 3: Substitute the molar concentrations of the ions, Ca^{2+} and SO_4^{2-} into the K_{sp} expression and solve.

$K_{sp}=(4.9x10^{-3} mol/L)\ (4.9x10^{-3} mol/L)$
$K_{sp}=2.4x10^{-5}$

Example:
Calculate the molar solubility of $PbCl_2$ in pure water at 25C. K_{sp} for $PbCl_2$ is 2×10^{-5}.

Step 1: Write the dissociation equation for $PbCl_2$.

$PbCl_{2(s)} \rightarrow Pb^{2+}_{(aq)} + 2\ Cl^-_{(aq)}$

Step 2: Set up an ICE box and fill in the values for the unknown ions.

Equation:	$PbCl_{2(s)}$	$\rightarrow$ $Pb^{2+}_{(aq)}$	+ $2\ Cl^-_{(aq)}$
Initial (mol/L)	---	0	0
Change (mol/L)	---	+ x	+ 2x
Equilibrium (mol/L)	---	x	2x

Step 3: Write the K_{sp} expression and substitute the known values into the expression. Then solve for x.

$K_{sp}=[Pb^{2+}][Cl^-]^2$
$2x10^{-5} = 4x^3$
$x^3 = 5x10^{-6}$
$x = 1.7x10^{-2}$ mol/L

K_{sp} Problems

1. If the K_{sp} of $CaCO_3$ is 8.70 x 10^{-9}, what is the calcium ion concentration?

2. Calculate the K_{sp} of Na_2SO_4 if the sulphate ion concentration is 0.0032 mol/L in a saturated solution.

3. Determine the $[IO_3^-]$ in a saturated $Cu(IO_3)_2$ solution if the K_{sp} of 1.47 x 10^{-7}.

4. Calculate the $[H^+]$ of a saturated solution of H_3PO_4 with a K_{sp} of 4.78 x 10^{-4} assuming 100% ionization of the acid.

5. The K_{sp} of $Al(OH)_3$ is 1.26 x 10^{-3}. Determine the aluminium ion concentration and hydroxide ion concentration.

1. 9.3 x 10^{-5} mol/L 2. 1.31 x 10^{-7} 3. 6.6 x 10^{-3} mol/L 4. 0 .195 mol/L 5. $[Al^{3+}]$ = .083 mol/L, $[OH^-]$ = 0.249

The Common Ion Effect

So far, we have discussed the solubility and K_{sp} of substances in pure water. Now we will examine what happens when we add a common ion.

The K_{sp} of AgCl is 1.8×10^{-10}.

$AgCl_{(s)} \leftrightarrows Ag^{+}_{(aq)} + Cl^{-}_{(aq)}$

In pure water, the solubility of the Ag^{+} and Cl^{-} ions are:

$$K_{sp} = [Ag^{+}][Cl^{-}]$$
$$1.8 \times 10^{-10} = (x)(x)$$
$$1.8 \times 10^{-10} = x^{2}$$
$$x = 1.3 \times 10^{-5}\ mol/L$$

AgCl is considered insoluble and most will precipitate, only a very small concentration of ions are present in solution.

What happens if we add a solution of NaCl to the beaker?

$$NaCl_{(s)} \leftrightarrows Na^{+}_{(aq)} + Cl^{-}_{(aq)}$$

This equilibrium will react according to Le Chatelier's Principle. If we add ions to the right hand side, the system will shift to produce more precipitate on the left hand side.

The result will be more $AgCl_{(s)}$ in the beaker, and less Ag^{+} ions in solution.

The Common Ion Effect

Example:
Calculate the molar solubility of silver chloride in a 1.5×10^{-3} mol/L silver nitrate solution. K_{sp} for AgCl is 1.6×10^{-10}.

Note: The common ion is Ag^+, which is present in AgCl and $AgNO_3$. The presence of the common ion affects the solubility of AgCl but not the K_{sp} value because it is an equilibrium constant.

$AgNO_3$ dissociates completely as given by the equation, $AgNO_3(s) \rightarrow Ag^+_{(aq)} + NO_3^-{}_{(aq)}$. Since the concentration of $AgNO_3$ is given as 1.5×10^{-3} mol/L, then $[Ag^+]$ is 1.5×10^{-3} mol/L.

Step 1: Write the dissociation equation for AgCl.

$$AgCl_{(s)} \rightarrow Ag^+_{(aq)} + Cl^-_{(aq)}$$

Step 2: Set up an ICE box. *(Remember that there are two sources for Ag^+)*

Equation:	$AgCl_{(s)}$	$\rightarrow$ $Ag^+_{(aq)}$ +	$Cl^-_{(aq)}$
Initial (mol/L)	---	$1.5\text{x}10^{-3}$	0
Change (mol/L)	---	+ x	+ x
Equilibrium (mol/L)	---	$1.5\text{x}10^{-3}$ + x	x

Step 3: Write the K_{sp} equation, and substitute in the known values. Then solve for x.

$K_{sp}=[Ag^+][Cl^-]$
$1.6\text{x}10^{-10} = (1.5\text{x}10^{-3} + x)(x)$

This 'x' can be ignored because the amount of Ag^+ ion that can dissolve from AgCl is very small compared to the amount of Ag^+ generated from $AgNO_3$.

$1.6\text{x}10^{-10} = (1.5\text{x}10^{-3})(x)$
$x = 1.1\text{x}10^{-7}$
$[AgCl] = 1.1\text{x}10^{-7}$ mol/L

The molar solubility of AgCl in a $1.5\text{x}10^{-3}$ mol/L solution $AgNO_{3(aq)}$ is $1.1\text{x}10^{-7}$ mol/L

Common Ion Effect Problems

1. What is the $[Ba^{2+}]$ in a saturated $BaCO_3$ solution if 0.100 mol/L Na_2CO_3 is added? The K_{sp} of $BaCO_3 = 8.1 \times 10^{-8}$.

2. Determine the $[Cl^-]$ in a saturated AgCl solution if 0.200 mol/L $AgNO_3$ is added. The K_{sp} of AgCl = 1.56×10^{-10}.

3. To a saturated LiBr solution, 0.03 mol/L NaBr is added. If the K_{sp} of LiBr = 1.3×10^{-11}, what is the $[Li^+]$?

4. Calculate the solubility (in mol/L) of Ag^+ ions when Ag_2CrO_4 is dissolved
   a) in pure water
   b) in a 0.005 M solution of K_2CrO_4

   (The K_{sp} of Ag_2CrO_4 is 9.0×10^{-12})

1) 8.1×10^{-7} M 2) 7.8×10^{-10} M 3) 4.3×10^{-10} 4) a) 2.6×10^{-4} M b) 4.2×10^{-5} M

K_{sp} Worksheet

1. Write the equilibrium dissociation equations for each of the following ionic solids.
   a. Lead iodide, PbI_2
   b. Calcium hydroxide, $Ca(OH)_2$
   c. Barium chromate, $BaCrO_4$
   d. silver carbonate, Ag_2CO_3
   e. gold(III) iodate, $Au(IO_3)_3$
   f. iron(II) phosphate, $Fe_3(PO_4)_2$

2. Calculate the K_{sp} for:
   a. $SrCO_3$ which has a molar solubility of 1.0×10^{-5} M.
   b. Ag_2CO_3 which has a molar solubility of 1.3×10^{-4} M.
   c. CrF_3 given that a saturated solution contains 0.00751 g per 100.0 mL of solution.

3. Calculate the molar solubility of:
   a. $CuCrO_4$ given the K_{sp} of $3.6 \times 10^{-6}\ M^2$.
   b. $La(IO_3)_3$ given the K_{sp} of $6.1 \times 10^{-12} M^4$.

4. The K_{sp} of Ag_2CrO_4 is $1.1 \times 10^{-12}\ M^3$. If you were to heat 500.0 mL of a saturated solution to dryness, how many grams of Ag_2CrO_4 would remain behind?

5. The K_{sp} of PbI_2 is $7.9 \times 10^{-9}\ M^3$. Calculate its molar solubility in:
   a. Water
   b. 0.10 M NaI solution
   c. 0.10 M $Pb(NO_3)_2$
   d. 0.10 M MgI_2 solution

6. Use appropriate calculations to determine whether a precipitate will form when:
   a. 100.0 mL of a 0.0010 M $BaCl_2$ solution is mixed with 25.0 mL of a 0.000010 M $AgNO_3$ solution. $K_{sp}(AgCl) = 1.8 \times 10^{-10}\ M^2$
   b. 10.0 mL of a 2.5×10^{-3} M $Al_2(SO_4)_3$ solution is added to 85.0 mL of a 3.5×10^{-4} M $AgNO_3$ solution. $K_{sp}(Ag_2SO_4) = 1.5 \times 10^{-5} M^3$
   c. 0.500 g of $MgCl_2$ is added to 500.0 mL of a 0.0100 M NaF solution. $K_{sp}(MgF_2) = 6.6 \times 10^{-9}\ M^3$

Using K_{sp} to Determine if a Precipitate Will Form

Example:
The K_{sp} for $Ca_3(PO_4)_2$ in water is 2.0×10^{-29}. The approximate $[Ca^{2+}]$ in the blood is 1.2×10^{-3} M, and the approximate $[PO_4^{3-}]$ is 6.7×10^{-9} M. Do you expect a precipitate of $Ca_3(PO_4)_2$ to form in the blood?

Determine the K_{sp} of $Ca_3(PO_4)_2$ using data from the question.

$$Ca_3(PO_4)_{2(s)} \leftrightarrows 3\ Ca^{2+}_{(aq)} + 2\ PO_4^{3-}{}_{(aq)}$$

$K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2$
$K_{sp} = (1.2 \times 10^{-3})^3(6.7 \times 10^{-9})^2$
$K_{sp} = 7.8 \times 10^{-26}$

This K_{sp} value is ***greater*** than the K_{sp} of $Ca_3(PO_4)_2$ given in the question, therefore a precipitate will form.

A larger K_{sp} means there are more ions in solution than are necessary for saturation, **"supersatured"** – tendency to precipitate.

Predicting Precipitates Using K_{sp}

1. Predict whether a precipitate of PbF_2 (Ksp = $3.3x10^{-8}$) will form if 100 mL of 0.10 mol/L $Pb(NO_3)_2$ is added to 100 mL of 0.03 mol/L of NaF.

2. Predict whether a precipitate of Ag_2SO_4 (Ksp = $1.2x10^{-5}$) will form if 1.0 L of 0.025 mol/L K_2SO_4 is added to 1.0 L of 0.01 mol/L of $AgNO_3$.

3. Predict whether a precipitate of $Mg(OH)_2$ (Ksp = $5.6x10^{-12}$) will form if 50 mL of 0.20 mol/L $MgCl_2$ is added to 50 mL of 0.0025 mol/L of NaOH.

1. precipitate forms 2. no precipitate forms 3. precipitate forms

Exercise

Answer the following questions. Be sure to show all your work.

1. Silver iodide, AgI, has a solubility product of 8.5×10^{-17}. What is the solubility, in moles per Litre, of AgI in
   a. pure water
   b. 0.010 mol/L HI
   c. 0.010 mol/L MgI_2
   d. 0.010 mol/L $AgNO_3$

2. Magnesium fluoride, MgF_2, has a solubility product of 8.0×10^{-8}. Calculate the solubility, in mol/L, of magnesium fluoride in
   a. pure water
   b. 0.50 mol/L NaF
   c. 0.50 mol/L $MgCl_2$

3. Gold (III) chloride, $AuCl_3$, has a Ksp of 3.2×10^{-25}. Calculate its solubility, in mol/L, in
   a. pure water
   b. 0.20 mol/L HCl
   c. 0.20 mol/L $MgCl_2$
   d. 0.20 mol/L $Au(NO_3)_3$

Precipitates

We have already learned that ionic compounds dissociate in water.

Precipitation occurs when two different ionic (unsaturated) solutions are combined and undergo a double replacement reaction in which one of the products is insoluble in water.

$$AB + CD \rightarrow AD + CB$$

In this situation either AD or CB could be a solid precipitate not soluble in water.

Complete these double replacement reactions.

$2NaCl_{(aq)} + Pb(NO_3)_{2\,(aq)} \rightarrow 2NaNO_{3\,(\ \ )} + PbCl_{2\,(\ \ )}$

$BaBr_{2\,(aq)} + Na_2SO_{4\,(aq)} \rightarrow$

$Na_2CO_{3\,(aq)} + FeCl_{2\,(aq)} \rightarrow$

$AgNO_{3\,(aq)} + FeI_{2\,(aq)} \rightarrow$

Use the solubility rules to determine which products are insoluble and will form a precipitate. **Write the Ksp equations for the precipitates.**

From the front of the room pick up:
A large watch glass
A water bottle
A salt package
Lead nitrate
Potassium iodide
Silver Nitrate

Place some water on your watch glass. Add some salt and some silver nitrate.

- What do you see?
- Write the chemical equation for this reaction.
- Using your solubility rules determine which product the precipitate you see is. Be sure to include the states of your products in your chemical equation.
- Calculate the solubility of your precipitate using the literature Ksp value (pg 35).

Clean your watch glass and out fresh water on it. Add some Lead nitrate and some potassium iodide.

- What do you see?
- Write the chemical equation for this reaction.
- Using your solubility rules determine which product the precipitate you see is. Be sure to include the states of your products in your chemical equation.
- Calculate the solubility of your precipitate using the literature Ksp value.

WHAT'S SOLUBLE AND WHAT'S NOT

TABLE OF SOLUBILITY IN WATER

	ACETATE	BROMIDE	CARBONATE	CHLORATE	**CHLORIDE**	CHROMATE	HYDROXIDE	IODIDE	**NITRATE**	OXALATE	OXIDE	**PHOSPHATE**	SILICATE	SULFATE	SULFIDE	SULFITE
ALUMINUM	S	S	-	S	S	-	I	S	S	I	I	I	I	S	-	-
AMMONIUM	S	S	S	S	S	S	S	S	S	S	-	S	-	S	S	S
ANTIMONY	-	P	-	-	P	-	P	P	-	-	I	-	-	-	I	-
ARSENOUS	-	S	-	-	S	-	S	P	-	-	P	-	-	-	I	-
BARIUM	S	S	I	S	S	I	S	P	S	I	S	I	I	I	S	I
BISMUTH	-	P	I	-	P	I	I	I	S	I	I	I	-	S	I	-
CADMIUM	S	S	I	S	S	-	I	S	S	I	P	I	-	S	I	S
CALCIUM	S	S	I	S	S	I	P	S	S	I	P	I	I	P	S	P
CHROMIUM	S	S	-	S	S	-	I	S	S	P	I	I	I	S	I	S
COBALT	S	S	I	S	S	I	I	S	S	I	I	I	I	S	I	I
COPPER	S	S	I	S	S	I	I	S	S	I	I	I	I	S	I	S
FERRIC (Fe3+)	-	S	-	-	S	-	I	S	S	I	I	I	I	S	I	-
FERROUS (Fe2+)	S	S	I	-	S	-	I	S	S	I	I	I	I	S	I	P
HYDROGEN	S	S	-	S	S	S	-	S	S	S	-	S	S	S	S	-
LEAD	S	P	I	S	I	I	I	P	S	I	I	I	I	I	I	I
MAGNESIUM	-	S	I	S	S	S	I	S	S	I	P	I	I	S	I	P
MANGANESE	S	S	I	-	S	-	I	S	S	P	I	P	I	S	I	-
MERCURIC (Hg2+)	S	S	I	S	S	P	I	I	S	I	I	I	-	S	I	-
MERCUROUS (Hg+)	P	I	I	S	I	P	-	I	S	I	I	I	-	P	I	-
NICKEL	S	S	I	-	S	-	I	S	S	-	I	I	-	S	I	I
POTASSIUM	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S
SILVER	-	I	I	S	I	I	I	I	S	I	I	I	-	P	I	S
SODIUM	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S
STRONTIUM	S	S	I	S	S	P	P	S	S	P	I	I	I	P	S	-
TIN	-	S	I	S	S	-	I	S	S	-	I	I	-	S	I	P
ZINC	S	S	I	S	S	-	I	S	S	I	I	I	I	S	I	P

S - SOLUBLE IN WATER

I - INSOLUBLE IN WATER

P - SLIGHTLY SOLUBLE IN WATER

- COMPOUND DOES NOT EXIST OR DECOMPOSES IN WATER

GENERAL RULES OF SOLUBILITY

1. ALL AMMONIUM, POTASSIUM AND SODIUM COMPOUNDS ARE SOLUBLE IN WATER

2. ALL ACETATES, CHLORATES AND NITRATES ARE SOLUBLE IN WATER

3. ALL CHLORIDES ARE SOLUBLE IN WATER EXCEPT THOSE OF SILVER, MERCUROUS MERCURY, AND LEAD

4. ALL SULFATES ARE SOLUBLE IN WATER EXCEPT THOSE OF BARIUM AND LEAD. CALCIUM, STRONTIUM, AND SILVER SULFATES ARE ONLY SLIGHTLY SOLUBLE

5. CARBONATES, PHOSPHATES, OXIDES, SILICATES, SULFIDES, AND SULFATES ARE GENERALLY INSOLUBLE WITH THE EXCEPTIONS OF THOSE OF AMMONIUM, POTASSIUM AND SODIUM.

6. ALL HYDROXIDES ARE INSOLUBLE EXCEPT THOSE OF AMMONIUM, POTASSIUM, SODIUM, BARIUM, CALCIUM AND STRONTIUM. THOSE OF BARIUM, CALCIUM , AND STRONTIUM ARE ONLY SLIGHTLY SOLUBLE IN WATER.

Some Solubility Product Constant (K_{sp}) Values at 25 ^oC

Salt	K_{sp}	Salt	K_{sp}	Salt	K_{sp}
Bromides		**Carbonates**		**Oxalates**	
$PbBr_2$	6.6×10^{-6}	$MgCO_3$	6.8×10^{-6}	MgC_2O_4	4.8×10^{-6}
$CuBr$	6.3×10^{-9}	$NiCO_3$	1.3×10^{-7}	FeC_2O_4	2×10^{-7}
$AgBr$	5.4×10^{-13}	$CaCO_3$	5.0×10^{-9}	NiC_2O_4	1×10^{-7}
Hg_2Br_2	6.4×10^{-23}	$SrCO_3$	5.6×10^{-10}	SrC_2O_4	5×10^{-8}
Chlorides		$MnCO_3$	2.2×10^{-11}	CuC_2O_4	3×10^{-8}
$PbCl_2$	1.2×10^{-5}	$CuCO_3$	2.5×10^{-10}	BaC_2O_4	1.6×10^{-7}
$CuCl$	1.7×10^{-7}	$CoCO_3$	1.0×10^{-10}	CdC_2O_4	1.4×10^{-8}
$AgCl$	1.8×10^{-10}	$FeCO_3$	2.1×10^{-11}	ZnC_2O_4	1.4×10^{-9}
Hg_2Cl_2	1.4×10^{-18}	$ZnCO_3$	1.2×10^{-10}	CaC_2O_4	2.3×10^{-9}
Fluorides		Ag_2CO_3	8.1×10^{-12}	$Ag_2C_2O_4$	3.5×10^{-11}
BaF_2	1.8×10^{-7}	$CdCO_3$	6.2×10^{-12}	PbC_2O_4	4.8×10^{-12}
MgF_2	7.4×10^{-11}	$PbCO_3$	7.4×10^{-14}	$Hg_2C_2O_4$	1.8×10^{-13}
SrF_2	2.5×10^{-9}	**Hydroxides**		MnC_2O_4	1×10^{-15}
CaF_2	1.5×10^{-10}	$Ba(OH)_2$	5.0×10^{-3}	**Phosphates**	
Iodides		$Sr(OH)_2$	6.4×10^{-3}	Ag_3PO_4	8.9×10^{-17}
PbI_2	8.5×10^{-9}	$Ca(OH)_2$	4.7×10^{-6}	$AlPO_4$	9.8×10^{-21}
CuI	1.1×10^{-12}	$Mg(OH)_2$	5.6×10^{-12}	$Mn_3(PO_4)_2$	1×10^{-22}
AgI	8.5×10^{-17}	$Mn(OH)_2$	2.1×10^{-13}	$Ba_3(PO_4)_2$	3×10^{-23}
Hg_2I_2	4.5×10^{-29}	$Cd(OH)_2$	5.3×10^{-15}	$BiPO_4$	1.3×10^{-23}
Sulfates		$Pb(OH)_2$	1.2×10^{-15}	$Sr_3(PO_4)_2$	4×10^{-28}
$CaSO_4$	7.1×10^{-5}	$Fe(OH)_2$	4.9×10^{-17}	$Pb_3(PO_4)_2$	7.9×10^{-43}
Ag_2SO_4	1.2×10^{-5}	$Ni(OH)_2$	5.5×10^{-16}	**Chromates**	
Hg_2SO_4	6.8×10^{-7}	$Co(OH)_2$	1.1×10^{-15}	$CaCrO_4$	7.1×10^{-4}
$SrSO_4$	3.5×10^{-7}	$Zn(OH)_2$	4.1×10^{-17}	$SrCrO_4$	2.2×10^{-5}
$PbSO_4$	1.8×10^{-8}	$Cu(OH)_2$	1.6×10^{-19}	Hg_2CrO_4	2.0×10^{-9}
$BaSO_4$	1.1×10^{-10}	$Hg(OH)_2$	3.1×10^{-26}	$BaCrO_4$	1.2×10^{-10}
Acetates		$Sn(OH)_2$	5.4×10^{-27}	Ag_2CrO_4	2.0×10^{-12}
$Ag(CH_3COO)$	4.4×10^{-3}	$Cr(OH)_3$	6.7×10^{-31}	$PbCrO_4$	2.8×10^{-13}
$Hg_2(CH_3COO)_2$	4×10^{-10}	$Al(OH)_3$	1.9×10^{-33}		
		$Fe(OH)_3$	2.6×10^{-39}		