C4S CHEMICAL EQUILIBRIUM LESSON 4: LE CHATELIER'S PRINCIPLE

Introduction

It is important to know the factors that will affect or control the position of equilibrium. Chemists and chemical engineers responsible for the development and manufacturing of chemicals must understand the conditions which will optimize the amount of product as well as being economical. In this lesson, we will study those factors which control the equilibrium position of a system.

Definition

Henri Louis Le Chatelier (1850 - 1936) was a French chemist and a mining engineer. He spent much of his time studying flames in order to prevent mine explosions. He also invented two new ways of measuring very high temperatures.

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.

Concentration Changes

In a system at equilibrium, a change in the concentration of products or reactants present at equilibrium, constitutes a stress.

At equilibrium, the ratio of product to reactant concentrations is constant.

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

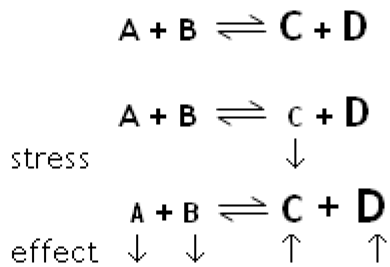
$$\begin{array}{lccccccc} & A & + & B & \rightleftharpoons & C & + & D \\ \text{stress} & \uparrow & & & & & & \end{array}$$

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.

$$\begin{array}{lccccccc} & A & + & B & \rightleftharpoons & C & + & D \\ \text{effect} & \downarrow & & \downarrow & & \uparrow & & \uparrow \end{array}$$

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.



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 system consumes some of the added product. The reverse rate is favoured until the product to reactant ratio is equal to K once again.

According to Le Chatelier's Principle, removing reactant causes a system at equilibrium to shift towards the left (reactants) in order to replace some of the lost reactant.

Iron-Thiocyanate Equilibrium

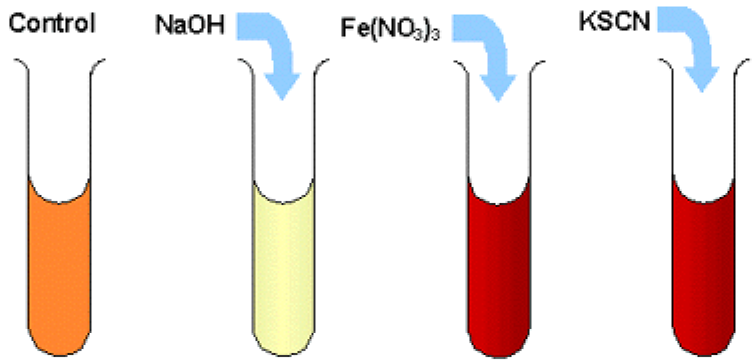
A standard laboratory example for demonstrating the effect of changing concentrations on equilibria is shown below:

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

pale yellow red

The position of equilibrium can be determined from the colour of the solution. If the equilibrium lies to the right more FeSCN2+ 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 equilibriuim 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.

The colour change indicates a shift in the equilibrium to the left, reducing the $FeSCN^{2+}$ ion concentration. Precipitating out the iron ions reduces the iron ion concentration. The system responds to the change by replacing some of the "lost" iron by favouring the reverse reaction.

Chickens and Pop

Eggshells are made of calcium carbonate, $CaCO_3(s)$ which is made from carbon dioxide, a product of cellular respiration.

Respiration causes CO_2 to be dissolved in the blood. As chickens breathe out, carbon dioxide leaves the blood. The equilibrium is shown below;

$$CO_2(g) \rightleftharpoons CO_2(aq)$$
(chicken breath)

When the carbon dioxide dissolves in the blood it reacts with the water to form carbonic acid, which ionizes in water.

$$H_2O(l) + CO_2(aq) \rightleftharpoons H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq) \rightleftharpoons CO_3^{2-}(aq) + 2\ H^+(aq)$$

The carbonate ions react with calcium to form insoluble calcium carbonate.

$$CO_3^{2-}(aq) + Ca^{2+}(aq) \rightleftharpoons CaCO_3(s)$$
(in the blood) (eggshell)

Therefore the net equation would be:

$$H_2O(l) + CO_2(g) + Ca^{2+}(aq) \rightleftharpoons 2\ H^+(aq) + CaCO_3(s)$$

When chickens get hot, they pant, and decrease the concentration of carbon dioxide in the blood. To offset the stress, the equilibrium will shift in the reverse direction and decrease the amount of calcium carbonate available to make eggshells. This yields eggs with thin shells that break easily. Ted Odom, a graduate student at the University of Illinois, found that giving chickens carbonated water to drink will shift equilibrium in the forward direction and minimize the effects of panting on warm days. This allows farmers to minimize the effects without having to install expensive air conditioning in chicken coops.

Pressure Changes

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

Let’s first review some properties of gases:

- Boyle's Law says that the pressure of a system can be changed by increasing or reducing the volume of the reaction container. Increasing the size of the container reduces the pressure, while decreasing the size of the container increases the pressure of the system.
- Avogadro's Law says that the pressure of a system is directly related to the number of gaseous particles in the container; the greater the number of gaseous particles, the greater the pressure and vice versa.

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.

Check out the example on the next page.

Pressure Change Example

For the reaction

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

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.

The system can reduce molecules by favouring the forward reaction. There are four moles of 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, increasing the concentration of NH_3 and reducing the concentration of N_2 and H_2.

The equilibrium position shifts right. There will be more product and less reactant after the change than before.

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. There are more gaseous reactants than products.

The equilibrium shifts left, favouring the reverse reaction and increasing the concentration of reactants while reducing the concentration of products.

Hydrogen Iodide Equilibrium

For the following reaction

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

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

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**.

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) or a reactant (endothermic reactions) 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:

$$N_2O_4(g) \rightleftharpoons 2\ NO_2(g) \quad \Delta H = +58\ kJ$$

colourless brown

or

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

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 N2O4 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 which heat is a product (exothermic). The equilibrium position shifts towards the left. This increases the concentration of N_2O_4 and reduces the concentration of NO_2.

This is evident since NO_2 is a brown coloured gas, while N_2O_4 is colourless. As the temperature is increased the gas becomes brown and as the reaction chamber is cooled, the gas turns colourless.

NO_2 and N_2O_4 are produced in the exhaust of gasoline powered engines. These gases are partly responsible for smog. On hot days the amount of NO_2 is increased and is responsible for the brownish haze of smog. Large cities will often have air quality advisories on hot days due to the presence of NO_2. NO_2 tends to react with water in the lungs and irritates the lungs of people with breathing problems, such as asthma.

Temperature and K

The equilibrium constant is temperature dependent. This is evident from the previous page where temperature changes can shift the equilibrium concentrations of reactants a products, while keeping volume constant.

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.

Effect of a Catalyst

We saw in the previous module 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.

Click on the link below to view a tutorial on Le Chatellier's Principle:

Le Chatelier's Principle Tutorial

Exercise

Answer each question below. Explain why each change occurs.

1. For the reaction

$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g) \ \Delta H = -92.5 \text{ kJ}$$

predict the effect on the position of the equilibrium that results from

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

$$CH_4(g) + H_2O(g) + 49.3 \text{ kJ} \rightleftharpoons CO(g) + 3\ H_2(g)$$

predict the effect on the position of the equilibrium that results from

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

$9.4 \text{ kJ} + 2\ HI(g) \rightleftharpoons H_2(g) + I_2(g)$

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
$CO(g) + 2\ H_2(g) \rightleftharpoons CH_3OH(g) + \text{energy}$

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

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

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

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

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.

Answer Key

1. a) Decreasing the volume of the container increases the total pressure of the system. According to Le Chatelier's Principle, the system will lower the pressure by reducing the number of particles. This causes the equilibrium to shift right (towards products) because the right side of the equation has fewer particles.

b) Adding chlorine gas to the system increases the concentration of a reactant. According to Le Chatelier's Principle, the system will use up the added reactant by shifting towards the products (right).

c) According to Le Chatelier's Principle, increasing the temperature tends to favour the endothermic reaction. This system will respond by shifting the equilibrium to the left (reactants) in order to use the added heat.

d) Increasing the volume of the container reduces the pressure of the system. According to Le Chatelier's Principle, the system will respond by increasing the pressure. The system will shift to the left (reactants), since the reactants have more particles.

e) A catalyst lowers the activtion energy of both forward and reverse reactions equally. Adding a catalyst does not affect the equilibrium position, just the speed with which equilibrium is reached.

**Note: Question #1 describes how each answer should be written as a full answer. The following questions will only provide the answers, not the explanations.

2. a) Increasing temperature favours the endothermic reaction. Therefore the equilibrium shifts right (towards products).

   b) Decreasing temperature causes a shift to the left (reactants), in order to replace lost heat.

   c) Decreasing the pressure shifts equilibrium to the right (products).

   d) Decreasing the volume of the container increases pressure, shifting equilibrium to the left. This increases pressure by increasing particles.

e) Adding a solid drying agent such as $CaCl_2$ which reacts with $H_2O(g)$ reduces water concentration. Since water is a reactant, the system will shift towards the left (reactants) to replace the lost reactant.

3. a) increases [HI]

   b) no change in [HI] since both sides have 2 particles each.

   c) decreases [HI]

   d) No change in [HI] if a catalyst is added
4. a) A decrease in temperature increases $[CH_3OH]$.

   b) An increase in pressure, increases $[CH_3OH]$.

   c) Addition of $H_2(g)$ increases $[CH_3OH]$.

   d) Addition of a catalyst does not affect equilibrium $[CH_3OH]$.
5. a) If O_2 is added, $[NO_2]$ increases to use up added oxygen.

   b) If NO is removed, $[NO_2]$ decreases to replace lost NO.

   c) If energy is added, $[NO_2]$ is decreased to use up added heat.
6. a) An increase in pressure will decrease the $[NO_2]$.

   b) An increase in temperature will increases the $[NO_2]$.

   c) The addition of a catalyst will not affect the equilibrium $[NO_2]$.