12.2 Chemical Equilibrium

Chemical reactions are reversible

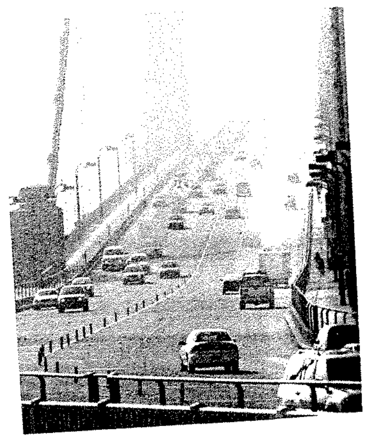
Up until now we have treated chemical reactions as though they only go in one direction, from reactants to products. In this section you will learn that chemical reactions are reversible. The fact that reactions are capable of going back and forth allows them to achieve a "balance", known as **equilibrium**. When equilibrium has been established in a chemical system there is no overall change in the amounts of reactants and products.

Equilibrium

To understand the concept of equilibrium it is helpful to develop the idea of chemicals forming products and reactants simultaneously. As reactants are forming products, products are also forming reactants, so we can picture a chemical reaction moving forward from left to right and backwards from right to left at the same time!

Equilibrium is like a two way bridge

To further understand this new concept of equilibrium, lets look a bridge. In this example a bridge with a steady traffic flow in both directions, represents a chemical reaction.



During a busy commute time, the traffic flowing in both directions on the bridge, is steady. The number of cars moving across the bridge into the city, and out of the city stays relatively constant.

When the number of cars moving into and out of the city, across the bridge, is constant we can say the system has established a balance. In contrast, a balance could not be established if the traffic flow was only in one direction, say into the city, or if the traffic flow continually changed.

$$\text{Traffic in the city} \underset{\text{cars moving in}}{\overset{\text{cars moving out}}{\rightleftharpoons}} \text{Traffic outside the city}$$

The key to understanding equilibrium is to realize that both the forward and the reverse reaction are happening together simultaneously. The result is that the *amount* of product and reactant remain constant over time, but the molecules are continuously being exchanged, just like the cars in and out of the city

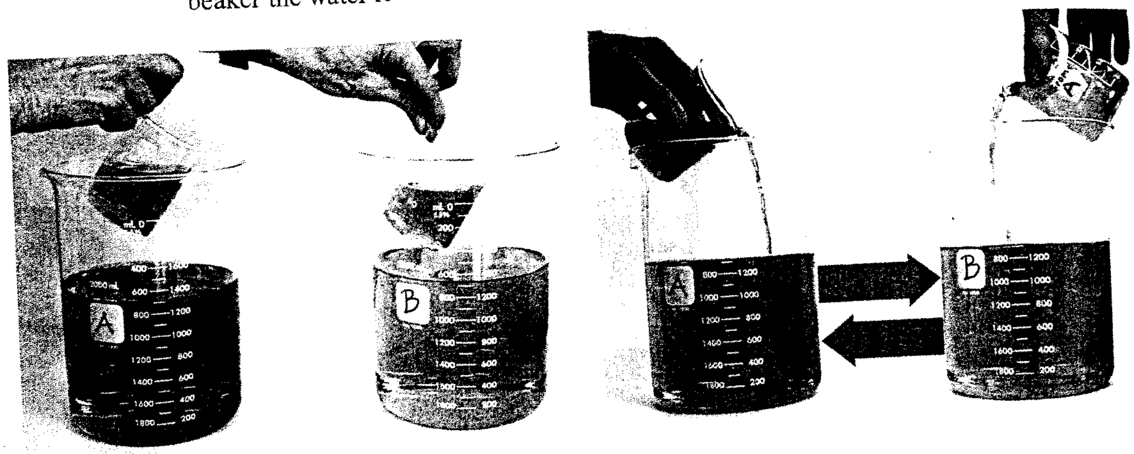
Chemistry terms

equilibrium - a "balance" in a chemical system. At equilibrium the rate of the forward reaction is equal to the rate of the reverse reaction, and the concentration of reactants and products remain constant over time.

Equilibrium is dynamic

Equilibrium systems are always changing.

One common misconception about equilibrium is that it is static and unchanging once it has been reached. This is because the system does not appear to change. To explain this it is helpful to consider a simple demonstration with beakers of water. Look a the picture of the beakers below. Notice they both have the same amount of water in them. If we remove 50mL of water from each beaker and we simultaneously pour it in to the other beaker the water levels in both beakers will still remain the same.



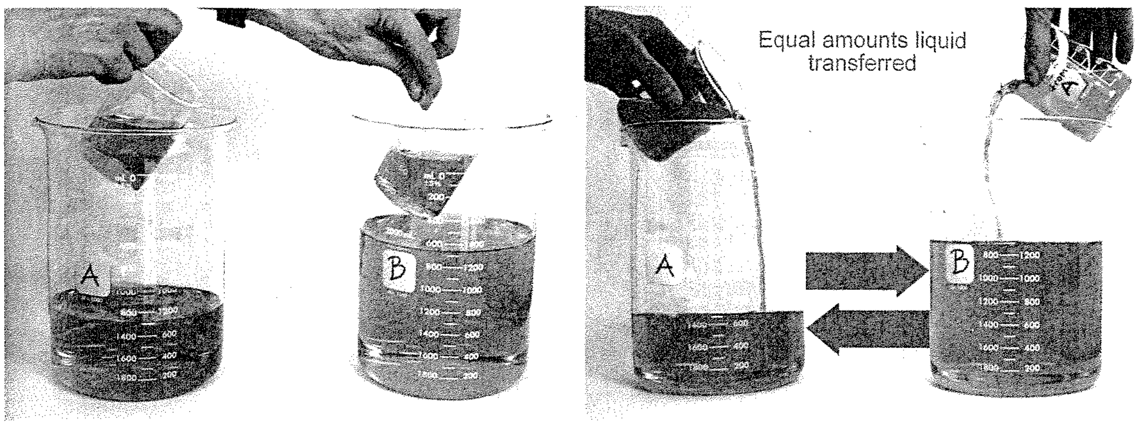
It looks like nothing is happening!

So while molecules of water moved from beaker A to beaker B, there was no noticeable change in either beaker. If you look at the beakers before and after the transfer of water you would not know that they were different. However we know that water molecules were transferred from beaker A to beaker B. In chemical reactions we are thinking about the rate of the forward reaction being equal to the rate of the reverse, this example mimics the equal rate by transferring equal amounts of water at the same time, so that the rate of change is equal over time. This is what fools us into thinking nothing happened. A chemical reaction has different chemicals that make up the forward and reverse reactions, however the rate at which the forward and reverse reaction take place is constant in equilibrium, so there is no overall observable change. Just like the beakers of water above.

It is important to emphasize that a balance is achieved between the two beakers. The amounts of water transferred are the same between the two beakers. In this example we started with beakers A and B having the same amounts of water in them. This would be similar to a chemical reaction where the amount of product and reactant are present in equal amounts. As you will see on the next page the equilibrium starting position and balance may not be the same. However, equilibrium still occurs.

Equilibrium balance

Balance is established no matter where the equilibrium system begins.



Here you can see that beakers A and B start with unequal amounts of liquid. However, the same amount of liquid is transferred between beakers A and B, which mimics the "rate" of the forward and reverse reaction being equal over time.

Equilibrium does not mean there must be equal amounts of reactants and products

Equilibrium simply means that a balance has been established. The "balance" is often different for different chemical reactions. Even though the beakers contain different amounts of reactant and product the water levels remain the same as long as the "rate" of transfer between the two is equal. Equal numbers of molecules are being exchanged between both beakers. The amount of reactant and product are not "equal" as shown by the unequal levels of liquid in the beakers.

Non-equilibrium

In a case of non equilibrium the amounts of water transferred would be *unequal* and over time *you would see a net change in the water levels*. The water levels would continue to become more unbalanced as "unequal" amounts of liquid are transferred. What would happen over time? We would notice that the water levels would noticeably change over time. One beaker would over-flow and one would become empty. In this case, there would be no balance achieved, because the rate of transfer is not equal between the beakers. Of course it is often impossible for us to see the molecules being exchanged back and forth, so to our eyes it appears as though nothing is happening. In the lab we rely on color changes and sampling amounts as they change over time. To measure the change over time requires some sensitive equipment, such as a spectrophotometer.

Le Chatelier's principle

Chemists carefully study ways to influence equilibrium positions. In industry and in the environment it can be important to understand how to make a chemical reaction move more in one direction. What factors affect the direction an equilibrium reaction "favors"? How can we influence the reaction and make it go in the direction we desire? Four variables affect the direction of equilibrium: concentration, temperature, pressure and volume. In this section we will study how changes in conditions affect the equilibrium position.

Systems shift to "partially" offset the stress

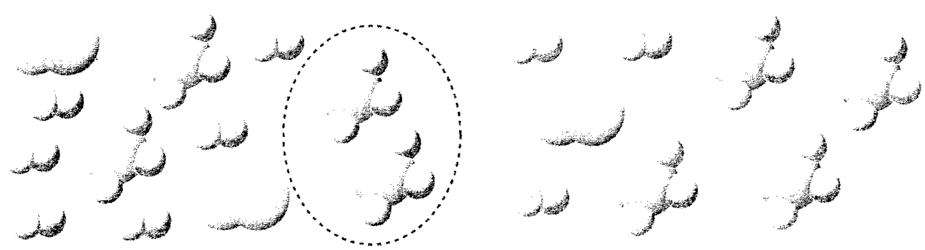
A French chemist, Henri LeChatelier, proposed a good general rule that allows us to predict how an equilibrium reaction will respond to changes. **Le Chatelier's principle** states that when a "change" is placed on a system at equilibrium, the system will shift in a direction that partially offsets the "change". The change placed on an equilibrium system refers to changes in concentration, pressure, volume or temperature.

The "change" causes the equilibrium balance to be disturbed.

We avoid stress too!

Le Chatelier's principle is very applicable to our everyday lives! Just think about it. Most of us tend to avoid, or move away from things that cause us stress. Changes in our environment cause us to adjust our behavior. Chemical reactions behave the same way! Remember that equilibrium is a "balance" so anything that changes the balance would cause an adjustment

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$



2 NH_3 are removed.
Reaction shifts to the right..

Some reactants are used to make more NH_3 to compensate for the removal.

Chemistry terms

Le Chateliers principle - states that when a "change" is placed on a system at equilibrium, the system will shift in a direction that partially offsets the "change". The change can be defined as a change in temperature, concentration, volume or pressure.

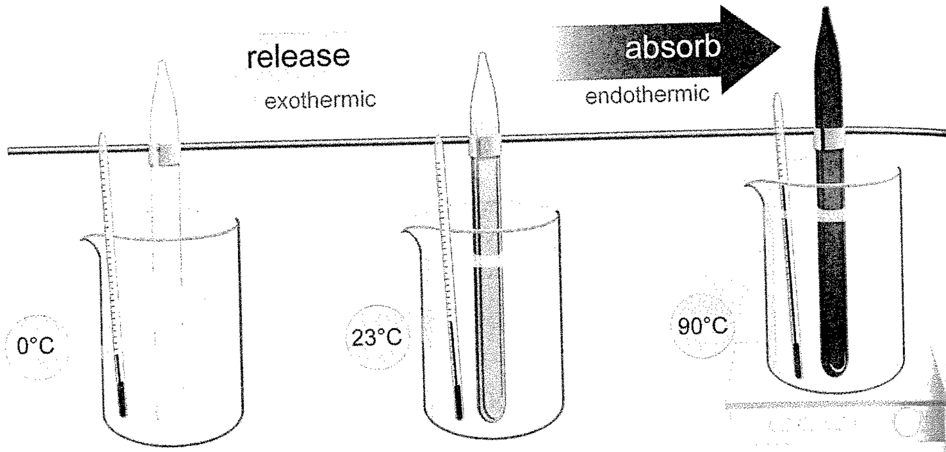
The effect of a change in temperature

Reversible reactions shift to absorb or release heat

Using the familiar equilibrium system for the N_2O_4/NO_2 system:

$$N_2O_4(g) + 58.0 \text{ KJ/mole} \rightleftharpoons 2NO_2(g)$$

clear red-brown



Here the reaction is absorbing heat, in the forward direction.

How does this system react to change in temperature?

1)An increase in temperature will cause the system to shift to decrease the temperature. Think about what you do if you are hot? You might remove your jacket or a layer of clothing, right? A chemical reaction "cools off" by taking in some of the added heat, and holding it in the chemical bonds, thereby absorbing some of the added heat. The endothermic side holds more heat in the bonds of the chemicals, the exothermic side holds less heat in the bonds of its chemicals. A chemical reaction gets rid of some of the added heat by "storing" it. The N_2O_4/NO_2 system is endothermic in the forward direction, so the reaction shifts toward products to partially off-set the increase in temperature. The picture above shows us that the system becomes a darker red-brown when placed in hot water.

2)A decrease in temperature will cause the system to want to release some heat to counter act the change. If the system is cooled down then it wants to compensate by heating up a little. How does the system release heat? It shifts to the exothermic side and releases some of the "stored" heat from the chemical bonds. Here the exothermic side is the reactants side: $N_2O_4(g)$ + 58.0 kJ/mole $\rightleftharpoons$ $2NO_2(g)$ When going from right to left using this chemical reaction heat is released and this partially compensates for the decrease in temperature. This reaction tells us that as 2 moles of $NO_2(g)$ form 1 mole of the reactant $N_2O_4(g)$, 58.0 kJ of heat is released.

Effect of change in concentration

Equilibrium shifts to counter act changes in concentration

Increasing or decreasing the concentration of the reactants or products, changes the amounts available for the overall reaction. If the amounts decrease the reaction will shift to increase them. If the amounts increase the reaction will shift to decrease them.

1) If the amount of SO_2 increases, the system will shift to the right, the products side to consume some of the added reactant.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

Reactants → Product (Shifts Right)

In a reversible equilibrium reaction, forming product, means "using up" or consuming reactants

2) If the amount of SO_2 is decreased, the system will shift to the left, the reactants side to produce some of the lost reactant.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

Reactants ← Product (Shifts Left)

Forming reactants, means consuming some of the products

Just remember if there is an increase in concentration Le Chatelier's principle says that the system will shift to decrease some of the concentration. The reverse is also true.

Solved problem

Using the following equilibrium system: $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

Predict the direction the system will shift, as a result of an increase in the concentration of $Cl_2(g)$.

Asked: *Predict the direction the system will shift?*

Given: *Increase in* $Cl_2(g)$

Relationships: *Note that* $Cl_2(g)$ *is a product on the right side of the equation.*

Solve: *The system will shift toward the reactant to consume some of the added* $Cl_2(g)$.

Relationships: *Shifts left to produce some* PCl_5

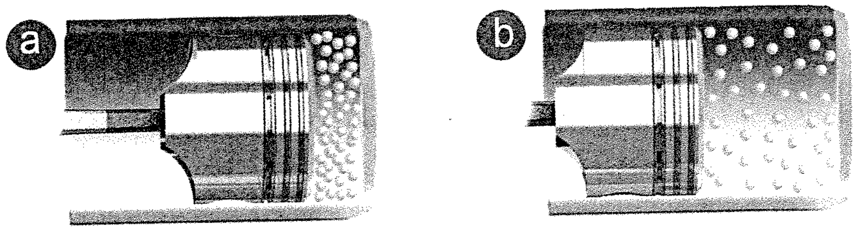
Discussion: *Partially off-sets the increase in* $Cl_2(g)$

Effect of change in pressure or volume

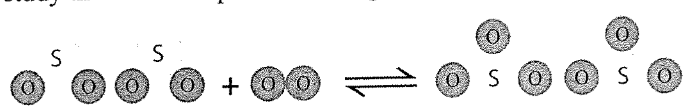
Changes in pressure or volume only effect gaseous equilibrium systems. To understand how a change in pressure or volume can influence an equilibrium system we will first look a how pressure and volume are related. In the example below we will assume we have a container of fixed volume, with rigid walls that cannot expand or contract.

Gas particles can compress or expand when inside a piston

The picture below shows a piston with a gas trapped inside. In figure a, when the pressure on the gas is increased, the volume of the gas decreases. On the other hand in figure b, when the pressure on the gas decreases, the volume of the gas is increases and the gas expands.



We can study the effects of pressure changes on the following equilibrium system:



$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

2 moles 1 mole 2 moles

Consider the system to be in a container that has a movable piston, like the one shown above.

What happens when pressure changes?

1) Increased Pressure on the System: Le Chatelier's principle predicts the system will adjust to partially decrease the pressure. Chemical reactions do this by shifting to the side of the reaction with fewer moles. In this case that would be the products side. Two moles of SO_3 gas exerts less pressure than 3 moles of the reactant gases (2 moles SO_2 plus one mole $O_2(g)$). The fewer the gas particles the lower pressure. Think of each individual gas particle as a force that pushes, the more particles of a gas the higher the pressure.

2) Decreased Pressure on the System: Here the reaction shifts to the side with more moles to try to raise the pressure. The side with more moles in this case would be the left side or the reactants.

3) If the total moles of gas are equal on both sides of the gaseous equilibrium equation then there would be no shift, because neither direction would partially off set the change.