Reversible Reactions and Equilibrium

Reversible Reactions

A reversible reaction is one where the conversion of reactants to products and the conversion of products to reactants occur simultaneously.

Example:

Forward Reaction $2SO_{2(g)} + O_{2(g)} \longrightarrow 2SO_{3(g)}$

Reverse Reaction $2SO_{2(g)} + O_{2(g)} \longleftarrow 2SO_{3(g)}$

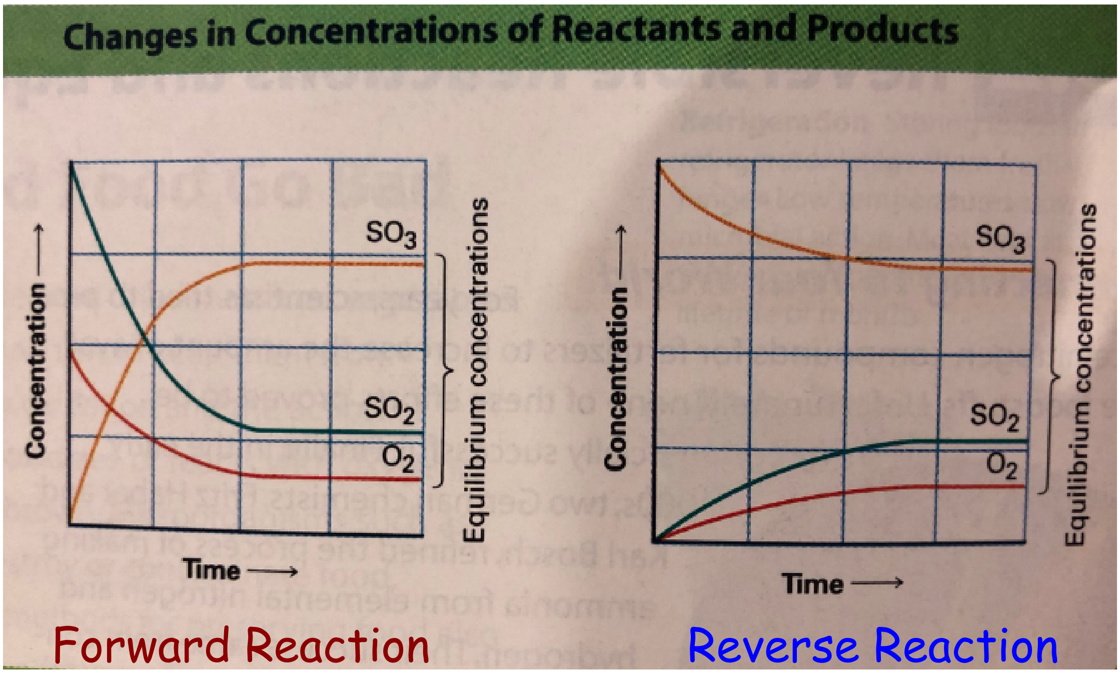
The reactions are read based on the arrows. The forward reaction is a combination reaction. The reverse reaction is a decomposition reaction.

The two equations can be written simultaneously by using a double arrow.

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

The double arrow tells you the reaction is reversible.

Take a look at the graph on pg 550

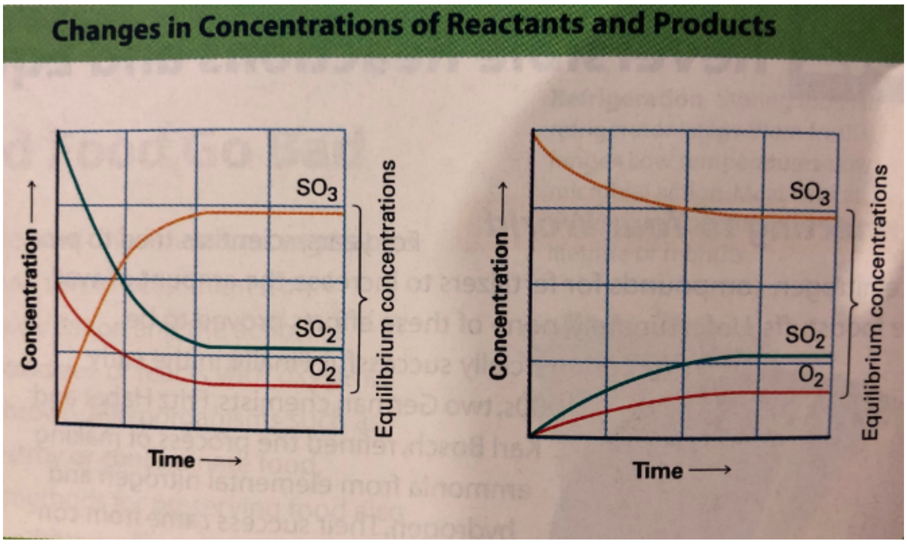


When the rates of the forward and the reverse reactions are equal, the reaction has reached a state of balance called **chemical equilibrium**.

At chemical equilibrium, no net change occurs in the actual amounts of the components of the system.

The amount of SO_3 in the equilibrium mixture is the maximum amount that can be produced by this reaction under the conditions of the reaction.

Although the rates of the forward and reverse reactions are equal at chemical equilibrium, the concentrations of the components are not always equal.



In the graph, SO_3 has a much higher equilibrium concentration than that of SO_2 and O_2.

Where the concentrations end up at equilibrium is called the **equilibrium position** of a reaction. This shows whether the reactants or products are favored in a reversible reaction.

If A reacts to give B in a reversible reaction...

$$A \rightleftharpoons B$$

If the equilibrium mixture contains more B than A, then the formation of B is said to be favored.

$$A \rightleftharpoons B$$

If A has a higher equilibrium concentration then A would be more favored in the reaction.

$$A \rightleftharpoons B$$

In general, the longer of the two arrows indicates which reaction is more favorable.

Factors Affecting Equilibrium: Le Chatelier's Principle

French chemist Henry Le Chatelier studied how equilibrium positions shift as a result of changing conditions.

Le Chatelier's Principle: If a stress is applied to a system in dynamic equilibrium, the system changes in a way that relieves the stress.

Different stress factors include changes in concentration, temperature, and pressure.

Concentration - Changing the amount of any reactant or product in a system at equilibrium disturbs the reaction. The system adjusts to minimize the change.

If *products are added* to a reaction in equilibrium, it pushes the reversible reaction in the *direction of the reactants*. *Removing a product* pushes the reversible reaction in the *direction of the products*.

Temperature

<u>Increasing the temperature</u> causes the equilibrium position of a reaction to shift in the *<u>direction that absorbs heat</u>*.

$$2SO_2(g) + O_2(g) \underset{\substack{\text{Remove heat (cool)} \\ \text{Direction of shift} \rightarrow}}{\overset{\substack{\text{Add heat} \\ \leftarrow \text{Direction of shift}}}{\rightleftharpoons}} 2SO_3(g) + \text{heat}$$

Exothermic reactions (which release heat) are favored if heat is removed.

Endothermic reactions (which consume heat) are favored if heat is added. So higher temperatures increase endothermic reactions.

Pressure

It affects only gaseous reversible reactions in equilibrium that have an unequal number of moles in the products and reactants.

Increasing the pressure on the system drives the reaction to produce fewer moles. The results is a shift in the equilibrium position that *favors the side with the fewest moles*.

Similarly, *decreasing the pressure* on the system would encourage the reaction to fill the empty space and would *favor the side with the most moles*.

Example

What effects do each of the following changes have on the equilibrium position for this reversible reaction?

$$PCl_{5(g)} + heat \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$$

a) addition of Cl_2
b) increase in pressure
c) removal of heat
d) removal of PCl_3 as it is formed

Equilibrium Constants

Chemists express the position of equilibrium in terms of numerical values. These values relate the amounts of reactants to products at equilibrium.

In general, at equilibrium we have

$$aA + bB \rightleftharpoons cC + dD$$

The equilibrium constant (K_{eq}) is the ratio of product concentrations to reactant concentrations at equilibrium.

The expression to solve for the equilibrium constant is

$$K_{eq} = \frac{[C]^c \times [D]^d}{[A]^a \times [B]^b}$$

coefficients in the balanced chemical equation

concentration of substance in mol/L

If the temperature of the reaction changes, then K_{eq} also changes.

If $K_{eq} > 1$, the products are favored at equilibrium

If $K_{eq} < 1$, the reactants are favored at equilibrium.

Example Problem

The colorless gas dinitrogen tetroxide (N_2O_4) and the dark brown gas nitrogen dioxide (NO_2) exist in equilibrium with each other.

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$$

A liter of a gas mixture at equilibrium at 10°C contains 0.0045 mol of N_2O_4 and 0.030 mol of NO_2. Write the expression for the equilibrium constant and calculate the equilibrium constant (K_{eq}) for the reaction.

Example 2

One mol of colorless hydrogen gas and 1.00 mol of violet iodine vapor are sealed in a 1-L flask and allowed to react at 450°C. At equilibrium, 1.56 mol of colorless hydrogen iodide is present, together with some of the reactant gases. Calculate K_{eq} for the reaction.

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

Example 3

Bromine chloride (BrCl) decomposes to form bromine and chlorine

$$2BrCl \rightleftharpoons Br_{2(g)} + Cl_{2(g)}$$

At a certain temperature, K_{eq} for this reaction is 11.1. Pure BrCl is placed in a 1-L container and analysis shows that the reaction mixture contains 4.00 moles of Cl_2. How many moles of Br_2 and BrCl are also present in the equilibrium mixture?

Try questions #6-16 on pages 555-559