Chapter 7 Reaction Rates and Equilibrium

Reaction Rates

The rate of a chemical reaction is the change in the amount of a reactant or product of the reaction with time.

The rates of chemical reactions differ enormously depending on the reaction and conditions.

Rates of chemical change must be measured for each chemical reaction under given conditions.

Molecular Collisions

Reacting particles must come into contact with one another in order to react or change chemically; that is, they must collide.

Some collisions lead to reaction (effective collisions) and others do not. There are two main reasons.

> Some of the collisions are not energetic enough. The kinetic energy of the colliding particles must usually be high enough to break bonds. The minimum energy necessary to lead to reaction is called the activation energy.
> In some cases the colliding molecules, or other particles, do not have appropriate orientation to one another in the collision to lead to a reaction.

Activation Energy and Energy Diagrams

Reactants must have enough energy to overcome the activation energy barrier in order to become products.

You must draw and interpret energy diagrams for chemical reactions.

Energy of reactants
Energy of products
Transition state
Activation energy
Energy of reaction

Understand in terms of bonds broken and the reformation of bonds.

The lower the activation energy the faster the reaction; the higher the activation energy the slower the reaction.

Factors Affecting Rates of Reaction

For most reactions the rate is increased with increase in the concentration of one or more of the reactants due to increasing the rate of collision between the reacting particles.

Reaction rate is generally increased with increasing temperature since more reactant collisions are sufficiently energetic to supply the required activation energy for the reaction.

A catalyst is a substance that increases the rate of a chemical reaction without being consumed in the reaction. Catalysts operate by changing the reaction pathway to one that has a lower activation energy. Consequently, more reactants have energy greater than the activation energy.

Reversible Reactions and Equilibrium

A reversible reaction can be made to go in the direction of product formation, or having formed products, can be made to produce the substances that were originally the reactants.

When products form reactants at the same rate that reactants form products (in a closed vessel), equilibrium is established and no further net reaction will occur until the amount of a reactant or product is changed.

Equilibrium Constants

Consider the symbolic reaction at equilibrium

$$aA + bB + \ldots == cC + dD + \ldots$$

The following quantitative expression can be written

$$K = [C]^c [D]^d \ldots / [A]^a [B]^b \ldots$$

In which capitol letters represent chemical species and the brackets denote molar concentration of the species. The lower case letters are the stiochiometric coefficients. The K is a constant for a given reaction and is called the equilibrium constant.

The equilibrium constant depends on temperature but not on the amount of reactants and/or products that are initially mixed.

A high equilibrium constant indicates that much more product is formed for the reaction as written, that is, the reaction goes nearly to completion in the direction written.

Conversely, a small equilibrium constant (value << 1) indicates that little product is formed for the reaction in the direction written.

There is no relationship between the rate of a reaction and the value of K.

Le Chatelier's Principle

Le Chateliers principle states that if a system at equilibrium experiences an external stress, the system will change in a way as to partially relieve the strain.

The following external changes will cause a reaction at equilibrium to change or shift the equilibrium:

- Addition of reaction components
  - Reaction occurs in a direction that restores the K.
  - Addition of one or more reactants leads to the formation of more product.
  - Addition of one or more products leads to formation of more reactant.
- Removal of a reaction component
  - Removal of one or more of the reactants from a reaction at equilibrium leads to formation of more of the reactants.
  - Removal of on or more of the products of a reaction at equilibrium causes reaction to proceed toward formation of products.
- Change in temperature
  - Increasing the temperature of an exothermic reaction at equilibrium suppresses the formation of products and increases the amount of the reactants.
  - Increasing the temperature of an endothermic reaction at equilibrium leads to formation of more of the products.
- Addition of a catalyst
  - The addition of a catalyst has no effect on the position of equilibrium.