CHEMICAL KINETICS

RATE OF REACTIONS AND ITS DEPENDENCE

CHEMICAL KINETICS

Chemical kinetics is the study and discussion of chemical reactions with respect to *reaction rates, effect of various variables, re-arrangement of atoms, formation of intermediates etc*. The topics discussed in this chapter are used as tools for the study of chemical reaction.

At the macroscopic level, we are interested in amounts reacted, formed, and the rates of their formation. At the molecular or microscopic level, the following considerations must also be made in the discussion of **chemical reaction mechanism**.

- Molecules or atoms of reactants must collide with each other in chemical reactions.
- The molecules must have sufficient energy (discussed in terms of activation energy) to initiate the reaction.
- In some cases, the orientation of the molecules during the collision must also be considered.

Reaction Rates

Chemical reaction rates are the rates of change in concentrations or amounts of either reactants or products. For changes in amounts, the units can be one of mol/s, g/s, lb/s, kg/day etc. For changes in concentrations, the units can be one of mol/(L s), g/(L s), %/s etc.

With respect to reaction rates, we may deal with *average rates, instantaneous rates, or initial rates* depending on the experimental conditions.

Thermodynamics and kinetics are two factors that affect reaction rates. The study of energy gained or released in chemical reactions is called **thermodynamics**, and such energy data are called thermodynamic data.

However, thermodynamic data have no direct correlation with reaction rates, for which the **kinetic factor** is perhaps more important. For example, at room temperature (a wide range of temperatures), thermodynamic data indicates that diamond shall convert to graphite, but in reality, the conversion rate is so slow that most people think that *diamond is forever*.

Factors Influence Reaction Rates

Many factors influence rates of chemical reactions, and these are summarized below. Much more extensive discussion will be given in other pages.

1. **Nature of Reactants**
   Acid-base reactions, formation of salts, and exchange of ions are fast reactions. Reactions in which large molecules are formed or break apart are usually slow. Reactions breaking strong covalent bonds are also slow.

2. **Temperature**
   Usually, the higher the temperature, the faster the reaction. The temperature effect is discussed in terms of Activation energy.
3. **Concentration Effect**
   The dependences of reaction rates on concentrations are called rate laws. Rate laws are expressions of rates in terms of concentrations of reactants. Keep in mind that rate laws can be in differential forms or integrated forms. They are called differential rate laws and integrated rate laws. The following is a brief summary of topics regarding rate laws.
   - rate laws: differential and integrated rate laws.
   - Integrated rate laws: First Order Reactions
     Second Order Reactions

   Rate laws apply to **homogeneous reactions** in which all reactants and products are in one phase (solution).

4. **Heterogeneous reactions**: reactants are present in more than one phase
   For heterogeneous reactions, the rates are affected by surface areas.
5. **Catalysts**: substances used to facilitate reactions
   By the nature of the term, catalysts play important roles in chemical reactions.

CONCENTRATION DEPENDENCE: THE RATE LAW

The concentration dependence of the kinetics of a chemical reaction is described by its ***rate law***. The rate law for a reaction in the form of:

$aA + bB + cC... \longrightarrow dD + eE + fF....$

is usually:

rate = $k[A]^x [B]^y [C]^z$ ....

where k is the ***rate constant***,

[ ] is the molarity of the reactant,

x, y, and z are the ***reaction orders*** with respect to A, B and C, respectively.

The *overall order of the reaction* is $x+y+z$.

The rate law is always determined experimentally.

THERE ARE TWO WAYS OF DOING THIS

- ✓ **EXPERMINETAL TRIAL**
- ✓ **INTEGRATED RATE LAW**

The Rate Law Versus the Stoichiometry of a Reaction

In the 1930s, Sir Christopher Ingold and coworkers at the University of London studied the kinetics of substitution reactions such as the following.
$CH_3Br(aq) + OH^-(aq) \rightleftharpoons CH_3OH(aq) + Br^-(aq)$
They found that the rate of this reaction is proportional to the concentrations of both reactants.
Rate = $k(CH_3Br)(OH^-)$
When they ran a similar reaction on a slightly different starting material, they got similar products.
$(CH_3)_3CBr(aq) + OH^-(aq) \rightleftharpoons (CH_3)_3COH(aq) + Br^-(aq)$
But now the rate of reaction was proportional to the concentration of only one of the reactants.
Rate = $k((CH_3)_3CBr)$
These results illustrate an important point: The rate law for a reaction cannot be predicted from the stoichiometry of the reaction; it must be determined experimentally. Sometimes, the rate law is consistent with what we expect from the stoichiometry of the reaction.

$$2\ HI(g) \rightleftharpoons H_2(g) + I_2(g) \qquad \text{Rate} = k(HI)^2$$

Often, however, it is not.

$$2\ N_2O_5(g) \rightarrow 4\ NO_2(g) + O_2(g) \qquad \text{Rate} = k(N_2O_5)$$

Molecularity & Order of a Reaction

Some reactions occur in a single step. The reaction in which a chlorine atom is transferred from $ClNO_2$ to NO to form NO_2 and ClNO is a good example of a one-step reaction.

$ClNO_2(g) + NO(g) \rightleftharpoons NO_2(g) + ClNO(g)$

Other reactions occur by a series of individual steps. N_2O_5, for example, decomposes to NO_2 and O_2 by a three-step mechanism.

Step 1: $N_2O_5 \rightleftharpoons NO_2 + NO_3$

Step 2: $NO_2 + NO_3 \rightleftharpoons NO_2 + NO + O_2$

Step 3: $NO + NO_3 \rightleftharpoons 2\ NO_2$

The steps in a reaction are classified in terms of **molecularity**, which describes the number of molecules consumed. When a single molecule is consumed, the step is called **unimolecular**. When two molecules are consumed, it is **bimolecular**.

Reactions can also be classified in terms of their **order**. The decomposition of N_2O_5 is a **first-order reaction** because the rate of reaction depends on the concentration of N_2O_5 raised to the first power.

Rate = $k(N_2O_5)$

The decomposition of HI is a **second-order reaction** because the rate of reaction depends on the concentration of HI raised to the second power.

Rate = $k(HI)^2$

When the rate of a reaction depends on more than one reagent, we classify the reaction in terms of the order of each reagent.

- ✓ The difference between the molecularity and the order of a reaction is important.
- ✓ The molecularity of a reaction, or a step within a reaction, describes what happens on the molecular level.
- ✓ The order of a reaction describes what happens on the macroscopic scale.
- ✓ We determine the order of a reaction by watching the products of a reaction appear or the reactants disappear.
- ✓ The molecularity of the reaction is something we deduce to explain these experimental results.

EXAMPLE:

For a reaction:

$BrO_3^- + 5Br^- + 6H^+ \longrightarrow 3Br_2 + 3H_2O$

a set of experiments are performed, with different initial conditions. The experiments are designed to investigate the concentration effect of one of the reactants, while keeping the others constant.

Experiment	**[BrO_3^-] (M)**	**[Br^-] (M)**	**[H^+] (M)**	**Initial Rate (M/s)**
1	0.10	0.10	0.10	8.0×10^{-4}
2	0.20	0.10	0.10	1.6×10^{-3}
3	0.20	0.20	0.10	3.2×10^{-3}
4	0.10	0.10	0.20	3.2×10^{-3}

In experiment 1 and experiment 2, Br^- has a a concentration of 0.10 M and H^+ has a concentration of 0.10 M. Now look at the concentrations of BrO_3^- and decide how it was changed. The BrO_3^-concentration is doubled. Then you have to compare it to the quotient of the initial rates. So:

$1.6 \times 10^{-3} / 8.0 \times 10^{-4}$ = 2 times faster
$[2BrO_3^-]^x$ = 2 times rate, so $x = 1$; the order for BrO_3^- is first.

In both experiment 2 and experiment 3, BrO_3^- has a concentration of 0.20 M and H^+ has a concentration of 0.10 M. Now look at the concentration of Br^- and decide how it was changed and what effect it had on the reaction rate. The concentration$_1$ was doubled, and the rate doubled. This is found by taking the quotient of the initial rates:

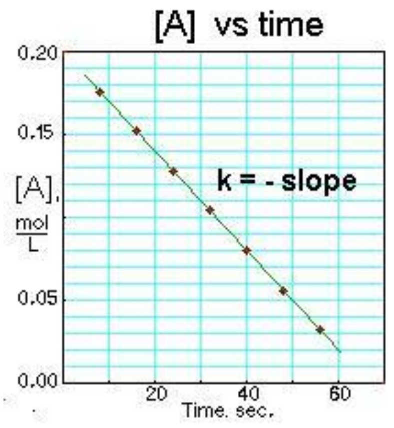
$3.2 \times 10^{-3} / 1.6 \times 10^{-3}$ = 2 times faster
$[2Br^-]^y$ = 2 times rate, so $y = 1$; the order for Br^- is first.

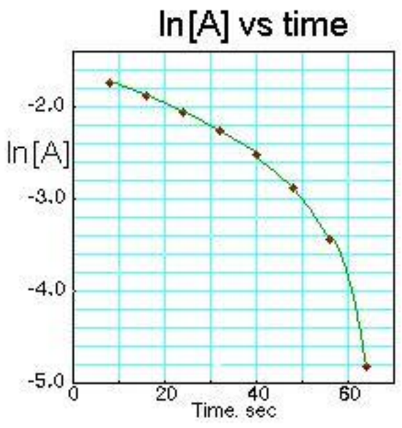
Finally, In both experiment 1 and experiment 4, BrO_3^- has a concentration of 0.10 M and Br^- has a concentration of 0.10 M. Now look at the concentrations of H^+ and decide how it was changed and what effect it had on the reaction rate. The concentration$_1$ was doubled, and the rate goes up by four times. This is found by taking the quotient of the initial rates:

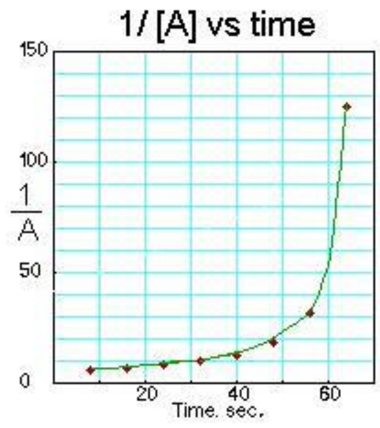
$3.2 \times 10^{-3} / 8.0 \times 10^{-4}$ = 4 times faster
$[2H^+]^z$ = 4 times rate, so $z = 2$; the order for H^+ is second

INTEGRATED RATE LAWS

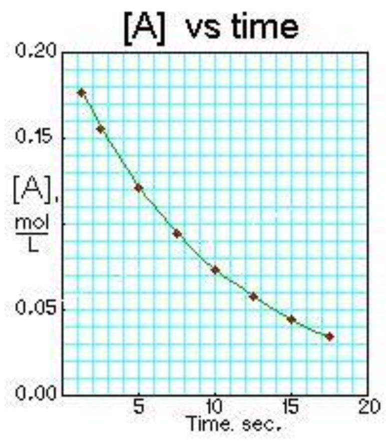
ZERO ORDER REACTION

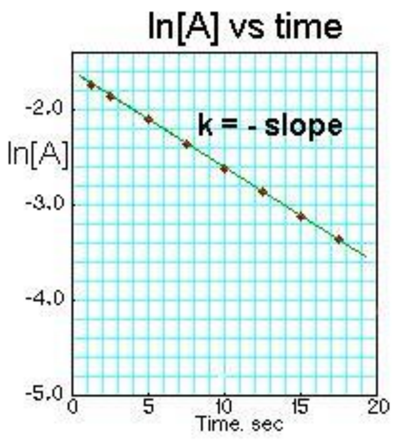


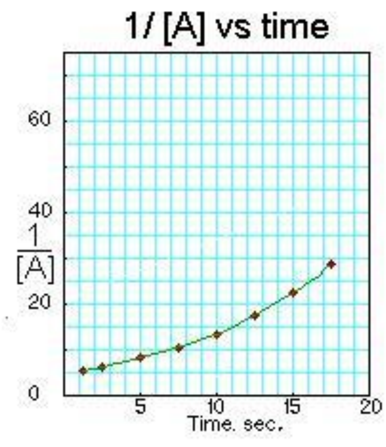




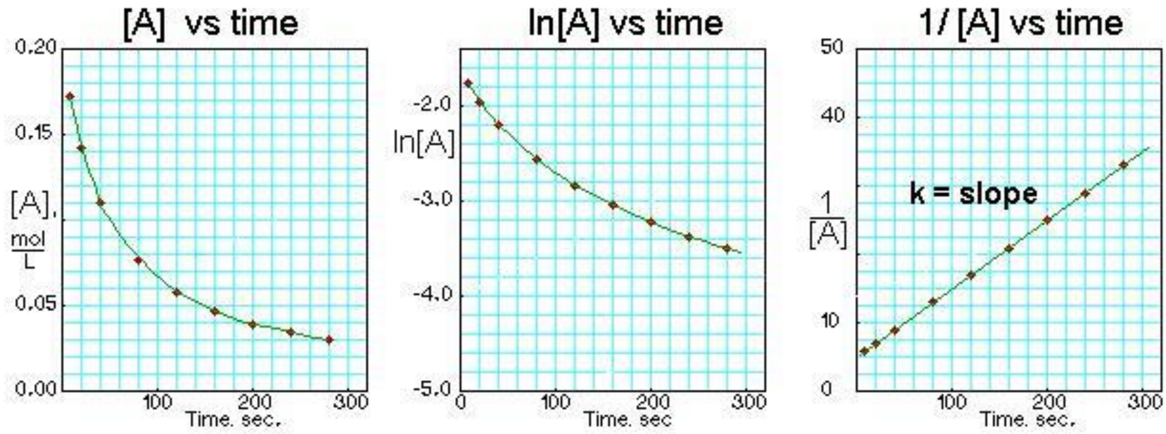
FIRST ORDER REACTION







SECOND ORDER REACTION(UNIMOLECULAR)



The Arrhenius Equation

chemical intuition suggest that the higher the temperature, the faster a given chemical reaction will proceed.

Quantitatively this relationship between the rate a reaction proceeds and its temperature is determined by the Arrhenius Equation.

At higher temperatures, the probability that two molecules will collide is higher. This higher collision rate results in a higher kinetic energy, which has an effect on the activation energy of the reaction.

The activation energy is the amount of energy required to ensure that a reaction happens.
Arrhenius Deduced a relation between the temperature and the rate of the reaction known as The Arrhenius equation which is

$$k = Ae^{-E_a/RT}$$

where k is the rate coefficient, A is a constant, E_a is the activation energy, R is the universal gas constant, and T is the temperature (in kelvin).

R has the value of 8.314×10^{-3} kJ $mol^{-1}K^{-1}$

Taking the logarithms of both sides and separating the exponential and pre-exponential terms yields

$$\ln k = \ln \left(Ae^{-E_a/RT}\right) = \ln A + \ln\left(e^{-E_a/RT}\right)$$

$$\boxed{\ln k = \ln A - \frac{E_a}{RT}}$$

which is the equation of a straight line whose slope is $-E_a/R$. This affords a simple way of determining the activation energy from values of k observed at different temperatures; we just plot $\ln k$ as a function of $1/T$.