

CHEMICAL KINETICS

Objectives

- Order and molecularity
- Kinetics of first and second order reaction
- Pseudo unimolecular reaction
- Arrhenius equation

1.1 Chemical Kinetics

Chemical kinetics is the branch of physical chemistry which deals with a study of the speed of chemical reactions. Such studies also enable us to understand the mechanism by which the reaction occurs. Thus, in chemical kinetics we can also determine the rate of chemical reaction.

From the kinetic stand point the reactions are classified into two groups:

a) homogeneous reactions which occur entirely in one phase b) heterogeneous reactions where the transformation takes place on the surface of a catalyst or the walls of a container.

1.2 Rate of reaction

The rate of reaction i.e. the velocity of a reaction is the amount of a chemical change occurring per unit time.

The rate is generally expressed as the decrease in concentration of a reactant or as the increase in concentration of the product. If C the concentration of a reactant at any time t is, the rate is $-\frac{dC}{dt}$ or if the concentration of a product be x at any time t , the rate would be $\frac{dx}{dt}$.

The time is usually expressed in seconds. The rate will have units of concentration divided by time.

The concentrations are taken in gm-moles/litre, hence rate is moles/litre/second.

Factors influencing the rate of reaction

Rate of a chemical reaction is influenced by the following factors

(i) Temperature (ii) Concentration of the reactants (iii) Nature of reactants (iv) Catalysts (v) Radiation

(i) Temperature

In most cases, the rate of a reaction in a homogeneous reaction is approximately doubled or tripled by an increase in temperature of only 100 C. In some cases the rise in reaction rates are even higher.

(ii) Concentration of the reactants

At a fixed temperature and in the absence of catalyst, the rate of given reaction increases with increased concentration of reactants. With increasing concentration of the reactant

the number of molecules per unit volume is increased, thus the collision frequency is increased, which ultimately causes increased reaction rate.

(iii) Nature of reactants

A chemical reaction involves the rearrangement of atoms between the reacting molecules to the product. Old bonds are broken and new bonds are formed. Consequently, the nature and the strength of the bonds in reactant molecules greatly influence the rate of its transformation into products. The reaction in which involve lesser bond rearrangement proceeds much faster than those which involve larger bond rearrangement.

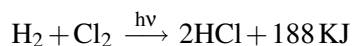
(iv) Catalysts

The rate of a chemical reaction is increased in presence of a catalyst which ultimately enhanced the speed of a chemical reaction.

(v) Radiation

The rate of a number of chemical reactions increases when radiations of specific wave length are absorbed by the reacting molecules. Such reactions are called photochemical reactions.

For example, chlorine may be mixed safely with hydrogen in dark, since the reaction between the two is very slow. However when the mixture is exposed to light, the reaction is explosive.



SKILL TEST

1. What do you mean by chemical kinetics?
2. What do you mean by rate of a reaction?
3. What is specific reaction rate or velocity constant (k)?
4. What are the factors that can change the value of K?

1.3 Order of reaction

The order is the number of concentration terms on which reaction rates depends. Thus, if the rate of a reaction depends on the first power of the concentration of reactant, i.e.
 $\text{Rate} = K C^1$

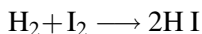
Thus the reaction is said to be of the **first order**. When the rate is proportional to the product of two reactant concentrations or the square of the concentration of a reactant, the reaction is of the **second order**.

For example, the decomposition of hydroiodic acid

$$\text{Rate} = K C_{HI}^2$$

$$\text{Rate} = K C_{HI}^2$$

and the hydrogen - iodine reaction



$$\text{Rate} = K C_{H_2} C_{I_2}$$

Here both are **second order** reactions.

If the reaction rate is experimentally found to be represented by

$$-\frac{dC}{dt} = K C^n$$

The order of the reaction is n .

If several reactants A, B, C,etc are involved and it is observed experimentally that the rate of the process is given by,

$$-\frac{dc}{dt} = K C_A^\alpha C_B^\beta C_C^\gamma \dots\dots$$

Then the order of the reaction would be $n = \alpha + \beta + \gamma + \dots\dots$

The reaction is said to be α th order with respect to A, β th order with respect to B etc.

But there are reactions in which the order is fractional i.e. $n = \frac{1}{2}, \frac{3}{2}$ etc.. For example, the ortho – para hydrogen conversion, its rate is expressed by $-\frac{d[H_2]}{dt} = K C_{H_2}^{3/2}$

1.4 Molecularity of a reaction

The molecularity of a reaction is defined as the number of molecules or atoms which take part in the process of a chemical change.

The reaction is said to be **unimolecular**, **bimolecular**, **termolecular** according to one, two, or three molecules are involved in the process of a chemical change.

The term unimolecular was used for all first order reactions, the term bimolecular for 2nd order reactions etc.

SKILL TEST

1. What do you mean by the order of a reaction?
2. What is the molecularity of a reaction?
3. Can order of a reaction be fractional?
4. Is it possible for a reaction to have identical values for molecularity and order?

1.5 Zero Order Kinetics

A chemical reaction whose rate does not depend on concentration of reactants is called a zero order chemical reaction.

The rate of the reaction can be written as

$$\frac{dx}{dt} = \text{Constant}$$

$$\Rightarrow \frac{dx}{dt} = K$$

$$\text{or, } dx = K dt$$

$$\text{On integration, } \int dx = K \int dt$$

$$\text{or, } x = Kt + Z \text{ (Integration Constant).}$$

$$\text{When } t = 0, x = 0 \text{ hence } Z = 0$$

$$\text{So, } x = Kt$$

$$\text{Or, } K = \frac{x}{t}$$

A plot of x versus t should give a straight line passing through the origin as shown in the figure and the slope of this straight line is K .

Example: Photochemical combination of H_2 and Cl_2 to form HCl .

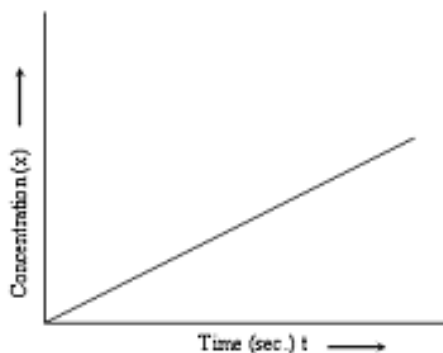
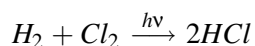


Figure 1.1: Plot of concentration against t for a reaction



The rate of this reaction does not depend on concentration.

1.6 First Order Kinetics

A reaction of the first order is represented as



where X is the reactant and Y the product. The rate of the reaction will be directly proportional to the concentration i.e.,

$$(1.1) \quad -\frac{dc}{dt} = KC$$

in which C is the concentration of the reactant at any time t and K is a constant, called the velocity constant or specific reaction rate.

$$\text{Thus } -\frac{dc}{C} = K dt$$

On integration $-\int \frac{dc}{C} = K \int dt$

$-\ln c = kt + Z$ (Integration Constant).

If at the start of the reaction the initial concentration of the reactant is C_o then we have at $t = 0$, $C = C_o$

Substituting $-\ln C_o = Z$

$$-\ln C = Kt - \ln C_o$$

$$\ln \frac{C_o}{C} = Kt$$

Or $\frac{C}{C_o} = e^{-Kt}$ Or

$$(1.2) \quad C = C_o e^{-Kt}$$

The concentration C therefore diminishes exponentially with time.

We may also write

$$(1.3) \quad C_o - C = C_o(1 - e^{-Kt})$$

The rate equation may also be conveniently expressed in an alternative form, by expressing the rate in terms of the product. When x moles per unit volume of product Y is formed from the reactant, the concentration of the reactant is $(a - x)$, where a is the initial concentration of the reactants. So

$$-\frac{d}{dt}(a - x) = K(a - x)$$

$$\frac{dx}{dt} = K(a - x)$$

$$\frac{dx}{a - x} = K dt$$

On integration $\int \frac{dx}{a - x} = K \int dt$

or, $-\ln(a - x) = Kt + Z'$ (Integration Constant)

When $t = 0, x = 0$, hence $-\ln a = Z'$