CHEMICAL KINETICS

THE RATE OF A CHEMICAL REACTION

Chemical kinetics is the branch of physical chemistry that is concerned with understanding the rates of chemical reactions. It is to be contrasted with thermodynamics, which deals with the direction in which a process occurs but in itself tells nothing about its rate.

The rate of chemical reaction is the speed or rate of the change in concentration of a reactant or product per unit time. To be specific, it can be expressed in terms of: (i) The rate of decrease in concentration of any of the reactants. (ii) The rate of increase in the concentration of any of the products. Generally, a reaction rate involves the change in the concentration of a substance over a given period of time. You calculate the rate of reaction by dividing the change in concentration by the elapsed time. You can also determine the rate of a reaction graphically, by finding the slope of the concentration curve.

Factors that Affect the Reaction Rate Constant

1. **Temperature:** At higher temperatures, reactant molecules have more kinetic energy, move faster, and collide more often and with greater energy
    - **Collision Theory:** When two chemicals react, their molecules have to collide with each other with sufficient energy for the reaction to take place.
    - **Kinetic Theory:** Increasing temperature means the molecules move faster.
2. **Concentrations of reactants**
    - As the concentration of reactants increases,

    so does the likelihood that reactant molecules will collide.
3. **Catalysts**
    - Speed up reactions by lowering activation energy
4. **Surface area of a solid reactant**
    - Bread and Butter theory: more area for reactants to be in contact
5. **Pressure of gaseous reactants or products**
    - Increased number of collisions

Chemical kinetics is the study of the rates of chemical reactions or how fast reactions occur. The primary requirement for a reaction to occur is that the reactant particles (atoms or molecules) must collide and interact with each other in some way. This is the central idea of the **collision model**, which is used to explain many of the observations made about chemical kinetics.

In order to produce an effective collision, reactant particles must possess some minimum amount of energy. This energy, used to initiate the reaction, is called the activation energy. For every sample of reactant particles there will be some that possess this amount of energy.

One way is according to the molecularity, which defines the number of molecules that are altered in a reaction: a reaction $A \rightarrow P$ is monomolecular and a reaction $A + B \rightarrow P$ is bimolecular. One-step reactions of higher molecularity are extremely rare, if they occur at all, but a reaction $A + B + C \rightarrow P$ would be tri-molecular. Alternatively one can classify a reaction according to its order, a description of its kinetics that defines how many concentration terms must be multiplied together to get an expression for the rate of reaction. Hence, in a first-order reaction the rate is proportional to one concentration; in a second-order reaction it is proportional to the product of two concentrations or to the square of one concentration; and so on**.**

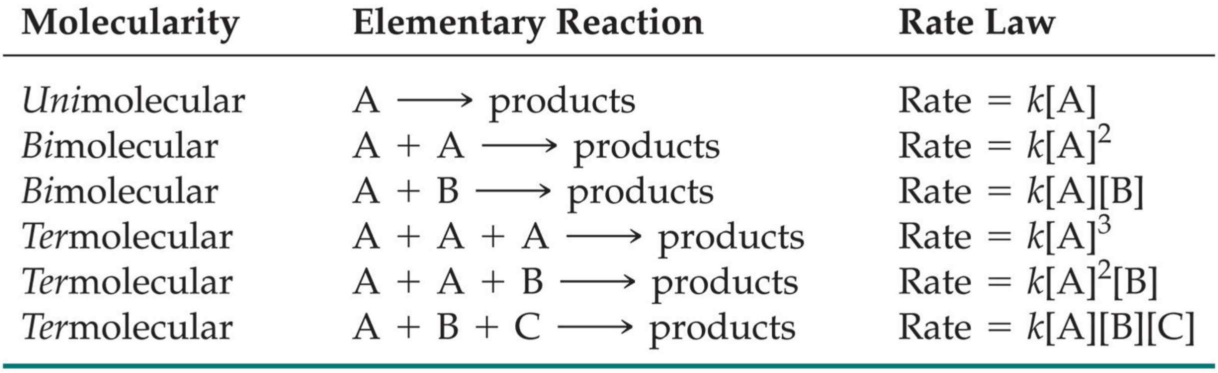
Chemical reactions can be classified according to the properties of their reaction rates, as:

1- Zero-order if the reaction rate does not depend on the concentration of the reactant(s).

2- First-order (uni-molecular) if the reaction rate depends on the concentration of only one reactant.

3- Second-order (Bimolecular) if the reaction rate depends on the square of the concentration of a single reactant, or the product of the concentrations of two reactants.

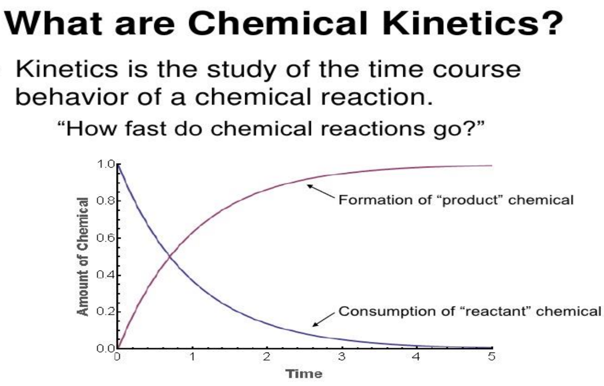
4- Third-order (ter-molecular) if the reaction rate depends on the product of the concentrations of three reactants.



Molecularity	Elementary Reaction	Rate Law
*Uni*molecular	$A \longrightarrow$ products	Rate $= k[A]$
*Bi*molecular	$A + A \longrightarrow$ products	Rate $= k[A]^2$
*Bi*molecular	$A + B \longrightarrow$ products	Rate $= k[A][B]$
*Ter*molecular	$A + A + A \longrightarrow$ products	Rate $= k[A]^3$
*Ter*molecular	$A + A + B \longrightarrow$ products	Rate $= k[A]^2[B]$
*Ter*molecular	$A + B + C \longrightarrow$ products	Rate $= k[A][B][C]$

We will discuss the following:

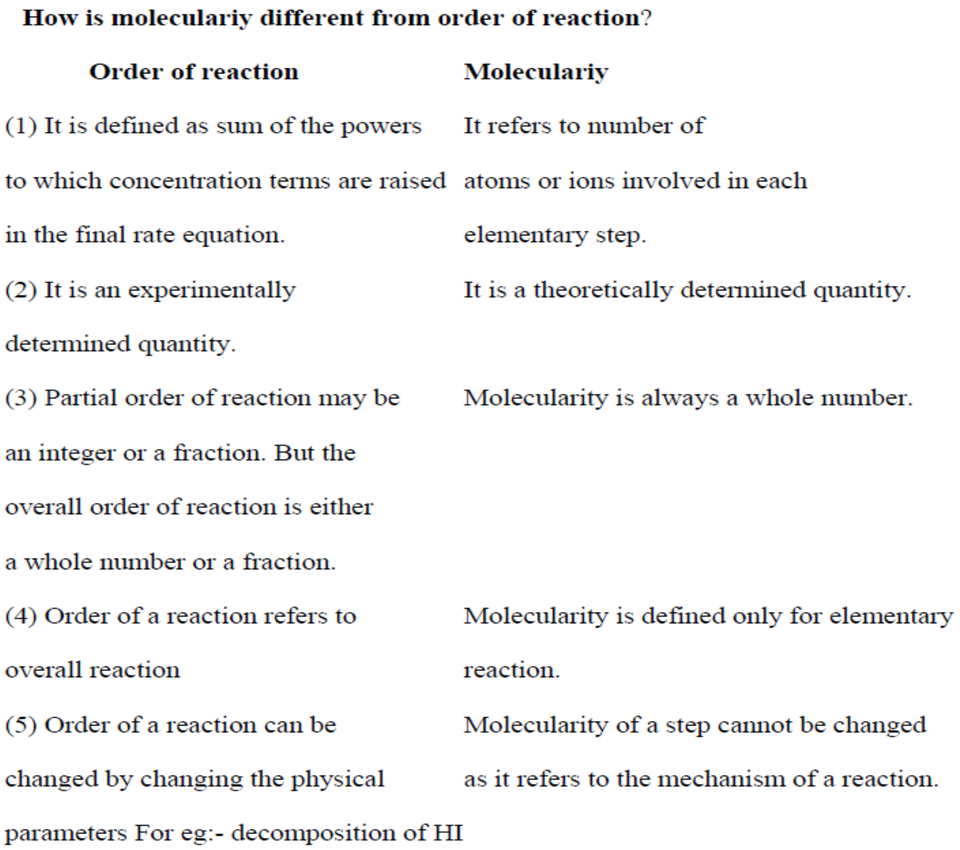
Reaction Rates	How we measure rates.
Rate Laws	How the rate depends on amounts of reactants.
Integrated Rate Laws	How to calculate amount left or time to reach a given amount.
Half-life	How long it takes to react 50% of reactants.
Arrhenius Equation	How rate constant changes with temperature.
Mechanisms	Link between rate and molecular scale processes.



What are Chemical Kinetics?

- Kinetics is the study of the time course behavior of a chemical reaction.

  "How fast do chemical reactions go?"



How is molecularìy different from order of reaction?

Order of reaction	**Moleculariy**
(1) It is defined as sum of the powers to which concentration terms are raised in the final rate equation.	It refers to number of atoms or ions involved in each elementary step.
(2) It is an experimentally determined quantity.	It is a theoretically determined quantity.
(3) Partial order of reaction may be an integer or a fraction. But the overall order of reaction is either a whole number or a fraction.	Molecularity is always a whole number.
(4) Order of a reaction refers to overall reaction	Molecularity is defined only for elementary reaction.
(5) Order of a reaction can be changed by changing the physical parameters For eg:- decomposition of HI	Molecularity of a step cannot be changed as it refers to the mechanism of a reaction.

1- Zero Order Reactions

Zero-order reactions are typically found when a material that is required for the reaction to proceed, such as a surface or a catalyst, is saturated by the reactants. The rate law for a zero-order reaction is rate = k, where k is the rate constant.

Zero-Order reaction : Reactions in which rate of reaction is found to be independent of the concentration of reactant is termed as zero order reaction.

A zero order reaction is represented as:

$A \rightarrow B$

Rate of this reaction is:

$$\text{Rate} = -\frac{d[A]}{dt} = \frac{d[B]}{dt} = k[A]^0$$

$$\text{Rate} = -\frac{d(a-x)}{dt} = \frac{dx}{dt} = k(a)^0 = k$$

$$\text{or } \frac{dx}{dt} = k$$

$$\text{or } dx = kdt$$

Integration of this equation within the limits

$$\int_{x=0}^{x} dx = \int_{t=0}^{t} kdt$$

$$\boxed{x = kt} \qquad \text{or} \qquad \boxed{k = \frac{x}{t}} \qquad t_{½} = \frac{a}{2k}$$

The S.I. unit of k is moles/dm^3/s.

e.g. enzyme catalysed reaction.

$$\text{substrate} \xrightarrow{\text{enzyme}} \text{Product}$$

$$\text{Rate} = k\ [\text{enzyme}]^1\ [\text{substrate}]^0$$

A → Product

Example: decomposing of H_2O_2 using MnO_2 as a catalyst.

$$H_2O_2 \rightarrow H_2O + ½\ O_2$$

$$V_t = V_o + K\ t$$

Where (V_t) is the volume of oxygen evolved at time (t), (V_o) is the volume of oxygen evolved at (t = 0), i.e. before the actual start of the reaction and (K) is the rate constant of the reaction which can be computed from the slope of the V_t - t plot.

2- First Order Reaction

A $\rightarrow$ Product. Or A + B $\rightarrow$ Product.

a 0, at *t* = 0.

(*a* –*x*) *x*, at $t = t_t$,

$$\frac{dx}{dt} = k(a-x) \ , \qquad \int \frac{dx}{(a-x)^n} = k\int dt \qquad .... \quad (1)$$

$$-ln(a-x) = kt - lna, \ (or) \ -log(a-x) = \frac{k}{2.303}\,t - loga \quad ..... \ (2)$$

$$k = \frac{2.303}{t}\log\frac{a}{a-x} \quad ...... \quad (3) \qquad t_{\frac{1}{2}} = \frac{0.693}{k}\ s^{-1}$$

Example: Hydrolysis of ester in acid medium.

$CH_3COOCH_3 + H_2O + HCl \rightarrow CH_3COOH + CH_3OH$.

$$\text{Rate} = -\frac{d(a-x)}{dt} = \frac{dx}{dt} = k(a-x)^1 \qquad \frac{dx}{dt} = k(a-x) \qquad \frac{dx}{(a-x)} = k\,dt$$

$$\int_{x=0}^{x=x}\frac{dx}{(a-x)} = \int_{t=0}^{t} k\,dt \qquad -\ln(a-x)\Big|_0^x = kt\Big|_0^t$$

$$\text{or } \ln\frac{a}{(a-x)} = kt \qquad \text{or } \boxed{k = \frac{2.303}{t}\log\frac{a}{(a-x)}} \qquad \boxed{t_{½} = \frac{0.693}{k}}$$

Half live time ($t_{1/2}$).

Example: The initial concentration of N_2O_5 in the following first order reaction: N_2O_5 (g) → 2 NO_2 (g) + 1/2 O_2 (g) was 1.24 × 10^{-2} mol./L at 318 K. The concentration of N_2O_5 after 60 minutes was 0.20 × 10^{-2} mol./L. Calculate the rate constant of the reaction at 318 K.

Answer: For a first order reaction: $\log\frac{R1}{R2} = \frac{k(t_2-t_1)}{2.303}$, $\therefore k = \frac{2.303}{(t_2-t_1)}\log\frac{R1}{R2}$

$$\therefore k = \frac{2.303}{(60-0)}\log\frac{(1.24 \ x \ 10^{-2})}{(0.2 \ x \ 10^{-2})} = 0.304 \ min^{-1}$$

Pseudo First Order Reaction

The order of a reaction is sometimes altered by conditions. Consider a chemical reaction between two substances when one reactant is present in large excess. During the hydrolysis of 0.01 mol of ethyl acetate with 10 mol. of water, amounts of the various constituents at the beginning (*t* = 0) and completion (*t*) of the reaction are given as under.

	$CH_3COOC_2H_5$	$+ H_2O$	$\xrightarrow{H^+}$	CH_3COOH	$+$	C_2H_5OH
$t = 0$	0.01 mol	10 mol		0 mol		0 mol
t	0 mol	9.9 mol		0.01 mol		0.01 mol

The concentration of water does not get altered much during the course of the reaction. So, in the rate equation

$$\text{Rate} = k' [CH_3COOC_2H_5] [H_2O]$$

the term $[H_2O]$ can be taken as constant. The equation, thus, becomes

$$\text{Rate} = k [CH_3COOC_2H_5]$$

where $k = k' [H_2O]$

and the reaction behaves as first order reaction. Such reactions are called pseudo first order reactions.

Inversion of cane sugar is another pseudo first order reaction.

$C_{12}H_{22}O_{11}$	$+$	H_2O	H^+	$C_6H_{12}O_6$	$+$	$C_6H_{12}O_6$
Cane sugar				Glucose		Fructose

$$\text{Rate} = k \; [C_{12}H_{22}O_{11}]$$