Chemical Kinetics

■ Chemical Kinetics:

$\rightarrow$ The branch of Physical chemistry which deals with the rate of reactions is called Chemical Kinetics.

■ Reaction Rate:

$\rightarrow$ The rate of a reaction tells as to what speed the reaction occurs.

Let us consider a simple reaction

$$A \rightarrow B$$

The concentration of the reactant **A decreases** and that of **B increases** as time passes.

The rate of reactions is defined as **the change in concentration of any of reactant or products per unit time**. For the given reaction the rate of reaction may be equal to the rate of disappearance of A which is equal to the rate of appearance of B.

→ Thus

rate of reaction = rate of disappearance of A

= rate of appearance of B

Or

$$\text{rate} = -\frac{d[A]}{dt}$$

$$= +\frac{d[B]}{dt}$$

where [ ] represents the concentration in moles per litre whereas ‘d’ represents infinitesimally small change in concentration. Negative sign shows the concentration of the reactant A decreases whereas the positive sign indicates the increase in concentration of the product B.

■ Rate Laws:

→ At a fixed temperature the rate of a given reaction depends on concentration of reactants.

It is shown that; **the rate of a reaction is directly proportional to the reactant concentrations, each concentration being raised to some power.**

Thus for a substance A undergoing reaction,

$$\text{rate} \propto [A]^n \quad \text{or,} \quad \text{rate} = k\,[A]^n$$

An expression which shows how the reaction rate is related to concentrations is called the rate law or rate equation.

The power (exponent) of concentration n in the rate law is usually a small whole number integer (1, 2, 3) or fractional. The proportionality constant k is called the **rate constant** for the reaction.

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	REACTIONS	RATE LAW
(1)	$2N_2O_5 \longrightarrow 4NO_2 + O_2$	rate $= k[N_2O_5]$
(2)	$H_2 + I_2 \longrightarrow 2HI$	rate $= k[H_2][I_2]$
(3)	$2NO_2 \longrightarrow 2NO + O_2$	rate $= k[NO_2]^2$
(4)	$2NO + 2H_2 \longrightarrow N_2 + 2H_2O$	rate $= k[H_2][NO]^2$

■ Order of a Reaction:

The order of a reaction is defined as the sum of the powers of concentrations in the rate law.

Let us consider the example of a reaction which has the rate law

$$\text{rate} = k\,[A]^m\,[B]^n \quad ...(1)$$

The order of such a reaction is (m + n).

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■ Examples of reaction order:

RATE LAW	REACTION ORDER
$\text{rate} = k[N_2O_5]$	1
$\text{rate} = k[H_2][I_2]$	$1+1=2$
$\text{rate} = k[NO_2]^2$	2
$\text{rate} = k[[H_2][NO]^2$	$1+2=3$
$\text{rate} = k[CHCl_3][Cl_2]^{1/2}$	$1+\frac{1}{2}=1\frac{1}{2}$

■ Molecularity of a Reaction:

Chemical reactions may be classed into two types :

(a) Elementary reactions

(b) Complex reactions

An elementary reaction is a simple reaction which occurs in a single step.

A complex reaction is that which occurs in two or more steps.

■ Molecularity of an Elementary Reaction:

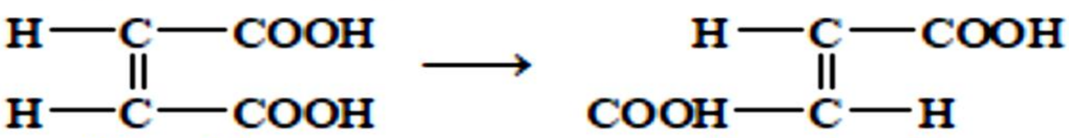
→ The molecularity of an elementary reaction is defined as : the number of reactant molecules involved in a reaction.

(*a*) **Unimolecular reactions : (molecularity = 1)**

$$A \longrightarrow \text{product}$$

Examples are : (*i*) $Br_2 \longrightarrow 2Br$

(*ii*)



maleic acid fumaric acid

(*b*) **Bimolecular reactions : (molecularity = 2)**

$$A + B \longrightarrow \text{products}$$
$$A + A \longrightarrow \text{products}$$

Examples are :

(*i*) $\underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + H_2O \longrightarrow \underset{\text{acetic acid}}{CH_3COOH} + \underset{\text{ethyl alcohol}}{C_2H_5OH}$

(*ii*) $2HI \longrightarrow H_2 + I_2$

(*c*) **Termolecular reactions : (molecularity = 3)**

$$A + B + C \longrightarrow \text{products}$$

Examples are :

$$2NO + O_2 \longrightarrow 2NO_2$$
$$2NO + Cl_2 \longrightarrow 2NOCl$$

Differences Between Order and Molecularity:

Order of a Reaction	Molecularity of a Reaction
1. It is the sum of powers of the concentration terms in the rate law expression.	1. It is number of reacting species undergoing simultaneous collision in the elementary or simple reaction.
2. It is an experimentally determined value.	2. It is a theoretical concept.
3. It can have fractional value.	3. It is always a whole number.
4. It can assume zero value.	4. It can not have zero value.
5. Order of a reaction can change with the conditions such as pressure, temperature, concentration.	5. Molecularity is invariant for a chemical equation.