Chemical Kinetics

REACTION RATE

The rate of a reaction tells as to what speed the reaction occurs. Let us consider a simple reaction

$$A \longrightarrow B$$

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

$$\text{rate of reaction} = \text{rate of disappearance of } A$$
$$= \text{rate of appearance of } B$$

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.

UNITS OF RATE

Reactions rate has the units of concentration divided by time. We express concentrations in moles per litre (mol/litre or mol/1 or mol 1^{-1}) but time may be given in any convenient unit second (s), minutes (min), hours (h), days (d) or possible years. Therefore, the units of reaction rates may be

mole/litre sec	or	mol 1^{-1} s
mole/litre min	or	mol 1^{-1} min^{-1}
mole/litre hour	or	mol 1^{-1} h^{-1} and, so on

Average Rate of Reaction is a Function of Time

Let us consider the reaction between carbon monoxide (CO) and nitrogen dioxide.

$$CO(g) + NO_2(g) \longrightarrow CO_2(g) + NO(g)$$

The average rate of reaction may be expressed as

$$\text{rate} = \frac{-\Delta[CO]}{\Delta t} = -\frac{d[CO]}{dt}$$

The concentration of CO was found experimentally every 10 seconds. The results of such an experiment are listed below.

Conc. of CO	0.100	0.067	0.050	0.040	0.033
Time (sec)	0	10	20	30	40

RATE LAWS

At a fixed temperature the rate of a given reaction depends on concentration of reactants. The exact relation between concentration and rate is determined by measuring the reaction rate with different initial reactant concentrations. By a study of numerous reactions 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,

rate $\quad \text{rate} \propto [A]^n$

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

For a reaction

$$2A + B \longrightarrow \text{products}$$

the reaction rate with respect to *A* or *B* is determined by varying the concentration of one reactant, keeping that of the other constant. Thus the rate of reaction may be expressed as

$$\text{rate} = k\,[A]^m\,[B]^n \qquad ...(2)$$

Expressions such as (1) and (2) tell the relation between the rate of a reaction and reactant concentrations.

Examples of rate law :

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

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

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

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

The order of a reaction can also be defined with respect to a single reactant. Thus the reaction order with respect to A is m and with respect to B it is n. The **overall order of reaction** $(m + n)$ may range from 1 to 3 and can be fractional.

Examples of reaction order :

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

ZERO ORDER REACTION

A reactant whose concentration does not affect the reaction rate is not included in the rate law. In effect, the concentration of such a reactant has the power 0. Thus $[A]^0 = 1$.

A zero order reaction is one whose rate is independent of concentration. For example, the rate law for the reaction

$$NO_2 + CO \longrightarrow NO + CO_2$$

at 200° C is

$$\text{rate} = k\,[NO_2]^2$$

Here the rate does not depend on [CO], so this is not included in the rate law and the power of [CO] is understood to be zero. The reaction is **zeroth order** with respect to CO. The reaction is second order with respect to $[NO_2]$. The overall reaction order is $2 + 0 = 2$.

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*) $Br_2 \longrightarrow 2Br$

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

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

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

Examples are :

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

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

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

Examples are :

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

MOLECULARITY *VERSUS* ORDER OF REACTION

The term molecularity is often confused with order of a reaction.

The total number of molecules or atoms which take part in a reaction as represented by the chemical equation, is known as the **molecularity of reaction.**

The sum of the powers to which the concentrations are raised in the rate law is known as the **order of reaction.**

Molecularity and Order are Identical for Elementary Reactions or Steps

The rate of an elementary reaction is proportional to the number of collisions between molecules (or atoms) of reactions. The number of collisions in turn is proportional to the concentration of each reactant molecule (or atom). Thus for a reaction.

$$2A + B \longrightarrow \text{products}$$

$$\text{rate} \propto [A]\,[A]\,[B]$$

or $$\text{rate} = k\,[A]^2\,[B] \qquad \textit{(rate law)}$$

Two molecules of A and one molecule of B are participating in the reaction and, therefore, molecularity of the reaction is 2 + 1 = 3. The sum of powers in the rate law is 2 + 1 and hence the reaction order is also 3. Thus **the molecularity and order for an elementary reaction are equal.**

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.