CHEMICAL KINETICS

FACTORS INFLUENCING RATE OF A REACTION

❖ Factors influence the rate of reaction: -

Concentration:
The law of mass action states that as the concentration of reactants increases, the reaction proceeds more rapidly.

Pressure (Gaseous reaction): Increasing pressure leads to a decrease in volume, an increase in concentration, and consequently, an acceleration in the rate of reaction.

Temperature: A general observation is that an increase in temperature corresponds to an increase in the reaction rate.

Nature of the reactants: The rate is contingent upon the specific bonds involved, hence varying with the nature of the reactants.

$$(g > l > s)$$

Surface area of the reactants: In heterogeneous reactions, finer powder forms of reactants exhibit higher velocity, providing more active centers.

Catalyst: A catalyst has a profound impact on the reaction rate.

Elementary or complex reactions: -

Elementary reactions

Chemical reactions occurring in a single step are termed simple reactions or elementary reactions. Nonetheless, certain simple reactions may involve multiple side reactions, leading to the formation of various products. Elementary reactions are characterized by taking place in a single step, without any intermediate steps. In such reactions, the order of the reaction aligns with the coefficient of the reaction.

Types of elementary reactions

In general, three categories define elementary reactions, each occurring in various molecules and substances. These categories are unimolecular, bimolecular, and tetramolecular reactions.

Unimolecular Reaction: This type of reaction occurs when a reaction involves only one molecule. The molecule collides with itself, leading to the formation of one or more substances. Unimolecular reactions are classified as first-order reactions since they involve only one reactant. An illustrative example of unimolecular reactions is radioactive decay.

$$A \rightarrow B$$

were

$$A = \text{reactant}$$
$$B = \text{product}$$

rate of chemical reaction, $r = k [A]$

k = reaction rate constant

Bimolecular reaction:

The kind of reaction that occurs when two molecules collide to produce one or more types of products is known as a bimolecular reaction. This type of reaction is known as a second-order reaction. A perfect example of a bimolecular reaction is an organic reaction.

$$2A \rightarrow B$$

Where,

2A = two molecules of reactant

B = product that is formed

Rate of chemical reaction, $r = k [A]2$

k = reaction rate constant

Tetramolecular reactions:

When three molecules collide and produce specific products, it is known as a tetramolecular reaction. These reactions are not common as they require certain conditions to take place. The reacting molecules must be in the proper orientation, and they must have a high energy level to sufficiently collide with each other and form products. This type of reaction is known as a third-order reaction.

Example-

$A + A + A \rightarrow B$ where Rate = $k [A]3$

$A + A + B \rightarrow C$ where Rate = $k [A]2 [B]$

$A + B + C \rightarrow D$ where Rate = $k [A] [B] [C]$

k = reaction rate constant

Complex reactions

A compound reaction occurs when the conversion of reactants into products unfolds through multiple or more than one step. Side reactions often accompany complex reactions, and the overall process involves several steps to yield the desired end product.

Types of complex reactions

In general, complex reactions can be categorized into three types: consecutive or sequential reactions, parallel reactions, and opposing reactions. The following provides an explanation for each type along with a complex reaction example:

Consecutive or sequential reactions: These reactions involve the formation of an intermediate compound by the reactant, followed by the conversion of the intermediate compound into the product through various steps. In such reactions, the transformation from reactants to products doesn't occur directly; instead, it entails a series of steps leading to the formation of the final products.

$A \rightarrow B$ …………… (k1)

$B \rightarrow C$ ……………. (k2)

Where,

A = reactant
B = intermediate
C = product
k1 = first step's-rate constant
k2 = second step's-rate constant

Parallel reactions:

Termed as side reactions, these processes occur when a reactant undergoes reactions through multiple pathways. In this type of reaction, two or more products are formed.

For example, consider a reaction where reactant A transforms into three distinct products, namely B, C, and D, through separate pathways. Each pathway is characterized by different rate constants, denoted as k1, k2, and k3. Among these pathways, one is the primary or main reaction, while the others are considered side or parallel reactions. The main reaction yields the highest concentration of the desired product, while the alternative products are formed in lower concentrations.

Bromination of bromobenzene is an example of a parallel reaction.

Opposing reactions, also referred to as reversible reactions, exhibit activity in both forward and backward directions. The reaction mechanism for an opposing reaction is represented as:

$$A + B — Kf– > < –Kr — C + D$$

Here, A and B denote the reactants, while C and D represent the products. kf is the rate constant for the forward reaction, and kr is the rate constant for the reversible reaction.

An illustration of an opposing reaction is the reaction between CO and NO_2 gases.

Distinguishing features between elementary and complex reactions.

Here are some of the key differences between elementary and complex reactions.

Complex reaction	elementary reaction
Occurs in multi (or) many steps	Occurs in single step
Overall order values are large	Overall order values are small.
Sometimes fractional orders such as $\frac{1}{2}, \frac{1}{3}, \frac{3}{2}$	Total and pseudo-order values lie between 0,1,2
Many side reactions are present.	No side reactions
Series of transition states	One transition state
In some complex reactions products are not formed in steps directly involving the reactants	Products are formed directly from the reactants
Experimental overall rate constant value, differ from the calculated values. Theories of reaction rates do not agree with complex reactions.	Experimental rate constant values accept with the calculated values. Theories of reaction rates apply fine on simple reactions.
Examples are Reaction between H_2 AND Br_2	Examples are cis-trans isomerization

Order of reaction:

The order of a reaction is determined by the sum of the powers of the concentration terms that experimentally influence the rate of the reaction.

For instance, Order of reaction = x + y

In this context, the order of reaction can be characterized as the cumulative sum of the exponents (powers) applied to the concentration terms within the rate law equation, reflecting the observed rate of the reaction.

Thus, reaction is said to be of the first order if its rate is given by the expression of the type,

$$r = k_1 C_A$$

Second order if the rate is given by the expression of the type,

$$r = k_2 C^2_A$$

$$r = k_2 C_A C_B$$

third order if the rate is given by the expression of the type

$$r = k_3 C_A^3 \text{ or } r = k_3 C_A^2 C_B \text{ or } r = k_3 C_A C_B^2 \text{ or } k_3 C_A C_B C_C \text{ and so on}$$

For zero order reaction, the rate equation is written as $R = k_0$. It is to be noted that the order of reaction is essentially an experimental quantity.

Note: Order may be zero, fractional, integer or negative.

Examples showing different values of order of reactions:

S. No Reaction	Rate law	Order
$2N_2O_5\ (g) \rightarrow 4NO_2\ (g) + O_2\ (g)$	$R = K\ [N_2O_5]^1$	1
$5Br^-\ (aq) + BrO_3^-\ (aq) + 6H^+\ (aq)$		
$\rightarrow 3Br_2\ (\ell) + 3H_2O\ (\ell)$	$R = K[Br^-][BrO_3^-][H^+]^2$	1+1+2= 4
H_2 (Para) $\rightarrow H_2$ (ortho)	$R = K\ [H_{2(Para)}]^{3/2}$	3/2
$NO_2(g) + CO\ (g)$		
$\rightarrow NO\ (g) + CO_2\ (g)$	$R = K\ [NO_2]^2\ [CO]^0$	2 + 0 = 2
$2O_3\ (g) \rightarrow 3O_2\ (g)$	$R = K\ [O_3]^2\ [O_2]^{-1}$	2 – 1 = 1
$H_2 + Cl_2 \xrightarrow{hv} 2\ HCl$	$R = K\ [H_2]^0[Cl_2]^0$	0 + 0 = 0

The Reaction (ii) does not occur in a single step because it is highly improbable for all 12 reactant molecules to simultaneously undergo a state of encounter. Such a reaction is termed a complex reaction and unfolds through a series of elementary reactions. In an elementary reaction, the sum of stoichiometric coefficients equals the order of the reaction. However, for complex reactions, the order needs to be determined through experimental evaluation.

Molecularity of a reaction:

'Molecularity' is characterized as the count of molecules, atoms, or radicals that must collide simultaneously for the reaction to occur. This value is always a positive whole number and cannot be negative.

In the elementary processes:

Participating species		Molecularity
One species participates	....	unimolecular,1
Two species participates	....	bimolecular, 2
Three species participates	....	trimolecular, 3

Ex.

$N_2O_4 \rightarrow 2NO_2$	......	unimolecular
$H_2 + I_2 \rightarrow 2HI$	......	bimolecular
$2FeCl_3 + SnCl_2 \rightarrow 2FeCl_2 + SnCl_4$	......	trimolecular

Note: If the reaction takes place in two or more steps, then the overall molecularity of the reaction is monitored by the slow or rate determining step.

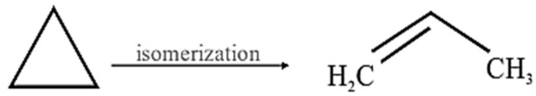
Difference between molecularity and order of reaction:

S. No	Molecularity	Order of reaction
1	Molecularity can neither be zero nor fractional	Order of reaction can be zero frictional or integer
2	It is a number of molecules of reactance of concentration term taking part in elementary step of reaction.	It is some of power raised or the rate expression.
3	It cannot have a negative value	Order of a reaction may have negative value
4	Molecularity Is a theoretical property	Order of Is a experimental property
5	Molecularity Concern with mechanism	Order of concern s with kinetic rate law

Ex.

Reaction	Rate law	Order
$CH_3CHO \rightarrow CH_4 + CO$	Rate μ $[CH_3CHO]^{3/2}$	1.5
$NH_3 \rightarrow N_2 + H_2$	Rate μ $[NH_3]^0$	0
$2Hl \rightarrow H_2 + I_2$	Rate μ $[HI]^0$, i.e., Rate = k	0

Order may change with change in experimental conditions while molecularity can't.



Ex. This reaction follows first order kinetics at high pressure and 2nd order kinetics at low pressure of cyclopropane.