CHEMICAL KINETICS

FACTORS INFLUENCING RATE OF A REACTION

- **Factors influence the rate of reaction: -**

Concentration:

Law of mass action enunciates that greater is the conc. of the reactants, the more rapidly the reaction proceeds.

Pressure (Gaseous reaction):

On increasing the pressure, volume decreases and conc. increases and hence the rate increases.

Temperature:

It is generally observed that rise in temperature increases the reaction rate.

Nature of the reactants:

The rate depends upon specific bonds involved and hence on the nature of reactants.

$g > \ell > s$

Surface area of the reactants:

In heterogeneous reactions, more powdered is the form of reactants, more is the velocity. [as more active centres are provided]

Catalyst: Affects the rate immensely.

Elementary or complex reactions: -

Elementary reactions

Chemical reactions that take place in only a single step are known as simple reactions or elementary reactions. However, in some simple reactions, multiple side reactions occur along with the main reaction, resulting in product formation. Elementary reactions can be defined as reactions that involve no intermediate steps, thus occurring in one single step. In this type of reaction, the order of the reaction is similar to the coefficient of the reaction.

Types of elementary reactions

Generally, there are three types of elementary reactions that take place in different molecules and substances. These are unimolecular, biomolecular, and tetramolecular reactions.

Unimolecular reaction:

This occurs when a reaction consists of only one molecule. This molecule collides with itself to form one or more substances. These reactions are known as first-order reactions because they have only one reactant. Radioactive decay is one of the best examples of unimolecular reactions.

$A \rightarrow B$

were

A = reactant

B = 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 complex reaction takes place when the reactants are converted into products in multiple steps or more than one step. Some side reactions take place when complex reactions occur. Additionally, a number of steps are involved in the reaction to form the right product.

Types of complex reactions

Generally, there are three types of complex reactions. These are consecutive or sequential reactions, parallel reactions, and opposing reactions. Here, we have explained each reaction with a complex reaction example given.

Consecutive or sequential reactions: The reactions in which the reactant forms an intermediate compound and then the intermediate compound is converted into the product in various steps are known as consecutive or sequential reactions. However, the reactants are not converted to the products directly in such a reaction. But it involves an array of steps in which the products are formed.

$A \rightarrow B$ …………… (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:

Also known as side reactions, these reactions take place when a reactant reacts in more than a single pathway. In such a reaction, the products formed are two or more. For instance, in such a reaction, a reactant A reacts to form three different products, B, C, and D, through different pathways. All the pathways have different rate constants, k1, k2, and k3. In these three reactions, one reaction is main, whereas others are side or parallel reactions. The main reaction gives maximum yield, whereas other products are formed in lower concentrations.

Bromination of bromobenzene is an example of a parallel reaction.

Opposing reactions: Also known as reversible reactions, these reactions are known to work in both forward and backward reactions. The reaction mechanism of an opposing reaction looks like

A + B — Kf– >< –Kr —C + D

Where A and B are reactants, C and D are products, kf is the rate constant of forward reaction, and kr is the rate constant of a reversible reaction.

The reaction between CO and NO2 gasses is an example of an opposing reaction.

Key differences 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 sum of the power of the concentration terms on which the rate of reaction actually depends as observed experimentally is called the order of the reaction. For example,

Order of reaction $= x + y$

Thus, the order of reaction may also be defined as the sum of the exponents (powers) to which the concentration terms in the rate law equation are raised in order to express 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,

$r = k_1C_A$

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

$r = k_2C^2{}_A$

$r = k_2C_AC_B$

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

$r = k_3C_A{}^3$ or $r = k_3C_A{}^2C_B$ or $r = k_3C_AC_B{}^2$ or $k_3C_AC_BC_C$ 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 take place in one single step. It is almost impossible for all the 12 molecules of the reactants to be in a state of encounter simultaneously. Such a reaction is called complex reaction and takes places in a sequence of a number of elementary reactions. For an elementary reaction the sum of stoichiometric coefficients = order of the reactions. But for complex reactions order is to be experimentally calculated.

Molecularity of a reaction :

''Molecularity is defined as the number of molecules, atoms, or radicals that must collide simultaneously in order for the reaction to take place.'' It is always a 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 ® $2NO_2$ ...... unimolecular

$H_2 + I_2$ ® $2HI$ ...... bimolecular

$2FeCl_3 + SnCl_2$ ® $2FeCl_2 + SnCl_4$ ...... trimolecular

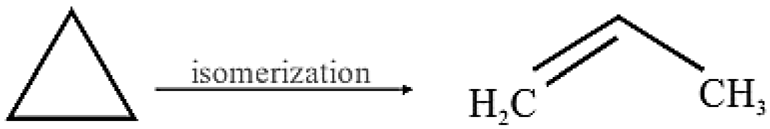
Note: If the reaction takes place in two or more steps then the overall molecularity of the reaction is monitored by the slow or rate determining step.

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 can not 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.