



Chemical Kinetics

Chemical Kinetics

- Study of rate of reactions and factors affecting it like temperature, pressure, catalyst and radiations is called chemical kinetics.
 - On the basis of rate, reactions can be of slow, moderate and very fast type.
 - Very fast reactions take 10^{-14} to 10^{-16} seconds for their completion, for example, ionic reactions, such as the one shown below:
- $$\text{NaCl} + \text{AgNO}_3 \longrightarrow \text{AgCl} + \text{NaNO}_3$$
- Fast reactions are not studied under kinetics. These are studied by flash-photolysis and spectrographic methods.
 - Blackening of white lead, Rusting of iron, formation of water at room temperature burning of coal and are not studied under kinetics.
 - Reactions with moderate speed, like molecular reactions, are studied under kinetics. For e.g., hydrolysis of ester or sugar.

Rate of Reaction

Rate of reaction is defined as the rate of change of concentration of a reactant or a product per unit time.

$$\text{Rate of reaction} = \frac{[C_2] - [C_1]}{t_2 - t_1}$$

- Rate of reaction decreases with time because concentration of the reactant also decreases. This can be observed from the following reaction.



Here, rate of reaction is measured by the decrease in concentration of F_2 .

- Unit for rate of reaction is $\text{mol L}^{-1} \text{time}^{-1}$ or atm time^{-1} (gaseous substance).

Concept Ladder



Chemical Kinetics basically tells us about how fast or slow a reaction is. Reactions with moderate speed are studied using chemical kinetics.



Rack your Brain



Can we study the rate of neutralisation reaction of a strong acid and base using chemical kinetics?

Previous Year's Questions



For the reaction, $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$, if $\frac{d[\text{NH}_3]}{dt} = 2 \times 10^{-4} \text{ mol L}^{-1} \text{s}^{-1}$, the value of $\frac{-d[\text{H}_2]}{dt}$ would be

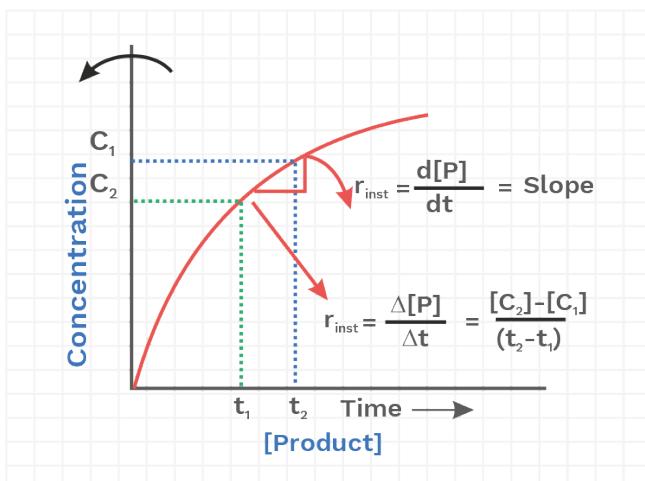
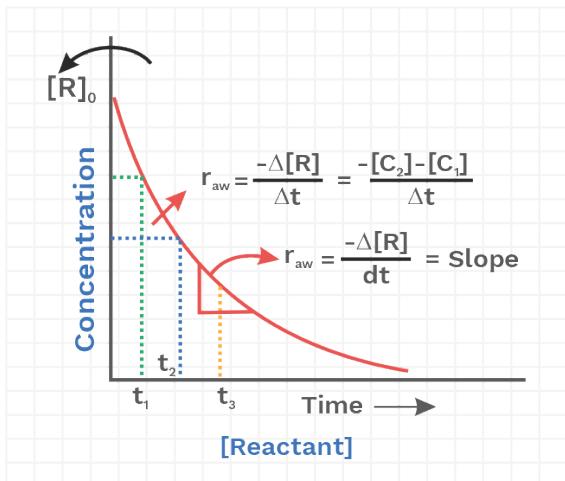
[AIPMT]

- (1) $4 \times 10^{-4} \text{ mol L}^{-1} \text{s}^{-1}$
- (2) $6 \times 10^{-4} \text{ mol L}^{-1} \text{s}^{-1}$
- (3) $1 \times 10^{-4} \text{ mol L}^{-1} \text{s}^{-1}$
- (4) $3 \times 10^{-4} \text{ mol L}^{-1} \text{s}^{-1}$



Average Rate of Reaction

As rate varies greatly with time so we use average reaction rate. By dividing the total change in concentration of reactant or product by a time interval, we actually get the average rate of the reaction.



Instantaneous Rate of Reaction

Instantaneous rate of reaction is equal to very small change in concentration ($d[x]$) during a very small interval of time (dt). It is given as $\frac{d[x]}{dt}$

Concept Ladder



Average rate of reaction is termed as the rate of reaction measured over the long time interval.

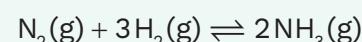
$$\text{Avg. rate } \frac{\Delta[x]}{\Delta t} = \frac{-\Delta[R]}{\Delta t} = \frac{\Delta[P]}{\Delta t}$$



Previous Year's Questions



For the chemical reaction,



the correct option is

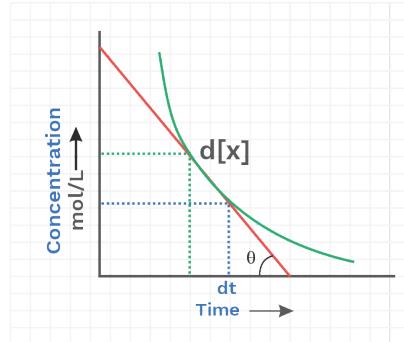
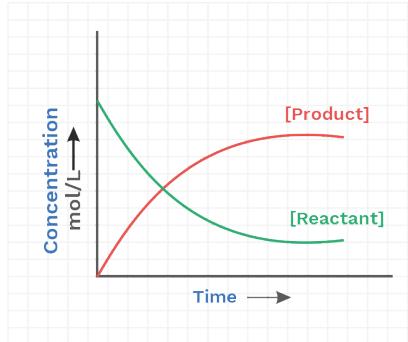
[NEET-2019]

- (1) $3 \frac{d[H_2]}{dt} = 2 \frac{d[NH_3]}{dt}$
- (2) $-\frac{1}{3} \frac{d[H_2]}{dt} = -\frac{1}{2} \frac{d[NH_3]}{dt}$
- (3) $-\frac{d[N_2]}{dt} = 2 \frac{d[NH_3]}{dt}$
- (4) $-\frac{d[N_2]}{dt} = \frac{1}{2} \frac{d[NH_3]}{dt}$

Definition

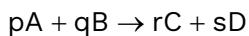


The instantaneous rate of reaction i.e., rate of reaction at any instant of time is the rate of change of concentration of any one of the reactants or products at that instant of time.



- $\frac{dx}{dt} = \tan \theta = -\text{slope}$
- It is written for any of the reactant or the product in terms of stoichiometric coefficients V_j as follows:

$$\frac{dx}{dt} = \frac{1}{V_j} \frac{d(J)}{dt}$$



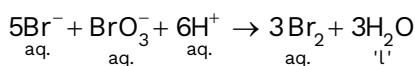
$$-\frac{1}{p} \frac{d[A]}{dt} = -\frac{1}{q} \frac{d[B]}{dt} = \frac{1}{r} \frac{d[C]}{dt} = \frac{1}{s} \frac{d[D]}{dt}$$

Taking $N_2 + 3H_2 \rightleftharpoons 2NH_3$ as an example, the instantaneous rate of reaction is calculated as follows:

$$\text{For } N_2, \frac{d[x]}{dt} = \frac{-d[N_2]}{dt}$$

$$\text{For } H_2, \frac{d[x]}{dt} = \frac{-d[H_2]}{dt}$$

$$\text{For } NH_3, \frac{d[x]}{dt} = \frac{d[NH_3]}{dt}$$



$$\begin{aligned} \text{Rate} &= \frac{-1}{5} \frac{d[Br^-]}{dt} = \frac{-d[BrO_3^-]}{dt} \\ &= \frac{-1}{6} \frac{d[H^+]}{dt} = \frac{1}{3} \frac{d[Br_2]}{dt} \frac{1}{3} \frac{d[H_2O]}{dt} \end{aligned}$$

Concept Ladder



The average rate of the reaction is the average of the all instantaneous reaction rates over a period of time during the reaction.



Rack your Brain



What is the slope of the tangents for reactants and products respectively in the plot of concentration vs time?



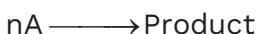
- For reactants, negative sign indicates decrease in concentration.
- For a reversible reaction at dynamic equilibrium, the net reaction rate is zero.

Features of Rate of Reaction

- Rate of reaction is always a positive quantity.
- It is proportional to the active masses of the reactant.
- It is measured by measuring active mass or molar concentration of a reactant or a product with respect to time.
- It varies with time, therefore it is better to use average reaction rate.

Specific Reaction Rate or Velocity Constant

Consider,



$$-\frac{dx}{dt} \propto [A]^n$$

$$\text{or } -\frac{dx}{dt} = k[A]^n$$

Rate law equation

If $[A]^n = 1$ then

$$-\frac{dx}{dt} = k \text{ (At a particular temperature)}$$

k = Rate constant or specific reaction rate

- At concentration value of unity, rate of reaction is equal to the value of rate constant.
- Rate constant, $k \propto$ Temperature (rate constant always increases with increase in temperature).
- Rate constant does not depend upon presence of a catalyst or on nature of reactant.
- Rate constant does not depend upon pressure, volume or concentration.
- Unit of rate constant is represented as (mole/litre) $^{1-n}$ time $^{-1}$ (Here n = Order of reaction).

Definition

According to the law of mass action, it states that the rate of chemical equation is directly proportional to the product of the active mass of the reactants, with each active mass term raised to the power equal to its respective stoichiometric coefficient in a balanced equation with a constant temperature which was later discarded.

Rack your Brain



Find out the units of rate constant for a 3rd order reaction.

Concept Ladder



The rate of reaction is directly proportional to the product of concentration of reactant and each concentration is raised to some power which may or may not be equal to stereochemistry experimentally.





Factors Affecting Rate of Reaction

Physical state of reactants

Gaseous state > liquid state > solid state
Decreasing order of rate of reaction

Temperature

For every rise of 10°C in temperature, rate or $\frac{dx}{dt}$ increases by two to three times or rate increases with temperature as the number of effective collisions increases.

$$\text{Temperature coefficient} = \frac{k_{t+10^{\circ}\text{C}}}{k_{t^{\circ}\text{C}}} + 10^{\circ}\text{C}$$

The value of temperature coefficient lies in between 2 to 3.

Increase in Rate of Reaction with Rise of Temperature

We know that all the molecules of the reactants do not have the same energy. According to Maxwell distribution curve for energies, if energies of the reacting molecules are plotted against the corresponding fractions ($\Delta N/N$) at a particular temperature T , a curve of the type shown in figure given below is obtained. Suppose the threshold energy is attained at the point E_t . Here and beyond this point E_t , all collisions will be effective and hence, a chemical reaction can take place. The shaded area under the curve AB gives the fraction of molecules having energies equal to or greater than the threshold energy. (F)

If the temperature is raised from T K to $(T + 10)$ K, the distribution curve shifts towards right, as shown, but the magnitude of the threshold energy will remain the same. Now, the shaded area beyond E_t becomes almost double (in some cases triple also) and the fraction of the molecules having energy equal to or greater than

Concept Ladder



Concentration of reactant, surface area, temperature, nature of reactant are some basic factors which affects the rate of reaction.



Rack your Brain



Why are reactions of higher order less in number?

Previous Year's Questions



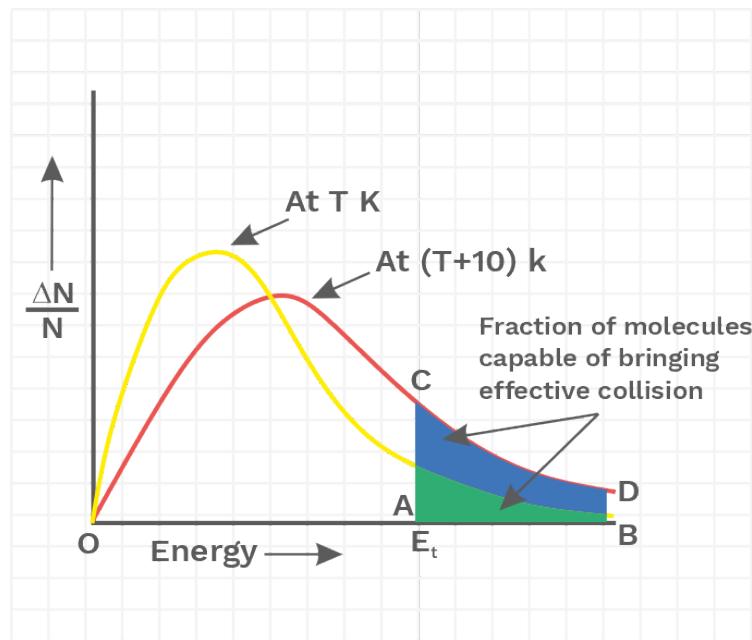
The decomposition of phosphine (PH_3) on tungsten at low pressure is a first-order reaction. It is because the

[NEET-2016]

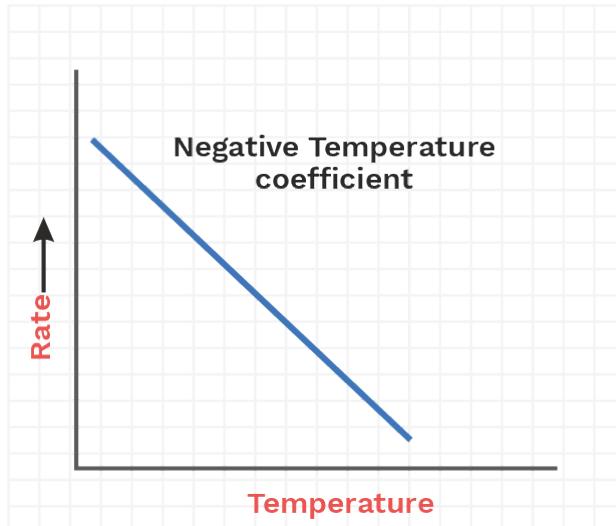
- (1) rate is proportional to the surface coverage
- (2) rate is inversely proportional to the surface coverage
- (3) rate is independent of the surface coverage
- (4) rate of decomposition is very slow.



threshold energy also becomes double or triple and hence, the reaction at $(T + 10)$ K, becomes much higher, (accordingly doubles or triples) than at T K.



- A negative temperature coefficient is observed only in the case of $2\text{NO} + \text{O}_2 \rightleftharpoons 2\text{NO}_2$



Previous Year's Questions



Which one of the following statements for the order of a reaction is incorrect?

[AIPMT-2011]

- Order can be determined only experimentally
- Order is not influenced by stoichiometric coefficient of the reactants
- Order of a reaction is sum of power to the concentration terms of reactants to express the rate of reaction.
- Order of reaction is always whole number.



Concentration

Rate of reaction ($\frac{dx}{dt}$) \propto Concentration.

Pressure

For gaseous reactants

$$\frac{dx}{dt} \propto \text{Pressure (as } P \propto C\text{)}$$

Surface area

In the case of heterogeneous reactions, greater is the surface area, faster is the rate of reaction due to presence of more number of active sites.

$$\frac{dx}{dt} \propto \text{Surface area}$$

Example

- (1) Coal dust burns fast than large coal piece
- (2) Wood shavings burn fast than a log of Wood

Nature of reactant and product

For ionic reactants, rate of reaction is fast, as activation energy is zero for these. Molecules have a slower reaction rate as they require higher activation energy.

Radiation

For a photochemical reaction

$$\frac{dx}{dt} \propto \text{Intensity of radiation}$$

Rate of reaction for photochemical reactions depends upon the intensity of light radiations and it increases by absorption of photons.

Positive catalyst

Positive catalyst increases rate of a reaction by providing an alternative path which requires a lesser activation energy.

- A negative catalyst decreases the rate of reaction.
- Catalysts are more effective in 'solid powdered form', which provides a greater surface area, that is, more number of active sites.

Concept Ladder



The rate of a reaction can be increased by increasing the temperature, concentration, surface area, pressure, intensity of radiation or by adding a catalyst.



Rack your Brain



Why boiling of an egg in an open vessel takes more time in a hill station?

Previous Year's Questions



For the reaction, $A + B \rightarrow \text{Products}$, it is observed that

- (i) on doubling the initial concentration of A only, the rate of reaction is also doubled and
- (ii) on doubling the initial concentration of both A and B, there is a change by a factor of 8 in the rate of the reaction.

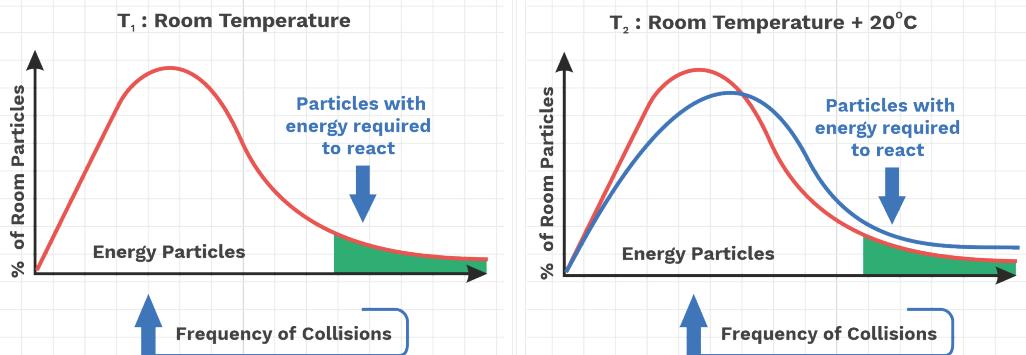
The rate of this reaction is

[AIPMT]

- (1) rate = $k[A][B]^2$
- (2) rate = $k[A]^2[B]^2$
- (3) rate = $k[A][B]$
- (4) rate = $k[A]^2[B]$



INCREASE TEMPERATURE OF REACTANTS



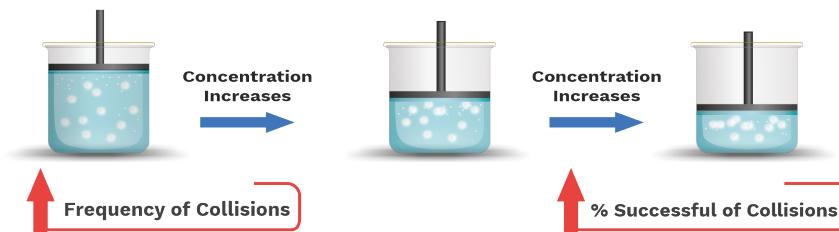
Increasing the temperature increases the kinetic energy of particles. This increases the frequency of particle collisions and a greater proportion of collisions will have the sufficient energy required to react.

INCREASE SURFACE AREA OF REACTANTS



Increasing surface area of solid reactants increases number of particles that are exposed and avail particles for collision, thus increasing the rate to react and as a consequence this increases the frequency of collision.

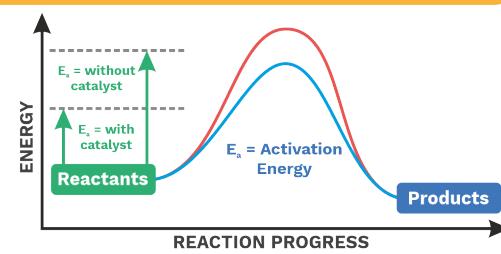
INCREASE PRESSURE OF REACTANTS

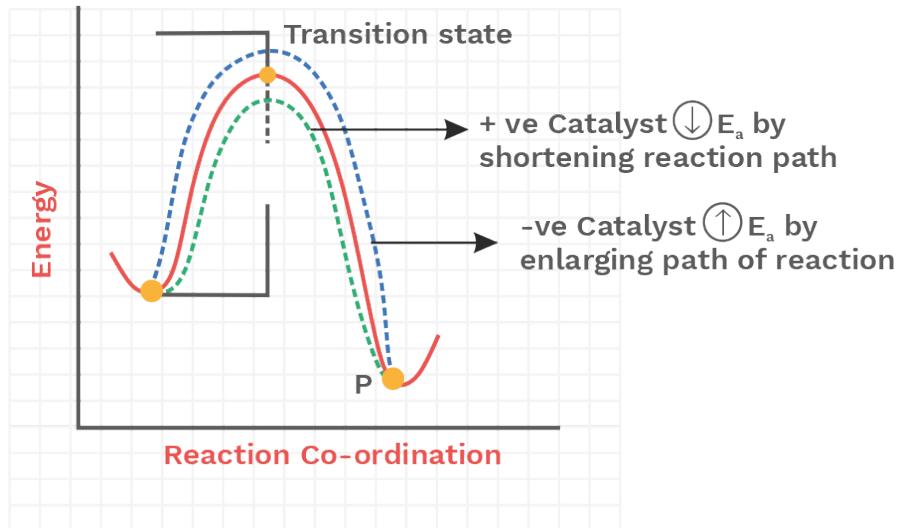


Increasing the pressure of a reaction involving gases, forces the gas particles to come closer. This will increase the frequency of particle collisions and therefore increases the rate of reaction.

USE A CATALYST IN A REACTION

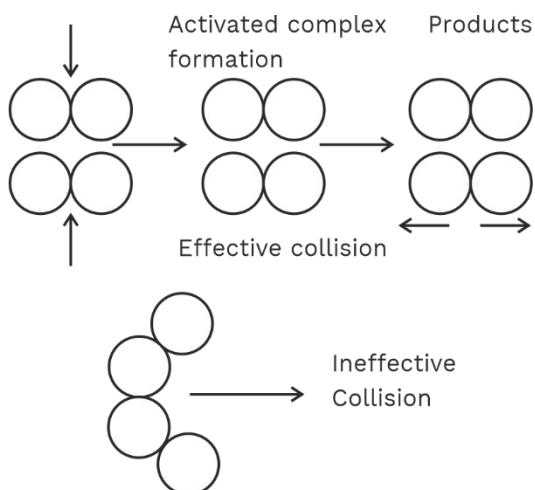
A catalyst provides an alternative route for the reaction with a lower activation energy. This means that particle collisions need less energy in order for a reaction to occur, thus increasing the rate of reaction.





Collision Theory

- A reaction takes place when the reacting molecules undergo collisions with each other. In other words, any chemical reaction is the result of effective collisions.
- For effective collisions
 - Colliding molecules must have sufficient kinetic energy.
 - Collision should be properly oriented.



- The minimum amount of energy needed to convert a reactant into product is known as threshold energy. This is the minimum amount of energy possessed by the reacting molecules, in order to have effective collisions for the formation of product.

Concept Ladder



The rate of reaction increases with increase in temperature because of the increase in the effective number of collisions.

Rack your Brain



A reaction has enough number of collisions having energy greater than threshold energy, still the reaction is very slow. Why?

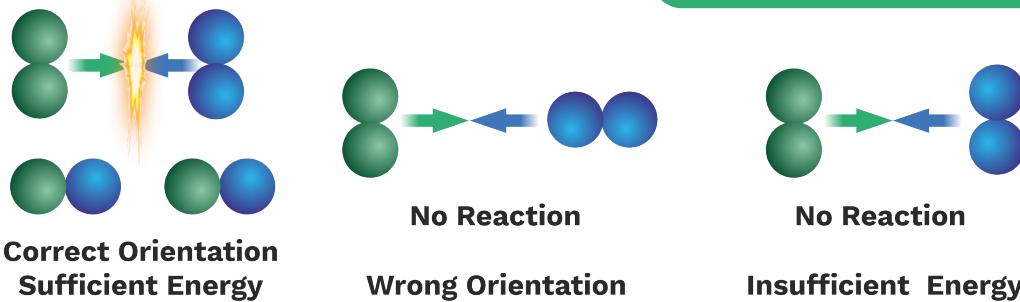


Chemical Kinetics

MAKING CHEMICAL REACTION HAPPEN FASTER

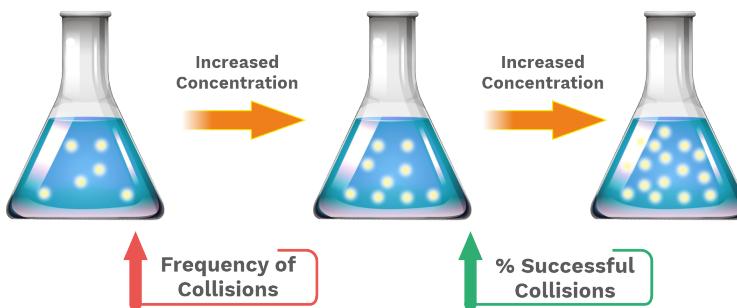
There are number of different things that we can change to make a chemical reaction faster. Here, we explain the concept of collision theory, and how it can be used to explain the effects of five different factors on the rate of a chemical reaction.

COLLISION THEORY



Collision theory states that for a reaction to occur, particles must collide with the correct orientation and with sufficient energy . Different factors affect the rate of the reaction by affecting the frequency of particle collisions, and the proportion of collisions that have enough energy to react.

INCREASED CONCENTRATION OF REACTANTS



Increasing the concentration of reactants in solution increases the rate of reaction as there are more number of particles to react. This increases the frequency of collision between particles.



- According to this theory, rate of reaction is given as

$$\text{Rate} = f Z$$

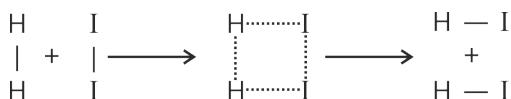
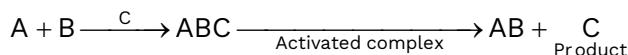
where, f = Fraction of molecules with potential energy greater than threshold energy.

$$f = e^{-E_a/RT}$$

P = Orientation factor

Z = Collision frequency

- Activated state or transition state theory or absolute rate theory was given by Henry Eyring.



Activation Energy

It is the minimum amount of additional external energy needed to change a reactant into product, or to make potential energy of the reactants equal to the threshold energy. It is denoted by E_a .

E_a = Threshold energy – Potential energy of reactants or Average kinetic energy of reactants

$$\text{Rate of Reaction} \propto \frac{1}{E_a}$$

Hence, lower the value of activation energy, faster will be the reaction.

Q1

The rate of a particular reaction quadruples when the temperature changes from 293 K to 313 K. Calculate activation energy.

Sol. $K_2/K_1 = 4$, $T_1 = 293$ K, $T_2 = 313$ K

$$\log \frac{K_2}{K_1} = -\frac{E_a}{2.303R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right]$$

Thus, on calculating and substituting values, we get

$$E_a = 52.86 \text{ KJ mol}^{-1}$$

Previous Year's Question

An increase in the concentration of the reactants of a reaction leads to change in [NEET-2014]

- heat of reaction
- threshold energy
- collision frequency
- activation energy

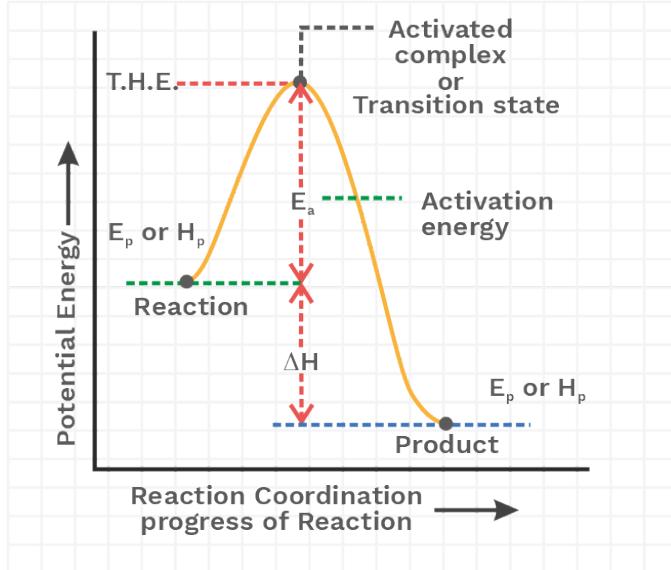


Concept Ladder



A catalyst speeds up the reaction by lowering the potential energy barrier and thus by decreasing the activation energy.





Arrhenius Equation

Arrhenius equation is used to evaluate energy of activation and to show the effect of temperature on rate constant as follows:

$$k = Ae^{-E_a/RT}$$

or alternatively,

$$\log_{10} k = \log_{10} A - \frac{E_a}{2.303 RT}$$

Here A is the Arrhenius or pre-exponential factor or frequency factor.

Here $e^{-E_a/RT}$ is known as Boltzmann factor.

- When E_a is zero or temperature is infinite (∞)
 $k = Ae^0 = A$
'A' signifies frequency of binary collisions or total number of collisions per unit volume per unit time.
- At two different temperatures T_1 and T_2 .

$$E_a = \frac{2.303 R T_1 T_2}{(T_2 - T_1)} \log_{10} \frac{k_2}{k_1}$$

$$\log_{10} \left(\frac{a}{a-x} \right) = \frac{E_a}{2.303 R} \frac{(T_2 - T_1)}{T_1 T_2}$$

Rack your Brain



Coal is a good fuel but it doesn't react with oxygen until a flame is applied. Why?

Concept Ladder



The Arrhenius equation is often used to compare the rate of constants measured at two different temperatures.



Previous Year's Question

The rate constants k_1 and k_2 for two different reaction are $1016e^{-2000/T}$ and $1015e^{-1000/T}$, respectively. The temperature at which $k_1 = k_2$ is

[NEET]

- 1000 K
- 2000/2.303 K
- 2000K
- 1000/2.303K



Graph Between $\log_{10} k$ and $1/T$

When a graph is plotted between $\log_{10} k$ and $1/T$, a straight line with a negative slope is obtained. Here, slope is equal to $-E_a / 2.303R$, that is, $E_a = -2.303 R$. Here, intercept is equal to $\log_{10} A$.

In Exothermic Reactions

Potential energy of reactant > potential energy of product E_a of backward reaction > E_a of forward reaction.

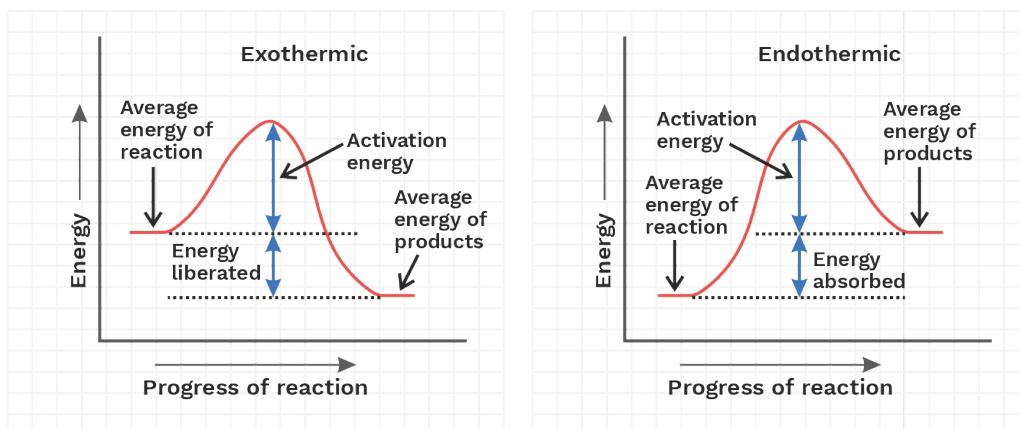


Previous Year's Questions

The rate of reaction between two reactants A and B decreases by a factor of 4 if the concentration of reactant B is doubled. The order of this reaction with respect to reactant B is

[AIPMT]

- | | |
|-------|--------|
| (1) 2 | (2) -2 |
| (3) 1 | (4) -1 |



Elementary and Complex Reactions

It is interesting to know that a balanced chemical equation never shows us a true picture of how the reaction is taking place as very rarely a reaction gets completed in only one step.

- The reaction which occurs in one step is known as an elementary reaction and when a sequence of such reactions (mechanism) provides us with the desired products then these reactions are termed as complex reactions.

Rack your Brain



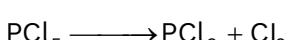
Can activation energy have zero or negative values? If not, why?



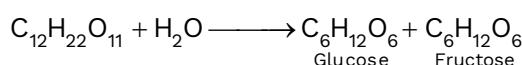
- Such reactions may be consecutive, reverse or side reactions. For example, in the complete combustion of an alkane the final products are always carbon dioxide and water. However, during this reaction a series of elementary reactions take place during which alcohols, aldehydes and acids are formed.

Molecularity

- Molecularity is the number of particles (atoms, ions or molecules) that must collide with one another simultaneously, which results in a chemical reaction.
- It is a theoretical value.
- It is always a whole number.
- It never determines the rate of reaction.
- It never depends upon external factors like temperature and pressure.
- Molecularity cannot be more than three as there is nearly no chance for more than three molecules to undergo an effective collision at a time.
- In a multistep reaction, molecularity is determined separately in each step.
- In case of complex reactions, (reactions taking place in a number of steps), the slowest step is called the rate determining step or rate limiting step.
- The overall molecularity of a complex reaction is equal to the molecularity of the slowest step.
- If molecularity of a reaction is 1 the reaction is called unimolecular as in the following reaction:



- If molecularity is 2, the reaction is called bimolecular.



- If molecularity is 3, the reaction is called termolecular



Concept Ladder



Reactions of higher order are very rare as the chances for the molecules to come together in a proper orientation to undergo effective collisions are very less.



Rack your Brain



The specific reaction rate is equal to the rate of reaction. Reaction is of which order?

Concept Ladder



Molecularity of a reaction is mostly between 1 to 3, but never zero. It is rare that molecularity exceeds 3.





Order of Reaction

Order of reaction is defined as number of reactants which determine rate of reaction, or alternatively, it is the number of reactants, whose molar concentration changes during the chemical reaction. It can also be defined as the sum of exponents, raised on active masses of reactants in a rate law equation.

Look at the example ahead,



For this, the rate law equation is

$$\text{Rate } k = [A]^m [B]^n$$

Hence, order = $m + n$

- It is an experimental value.
- It may be zero, negative or a fraction.
- It determines the rate of reaction.
- Order of reaction depends upon temperature, pressure and concentration. (external factors)
- Anything present in excess, is not counted in order of reaction, for example, in hydrolysis of ester and sugar, water is in excess, so it is neglected for order.
- Order of any reaction is determined by the slowest step of a reaction.
- High order reactions are rare due to less chance of effective collisions between molecules.

Mechanism:



$$\text{Rate} = K[O_3][O]$$

$$\text{As } [O] = K \frac{[O_3]}{[O_2]} \text{ from eq(i)}$$

So

$$\text{Rate} = K^1 [O_3]^2 [O_2]^{-1}$$

Hence, it is a first order reaction.

Concept Ladder



In rate law of expression the sum of powers to which the concentration terms are raised is known to be order of reaction.



Previous Year's Question



Which one of the following statement for the order of a reaction is incorrect? **[NEET]**

- (1) Order is not influenced by stoichiometric coefficient of the reactants
- (2) Order of reaction is sum of power to the concentration terms of reactants to express the rate of reaction
- (3) Order of reaction is always the whole number
- (4) Order can be determined by experiments only



Zero-order Reaction

In zero-order reactio. concentration of the reactants.

$$-\frac{dx}{dt} \propto [\text{Concentration}]^0$$



$$\frac{dx}{dt} = k(A)^\circ = k$$

On integrating it, we get

$$x = k.t + c$$

If $c = 0$ then

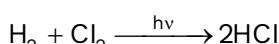
$$x = k.t$$

$$k = \frac{x}{t}$$

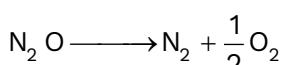
- Unit of is mol L⁻¹ time⁻¹

Examples of a zero-order reaction

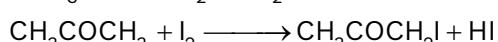
- Photochemical reactions



(studied over watch surface)



(studied over platinum surface)



(studied over gold surface)

- Iodination of acetone.
- Enzyme catalysed reactions.

Features of a zero-order reaction

- The concentration of the reactant decreases linearly with time
 $[A]_t = [A]_0 - kt$
- Rate = k (at all concentrations)
- $t_{1/2} \propto a_0$ (initial concentration)
- Here rate and concentration of reactants do not vary with time.

Concept Ladder



In the plot concentration vs time for a zero order reaction, the slope gives the value of rate constant and intercept gives the initial concentration.

Rack your Brain



What will be the plot of the rate of reaction vs time for a zero order reaction?

Previous Year's Question



In a zero order reaction, for every 10°C rise of temperature, the rate is doubled. If the temperature is increased from 10°C to 100°C, the rate of the reaction will become.

[NEET]

- 256 times
- 212 times
- 64 times
- 128 times



First-order Reaction

Here the reaction rate is determined by one concentration variable term only.

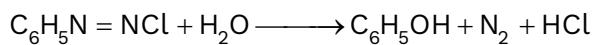
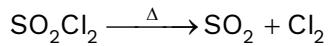
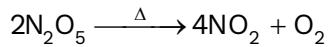
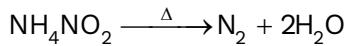
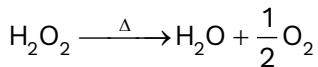
Here, t = Time period

k = Rate constant

A_r or a or N_0 = Initial amount

A or $a - x$ or N = Amount left after time t

Examples of a first-order reaction

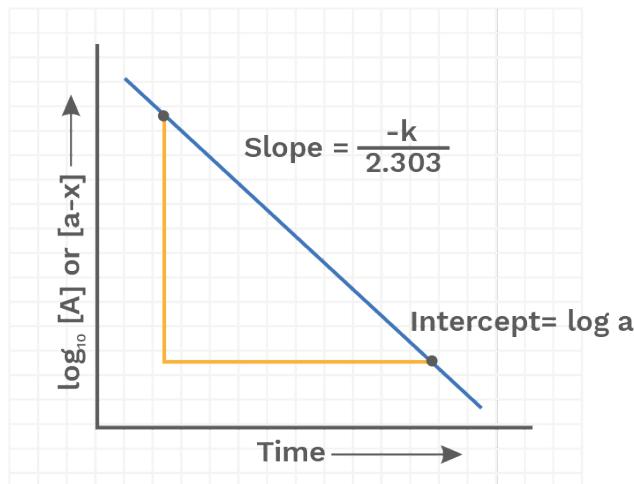


All radioactive disintegration processes are examples of 1st order.

Features of a first-order reaction

- Unit of k is time^{-1}
- k does not depend upon concentration units or change in concentration.
- $t_{1/2}$ does not depend upon initial concentration
(a). It depends only upon rate constant.

$$t_{1/2} = \frac{0.693}{k}$$



Concept Ladder



If $a \propto P_0$

$$(a - x) \propto 2P_0 - P_t$$

$$k = \frac{2.303}{t} \log_{10} \frac{P_0}{2P_0 - P_t}$$



Rack your Brain



How the plot of $[A]$ vs. t for a first order reaction looks like?

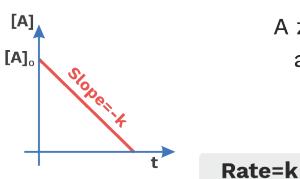
Concept Ladder



If the amount of substance left after one half life is $[A_0]/2$, then the amount of substance left after n - half lives is $[A_0]/2^n$.

ORDER OF REACTIONS

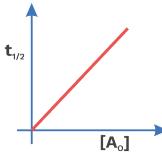
ZERO ORDER REACTIONS



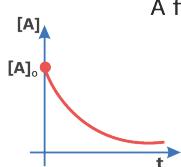
A zero order reaction has a constant rate that is independent of the concentration of the reactant(s).

Time in which half of initial amount is left

$$\text{Half life } (t_{1/2}) = \frac{[A]_0}{2k}$$



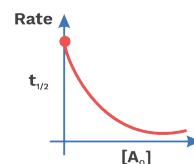
FIRST ORDER REACTIONS



A first-order reaction is a reaction that proceeds at a rate that depends linearly on only one reactant concentration.

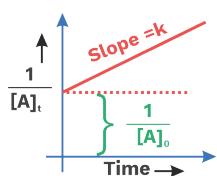
$$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$$

$$\text{Half life } (t_{1/2}) = \frac{0.693}{k} \quad [A] = \frac{[A]_0}{2^n}$$



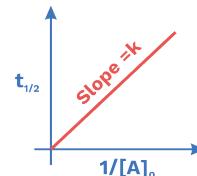
SECOND ORDER REACTIONS

A chemical reaction in which the rate of the reaction is determined by the concentration of two chemical reactants involved or the square of the concentration of one chemical reactant.



$$k = \frac{1}{[A]} - \frac{1}{[A]_0}$$

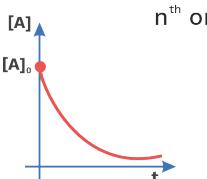
$$\text{Half life } (t_{1/2}) = \frac{1}{K[A]_0}$$



PSEUDO FIRST ORDER REACTIONS

If the **concentration** of a reactant remains constant (because it is a catalyst or it is in great excess with respect to the other reactants), its concentration can be included in the rate constant, obtaining a pseudo-first-order (or occasionally **pseudo-second-order**) rate equation. For example, the hydrolysis of sucrose in acid solution rate $r = k[\text{sucrose}]$. The true rate equation is third-order, $r = k [\text{sucrose}] [\text{H}^+] [\text{H}_2\text{O}]$: however, the **concentrations** of both the catalyst H^+ and the solvent H_2O are normally constant, so that the reaction is pseudo-first-order.

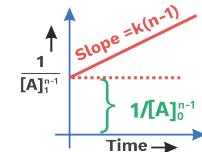
n^{th} order reactions



n^{th} order reaction is one which proceeds at the rate that depends on concentration of multiple reactants or on multiple steps.

$$\Rightarrow k = \frac{1}{(n-1)t} \left[\frac{1}{[A]_t^{n-1}} - \frac{1}{[A]_0^{n-1}} \right]$$

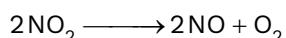
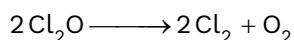
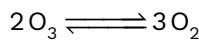
$$\text{Half life } (t_{1/2}) = \lim_{x \rightarrow n} \frac{2^{x-1}-1}{(x-1)K[A]_0^{x-1}}$$





Second-order Reaction

Examples of a second-order reaction



Features of a second-order reaction

- Unit of k is L mol⁻¹ time⁻¹

$$t_{1/2} \propto \frac{1}{a}$$

- When concentrations are same

$$k = \frac{1}{t} \frac{x}{a(a-x)}$$

- When concentrations are different

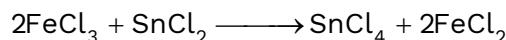
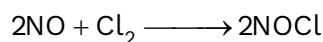
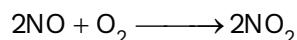
$$k = \frac{2.303}{t(a-b)} \log_{10} \frac{b(a-x)}{a(b-x)}$$

- The change in the unit of concentration, changes the value of k here.

Third-order Reaction

$$-\frac{dx}{dt} \propto [A]^3 \text{ or } [A]^1[B]^1[C]^1$$

Examples of a third-order reaction



Concept Ladder



The integrated rate equation for nth order is given by

$$K = \frac{1}{t(n-1)} \left[\frac{1}{[C]^{n-1}} - \frac{1}{[C_0]^{n-1}} \right]$$

Where n = 2,3....



Previous Year's Questions



The given reaction,
 $2\text{FeCl}_3 + \text{SnCl}_2 \rightarrow 2\text{FeCl}_3 + \text{SnCl}_4$
is an example of

[AIPMT]

- third order reaction
- first order reaction
- second order reaction
- none of these

Q2

What is the order of reaction whose rate constant has the same units as the rate of reaction?

Sol. Zero order



Features of a third-order reaction

$$k = \frac{1}{2t} \left[\frac{1}{(a-x)^2} - \frac{1}{a^2} \right]$$

$$t_{1/2} \propto \frac{1}{a^2}$$

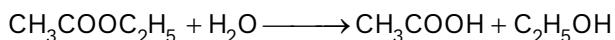
- The change in the unit of concentration changes the value of A here.
- Unit of k is $\text{L}^2 \text{ mol}^{-2} \text{ time}^{-1}$

Pseudo First-order Reactions

Pseudo first-order reactions are the reactions which are not truly of the first order but under certain conditions become reactions of the first order.

Here molecularity is more than 1, but order of reaction is always one. Few example of pseudo first-order reactions are as follows:

Hydrolysis of ethyl acetate



Rate constant (k) is given as

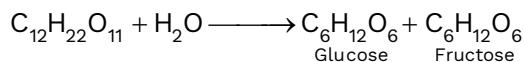
$$k = \frac{2.303}{t} \log_{10} \frac{V_\infty - V_0}{V_\infty - V_t}$$

Here V_∞ = Volume at infinite

V_0 = Initial volume

V_t = Volume at time t

Hydrolysis of sugar



Rate constant in this case is given as

$$k = \frac{2.303}{t} \log_{10} \frac{r_0 - r_\infty}{r_t - r_\infty}$$

Here r_0 = Initial optical rotation

r_∞ = Rotation at infinite dilution

r_t = Rotation at t time

Rack your Brain



The half life of a reaction is inversely proportional to the square of initial Concentration, what is the order of reaction ?

Concept Ladder



If one of the reactants is present in excess, its concentration does not change much with time through out the reaction, hence the reaction is considered as a pseudo first order reaction.

Rack your Brain



Hydrolysis of ethyl acetate with HCl is a first order reaction, why?



Methods for determining order of reaction

Order of a reaction is determined mainly by:

1. Initial concentration method
2. Integration method
3. Graphical method: When a graph is plotted between $1/(a - x)^{n-t}$ and time t, a straight line is formed.
4. Half-life method

$$\frac{(t_{1/2})_1}{(t_{1/2})_2} = \left[\frac{a_2}{a_1} \right]^{n-1}$$

or

$$n = 1 + \frac{\log(t_{1/2})_1 - \log(t_{1/2})_2}{\log[a_2] - \log[a_1]}$$

Here n is the order of reaction

5. Van't Hoff differential method

$$n = \frac{\log\left(\frac{-d[C_1]}{dt}\right) - \log\left(\frac{-d[C_2]}{dt}\right)}{\log[C_1] - \log[C_2]}$$

Photochemical reactions

Those reactions which take place only in the presence of light are called photochemical reactions, for example, photosynthesis and formation of HCl. They proceed by chain reaction mechanism using atoms or free radicals.

- For such reactions ΔG^0 (standard Gibbs free energy change) can be positive. For example, synthesis of carbohydrate and HCl formation.
- Red light has lowest energy. Some photochemical reactions can be initiated by red light.
- Such reactions are not affected by temperature, however, they are affected by intensity of light radiations.
- The retina in the eye undergoes geometrical isomerization by absorbing photons of light to enable sight.

Concept Ladder



The ozone layer that is found in the earth's stratosphere is formed by the photochemical dissociation of molecular oxygen into oxygen atoms and these atoms react with molecules of oxygen to form ozone.

Rack your Brain



What would accelerate a photochemical reaction more effectively : a catalyst or high intensity of light?

Previous Year's Questions



When initial concentration of a reactant is doubled in a reaction, its half-life period is not affected. The order of the reaction is

[AIPMT]

- (1) second
- (2) more than zero but less than first
- (3) zero
- (4) first



Photosensitizer

It is a substance which when added to a reaction mixture, helps to start the photochemical reaction, but it does not undergo any chemical change, for example, chlorophyll in photosynthesis and Hg vapours in dissociation of H₂.

Non – photoactive $\xrightarrow{\text{By photosensitizer}}$ Photoactive

Luminiscence

It is the emission of light unaccompanied by heat.

Cheilominiscence

It is the conversion of chemical energy in to cold-light energy, for example, in fire flies the light emitted is due to oxidation of luciferin protein by the enzyme luciferase (bioluminescence).

Fluorescence

Here emission of light stops instantaneously when radiation being projected on a fluorescent substance, is cut off, for example CaF₂.

Phosphorescence

Here emission of light occurs for some time even after light radiation being projected on a phosphorescence substance, is cut off. For example, ZnS.

Quantum efficiency (ϕ)

$$\phi = \frac{\text{Number of molecules reacting in a given time}}{\text{Number of quanta absorbed at the same time}}$$

- For HCl, ϕ is high (as both steps are exothermic).
- For HBr, ϕ is low (as second step is endothermic).

Concept Ladder



To begin a photochemical process, an atom or molecule must absorb a quantum of light energy from a photon. When this occurs, the energy of the atom or molecule increases above its normal level.

Definition

Quantum Efficiency is a measure of the number of product molecules formed by the quantum of energy absorbed from each photon.

Rack your Brain

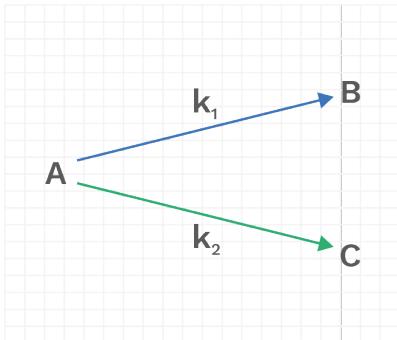


How quantum efficiency can be measured in terms of energy adsorbed by photons?



Rate law equation for reactions involving parallel and side reactions:

Here reactant reacts or decomposes in more than one way.



$$\text{Rate} = (k_1 + k_2) [A]$$

- Fraction yield of A = $k_1 / (k_1 + k_2)$
- Fraction yield of B = $k_2 / (k_1 + k_2)$
- Successive reaction: $A \xrightarrow{k_1} B \xrightarrow{k_2} C$
Here, rate of disappearance of A = $k_1 + k_2 [A]$
 $[A]_t = [A]_0 e^{-k_1 t}$

$$[B]_t = \frac{k_1 [A]_0}{k_2 - k_1} [A]_0 (e^{-k_1 t} - e^{-k_2 t})$$

Modified Arrhenius Equation

$$\frac{d \ln k}{dT} = \frac{E}{RT^2}$$

- The exponential form of the expression for a first order reaction is

$$[A] = [A]_0 e^{-kt}$$

It is called Wilhelmy's equation.

Definition

The reaction in which a substance reacts or decomposes in more than one way are called parallel or side reactions.

Previous Year's Questions

Activation energy (E_a) and rate constants (k_1 and k_2) of a chemical reaction at two different temperatures (T_1 and T_2) are related by

- [AIPMT]
- (1) $\ln \frac{k_2}{k_1} = -\frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$
 - (2) $\ln \frac{k_2}{k_1} = -\frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$
 - (3) $\ln \frac{k_2}{k_1} = -\frac{E_a}{R} \left(\frac{1}{T_2} + \frac{1}{T_1} \right)$
 - (4) $\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$

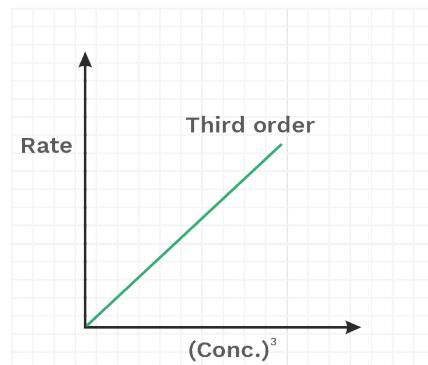
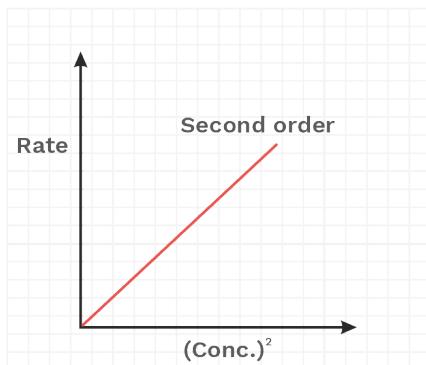
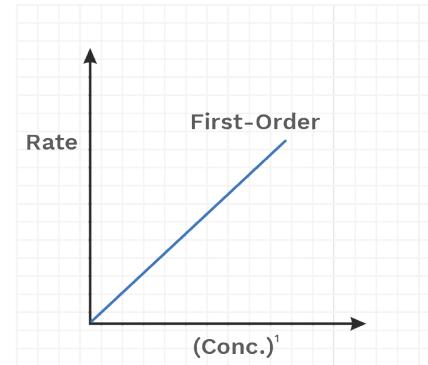
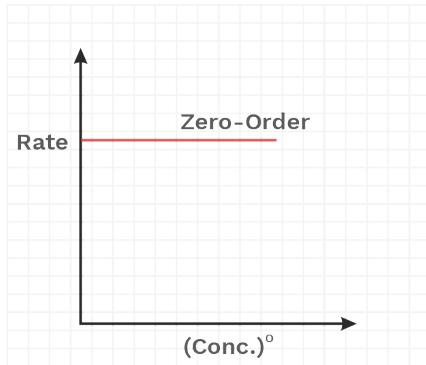
- Q3** The rate constant of a reaction at 700 K and 760 K are $0.011 \text{ M}^{-1} \text{ s}^{-1}$ and $0.105 \text{ M}^{-1} \text{ s}^{-1}$ respectively. Calculate the value of Arrhenius parameters.

Sol. 2.824×10^{10}

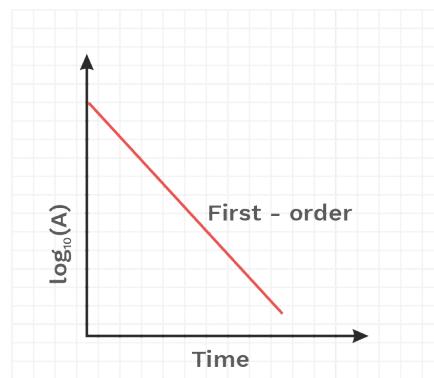
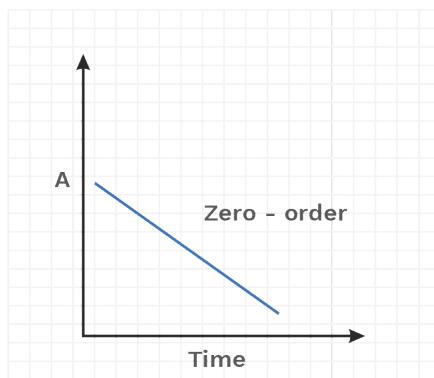


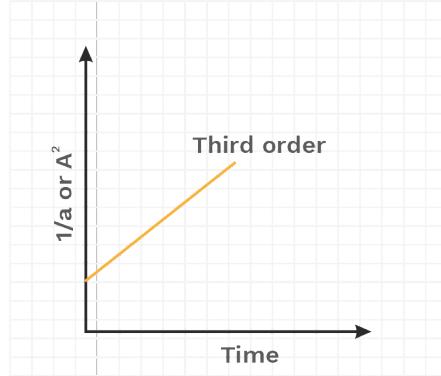
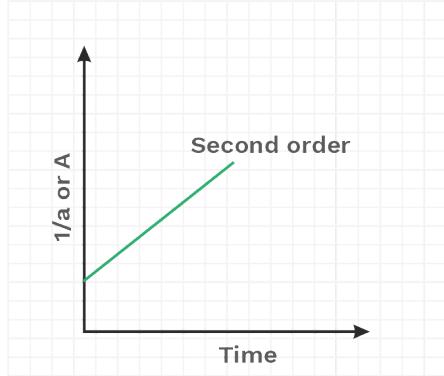
Some Important Graphs

Rate Versus Concentration

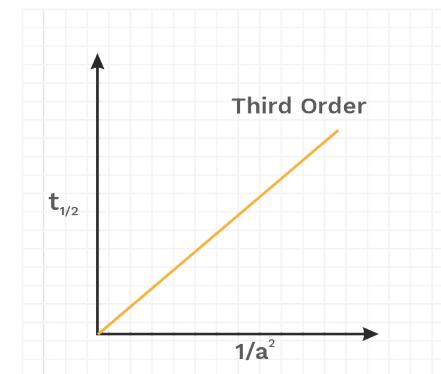
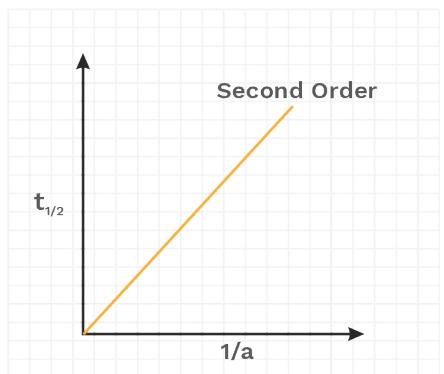
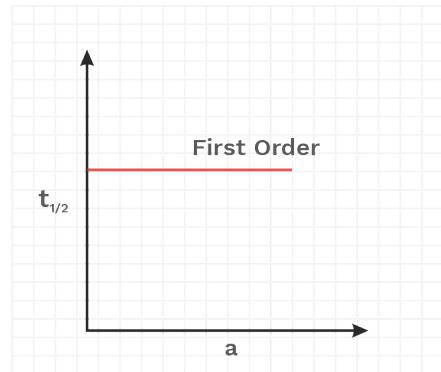
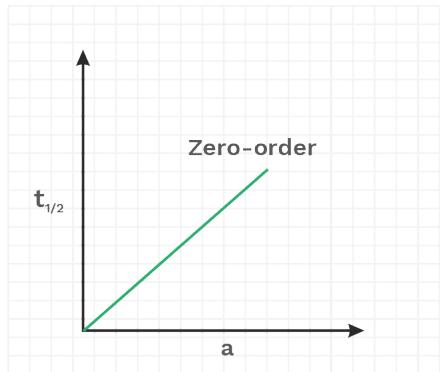


Integrated Rate Equation





Half-lives Versus Concentration $\left(t_{1/2} \text{ vs } \frac{1}{a^{n-1}} \right)$





Q4 For the reaction $R \rightarrow P$, the concentration of a reactant changes from 0.03 M to 0.02 M in 25 min. Calculate the average rate of reaction using units of time both in minutes and seconds.

Sol.

$$\text{Average rate} = -\frac{\Delta[R]}{\Delta t} = -\frac{[R]_2 - [R]_1}{t_2 - t_1} = -\frac{0.02\text{M} - 0.03\text{M}}{25\text{ min}} = -\frac{-0.01\text{M}}{25\text{ min}}$$

$$= 4 \times 10^{-4} \text{ mol.L}^{-1} \text{ min}^{-1} = \frac{0.01\text{M}}{25 \times 60 \text{ s}} = 6.66 \times 10^{-6} \text{ mol L}^{-1} \text{ sec}^{-1}$$

Q5 For the reaction $3H_2 + N_2 \rightarrow 2NH_3$, how are the rate of reaction expression $-\frac{d[H_2]}{dt}$ and $\frac{d[NH_3]}{dt}$ inter-related?

Sol.

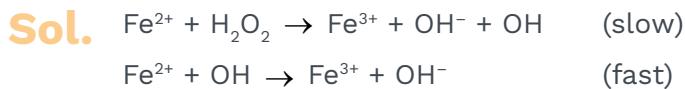
$$-\frac{1}{3} \frac{d[H_2]}{dt} = \frac{1}{2} \frac{d[NH_3]}{dt}$$

Q6 If the time required to decompose SO_2Cl_2 to half of its initial amount is 60 minutes and the decomposition is a first-order reaction, then calculate the rate constant of the reaction.

Sol. For a first-order reaction. $k = \frac{0.693}{t_{1/2}}$

$$\frac{0.693}{t_{1/2}} = \frac{0.693}{60 \text{ min}} = \frac{0.693}{60 \times 60 \text{ sec}} = 1.925 \times 10^{-4} \text{ s}^{-1}$$

Q7 For the reaction : $2Fe^{2+} + H_2O_2 \rightarrow 2Fe^{3+} + 2OH^-$
the rate of formation of Fe^{3+} is given by : rate = $K[Fe^{2+}][H_2O_2]$.
Suggest possible mechanism for the reaction.



Q8 The rate constant for a reaction of zero order A is $0.0030 \text{ mol L}^{-1} \text{ s}^{-1}$. How long will it take for the initial conc. of A to fall from 0.10M to 0.075M ?

Sol. For a zero order reaction

$$K = 0.0030 \text{ mol L}^{-1} \text{ s}^{-1}$$

$$[A]_0 = 0.10 \text{ M} \quad [A] = 0.075 \text{ M}$$

$$K = \frac{[A]_0 - [A]}{t}$$

$$t = \frac{0.10 - 0.075}{0.0030} = 8.33 \text{ s}$$

Q9 A first order reaction is 75% complete in 60 min. Find the half-life of this reaction.

$$k = \frac{2.303}{t} \log \frac{a}{(a-x)}$$

$$= \frac{2.303}{t} \log \frac{100}{100-75}$$

$$= \frac{2.303}{t} \log 4$$

$$= \frac{2.303}{60} \times 0.6020 = 0.0231$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.0231} = 30 \text{ min}$$

Q10 Calculate the factor by which the rate of reaction is increased for a temperature rise of 10°C from 25°C to 35°C . The energy of activation is 35 kcal mol^{-1} .



Sol. Given, $E_a = 35 \times 10^3$ cal mol⁻¹, $R = 1.987$ cal, $T_2 = 308$ K, $T_1 = 298$ K

$$\therefore 2.303 \log_{10} \frac{k_2}{k_1} = \frac{35 \times 10^3}{1.987} \left[\frac{308 - 298}{308 \times 298} \right]$$

$$\text{or } \left(\frac{k_2}{k_1} \right) = 6.812$$

$$\text{or } k_2 = 6.812 \times k_1$$

$$\therefore r_2 = 6.812 \times r_1 \quad \left(\because \frac{r_1}{r_2} = \frac{k_1}{k_2} \right)$$

Q11 For the reaction : $C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$

Write :

- (a) Rate of reaction expression
- (b) Molecularity

Sol.

$$\begin{aligned} \text{(a)} \quad \text{Rate} &= -\frac{d[C_{12}H_{22}O_{11}]}{dt} = -\frac{d[H_2O]}{dt} \\ &= \frac{d[C_{12}H_{22}O_{11}]}{dt} = \frac{d[C_6H_{12}O_6]}{dt} \end{aligned}$$

$$\text{(b)} \quad \text{Molecularity} = 2$$

Q12 For the reaction, $A \rightarrow B$, the rate of reaction becomes 27 times when the concentration of A is increased 3 times. What is the order of the reaction?

Sol.

$$r = k[A]^n$$

$$27r = k[3A]^n$$

$$\therefore \frac{27r}{r} = \frac{k[3A]^n}{k[A]^n}$$

$$\text{or } 3^3 = 3^n$$

$$\therefore \text{Order of the reaction} = 3$$



Q13 The rate constant for first order reaction is 60/s. How much time will it take to reduce the concentration of the reaction to 1/10 of its initial value?

Sol.

$$t = \frac{2.303}{K} \log \left[\frac{R_0}{R} \right]$$

$$t = \frac{2.303}{\frac{1}{10}} \log \left[\frac{R_0}{R} \right]$$

$$t = \frac{2.303}{60} \log 10$$

$$t = \frac{2.303}{60}$$

$$= 3.38 \times 10^{-2} \text{ s}^{-1}$$

Q14 The rate constant of a reaction is $1.5 \times 10^7 \text{ s}^{-1}$ at 50°C and $4.5 \times 10^7 \text{ sec}^{-1}$ at 100°C . Evaluate the Arrhenius parameter and E_a .

Sol.

$$2.303 \log \frac{k_2}{k_1} = \frac{E_a}{R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

$$\therefore 2.303 \log \frac{4.5 \times 10^7}{1.5 \times 10^7} = \frac{E_a}{8.314} \left[\frac{373 - 323}{373 \times 323} \right]$$

$$\therefore E_a = 2.2 \times 10^4 \text{ J mol}^{-1}$$

$$\text{Now, } k = A \cdot e^{-E_a/RT}$$

$$\therefore 4.5 \times 10^7 = A \cdot e^{\frac{-2.2 \times 10^4}{8.314 \times 373}}$$

$$A = 5.42 \times 10^{10} \text{ sec}^{-1}$$

Q15 For a reaction, $\text{Cl}^\bullet + \text{Cl}^\bullet \rightarrow \text{Cl}_2$, the pre-exponential factor is $2 \times 10^{13} \text{ sec}^{-1}$ at 298 K. Calculate the value of rate constant for the reaction.

Sol. E_a for free radical combination is zero. Thus,

$$K = A e^{-E_a/RT} \quad (\text{if } E_a = 0)$$

$$\therefore K = A = 2 \times 10^{13} \text{ sec}^{-1}$$



Summary

$$1. \text{ Rate of reaction} = \frac{[C_1] - [C_2]}{t_2 - t_1}$$

2. Instantaneous reaction rate is given as

$$\frac{dx}{dt} = \frac{1}{V_j} \frac{d[J]}{dt}$$



Rate of reaction

$$= -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{c} = \frac{1}{d} \frac{d[D]}{dt}$$

3. Activation energy E_a = Threshold energy – Potential energy of reactants

4. Arrhenius equation

$$k = Ae^{-E_a/RT}$$

or

$$\log_{10} k = \log_{10} A - \frac{E_a}{2.303 RT}$$

5. At two different temperatures T_1 and T_2

$$E_a = \frac{2.303 R T_1 T_2}{T_2 - T_1} \log_{10} \frac{k_2}{k_1}$$

$$\log_{10} \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \frac{(T_2 - T_1)}{T_1 T_2}$$

6. Order of reaction

$$\text{Rate} = k [A]^m [B]^n$$

$$\text{Order} = m + n$$

First-order reaction

$$-\frac{dx}{dt} \propto [A]^1$$

$$t = \frac{2.303}{k} \log_{10} \frac{a}{a-x} \text{ or } \frac{N_0}{N}$$



$$k = \frac{2.303}{t_2 - t_1} \log_{10} \frac{[a - x_1]}{[a - x_2]}$$

$$t = \frac{2.303}{k} \log \frac{r_0 - r_\infty}{r_t - r_\infty}$$

Second-order reaction

When concentrations are different

$$k = \frac{2.303}{t(a-b)} \log_{10} \frac{b(a-x)}{a(b-x)}$$

Half-life method

$$\frac{(t_{1/2})_1}{(t_{1/2})_2} = \left[\frac{a_2}{a_1} \right]^{n-1}$$

$$n = 1 + \frac{\log(t_{1/2})_1 - \log(t_{1/2})_2}{\log[a_2] - \log[a_1]}$$

Van't Hoff differential method

$$n = \frac{\log \left(\frac{-d[C_1]}{dt} \right) - \log \left(\frac{-d[C_2]}{dt} \right)}{\log [C_1] - \log [C_2]}$$

Pseudo-unimolecular reactions

$$k = \frac{2.303}{t} \log \frac{V_\infty - V_0}{V_\infty - V_t}$$

Here V_∞ = Volume at infinity

V_0 = Initial volume

V_t = Volume at t time

7. Modified arrhenius equation

$$\frac{d \ln k}{dT} = \frac{E}{RT^2}$$

8. Quantum efficiency

$$\phi = \frac{\text{Number of molecules in a given time}}{\text{Number of quanta absorbed at the same time}}$$