

Revision Notes

Class – 12 Chemistry

Chapter 4 – Chemical Kinetics

INTRODUCTION

Chemical Kinetics

(Kinesis: Movement)

The branch of chemistry which deals with the study of the rates of chemical reactions, the factors affecting the rates of the reactions and the mechanism by which the reactions proceed is called Chemical Kinetics.

Classification of reactions

On the basis of rates:

Very fast reactions e.g. precipitation of AgCl

Very slow reactions e.g. rusting of iron

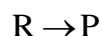
Reactions taking place at moderate speeds e.g. hydrolysis of starch

1. RATE OF A CHEMICAL REACTION

The rate of a reaction can be defined as the change in concentration of a reactant or a product in unit time.

1.1 Average rate

The rate of reaction measured over a definite time interval is called average rate of a reaction. Consider a hypothetical reaction,



$$\begin{aligned}\text{Average rate of reaction} &= \frac{(\text{Decrease in concentration of R})}{(\text{Time taken})} \\ &= \frac{[\Delta R]}{\Delta t}\end{aligned}$$

Or

$$\begin{aligned}\text{Average rate of reaction} &= \frac{(\text{Increase in concentration of P})}{(\text{Time taken})} \\ &= \frac{[\Delta P]}{\Delta t}\end{aligned}$$

1.2 Instantaneous rate

Rate of change of concentration of any one of the reactants or products at that particular instant of time is called instantaneous rate.

As

$$\Delta t \rightarrow 0$$

or

$$r_{\text{inst}} = \frac{-d[R]}{dt} = \frac{d[P]}{dt}$$

IMPORTANT: Rate of a reaction is always positive. Since, $[R]$ is a negative quantity (as concentration of reactants is decreasing), it is multiplied with -1 to make the rate of the reaction a positive quantity.

1.3 Units of rate of a reaction

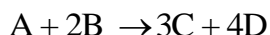
Units of rate are concentration time⁻¹

e.g. $\text{mol L}^{-1} \text{s}^{-1}$; atm s^{-1} (for gaseous reactions)

1.4 Overall rate of a reaction

When there are several reactants and products the individual rates of the various components may differ as they would depend on the stoichiometric coefficients.

For a reaction,



Rate of disappearance of B = 2 × Rate of disappearance of A (2:1)

Rate of formation of C = 3 × Rate of disappearance of A
(3:1)

Rate of formation of D = 4 × Rate of disappearance of A
(4:1)

To define a unique value for the overall rate of the reaction we divide the individual rates by the respective coefficients and equate their signs.

$$\begin{aligned}\text{Overall Rate} &= -A/t = (-1/2) B/t = (+1/3) C/t \\ &= (+1/4) D/t\end{aligned}$$

2. DEPENDENCE OF RATE ON CONCENTRATION

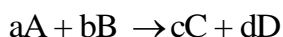
Factors Influencing Rate of a Reaction

concentration of reactants (pressure in case of gases),
temperature and
catalyst.

Dependence on Concentration:

2.1 Rate law

Consider a general reaction



The rate expression for this reaction is

$$\text{Rate} \propto [\text{A}]^x [\text{B}]^y$$

where exponents x and y may or may not be equal to the stoichiometric coefficients (a and b) of the reactants.

$$\text{Rate} = k[\text{A}]^x [\text{B}]^y$$

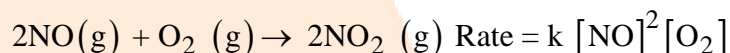
$$-d[\text{R}]/dt = k[\text{A}]^x [\text{B}]^y$$

Above equation is known as differential rate equation, k is a proportionality constant called rate constant.

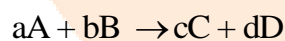
Rate law is the expression in which reaction rate is given in terms of molar concentration of reactants with each term raised to some power, which may or may not be same as the stoichiometric coefficient of the reacting species in a balanced chemical equation.

IMPORTANT

Rate law for any reaction cannot be predicted by merely looking at the balanced chemical equation, i.e., theoretically but must be determined experimentally.



2.2 Order of a Reaction



$$\text{Rate} = k[\text{A}]^x [\text{B}]^y$$

Sum of these exponents, i.e., x + y gives the overall order of a reaction where x and y represent the order with respect to the reactants A and B respectively. Hence, the sum of powers of the concentration of the reactants in the rate law expression is called the order of that chemical reaction.

Order of a reaction can be 0, 1, 2, 3 and even a fraction.

2.3 Units of rate constant

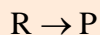
$$\text{Rate} = k[A]^x[B]^y$$

$$k = \frac{\text{Rate}}{[A]^x[B]^y} = \frac{\text{concentration}}{\text{time}} \times \frac{1}{(\text{concentration})^n}$$

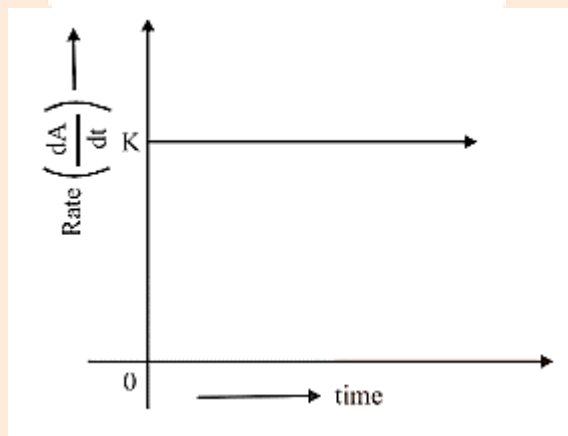
3. INTEGRATED RATE EQUATIONS

3.1 Zero order reaction

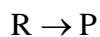
The rate of the reaction is proportional to zero power of the concentration of reactants.



$$\text{Rate} = -\frac{d[R]}{dt} = kR^0$$



Consider the reaction,



$$\text{Rate} = -\frac{d[R]}{dt} = k[R]^0$$

$$\text{Rate} = -\frac{d[R]}{dt} = k \times 1$$

$$d[R] = -kdt$$

Integrating both sides

$$[R] = -kt + I$$

where, I is the constant of integration.

At $t = 0$, the concentration of the reactant $R = [R]_0$, where $[R]_0$ is initial concentration of the reactant.

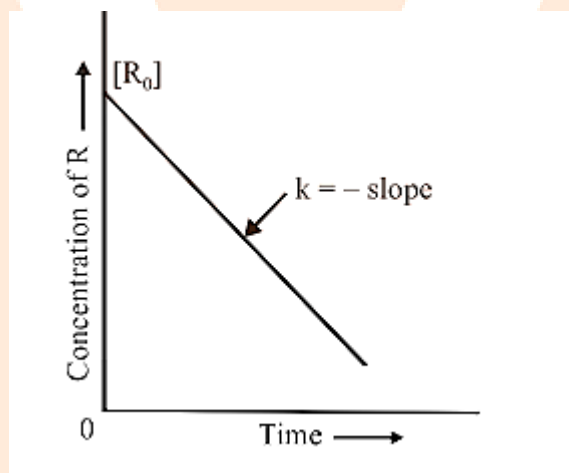
Substituting in equation

$$[R]_0 = -k \times 0 + I$$

$$[R]_0 = I$$

Substituting the value of I in the equation

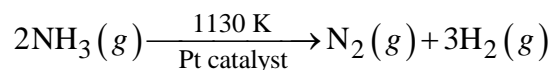
$$[R] = -kt + [R]_0$$



$$k = \frac{([R]_0) - ([R])}{t}$$

Example:

The decomposition of gaseous ammonia on a hot platinum surface at high pressure.



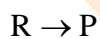
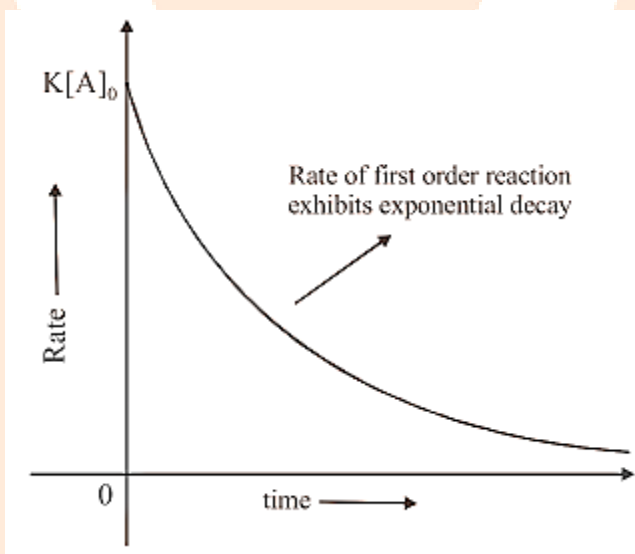
$$\begin{aligned}\text{Rate} &= k[\text{NH}_3]^0 \\ &= k\end{aligned}$$

Thermal decomposition of HI on gold surface

3.2 First order

The rate of the reaction is proportional to the first power of the concentration of the reactant R.

$$\begin{aligned}\text{Rate} &= \frac{-d[\text{R}]}{dt} \\ &= k[\text{R}]\end{aligned}$$



$$\text{Rate} = \frac{-d[\text{R}]}{dt} = k[\text{R}]$$

$$\frac{-d[\text{R}]}{[\text{R}]} = kdt$$

Integrating this equation, we get

$$\ln [\text{R}] = -kt + I \dots\dots (1)$$

Again, I is the constant of integration and its value can be determined easily.

When $t = 0$, $R = [R]_0$, where $[R]_0$ is the initial concentration of the reactant.

Therefore, equation can be written as

$$\ln [R]_0 = -k \times 0 + I$$

$$\ln [R]_0 = I$$

Substituting the value of I in equation

$$\ln [R] = -kt + \ln [R]_0 \dots\dots\dots (2)$$

Rearranging this equation

$$\ln \frac{[R]}{[R]_0} = -kt$$

or

$$k = \frac{1}{t} \ln \frac{[R]_0}{[R]} \dots\dots\dots (3)$$

At time t_1 from equation (2)

$$\ln [R]_1 = -kt_1 + \ln [R]_0$$

At time t_2

$$\ln [R]_2 = -kt_2 + \ln [R]_0$$

where, $[R]_1$ and $[R]_2$ are the concentrations of the reactants at time t_1 and t_2 respectively.

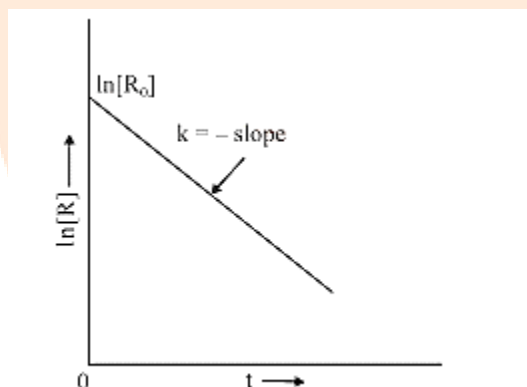
Subtracting

$$\ln [R]_1 - \ln [R]_2 = -kt_1 - (-kt_2)$$

$$\ln \frac{[R]_1}{[R]_2} = k(t_2 - t_1)$$

$$k = \frac{1}{(t_2 - t_1)} \ln \frac{[R]_1}{[R]_2}$$

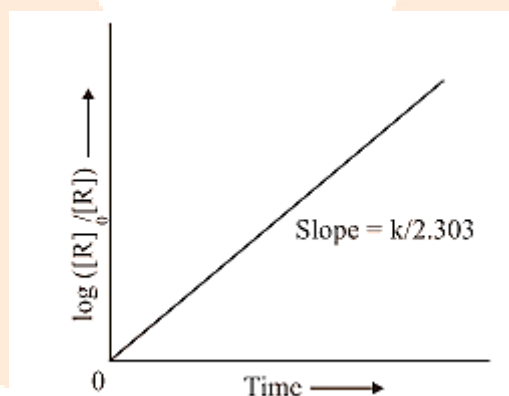
Comparing equation (2) with $y = mx + c$, if we plot $\ln [R]$ against t , we get a straight line with slope $= -k$ and intercept equal to $\ln [R]_0$



The first order rate equation (3) can also be written in the form

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

$$\log \frac{[R]_0}{[R]} = \frac{kt}{2.303}$$



3.3 Half-Life of a Reaction

The half-life of a reaction is the time in which the concentration of a reactant is reduced to one half of its initial concentration.

Represented as: $t_{1/2}$.

For a zero order reaction, rate constant is given by equation.

$$k = \frac{[R]_0 - [R]}{t}$$

At $t = t_{1/2}$, $[R] = \frac{1}{2}[R]_0$

The rate constant at $t_{1/2}$ becomes

$$k = \frac{[R]_0 - \frac{1}{2}[R]_0}{t_{1/2}}$$

$$t_{1/2} = \frac{[R]_0}{2k}$$

For the first order reaction,

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

At half time, $[R] = \frac{[R]_0}{2}$

So, the above equation becomes

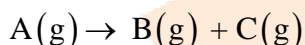
$$k = \frac{2.303}{t_{1/2}} \log \frac{[R]_0}{[R]_0/2}$$

Or

$$t_{1/2} = \frac{2.303}{k} \log 2$$

$$t_{1/2} = \frac{2.303}{k} \times 0.301$$

Total pressure $P_t = P_A + P_B + P_C$ (pressure units) p_A , p_B and p_C are the partial pressures of A, B and C, respectively. If x atm be the decrease in pressure of A at time t and one mole each of B and C is being formed, the increase in pressure of B and C will also be x atm each.



At $t = 0$ p_i atm 0 atm 0 atm

At time t $(p_i - x)$ atm x atm x atm

where, p_i is the initial pressure at time $t = 0$.

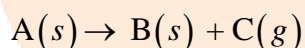
$$p_t = (p_i - x) + x + x = p_i + x$$

$$x = (p_t - p_i)$$

$$p_A = p_i - x = p_i - (p_t - p_i) \\ = 2p_i - p_t$$

$$k = \left(\frac{2.303}{t} \right) \left(\log \frac{p_i}{p_A} \right) \\ = \left(\frac{2.303}{t} \right) \left(\log \frac{p_i}{(2p_i - p_t)} \right)$$

For a first order gas phase reaction of the type :



The data given to us is:

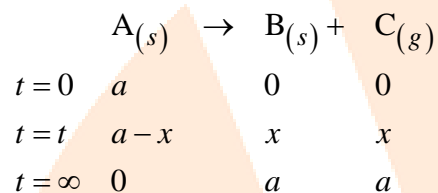
| Time | Pressure of gas C/Total Pressure |
|----------|----------------------------------|
| 0 | 0 |
| t | P_t |
| ∞ | P_∞ |

If we have to find the expression for k or verify that its a first order reaction then we will use the expression for k :

$$\ln \frac{a}{a-x} = kt$$

But we don't know the values for a or $a - x$ but we can find the above ratio by relating the given data with concentration values.

For gases, $P \propto$ number of moles



Now we can write;

$$P_t \propto x$$

$$P_{\infty} \propto a$$

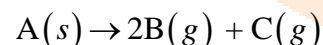
$$P_{\infty} - P_t \propto a - x$$

$$a/(a-x) = P_{\infty} / (P_{\infty} - P_t)$$

Now we can substitute this into the expression for k .

$$k = (1/t) \ln [P_{\infty} / (P_{\infty} - P_t)]$$

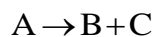
The above expression can be used to evaluate the value of k from the pressure data and also verify that the reaction is of first order by checking 2-3 data points. In the above analysis the expression would have been same for the following reactions as well as the constants will cancel out.



And the results will be same if the similar data is given in terms of volume.

Case 2: If one of reactants is titrated with a red/ox reagent:

Suppose we have a reaction of the type:



And suppose we detect the amount of A left by titrating it with some reagent and volume of that reagent reacting with the left over A is given at different time intervals:

| Time | Volume of the reagent |
|------|-----------------------|
| 0 | V_0 |
| t | V_t |

Now the volume of the reagent will be proportional to the moles of A present. Therefore:

$$V_0 \propto a$$

$$V_t \propto a - x$$

We can evaluate k:

$$k_t = \ln(V_0 / V_t)$$

If the same reagent reacts with all the reactants and products:

$$V_0 \propto a$$

$$V_t \propto a + x$$

$$2V_0 - V_t \propto a - x$$

$$kt = \ln(V_0 / (2V_0 - V_t))$$

3.6 Practical Methods of determining order of a reaction

i. Initial Rate Data Method:

We take different set of initial concentration and measure the initial rate. Then by keeping the concentration of one of the reactants constant and varying the other one we can study the effect on the rate and hence find out the order.

ii. Logarithmic data method:

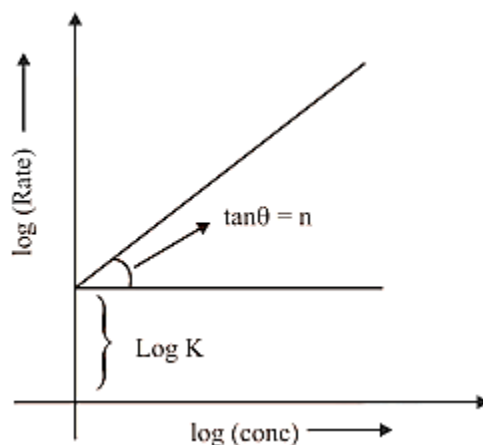
For any order, be it fractional or integral, if we plot $\log(\text{rate})$ vs $\log(\text{concentration})$ graph it will always be a straight line for the reactions of the type:

$A \rightarrow \text{products}$

$$\text{Rate, } r = k[A]^n$$

$$\log r = \log k + n \log [A]$$

We can take various data points and convert them to log values and plot them. We will obtain a straight line after curve-fitting with slope n and intercept $\log k$. And hence we can find out the order and rate constant from the graph.



iii. Half Life Method:

If we take various concentrations of reactant and measure half life for all of them then we can find out the order of the reaction by mere observation or with the help of some calculations.

$$t_{1/2} = [A]_0^{1-n}$$

If simple observation is not possible then we can calculate the order of the reaction by taking two data points and using log for calculating n .

iv. By integrated rate Equations:

If we have simple data of concentration and time we can use the integrated rate equations to find out the order. For this we will have to try and fit the data into the equation at various intervals and calculate the value of rate constants. If the values come out to be the same in all intervals then the data fits into the equation taken and we will know the order. For example, we have the following data:

Time: 0 t_1 t_2 t_3 t
 Conc: A_0 A_1 A_2 A_3 A_t

And if we assume that it can be of first order then we will calculate the values of k at minimum three data points by using the equation for first order:

$$(1/t) \ln (A_0/A_t) = k$$

Let these values be k_1 , k_2 and k_3 . If $k_1 = k_2 = k_3$ then it means that this data fits into the above equation hence the order is 1. If it doesn't we will have to try other equations as well.

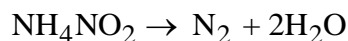
v. Isolation method:

In this method we try and eliminate one of the two reactants from the rate equation by taking it in excess. What happens is when the amount of a reactant is in excess its effect on the rate becomes marginal or negligible and then we can vary the concentration of the other reactant and observe its effect on rate and find out the order.

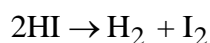
4. MOLECULARITY AND MECHANISM

4.1 Molecularity The number of reacting species (atoms, ions or molecules) taking part in an elementary reaction, which must collide simultaneously in order to bring about a chemical reaction is called molecularity of a reaction. Classification of reactions on the basis of Molecularity:

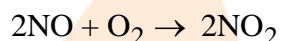
Unimolecular reactions: when one reacting species is involved, for example, decomposition of ammonium nitrite.



Bimolecular reactions: involve simultaneous collision between two species, for example, dissociation of hydrogen iodide.



Trimolecular or termolecular reactions: involve simultaneous collision between three reacting species, for example,



Reactions with molecularity greater than three are very rare.

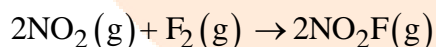
4.2 Mechanism

The reactions taking place in one step are called elementary reactions. When a sequence of elementary reactions (called mechanism) gives us the products, the reactions are called complex reactions. The different steps in which the complex reaction takes place is called the mechanism of the reaction.

Rate determining step:

The overall rate of the reaction is controlled by the slowest step in a reaction called the rate determining step. A complex reaction can be represented as a series of elementary steps.

For example



Experimentally, Rate of reaction $= k[\text{NO}_2][\text{F}_2]$

Probable mechanism:

Step-1:



Step-2:



Slow step: bimolecular

Hence, a bimolecular reaction.

Reaction intermediates: There are some species which are formed during the course of the reaction but do not appear in the overall reaction. They are called reaction intermediates.

e.g. NO_3 in the above example.

Distinction between Order and Molecularity of a reaction

Order

1. Order is the sum of the powers of the concentration of the reactants in the rate law expression.
2. It can be zero and even a fraction.
3. It is applicable to elementary as well as complex reactions.
4. It can be determined experimentally only and cannot be calculated.
5. For complex reaction, order is given by the slowest step.

Molecularity

1. Molecularity is the number of reacting species taking part in an elementary reaction, which must collide simultaneously in order to bring about a chemical reaction.
2. It cannot be zero or a non integer.
3. It is applicable only for elementary reactions. For complex reaction molecularity has no meaning.

4. It can be calculated by simply adding the molecules of the slowest step.
5. Generally, molecularity of the slowest step is same as the order of the overall reaction.

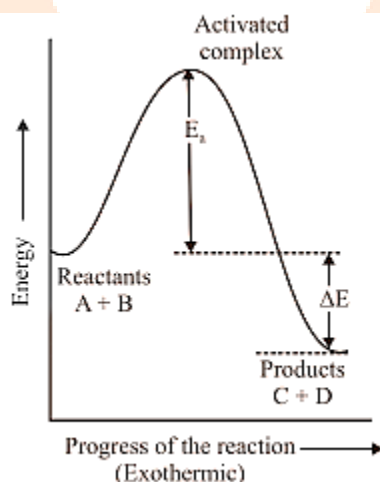
5. TEMPERATURE DEPENDENCE

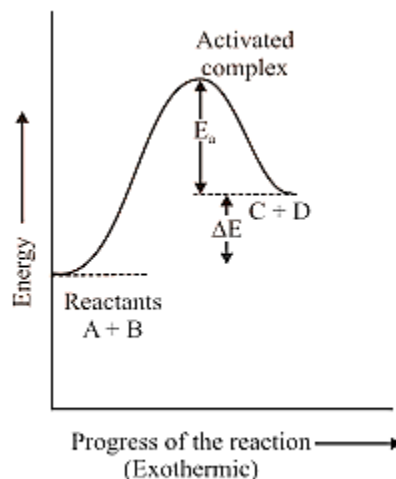
5.1 Activation Energy

According to collision theory, a reaction takes place because the reactant molecules collide with each other. The minimum energy which the colliding molecules must have in order that the collision between them may be effective is called threshold energy. The minimum extra amount of energy absorbed by the reactant molecules so that their energy becomes equal to threshold value is called activation energy.

Threshold energy = Activation energy + Energy possessed by the reactants

Less is the activation energy, faster is the reaction. In order that the reactants may change into products, they have to cross an energy barrier (corresponding to threshold energy). Reactant molecules absorb energy and form an intermediate called activated complex which immediately dissociates to form the products.



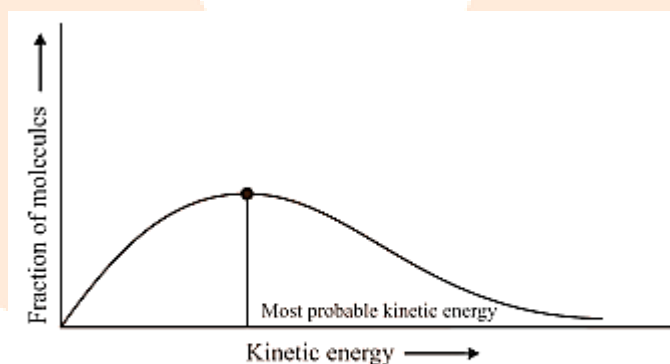


5.2 Temperature Dependence of the Rate of a Reaction

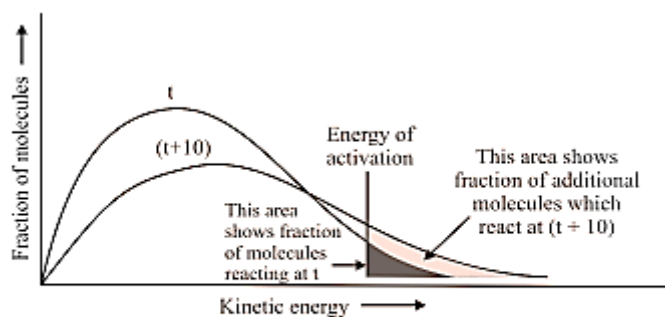
For a chemical reaction with rise in temperature by 10° , the rate constant is nearly doubled. Temperature coefficient = $(\text{Rate constant at } T + 10^\circ) / (\text{Rate constant at } T^\circ)$

Explanation:

At a particular temperature, if fractions of molecules are plotted versus corresponding kinetic energies, a graph of the type shown is obtained. The peak of the curve represents the kinetic energy possessed by the maximum fraction of molecules and is called most probable kinetic energy.



Distribution curve showing energies among gaseous molecules



Distribution curve showing temperature dependence of rate of a reaction

With increase in temperature:

- (i) maximum of the curve moves to the higher energy value i.e., most probable kinetic energy increases
- (ii) the curve spreads to the right i.e., there is a greater proportion of molecules with much higher energies.

The area under the curve remains constant since total probability must be one at all times. At $(t + 10)$, the area showing the fraction of molecules having energy equal to or greater than activation energy gets doubled leading to doubling the rate of a reaction.

Arrhenius equation

Quantitatively, the temperature dependence of the rate of a chemical reaction can be explained by Arrhenius equation

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

where A is the Arrhenius factor or the frequency factor or pre-exponential factor. R is gas constant and E_a is activation energy measured in joules/mole. The factor $e^{-E_a/RT}$ corresponds to the fraction of molecules that have kinetic energy greater than E_a . Thus, it has been found from Arrhenius equation that increasing the temperature or decreasing the activation energy will result in an increase in the rate of the reaction and an exponential increase in the rate constant. Taking natural logarithm of both sides of equation

$$\ln k = \ln A - \frac{E_a}{RT}$$

The plot of $\ln k$ vs $1/T$ gives a straight line with slope

$-\frac{E_a}{R}$ and intercept = $\ln A$. At temperature T_1 , equation is $\ln k_1 = \ln A - \frac{E_a}{RT_1}$. At temperature T_2 , equation is $\ln k_2 = \ln A - \frac{E_a}{RT_2}$ (since A is constant for a given reaction) k_1 and k_2 are the values of rate constants at temperatures T_1 and T_2 respectively. Subtracting equation from, we obtain $\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$

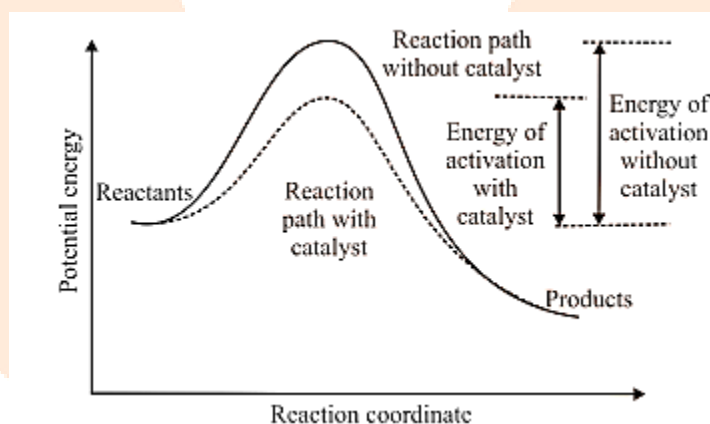
6. EFFECT OF CATALYST

A catalyst is a substance which alters the rate of a reaction without itself undergoing any permanent chemical change.

Action of the catalyst

According to intermediate complex theory, reactants first combine with catalyst to form intermediate complex which then decomposes to form the products and regenerating the catalyst.

Effect of catalyst on activation energy



Catalyst provides an alternate pathway by reducing the activation energy between reactants and products and hence lowering the potential energy barrier.

Important characteristics of catalyst:

A small amount of the catalyst can catalyse a large amount of reactants.

A catalyst does not alter Gibbs energy, G of a reaction.

It catalyses the spontaneous reactions but does not catalyse non-spontaneous reactions.

A catalyst does not change the equilibrium constant of a reaction rather, it helps in attaining the equilibrium faster.

7. COLLISION THEORY OF CHEMICAL REACTIONS

According to this theory, the reactant molecules are assumed to be hard spheres and reaction is postulated to occur when molecules collide with each other. Rate of reaction depends on the number of effective collisions which in turn depends on:

(i) Energy factor: colliding molecules must have energy more than threshold energy.

(ii) Steric or probability factor (P): colliding molecules must have proper orientations at the time of collision. Thus, the Arrhenius equation is modified to