Chemical Kinetics

The area of chemistry that concerns reaction rates and reaction mechanism

The focus of this lesson is to study the rates of chemical reactions and factors that influence these rates.

Understanding these factors will allow us to calculate, predict, and graph reactions. This includes changes in concentrations over time, initial reaction rates, instantaneous rates, average reaction rates, and half-lives of reactions.

What is chemical kinetics

- Chemical kinetics is the part of chemical science dealing with the study of the
- >rates of chemical reactions and
- the factors which affect the reaction rates.

TOPICS TO BE COVERED

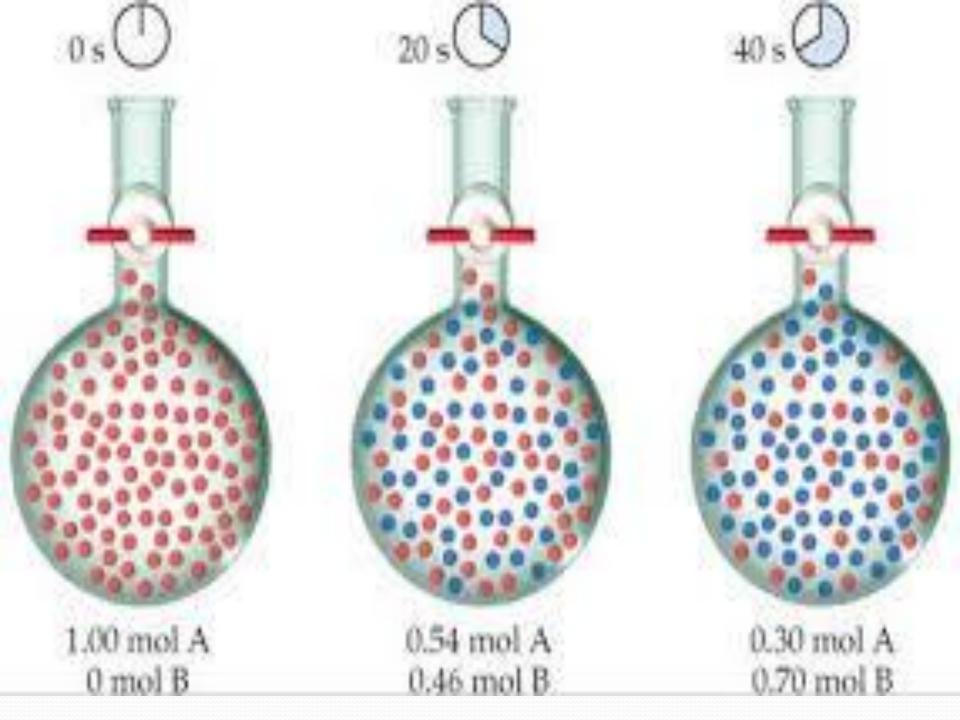
- What is Rate of reaction
- Average and Instantaneous rate
- Rate law or Rate Expression
- Specific rate constant
- Order of Reaction
- Methods to determine order of reaction
- Molecularity
- Pseudo first order reaction
- Collision theory of reaction
- Factor affecting rate of reaction
- Activation Energy, Arrhenius equation

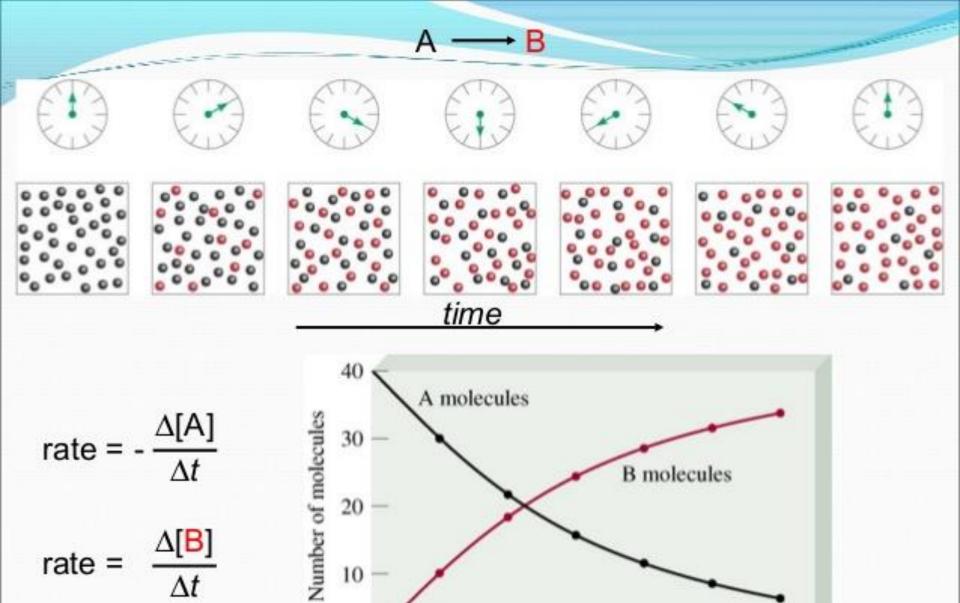
Reaction Rates

Rate of a chemical reaction = change in concentration (mol/L) of a reactant or product with time (s, min, hr);

Rate of Reaction=

Change in Concentration
Change in Time





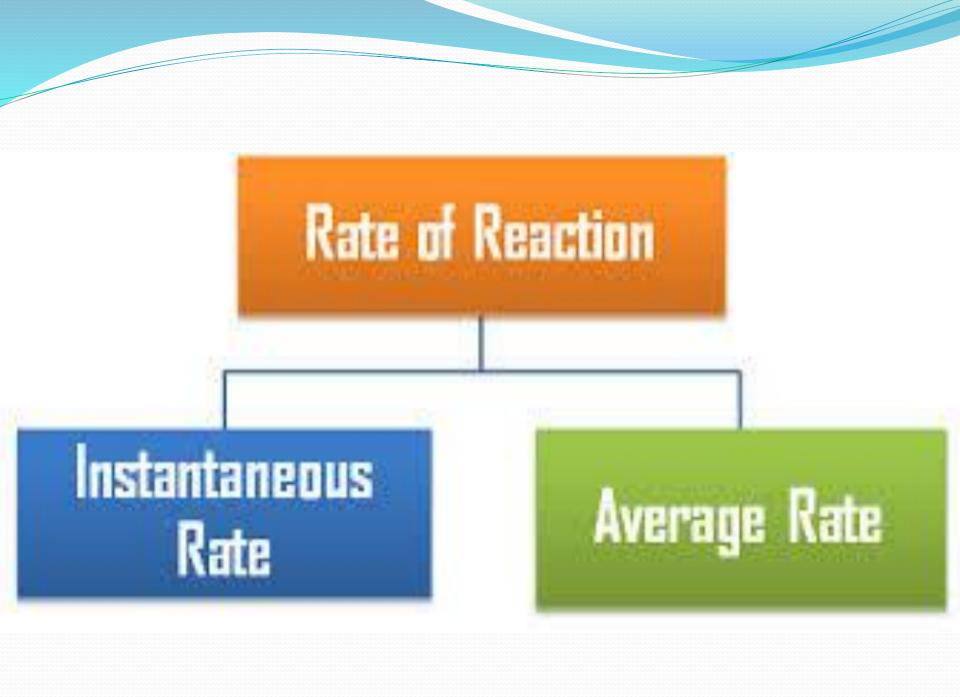
t(s)



Expressing the rate of the reaction:

Example, $aA + bB \rightarrow cC + dD$ The expression for the rate of the reaction is Rate, $R = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = +\frac{1}{c}\frac{d[C]}{dt} = +\frac{1}{d}\frac{d[D]}{dt}$ Rate of disappearance of A, $-\frac{d[A]}{dt} = a \times \text{rate of the reaction}$ Rate of disappearance of B, $-\frac{d[B]}{dt} = b \times \text{rate of the reaction}$ Rate of appearance of C, $+\frac{d[C]}{dt} = c \times \text{rate of the reaction}$

Rate of appearance of D, $+\frac{d[D]}{dt} = d \times rate$ of the reaction



Average rate of the reaction:

It is defined as the rate of change of concentration of the reactants (or products) over a specified measurable period of time.

For a reaction,
$$A \rightarrow B$$

If $[A]_1$ and $[A]_2$ be the concentration of the reactants A at time t_1 and t_2 respectively, then the rate of the reaction in terms of the reactant in time interval $(t_1 - t_2)$ is given by,

Average rate of reaction =
$$\frac{\text{change in concentration of A}}{\text{time interval}}$$
$$= \frac{[A]_2 - [A]_1}{t_2 - t_1}$$
$$= -\frac{\Delta[A]}{\Delta t}$$

Here $[A]_1 > [A]_2$

Therefore negative is used.

Similarly, if $[B]_1$ and $[B]_2$ be the concentration of product B at time t_1 and t_2 respectively, then the rate of reaction in terms of product B is given by,

Average rate of the reaction = $\frac{\text{change in concentration of B (products)}}{\text{time interval}}$

$$= \frac{[B]_{2} - [B]_{1}}{t_{2} - t_{1}} = + \frac{\Delta[B]}{\Delta t}$$

Here,[B], > [B], therefore positive sign is used

Figure..... in board

2. Instantaneous rate of the reaction:

It is defined as the rate of change in concentration of any one of the reactant or product at particular time. It gives the tendency of the reaction at a particular point of time during the course.

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Mathematically, Instantaneous rate =[Average \ rate]_{\Delta^t \to 0} \frac{dx}{dt} = Where dx= very small change in concentration dt= very small change in time For instantaneous rate, t_1 \approx t_2 \Delta t \to 0.
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Rate law and rate law equation:

For a general reaction,

aA + bB → products

Then according to the law of mass action,

Rate ∝ [A]a[B]b

Or, rate = K[A]a[B]b where K is constant called velocity constant.

However, experimentally is observed that the rate of this reaction may or may not depend upon all the 'a' concentration terms A and all the 'b' concentration terms of B.

Suppose, experimentally the rate of the reaction is found to depend upon 'x' concentration terms of A and 'y' concentration terms of B.

Then we may write,

Rate $\propto [A]^x[B]^y$ where, x is the order with respect to A and y is the order with respect to B.

Rate = $K[A]^{x}[B]^{y}$(i)

Where [A] and [B] are the molar concentration of A and B respectively and K is constant called rate constant. The above expression is called rate law.

The rate law is defined as "The mathematical expression which represents the experimentally measured rate of the reaction in terms of the concentration of the reacting species which influence the rate of the reaction."

Again, if all concentrations are taken as unity i.e.

[A]=[B]= 1 mol/L

Then rate = K(rate constant)

Hence, rate constant, may be defined as the rate of the reaction when the concentration of each reactant is taken as unity.

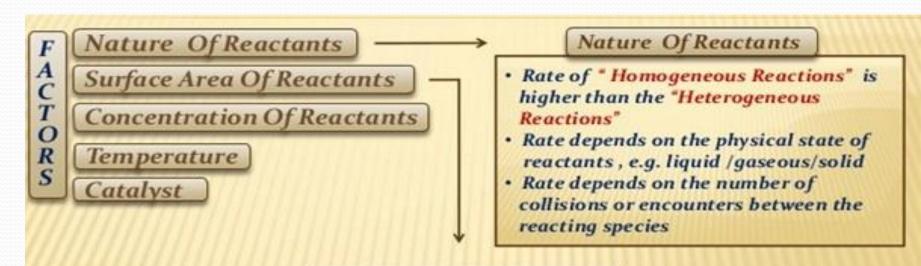
Characteristics of the rate constant(K)

- Rate constant is a measure of the rate of reaction. Higher the value of rate constant faster is the reaction.
- The value of rate constant 'K' is different for different reactions.
 Hence it is also called specific constant.
- For a particular reaction, the value of rate constant is independent of the concentration of the reactants.(zero order reaction)

Differences between rate of reaction and rate constant.

Rate of reaction	Rate constant
It is the change in concentration of the reactant or product per unit time.	 It is a constant of proportionality in the rate law equation and is equal to the rate of the reaction when the molar concentration of each reactants is unity.
The rate of reaction at any instant of time depends upon the molar concentration.	2. The rate constant is constant for a particular reaction at a particular temperature and may or may not depend upon the concentration of the reactants.
3. Its units are always molL-1time-1	3. Its units depend upon the order of the reaction

FACTORS AFFECTING THE RATES OF REACTION



The same mass of Steel wool bursts into flame

Surface Area Of Reactants

- Heterogeneous reaction occurs at interface of two phases of reactants
- If one reactant is Solid, rate increases with increase in surface area of solid phase reactant
- * Surface area increases, area of contact between reactants increasesrate of encounter between reactants increases - Rate increases
- Surface area of a solid can be increased by Sub-division i.e. dividing the bigger particles in smaller



CONCLUSION

- Main Factors which influence reaction rate:
 - Concentrations of Reactants Rates usually increase as reactant concentrations increase.
 - Reaction Temperature An increase in temperature increases the rate of a reaction.
 - Presence of a Catalyst (not all rxns have catalysts)
 - A catalyst is a substance which increases the rate of a reaction without being consumed in the overall reaction.
 - The concentration of the catalyst or its surface area (if insoluble) are variables which influence the rate.
 - Some catalysts are incredibly complex like enzymes; and others are quite simple: H+ + H₂O + CH₂ = CH₂ ------) CH₃-CH₂-OH + H+
 - Type of Reactants
 - "Surface Area of an Insoluble Reactant"

Order of the reaction:

The sum of the concentration terms on which the rate of a reaction actually depends as observed experimentally is called **order of the reaction**.

Or,

The power to which the concentration of the reactants is raised in the rate law equation is called **order of the reaction**.

Examples , let us consider a general reaction,

mA + nB → product

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Order of a reaction

Sum of the power of concentration.

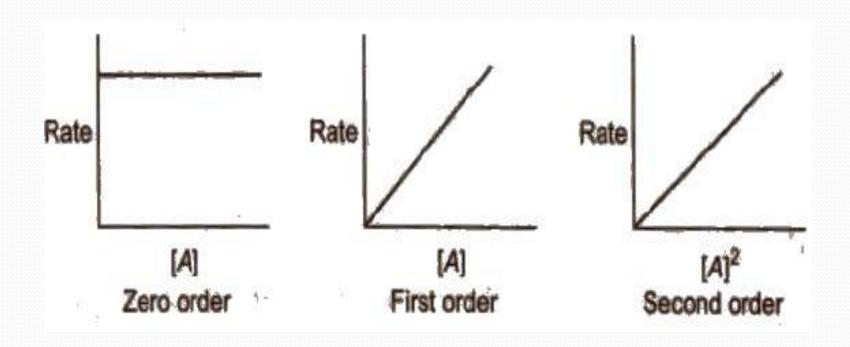
- The order of such a reaction is (m + n).
- Order of reaction:- positive, negative, zero and fractional.
- Example:

reaction order= 1+1= 2

Reaction order is determined by experiment.

Rate law	Reaction order
rate=k[N ₂ O ₅]	1
rate=k[H ₂][NO] ²	1+2=3
rate=k[CHCl ₃][Cl ₂] ^{1/2}	1+1/2=3/2

Methods to Determine Order of Reaction (i) Graphical method



(ii) Initial rate method:

In this method, the order of a reaction is determined by varying the concentration of one of the reactants while others are kept constant.

(iii) Integrated rate law method:

In this method out different integrated rate equation which gives the most constant value for the rate constant corresponds to a specific order of reaction.

INTEGRATED RATE EQUATION

For Zero Order Reaction:-

$$R \rightarrow P$$

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

$$Rate = -d[R] = dt \times k$$

$$d[R] = -k dt$$

$$Integrating both side$$

$$[R] = -kt + c \qquad(1)$$

$$where, c is the constant of integration$$

$$At t = 0, \quad R = R_0 = Initial concentration of reactant.$$

$$Substituting in equation (1)$$

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

$$Substituting the value of c in equation (1).$$

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

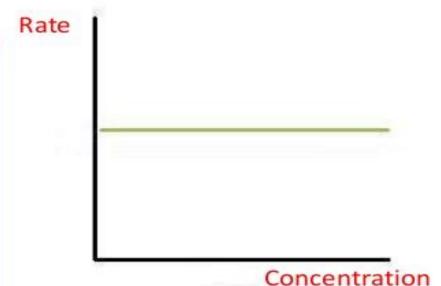
$$k = [R]_0 - [R]$$

Zero order reactions

In a zero order reaction you get a straight line as concentration does not change with rate

In this case the rate = rate constant

This means the reactant has no influence over the rate of reaction



My love for you is like a "ZERO ORDER REACTION" REACTION"

The reaction rate(my love for you) is independent of the concentration of reactant(your love for me)

So changing the concentration has no effect on the speed of reaction(my unconditional love for you)

• INTEGRATED RATE LAW FOR FIRST ORDER CHEMICAL REACTION:-

In this class of reactions, the rate of the reaction is proportional to the first power of the concentration of the reactant R. For example,

$$R \rightarrow P$$

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

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

Integrating this equation, we get

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

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 (4.8) can be written as

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

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

Substituting the value of I in equation 1
$$ln[R] = -kt + ln[R]_0$$
 2

Rearranging this equation

$$\ln \frac{[R]}{[R]_0} = -kt$$
or $k = \frac{1}{t} \ln \frac{[R]_0}{[R]}$

5

At time
$$t_1$$
 *ln[R]₁ = - kt_1 + *ln[R]₀ 4

At time
$$t_2$$

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

Subtracting 5 from 4

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

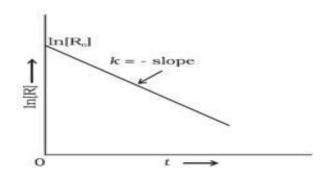
$$\ln \frac{[R]_1}{[R]_2} = k(t_2 - t_1)$$

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

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

Taking antilog of both sides

$$[R] = [R]_0 e^{-kt}$$
 7



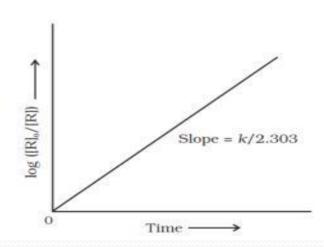
Comparing equation 2 with y = mx + c, if we plot $\ln [R]$ against t we get a straight line with slope = -k and intercept equal to $\ln [R]_0$

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

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

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

If we plot a graph between $\log [R]_0/[R]$ vs t, the slope = k/2.303



Rate law for first order reaction:

$$k=rac{2.303}{t}\lograc{[R_0]}{[R]}$$

where 'k' is rate constant or specific reaction rate, [Ro] is initial molar conc., [R] is final molar conc. after time 't'.

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

•where 'a' is initial conc. reacted in time 't' final conc., after time 't' is (a - x).

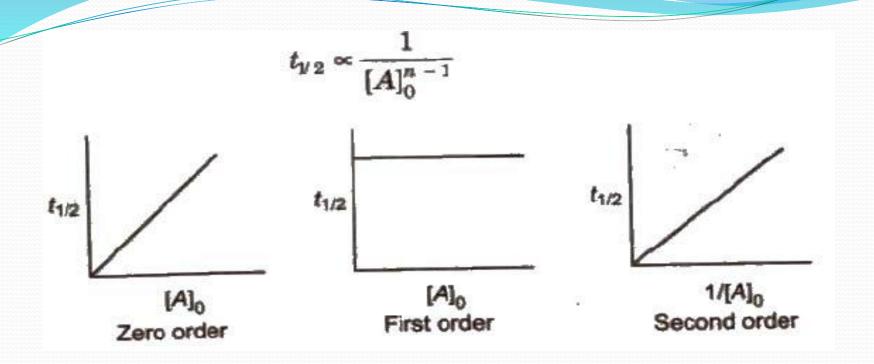
To calculate rate constant for first order gas phase reaction,

$$k = \frac{2.303}{t} \log \frac{p_1}{(2p_i - p_t)}$$

Where <u>pi</u> is initial pressure of A, <u>pt</u> is total pressure of gaseous mixture containing A , B, C

(iv) Half-life period (t_{1/2}):

method In general half-life period ($t_{1/2}$) of a reaction of nth order is related to initial concentration of the reactant as



This method is employed only when the rate law involved only one concentration term.

v) Ostwald's isolation method:

This method is employed in determining the order of complicated reactions by isolating one of the reactants so far as its influence on the reaction rate is concerned.

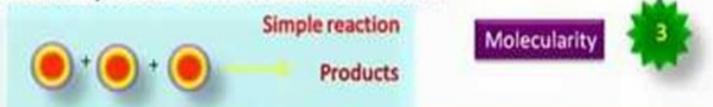
UNITS OF RATE CONSTANT

Reaction	Order	Units of rate constant
Zero order reaction	0	$\frac{\text{mol } L^{-1}}{\text{s}} \times \frac{1}{\left(\text{mol } L^{-1}\right)^{0}} = \text{mol } L^{-1} \text{s}^{-1}$
First order reaction	1	$\frac{\text{mol } L^{-1}}{\text{s}} \times \frac{1}{\left(\text{mol } L^{-1}\right)^{1}} = \text{s}^{-1}$
Second order reaction	2	$\frac{\text{mol } L^{-1}}{\text{s}} \times \frac{1}{\left(\text{mol } L^{-1}\right)^{2}} = \text{mol}^{-1}L \text{ s}^{-1}$

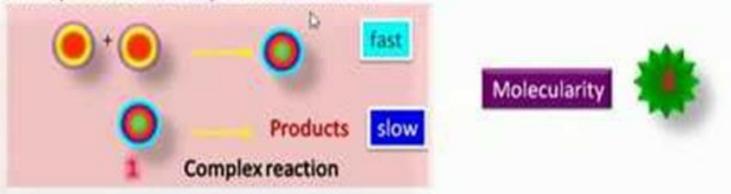
Molecularity

CHEMICAL KINETICS

It is the number of atoms, ions or molecules that must collide with one another simultaneously so as to result into a chemical reaction.



For simple reactions, the molecularity can usually be obtained from the Stoichiometry of the equation. It is always a whole number.



It can be calculated by simply adding the molecules of the slowest step.

The overall molecularity of a complex reaction has no significance. It is only slowest step whose molecularity has significance for the overall reaction.

DIFFERENCE BETWEEN MOLECULARITY AND ORDER OF REACTION

Molecularity

- Number of reacting species which collide to result in reaction
- Only positive integral values e.g 1,2,3
 never-ve
- Theoretical concept & value is derived from mechanism of reaction

Order

- Sum of powers to which concentrations are raised in the rate law expression
- · Zero, fractional or even be -ve
- Experimental fact & derived from rate law

Pseudo-order reaction:

The reactions which appear to be higher order but follow lower order kinetics are called pseudo-order reactions. In case of elementary reactions (which complete in one step), the order and molecularity are identical. Let us consider a general reaction.

In which the reactant B is present in a large excess. Since it is elementary, its rate law can be written as

Rate =
$$K[A][B]$$

As B is present in large excess, its concentration remains practically constant during the course of the reaction. Thus the rate law can be written as

Rate =
$$K'[A]$$

Temperature Dependence of Rate of a Reaction

For every 10°C rise in temperature, the rate of reaction becomes double, but only 16% collisions increases.

Temperature coefficient is the ratio of rate constant of a reaction at two temperature differing by 10. Temperature selected are usually 298 K and 308 K Temperature coefficient = \Re_t + 10/ \Re_t ≈ 2 to 3

It can be explained by Arrhenius equation.

Arrhenius Equation

Arrhenius equation is a mathematical expression to give a quantitative relationship between rate constant and temperature, and the expression is

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

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

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

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

where, A = frequency or Arrhenius factor. It is also called preexponential factor

R = gas constant

 E_a = activation energy

Important points about Arrhenius equation

(i) If \Re_2 and \Re_1 are rate constant at temperature T_2 and T_1 ; then

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

ii) Fraction of molecules with energy equal to or greater than the activation energy is called Boltzmann factor and is given by

$$x = \frac{n}{N} = e^{-E_{\alpha}/RT}$$

$$\log x = \frac{-E_{\alpha}}{2.303 RT}$$

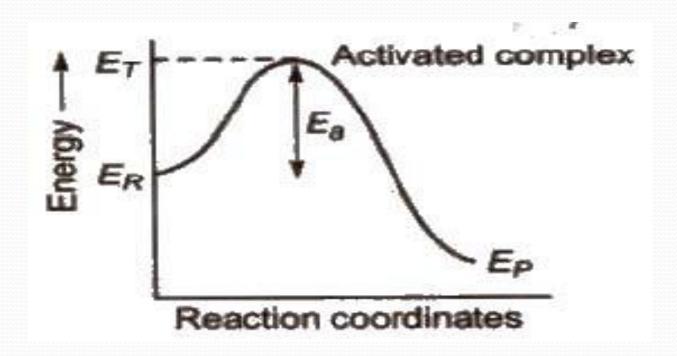
(iii) E_a is constant for a particular reaction.

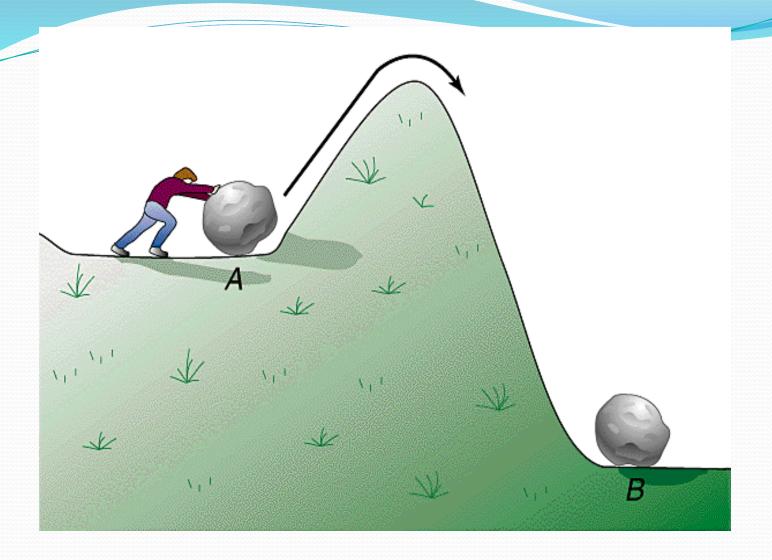
(iv) E_a does't depend on temperature, volume, pressure, etc., but gets affected by catalyst.

Activated complex (or transition state)

Activated complex is the highest energy unstable intermediate between the reactants and products and gets decomposed immediately (having very short life), to give the products.

In this state, bonds of reactant are not completely broken while the bonds of products are not completely formed.





Threshold energy (E_T)

The minimum amount of energy which the reactant must possess in order to convert into products is known as threshold energy.

Activation energy (E_a)

The additional amount of energy, required by the reactant so that their energy becomes equal to the threshold value is known as activation energy.

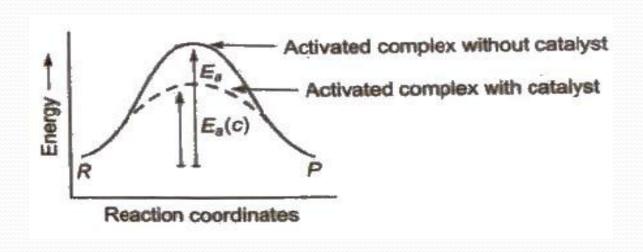
$$\Rightarrow E_a = E_T - E_R$$

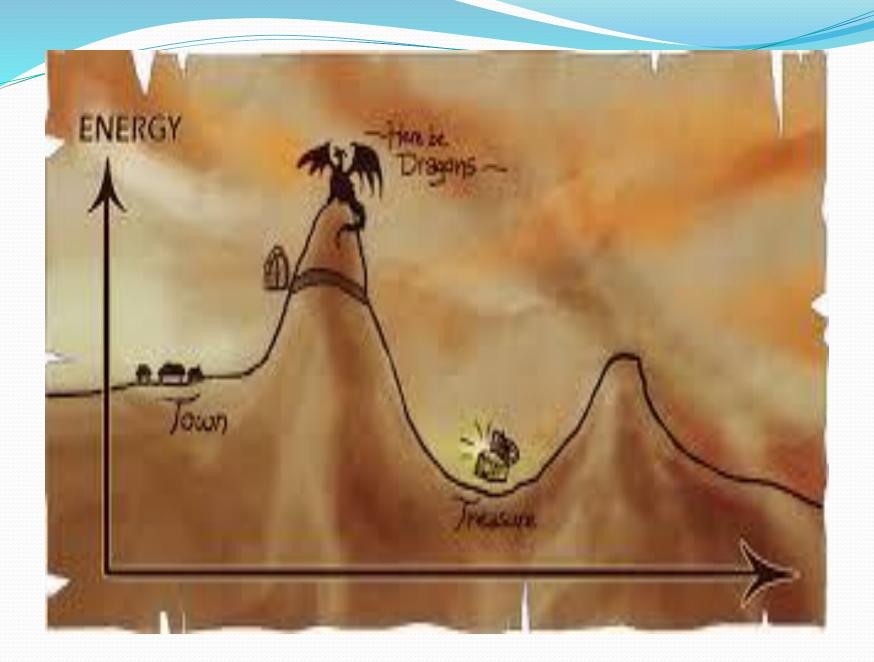
- *Lower the activation energy, faster is the reaction.
- *Different reactions have different rates because their activation energies are different.
- *Larger the value of Eo, smaller the value of rate constant and greater is the effect of a given temperature rise on K

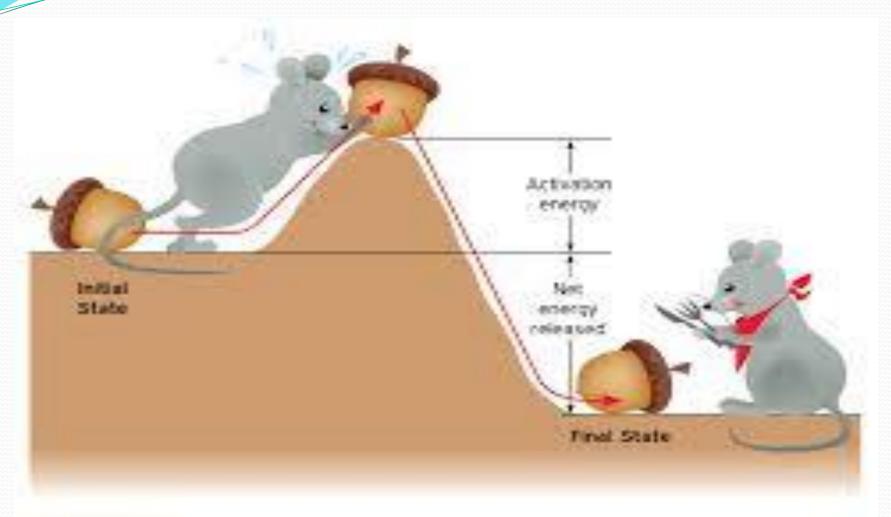
CATALYST:

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

In the chemical reactions, catalyst provides an alternate pathway or reaction mechanism by reducing the activation energy between reactants and products and hence. lowering the potential energy barrier as shown.







acorn must be hoisted over before it rolls down the mountain. Energy must be supplied to the acorn to get it into position to roll down. Similarly, energy must be supplied to reactants in order for them to "roll downhill" to products.

Theory of Reaction Rates

Collision Theory

According to this theory, the reactant molecules are assumed to be hard spheres and the reaction is postulated to occur, when molecules collide with each other.

The number of collisions between the reacting molecules taking place per second per unit volume is known as collision frequency (Z_{AB}) .

But only those collisions in which the colliding species are associated with certain minimum amount of energy and collide in proper orientation result in the product formation, such collisions are called **fruitful collisions or effective collision**.

Here,

 $\frac{\text{rate} = - (\text{dv/dt}) = \text{collision frequency x fraction of}}{\text{effective collision}}$

$$= Z_{AB} \times f$$

$$= Z_{AB} \times e^{-E_a/RT}$$

where, Z_{AB} represents the collision frequency of reactants, A and B

 $e^{-E_a/RT}$ represents the fraction of molecules with energies equal to or greater than E_a .

So, to account for effective collisions, another factor, P called the probability or steric factor is introduced.

So, rate =
$$PZ_{AB}e^{-E_a/RT}$$

SUM UP OF THE THEORY

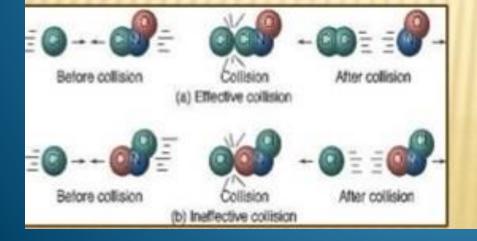
Collision Model

- Rxns occur when molecules undergo Collisions
- · All Collisions are not Effective
- Collisions of molecules with Sufficient Energy are only Effective

Orientation Barrier

Reactants must collide in favourable orientation to make & break bonds

E.g. Cl + NOCl -> NO + Cl,

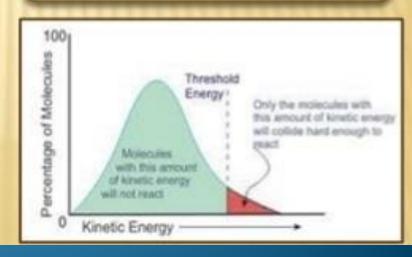


Effective Collisions

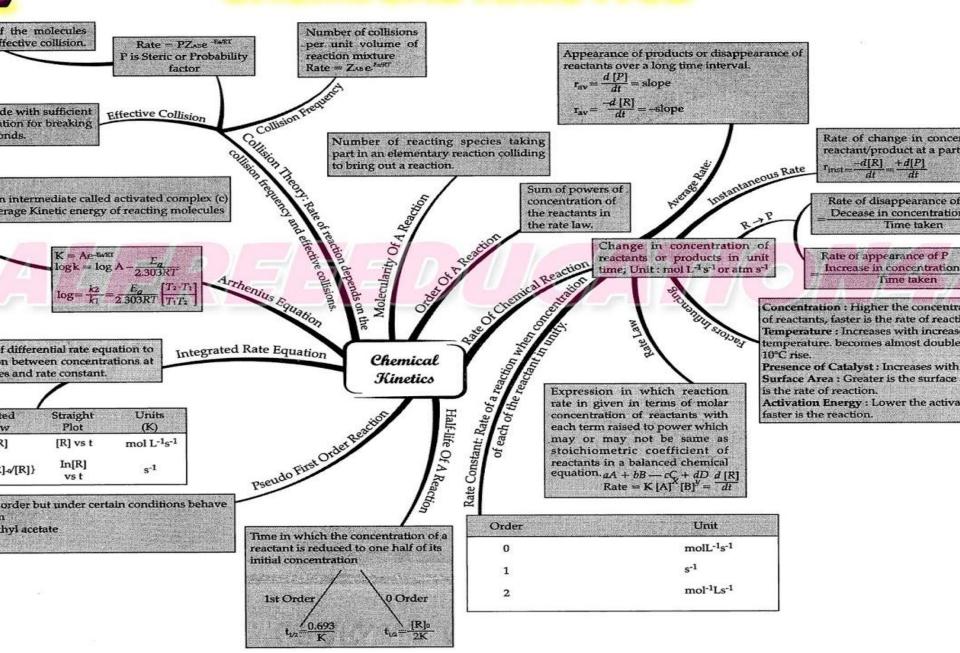
- Collisions which lead to product formation
- · Governed by 2 factors:

Energy Barrier

Molecules having energy greater than or equal to threshold energy will only form Product



CHEMICAL KINETICS



QUESTIONS

- . Define average rate and instantaneous rate.
- •What are the factors which affects the rate of reaction?
- Write three characteristics of rate constant.
- Define order and molecularity of reaction.
- •Write the difference between rate law and Law of Mass action.
- •Give two example each of
- (a) Zero order reaction
- (b) 1st order reaction.
- (c) 2nd order reaction
- Pseudo unimolecular reaction.
- •Also mention the units of rate constant from (a) to (c).
- •Explain the effect of temperature and catalyst on Rate constant.
- •Derive an expression for the rate constant of 1st order reaction by integrated rate law method.
- •Prove that for 1st order reaction, half life is independent of initial conc of reactant.

- Prove that for 1st order reaction, half life is independent of initial conc of reactant.
- For a reaction mM \rightarrow nN, the rate is given by $v = k[M]^3$. What is the change in the rate if the concentration of M is doubled?
- The rate of a reaction increases four times when the temperature changes from 300 K to 320 K. Calculate the energy of activation of the reaction, assuming that it does not change with temperature. (R = 8.314 JK⁻¹ mol⁻¹)
- A first order decomposition reaction takes 40 minutes for 30% decomposition. Calculate its t½ value.
- For the reaction $N_2O_5 \rightarrow 2NO_2 + \frac{1}{2}O_2$ the differential rate law follows a first order rate law follows a first order rate equation rate= $k [N_2O_5]$. Write the differential rate equations for the decomposition of N_2O_5 , formation of O_2 , and NO_2 in terms of the concentration of N_2O_5 .
- The differential rate law of a reaction aA→ Products is given as
 v = k[A]^x. For the reaction it is observed that the rate increases by a
 factor of 8 when the concentration of A is doubled. What is the value
 of x in the rate equation?

- For a reaction A → M it is observed that the rate of reaction doubles as the concentration of A is doubled. What is the order of the reaction?
- In a first order reaction the concentration of the reactant is reduced from 0.6 molL⁻¹ to 0.2 molL⁻¹ in 5 minutes. Calculate the rate constant of the reaction, when the initial concentration is 30 g per litre.
- For a first order reaction the specific rate is 10⁻²s⁻¹. What is the half life? If the initial concentration of the reactant is 1.0 mol L⁻¹, what is the initial rate, and what is the rate after one minute?
- For a first order reaction aA → mM, the rate constant is 0.1 s⁻¹. How much time it will take to reduce the concentration from initial value of 0.5 mol L⁻¹ to 0.05 mol L⁻¹?

- For a first order reaction prove that the time required for the completion of 99.9% of reaction is about ten times the time taken for the completion of 50% of this reaction.
- A reaction is of first order in reactant A and of second order in reactant B. How is the rate of the reaction affected when
 - (a) The concentration of B alone is increased to three times.
 - (b) The concentration of A and B are doubled?

- For a first order reaction the rate constant is 10⁻³s⁻¹. How much time would it take for 10 g of reactant to reduce to 5 g?
- The rate constant of a reaction is $2 \times 10^{-2} \, \text{s}^{-1}$ at 300 K and $8 \times 10^{-2} \, \text{s}^{-1}$ at 340 K. Calculate the energy of activation of the reaction.
- The rate of the reaction aA → mM, quadruples when the temperature is increased from 293 K to 313 K. Compute the energy of activation of the reaction.
- The half life of a first order reaction A → B is 8 minutes. How long will it take [A] to reach 25% of its initial concentration?

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