

CHEMICAL SKINETICS SCHOOL

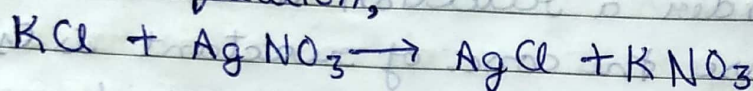
Types of reaction

There are 3 types of reaction on the basis of speed:

1. Very fast reaction

Reactions which takes place in micro seconds are called very fast reactions.

Example:- Ionic equation,



2. Very slow reaction

Reaction which takes place in some days or some months are called very slow reaction.

Example:- Rusting of iron.

3. Moderate speed reaction

Reactions which are neither very slow nor very fast but take place at moderate speed.

Example:- Chlorination of methane.

Explanation of difference in rate:

A reaction involves the breaking and making of bonds. Since different bond requires different amounts of energy for breaking and different amounts of energy are released when different kinds of new bonds are formed. Therefore different reactions have different rates.

SBG STUDY

Rate of reaction

Rate of reaction may be defined as the change in conc. of anyone reactant or product per unit time.

$$\text{Rate of reaction} = \frac{\text{change in conc.}}{\text{Time interval}}$$

$$\text{Unit of rate of reaction} = \text{mol L}^{-1} \text{s}^{-1} \text{ or mol L}^{-1} \text{min}^{-1}$$

Representation of rate of reaction

Consider a reaction R to P.

Suppose the conc. of reactant is C_1 at t_1 time and the conc. of reactant decrease and becomes C_2 at t_2 .

$$\text{Rate of reaction} = -\frac{(C_2 - C_1)}{(t_2 - t_1)}$$

where (-) represents decrease in concentration

Suppose the conc. of product at t_1 is C_1 and its conc. increase and become C_2 at t_2

$$\text{Rate of reaction} = +\frac{(C_2 - C_1)}{(t_2 - t_1)}$$

where (+) represents increase in concentration

Types of rate of reaction

There are 2 types of rate of reaction.

1. Instantaneous rate

It is the rate of reaction at a particular moment of time and measure as a very small conc. change over a very small time interval. It is represented by $\frac{dx}{dt}$

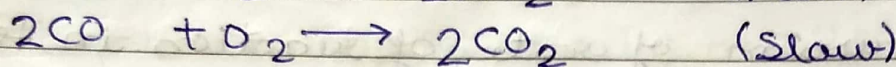
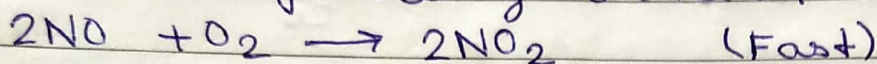
2. Average rate

It is the rate of reaction when the change in conc. is studied for a long time interval.

It is represented by $\Delta x / \Delta t$.

* Factors affecting rate of reaction1. Nature of reactant

Consider the following reaction:-



These reactions appear to be similar but the first is fast and second is slow.

This is because different amounts of energy are required for breaking of different bonds and different amounts of energy are released in the formation of different bond.

2. Conc. of reactant

Greater are the conc. of reactants, faster is the reaction.

3. Temperature

With increase in temperature, rate of reaction increase. In most of the case rate of reaction become double for 10° rise of temperature.

4. Presence of catalyst

Rate of reaction increase, by using of catalyst.

5. Surface area of reactant

Rate of reaction increase with increase in

surface area of reactant (i.e. finally divided reactant).

5. Presence of light

Presence of light \rightarrow Some reaction do not take place in dark but take place in the presence of light. Such reactions are called photochemical reactions.

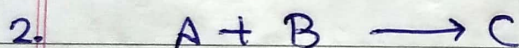
Expression of rate of reaction in term of different reactants and products.

1. Consider the following reaction:-



$$\text{Rate of reaction} = -\frac{d[R]}{dt} \quad \text{where } [R] = \text{molar conc. of } R$$

$$\text{Rate of reaction} = +\frac{d[P]}{dt}$$



$$\text{Rate of reaction} = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = +\frac{d[C]}{dt}$$

where $-\frac{d[A]}{dt}$ = rate of decomposition (or disappearance) of A.

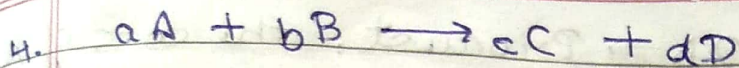
$-\frac{d[B]}{dt}$ = rate of disappearance of B.

$+\frac{d[C]}{dt}$ = rate of formation (or appearance) of C.



$$\text{rate of reaction} = -\frac{1}{2} \frac{d[A]}{dt}$$

$$\text{rate of reaction} = +\frac{d[B]}{dt} = +\frac{d[C]}{dt}$$

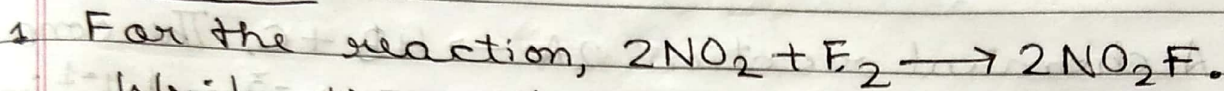


$$\text{rate of reaction} = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = +\frac{1}{c} \frac{d[C]}{dt} = +\frac{1}{d} \frac{d[D]}{dt}$$

where $-\frac{d[A]}{dt}$ = rate of decomposition of A

$+\frac{d[C]}{dt}$ = rate of formation of C

Problems:-



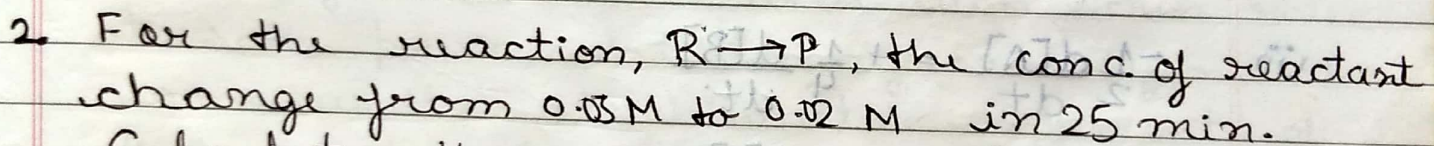
Write the rate of reaction in terms of:-

1. Rate of formation of NO_2F

2. Rate of decomposition of F_2

(i) Rate of reaction = $+\frac{1}{2} \frac{d[NO_2F]}{dt}$

(ii) Rate of reaction = $-\frac{d[F_2]}{dt}$



Calculate the average rate of reaction in min. and second.

$$\text{Average rate of reaction} = -\frac{\Delta[R]}{\Delta t}$$

$$= -\frac{(0.02 - 0.03)}{25}$$

$$= +4 \times 10^{-4} \text{ mol L}^{-1} \text{ min}^{-1}$$

$$\text{Average rate of reaction} = -\frac{(0.02 - 0.03)}{25 \times 60}$$

$$= +6.66 \times 10^{-6} \text{ mol L}^{-1} \text{ s}^{-1}$$

3. In a reaction, $2A \rightarrow \text{Product}$, the conc of A decrease from 0.5 mol L^{-1} to 0.4 mol L^{-1} in 10 min. Calculate the rate of reaction.

$$\begin{aligned} \text{Rate of reaction} &= -\frac{1}{2} \frac{d[A]}{dt} \\ &= -\frac{1}{2} \frac{(0.4 - 0.5)}{10} \\ &= +\frac{0.1}{20} = 5 \times 10^{-3} \text{ mol L}^{-1} \text{ min}^{-1} \end{aligned}$$

4. A chemical reaction $2A \rightarrow 4B + C$. The conc of B is found to increase by $5 \times 10^{-3} \text{ mol L}^{-1}$ in 10 sec. Calculate :- (i) rate of formation of B. (ii) rate of decomposition of A.

(i) Rate of formation of B = $+\frac{d[B]}{dt}$

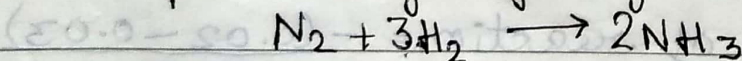
$$= \frac{5 \times 10^{-3}}{10} = 5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$

(ii) $-\frac{1}{2} \frac{d[A]}{dt} = +\frac{1}{4} \frac{d[B]}{dt}$

$$-\frac{d[A]}{dt} = +\frac{1}{2} \frac{d[B]}{dt}$$

$$\frac{-d[A]}{dt} = \frac{1}{2} \times 5 \times 10^{-4} = 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ sec}^{-1}$$

5. Express the rate of reaction in terms of decomposition of hydrogen for the reaction

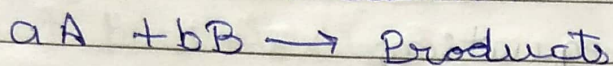


$$\text{Rate of reaction} = -\frac{1}{3} \frac{d[\text{H}_2]}{dt}$$

Rate law and law of mass action

According to law of mass action, rate of reaction is directly proportional to products of the conc. of the reactants, raise their power equal to stoichiometric coefficient in balance equation.

Consider a reaction:-



Acc. to law of mass action

$$\text{rate} = k [A]^a [B]^b$$

where k = rate constant or velocity constant

According to rate law,

$$\text{rate} = k [a]^\alpha [b]^\beta$$

- * Rate law is the expression which express the rate of reaction in terms of molar conc. of reactants with each term raise to some power, which may or may not be same as the stoichiometric coefficient of that reactant in the balance chemical equation.

Difference between rate law and law of mass action

Rate law states that the rate of reaction depends upon the conc. term on which the rate of reaction actually depend and observed experimentally.

Law of mass action is based upon the stoichiometric of the equation.

Order of reaction (n)

The sum of power of the conc. of reactant, express in rate law is called order of reaction.

Order of reaction may be integer, fractional and negative.

Consider a equation:-



Rate law equation,

$$\text{rate} = k[A]^\alpha[B]^\beta$$

$$\text{Order of reaction} = (\alpha + \beta)$$

Rate constant

Consider a reaction:-



Rate law equation,

$$\text{rate} = k[A]^\alpha[B]^\beta$$

Where k = rate constant

$$\text{if } [A] = [B] = 1 \text{ mol L}^{-1},$$

$$\text{rate} = k$$

Rate constant may be defined as the rate of reaction when the molar conc. of each is taken to be unity.

Unit of rate constant

$$\text{Unit of } k = (\text{mol}^{-1})^{1-n} \text{ time}^{-1}$$

- * For zero order reaction ($n=0$); $k = \text{mol}^{-1} \text{ time}^{-1}$
- * For first order reaction ($n=1$); $k = \text{time}^{-1}$
- * For second order reaction ($n=2$); $k = \text{L mol}^{-1} \text{ time}^{-1}$

Unit of rate of reaction in term of pressure

$$\text{Unit of rate of reaction} = \text{atm time}^{-1}$$

$$\text{or bar time}^{-1}$$

Unit of rate of constant in term of pressure
 Unit = $(\text{bar or atm})^{1-n} \text{time}^{-1}$

Difference between rate of reaction and rate constant
 Rate of reaction

- | | |
|---|---|
| <p>(i) Rate of reaction is the change in conc. of a reactant or product per unit time</p> <p>(ii) Its unit is $\text{mol L}^{-1} \text{time}^{-1}$</p> | <p>Rate constant</p> <p>(i) It is a proportionality constant in the rate law equation and is equal to the rate of reaction when the molar conc. of each element is unity.</p> <p>(ii) Its unit depends upon order of reaction i.e. $(\text{mol L}^{-1})^{1-n} \text{time}^{-1}$.</p> |
|---|---|

Problems:-

- The rate constant of a reaction is $3 \times 10^2 \text{ sec}^{-1}$. What is the order of reaction.
 Order of reaction = 1
- The rate of the reaction gives product is given by rate is equal to $k[A]^2[B]^{3/2}$. What is the order of reaction and unit of rate constant.
 Order of reaction = $\frac{5}{2}$.

$$\text{Unit of } k = (\text{mol L}^{-1})^{1-n} \text{time}^{-1} = (\text{mol L}^{-1})^{1-\frac{5}{2}} \text{time}^{-1} = (\text{mol L}^{-1})^{-\frac{3}{2}} \text{time}^{-1}$$

- In the reaction A gives B, the value of rate constant was found to be $1 \times 10^{-2} \text{ mol}^{-1} \text{ L s}^{-1}$. What is the order of reaction?
 Second order.

4. For the reaction, $2X \rightarrow X_2$, the rate of reaction becomes 27 times when the conc. of X is increased 3 times. What is the order of reaction?

Suppose rate law equation:-

$$\text{rate} = k[X]^n$$

if conc of X = $[3X]$, then $\text{rate}_2 = 27 \text{ rate}$

$$\text{rate}_2 = k[3X]^n$$

$$27 \text{ rate} = k[X]^n \times 3^n$$

$$27 \text{ rate} = 3^n \text{ rate}$$

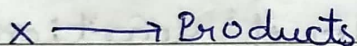
$$3^3 = 3^n$$

$$\boxed{n=3}$$

Order of reaction = 3

5. The rate of a gaseous reaction is half when the volume of the container is doubled. What is the order of reaction?

Suppose a reaction



rate law equation:-

$$\text{rate} = k[X]^n$$

If volume of container is doubled then conc. of reactant $X = \left[\frac{X}{2}\right]$ and $\text{rate}_2 = \frac{1}{2} \text{ rate}$

$$\text{rate}_2 = k\left[\frac{X}{2}\right]^n$$

$$\frac{1}{2} \text{ rate} = k[X]^n \times \left[\frac{1}{2}\right]^n$$

$$\frac{1}{2} \text{ rate} = \text{rate} \times \left(\frac{1}{2}\right)^n$$

$$\frac{1}{2} = \left(\frac{1}{2}\right)^n$$

$$\boxed{n=1}$$

6. For the reaction, $2A + B + C \rightarrow A_2B + C$, the rate law has been determined to be $k[A]^1[B]^2$ with $k = 2 \times 10^{-6} \text{ mol}^{-2} \text{ L}^2 \text{ s}^{-1}$. Calculate

the initial rate of reaction when the conc. of A is 0.1 mol L^{-1} , $[B] = 0.2 \text{ mol L}^{-1}$ and $[C] = 0.8 \text{ mol L}^{-1}$

$$\begin{aligned} \text{Initial rate} &= k[A]^1[B]^2 \\ &= 2 \times 10^{-6} \times (0.1)(0.2)^2 \\ &= 8 \times 10^{-9} \text{ mol L}^{-1} \text{ s}^{-1} \end{aligned}$$

6. A reaction is first order with respect to A and 2nd order with respect to B. Write differential rate equation? (i) How is the rate affected on increasing the rate 3 times (ii) How is the rate affected when the conc of A and B is doubled?

Given, $\text{rate} = k[A]^1[B]^2$

(i) $\frac{dx}{dt} = k[A]^1[B]^2$

(ii) if conc. of B = $[3B]$

$$\text{rate}_2 = k[A][3B]^2$$

$$\text{rate}_2 = 9k[A][B]^2$$

$$\text{rate}_2 = 9 \text{ rate}$$

(iii) if conc. of A = $[2A]$

if conc. of B = $[2B]$

$$\text{rate}_3 = k[2A]^1[2B]^2$$

$$\text{rate}_3 = 8k[A][B]^2$$

$$\text{rate}_3 = 8 \text{ rate}$$

7. The following rate data were obtained at 303 K for the following reaction: $2A + B \rightarrow C + D$

Exp.	[A]	[B]	Initial rate of formation of D / $\text{mol L}^{-1} \text{ s}^{-1}$
1.	0.1	0.1	6×10^{-3}
2.	0.3	0.2	7.2×10^{-2}
3.	0.3	0.4	2.88×10^{-1}
4.	0.4	0.1	2.4×10^{-2}

What is the rate law? What is the order with respect to each reactant, and overall order? Also calculate the rate constant and its unit?

Suppose rate law equation in terms of formation of B,

$$\text{Rate} = k[A]^\alpha[B]^\beta$$

From experiment 1: $6 \times 10^{-3} = k[0.1]^\alpha[0.1]^\beta \rightarrow (i)$

From experiment 2: $7.2 \times 10^{-2} = k[0.3]^\alpha[0.2]^\beta \rightarrow (ii)$

From experiment 3: $2.88 \times 10^{-1} = k[0.3]^\alpha[0.4]^\beta \rightarrow (iii)$

From experiment 4: $2.4 \times 10^{-2} = k[0.4]^\alpha[0.1]^\beta \rightarrow (iv)$

$$\frac{\text{equation (i)}}{\text{equation (iv)}} = \frac{6 \times 10^{-3}}{2.4 \times 10^{-2}} = \frac{k[0.1]^\alpha[0.1]^\beta}{k[0.4]^\alpha[0.1]^\beta}$$

$$= \left(\frac{1}{4}\right)^\alpha = \left(\frac{1}{4}\right)^\alpha$$

$$\alpha = 1$$

$$\frac{\text{equation (ii)}}{\text{equation (iii)}} = \frac{7.2 \times 10^{-2}}{2.88 \times 10^{-1}} = \frac{k[0.3]^\alpha[0.2]^\beta}{k[0.3]^\alpha[0.4]^\beta}$$

$$\frac{1}{4} = \left(\frac{1}{2}\right)^\beta$$

$$\left(\frac{1}{2}\right)^2 = \left(\frac{1}{2}\right)^\beta$$

$$\beta = 2 \quad (\text{rate} = k[A]^1[B]^2)$$

(i) Order of reaction w.r.t A = 1

Order of reaction w.r.t B = 2

Overall order = 3

From eq. (i),

$$6 \times 10^{-3} = k[0.1]^1[0.2]^2$$

$$k = 6 \text{ mol}^{-2} \text{ L}^2 \text{ s}^{-1}$$

Elementary reactions

Reactions which take place in one step are called elementary reactions.

Complex reactions

Reactions which take place in more than one step are called complex reaction.

Complex reactions take place in a sequence of a no. of steps. Each step of a complex reaction is called elementary reaction.

The different steps of a complex reaction do not take place at the same rate.

The overall rate of the reaction depends upon the slowest step. The slowest step of the reaction is called rate determining step (RDS).

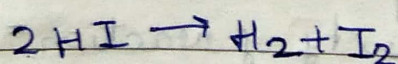
The representation of each step of a complex reaction is called mechanism of the reaction.

* Molecularity of a reaction

The no. of atoms, ions or molecules which must collide with one another simultaneously in elementary reaction so as to result into a chemical reaction is called molecularity of a reaction.

Molecularity of a reaction must always be a whole no. and never be 0 or fractional.

Example: For ~~an~~ elementary reaction:-



* Molecularity greater than 3 is not observed. This is because the probability that more

than 3 molecules can collide and react simultaneously is very small. Therefore

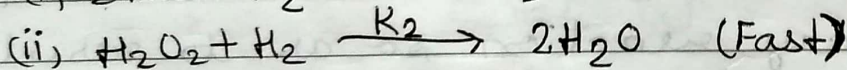
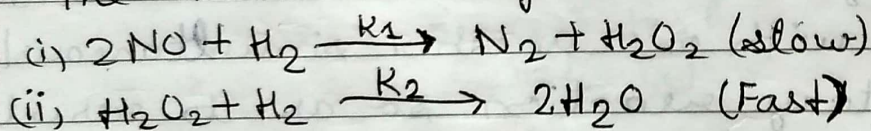
Difference between order of reaction and molecularity of reaction.

- | Order of reaction | Molecularity of reaction |
|---|---|
| 1. It is the sum of the power of conc. of reactant express in rate law. | 1. It is the no. of atoms, ions, or molecules that must collide with one another simultaneously so as to result into a chemical reaction. |
| 2. It can be fractional as well as zero. | 2. It cannot be fractional or zero. |
| 3. It can be determined experimentally only. | 3. It can be calculated by adding the molecule of the slowest step. |

Problem

1. Nitric oxide react with hydrogen to give dihydrogen and water: $2\text{NO} + 2\text{H}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O}$

The mechanism of reaction is:-



What is the rate law? What is the order of reaction and its molecularity.

From slow step,

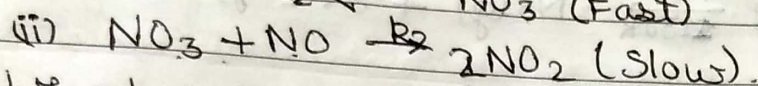
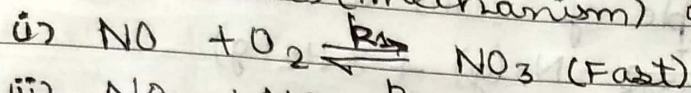
$$\text{rate} = K_1[\text{NO}]^2[\text{H}_2]^1$$

$$\text{Order of reaction} = 2 + 1 = 3$$

$$\text{Molecularity of reaction} = 3$$

2. Nitric oxide reacts with oxygen to give nitrogen dioxide, $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$.

The kinetics (mechanism) of the reaction is



(i) What is the predicted rate law?

(ii) What is the order of reaction and its molecularity

From slow step,

$$\text{rate} = K_2 [\text{NO}_3][\text{NO}] \rightarrow \text{①}$$

From fast step, $K_1 = \frac{[\text{NO}_3]}{[\text{NO}][\text{O}_2]}$

$$[\text{NO}_3] = K_1 [\text{NO}][\text{O}_2]$$

Substituting the value of $[\text{NO}_3]$ in eq. ①

$$\text{rate} = K_1 K_2 [\text{NO}][\text{O}_2][\text{NO}]$$

$$\text{rate} = K [\text{NO}]^2 [\text{O}_2]^1 \quad \text{where } K = K_1 K_2$$

(ii) Order of reaction = $2+1=3$

Molecularity of reaction = 2

* Half life

The time taken for half of the reaction to complete is called half reaction.

The time in which the conc. of reactant is reduced to half of its original value is called half life of the reaction.

It is represented by $t_{1/2}$

$$\text{Half life of } n^{\text{th}} \text{ order} \propto ([R]_0)^{1-n}$$

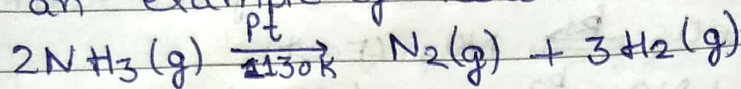
where $[R]_0$ = initial conc. of reactant

Zero order reaction

Zero order reaction means that the rate of reaction is proportional to zero power of the conc. of reactants.

Examples of zero order reaction

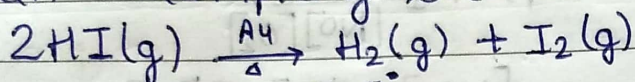
- (i) Decomposition of ammonia on platinum surface is an example of zero order reaction



$$\text{rate} = k[\text{NH}_3]^0$$

$$\boxed{\text{rate} = k}$$

- (ii) Thermal decomposition of HI on gold surface is an example of zero order reaction.

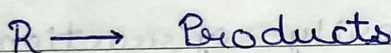


$$\text{rate} = k[\text{HI}]^0$$

$$\boxed{\text{rate} = k}$$

Integration of zero order reaction.

Consider a zero order reaction:-



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

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

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

Integrating both sides

$$\boxed{[\text{R}] = -kt + I} \rightarrow \text{①}$$

Where I = Integration constant

When $t=0$, then $[\text{R}] = [\text{R}]_0$

Putting these values in eq. ①

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

$$[\text{R}]_0 = I$$

Putting the value of I in eq. ①

$$[\text{R}] = -kt + [\text{R}]_0$$

$$kt = [\text{R}]_0 - [\text{R}]$$

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

Half life of zero order reaction

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

Putting these values in $K = \frac{[R]_0 - [R]}{t}$,

We get $K = \frac{[R]_0 - \frac{[R]_0}{2}}{t_{1/2}}$

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

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

i.e. $t_{1/2} \propto [R]_0$

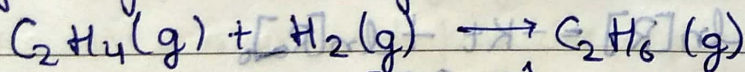
Half life of zero order reaction is proportional to initial conc. of reactant.

First order reaction

First order reaction means that the rate of reaction is proportional to the first power of the conc. of reactant.

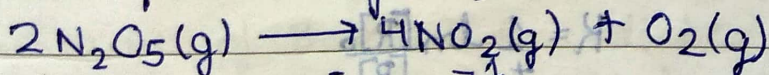
Examples

(i) Hydrogenation of ethene



$$\text{rate} = K [C_2H_4]^1$$

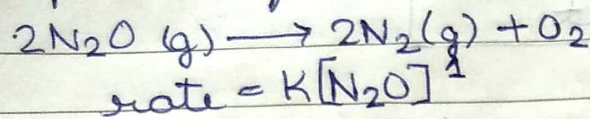
(ii) Decomposition of N_2O_5



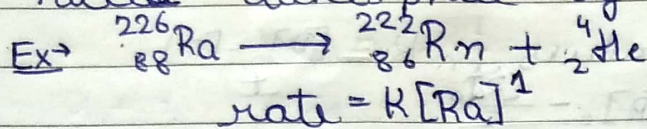
$$\text{rate} = K [N_2O_5]^1$$

$$K = \frac{[R]}{t}$$

(iii) Decomposition of N_2O

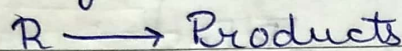


(iv) All natural and artificial ^{radioactive} decay of unstable nuclei takes place by first order kinetics.



Integration of first order reaction

Consider a first order reaction:-



$$-\frac{d[R]}{dt} = k[R]^1$$

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

Integrating both sides

$$\boxed{\ln[R] = -kt + I} \rightarrow \text{①}$$

where I = Integration constant

When $t=0$, then $[R] = [R]_0$

Putting these values in equation ①

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

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

Putting these value in ①

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

$$kt = \ln[R]_0 - \ln[R]$$

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

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

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

Half life of first order reaction:

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

Putting these values in $k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$, we get

$$k = \frac{2.303}{t_{1/2}} \log \frac{[R]_0}{[R]_{0/2}}$$

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

$$k = \frac{2.303 \times 0.3010}{t_{1/2}}$$

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

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

Half life of a first order reaction is independent of initial conc. of reactant.

First order gas phase reaction

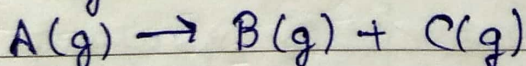
Consider a first order gas phase reaction:



Let p_i is the initial pressure of reactant A and p_t is the total pressure of gasses at time 't'.

Total pressure of gasses at time 't' is equal to the sum of partial pressure of gas A, B and C at time 't'.

If 'x' atm pressure of A decrease at time 't' then according to mole concept, the increase in pressure of B and C will be x atm each.



At $t=0$,

p_i

0

0

At time 't'

$p_i - x$

x

x

Total pressure at time 't' = $(p_t) = p_i - x + x + x$

$$p_t = p_i + x$$

$$x = p_t - p_i$$

$$\therefore (p_i - x) = p_i - p_t + p_i = 2p_i - p_t$$

We know that at constant temperature,

$$p_i \propto [R]_0$$

$$\text{and } (p_i - x) \propto [R]$$

Putting these value in $k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$,

We get,

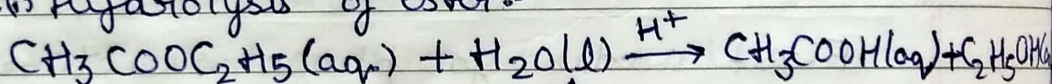
$$k = \frac{2.303}{t} \log \frac{p_i}{(p_i - x)}$$

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

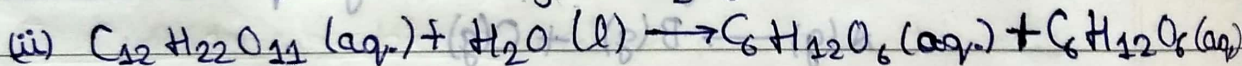
Pseudo first order reaction

A bi-molecular reaction whose order is 2 is called pseudo first order reaction.

Example: (i) Hydrolysis of ester:-



$$\text{rate} = k[\text{CH}_3\text{COOC}_2\text{H}_5]^1$$



Sucrose

Glucose

Fructose

$$\text{rate} = k[\text{C}_{12}\text{H}_{22}\text{O}_{11}]^1$$

Conditions for pseudo first order reaction

If anyone reactant is present in large amount conc. of reactant remains constant.

Graph

$$y = mx + c$$

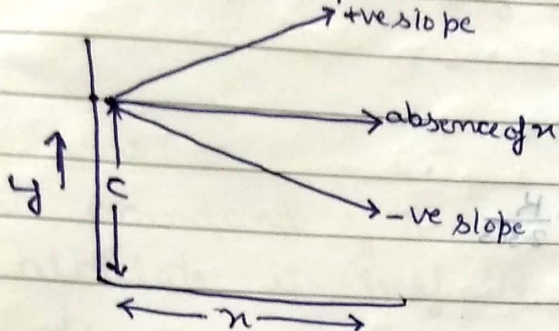
\downarrow Slope \downarrow Intercept

* Slope (m) = $\tan \theta$

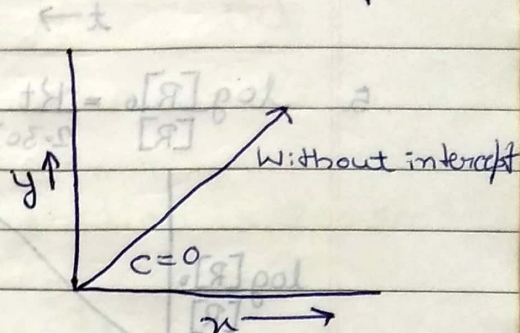
$$\text{Slope (m)} = \frac{y_2 - y_1}{x_2 - x_1}$$

* Intercept (C) = $y_2 - y_1$

(a) With intercept



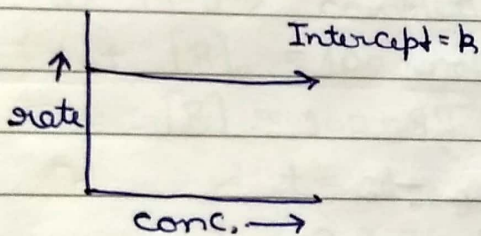
(b) Without intercept



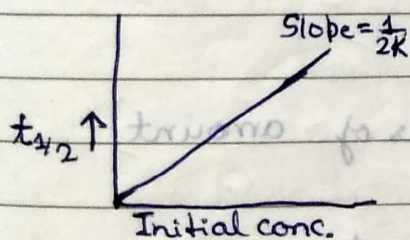
Graph of Zero order and first order reaction

Zero order reaction

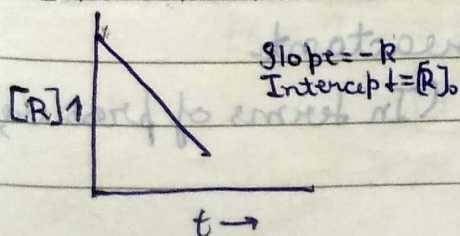
1. rate = $k[R]^0$
or rate = k



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

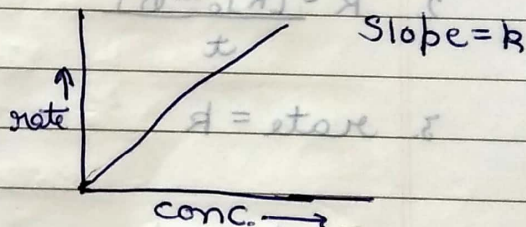


3. $[R] = -kt + [R]_0$

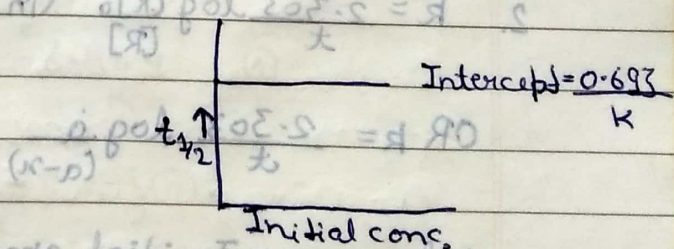


First order reaction

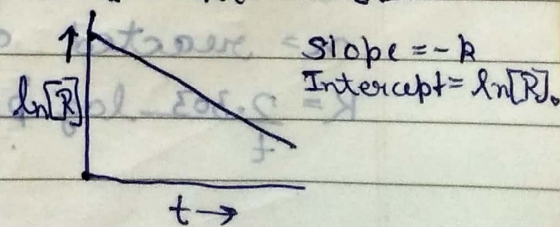
1. rate = $k[R]^1$



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



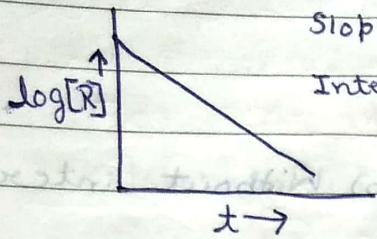
3. $\ln[R] = -kt + \ln[R]_0$



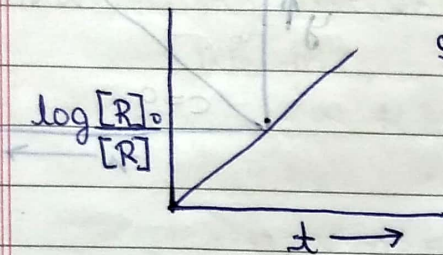
$$4. \log [R] = \frac{-kt}{2.303} + \log [R]_0$$

$$\text{Slope} = \frac{-k}{2.303}$$

$$\text{Intercept} = \log [R]_0$$



$$5. \frac{\log [R]_0}{[R]} = \frac{kt}{2.303}$$



$$\text{Slope} = \frac{k}{2.303}$$

Formula for zero and first order reaction

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

$$2. k = \frac{[R]_0 - [R]}{t}$$

$$3. \text{rate} = k$$

First order reaction

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

$$2. k = \frac{2.303 \log [R]_0}{t [R]} \quad (\text{in terms of conc.})$$

$$\text{OR } k = \frac{2.303 \log a}{t (a-x)} \quad (\text{in terms of amount})$$

where a = Initial amount of reactant

$a-x$ = remaining amount of reactant at time t .

x = reacted amount of reactant.

$$k = \frac{2.303 \log p_i}{t} \quad (\text{In terms of pressure})$$

$$3. \text{rate} = k[R]^1$$

$$\text{rate} = k(p_R)$$

where p_R = remaining pressure of reactant

$$4. \text{Fraction of remaining conc. of reactant} = \frac{[R]}{[R]_0}$$

Problems

1. Rate constant of a first order reaction is 200 sec^{-1} . Calculate its half life.

$$t_{1/2} = \frac{0.693}{200} \rightarrow t_{1/2} = 3.465 \times 10^{-3} \text{ sec.}$$

2. Shows that for a first order reaction the time required for 99.9% completion is the 10 times of its half life or $t_{99.9} = 10 t_{1/2}$.

For 99.9% completion

$$\text{let } [R]_0 = 100 \text{ mol L}^{-1}$$

$$[R] = 100 - 99.9\% = 0.1 \text{ mol L}^{-1}$$

$$t = t_{99.9\%}$$

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

$$k = \frac{2.303}{t_{99.9\%}} \log \frac{100}{0.1}$$

$$t_{99.9\%} = \frac{2.303 \times 3}{k} = \frac{6.909}{k} \rightarrow (1)$$

$$\text{For } t_{1/2} \Rightarrow t_{1/2} = \frac{0.693}{k} \rightarrow (2)$$

$$\frac{\text{Eqn. 1}}{\text{Eqn. 2}} = \frac{t_{99.9\%}}{t_{1/2}} = \frac{\frac{6.909}{k}}{\frac{0.693}{k}}$$

$$t_{99.9\%} = 10 t_{1/2}$$

3. Shows that for a first order reaction time required for 99% completion is the twice of time required for 90% completion OR $t_{99\%} = 2t_{90\%}$

For 99% completion:-

$$\text{Let } [R]_0 = 100 \text{ mol L}^{-1}$$

$$[R] = 100 - 99 = 1 \text{ mol L}^{-1}$$

$$t = t_{99\%}$$

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

$$k = \frac{2.303}{t_{99\%}} \log \frac{100}{1}$$

$$t_{99\%} = \frac{2.303 \times 2}{k} \rightarrow \text{①}$$

For 90% completion \Rightarrow

$$\text{Let } [R]_0 = 100 \text{ mol L}^{-1}$$

$$[R] = 100 - 90 \text{ mol L}^{-1} = 10 \text{ mol L}^{-1}$$

$$t = t_{90\%}$$

$$k = \frac{2.303}{t_{90\%}} \log \frac{100}{10}$$

$$t_{90\%} = \frac{2.303 \times 1}{k} \rightarrow \text{②}$$

$$\frac{\text{eq 1}}{\text{eq 2}} = \frac{t_{99\%}}{t_{90\%}} = \frac{\frac{2.303 \times 2}{k}}{\frac{2.303 \times 1}{k}}$$

$$t_{99\%} = 2t_{90\%}$$

4. Shows that for a first order reaction time required for 75% completion is the twice of time required for 50% completion OR

$$t_{75\%} = 2t_{50\%}$$

For 75% completion:-

$$\text{Let } [R]_0 = 100 \text{ mol L}^{-1}$$

$$[R] = 100 - 75 = 25 \text{ mol L}^{-1}$$

$$0.693 = 2.303 \times 0.301$$

$$t = t_{75\%}$$

$$k = \frac{2.303}{t_{75\%}} \log \frac{100}{25}$$

$$t_{75\%} = \frac{2.303}{k} \times 0.6021 \rightarrow \text{①}$$

For 50% completion:-

$$\text{Let } [R]_0 = 100 \text{ mol L}^{-1}$$

$$[R] = 100 - 50 = 50 \text{ mol L}^{-1}$$

$$t = t_{50\%}$$

$$k = \frac{2.303}{t_{50\%}} \log \frac{100}{50}$$

$$t_{50\%} = \frac{2.303}{k} \times 0.3010 \rightarrow \text{②}$$

$$\frac{\text{eqn ①}}{\text{eqn ②}} = \frac{\frac{2.303}{k} \times 0.6021}{\frac{2.303}{k} \times 0.3010} = \frac{t_{75\%}}{t_{50\%}}$$

$$t_{75\%} = 2 t_{50\%}$$

- 5 Shows that for a first order reaction time required by $3/4$ of a reaction is the twice of its half life or $t_{3/4} = 2 t_{1/2}$

For $3/4$ completion:-

$$\text{Let } [R]_0 = 1 \text{ mol L}^{-1}$$

$$[R] = 1 - \frac{3}{4} = \frac{1}{4} \text{ mol L}^{-1}$$

$$t = t_{3/4}$$

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

$$k = \frac{2.303}{t_{3/4}} \log \frac{1}{1/4}$$

$$t_{3/4} = \frac{2.303}{k} \log 4 = \frac{2.303}{k} \times 0.6021 \rightarrow \text{①}$$

For half life:-

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

$$\frac{\text{eqn ①}}{\text{eqn ②}} = \frac{t_{3/4}}{t_{1/2}} = \frac{2.303 \times 0.6021}{0.693 \times 0.301}$$

$$t_{3/4} = 2 t_{1/2}$$

Problems :-

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

For 1st order reaction

$$t_{75\%} = 2 t_{1/2}$$

$$60 = 2 t_{1/2}$$

$$t_{1/2} = 30 \text{ min.}$$

2. A first order decomposition reaction takes 40 min for 30% decomposition. Calculate its half life.

For 30% decomposition:-

$$\text{Let } [R]_0 = 100 \text{ mol L}^{-1}$$

$$[R] = 100 - 30 = 70 \text{ mol L}^{-1}$$

$$t = 40 \text{ min}$$

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

$$\frac{0.693}{t_{1/2}} = \frac{2.303}{40} \times \log \frac{100}{70}$$

$$\frac{0.301}{t_{1/2}} = \frac{1}{40} [\log 100 - \log 70]$$

$$\frac{0.301}{t_{1/2}} = \frac{1}{40} [2 - 1.8451]$$

$$\frac{0.301}{t_{1/2}} = \frac{1}{40} \times 0.1549$$

$$t_{1/2} = \frac{0.301 \times 40}{0.1549}$$

$$t_{1/2} = 77.86 \text{ min}$$

3. Time for half change for a first order is 25 min. What time will be required for 99% completion of the reaction.

For 99% decomposition:-

$$\text{Let } [R]_0 = 100 \text{ mol L}^{-1}$$

$$[R] = 100 - 99 = 1 \text{ mol L}^{-1}$$

$$t = ?$$

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

$$\frac{0.693}{t_{1/2}} = \frac{2.303}{t} \log \frac{100}{1}$$

$$\frac{0.301}{25} = \frac{2}{t}$$

$$t = \frac{2 \times 25}{0.301} = \frac{50}{0.3}$$

$$t = 166.67 \text{ min.}$$

4. The half life period of a 1st order reaction is 60 min. What % of the reactant will be left after 120 min.

$$t_{1/2} = 60 \text{ min}$$

$$\text{Let } [R]_0 = 100 \text{ mol L}^{-1}$$

$$[R] = ?$$

$$t = 120 \text{ min}$$

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

$$\frac{0.693}{t_{1/2}} = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$$

$$\frac{0.301}{60} = \frac{1}{120} \log \frac{100}{[R]}$$

$$0.6020 = \log 100 - \log [R]$$

$$0.6020 = 2 - \log [R]$$

$$\log[R] = 2 - 0.6020$$

$$\log[R] = 1.398$$

$$[R] = \text{Antilog}(1.398)$$

$$[R] = 2.500 \times 10^1$$

$$[R] = 25\%$$

- * 5. A reaction is 50% complete in 2 hours and 75% complete in 4 hours. What is the order of reaction?

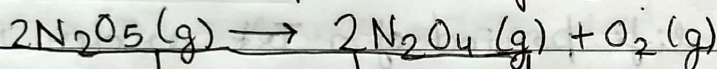
Given $t_{1/2} = 2 \text{ hours}$

$t_{75\%} = 4 \text{ hours}$

Therefore, half life of the reaction does not depend upon initial conc. of reactant.

Hence, it is a first order reaction.

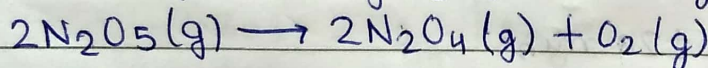
6. The following rate data were obtained for the thermal decomposition of N_2O_5 .



Time (s)	0	50
Total Pressure	0.2	0.25

Calculate the rate of reaction when the total pressure is 0.28 atm.

The decomposition of N_2O_5 is a first order reaction



At $t=0 \text{ sec}$ p_i 0 0

At time $t' \text{ sec}$ $p_i - 2x$ $2x$ x

Total pressure at time t' , $p_t = p_i - 2x + 2x + x$

$$x = p_t - p_i$$

$$\therefore (p_i - 2x) = p_i - 2(p_t - p_i) = 3p_i - 2p_t$$

We know that

$$p_i \propto [R]_0$$

$$\text{and } (p_i - 2x) \propto [R]$$

From rate constant of first order reaction,

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

we get, $K = \frac{2.303}{t} \log \frac{p_i}{p_i - 2x} = \frac{2.303}{t} \log \frac{p_i}{(3p_i - 2pt)}$

From given data, $p_i = 0.2 \text{ atm}$, $t = 50 \text{ sec}$, $p_i = 0.25 \text{ atm}$

$$K = \frac{2.303}{50} \log \frac{(0.2)}{(3 \times 0.2 - 2 \times 0.25)}$$

$$K = \frac{2.303}{50} \log \frac{0.2}{0.1} = \frac{0.693}{50} \text{ sec}^{-1}$$

When $pt = 0.28 \text{ atm}$

$$\text{rate} = k(p_R)'$$

$$\text{rate} = k(p_i - 2x)$$

$$\text{rate} = k(3p_i - 2pt)$$

$$\text{rate} = \frac{0.693}{50} (3 \times 0.2 - 2 \times 0.28)$$

$$\text{rate} = 5.54 \times 10^{-4} \text{ atm s}^{-1}$$

Threshold Energy

The minimum energy which the colliding molecule must have in order that the collision between them may be effective is called threshold energy.

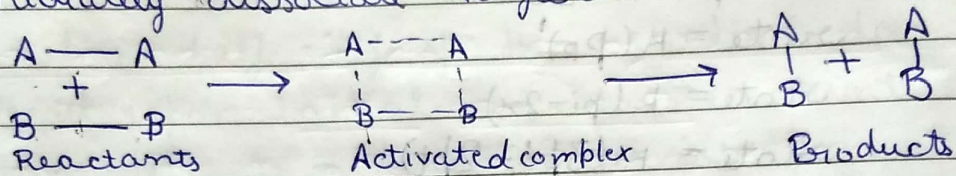
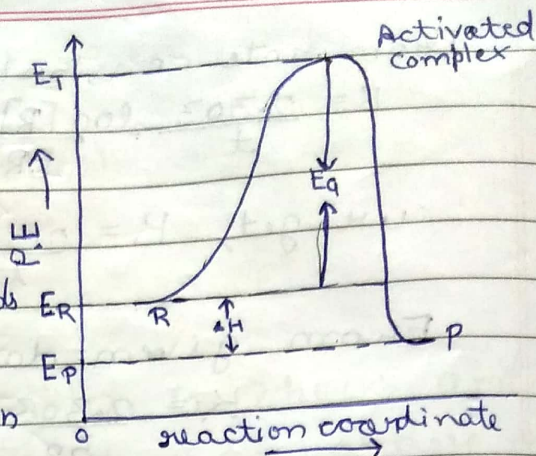
Activation Energy (E_a)

The minimum extra amount of energy absorbed by the reactant molecule so that their energy becomes equal to threshold energy.

$$\text{Activation energy} = \text{Threshold energy} - \text{Average kinetic energy of reactant}$$

Reaction Profile

It is believed that when the reactant molecules absorb energy, their bonds are broken and new bonds are formed between them. The intermediate thus formed is called activated complex or transition state complex. It is unstable and immediately dissociates to form the stable product.



Effect of temperature on rate of reaction or rate constant.

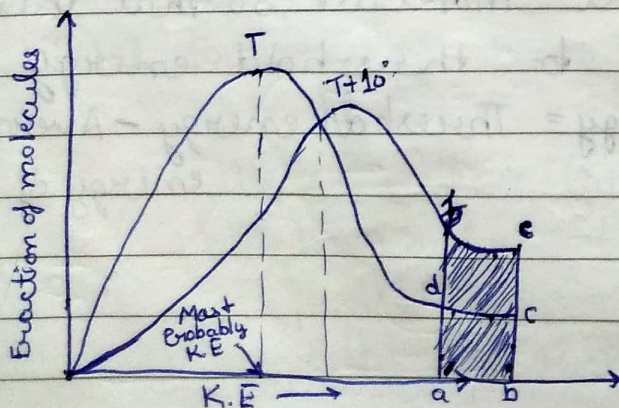
The effect of temperature on rate constant is expressed in terms of temperature coefficient.

Temperature coefficient is defined by the equation:

$$\text{Temperature coefficient} = \frac{\text{Rate constant at } T+10^\circ}{\text{Rate constant at } T (298 \text{ K})}$$

For most of reaction, $2 < n < 3$

Graphical Explanation



At a particular temperature (T), all the reacting molecules do not have the same K.E. If fraction of molecules are plotted against K.E, a graph of the type shown in figure is obtained. The peak of the curve represents the K.E possessed by the maximum fraction of molecules and is called most probable K.E. If the point 'a' represents threshold energy, the shaded area abcd represents the fraction of molecules greater than threshold energy.

When the temperature is increased to $T+10$, the curve shifts as shown in figure. The fraction of molecules having K.E greater than threshold value is represented by the shaded area abef which is almost double than the area abcd.

Therefore the increase in the rate of reaction with increase in temperature is due to increase in the no. of effective collision.

Arrhenius equation

Quantitatively, the effect of temperature on the rate of reaction or rate constant is expressed by an equation known as Arrhenius equation.

$$K = A e^{-E_a/RT}$$

where K = rate constant

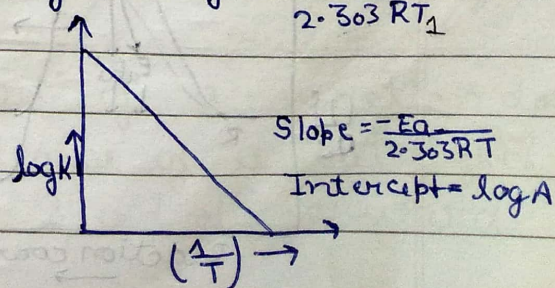
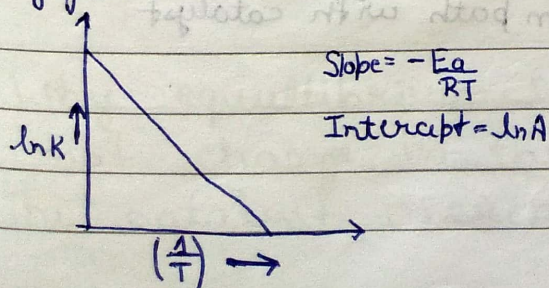
A = a constant called as frequency factor or pre-exponential factor.

E_a = Activation energy.

R = Gas Constant

T = Temperature in Kelvin.

log form: $\ln K = \ln A - E_a/RT \Rightarrow \log K_1 = \log A - \frac{E_a}{2.303 RT_1}$



At two different temperature:-

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

In case of catalyst \rightarrow

$$\log \frac{K_2}{K_1} = \frac{\Delta E_a}{2.303RT}$$

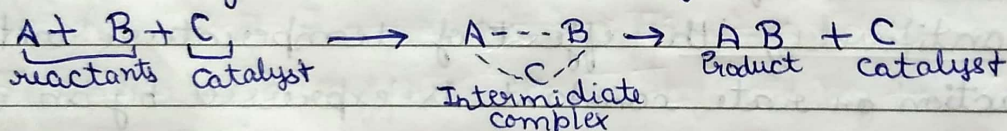
$$\text{where } \Delta E_a = E_a - E_a'$$

activation energy
without catalyst

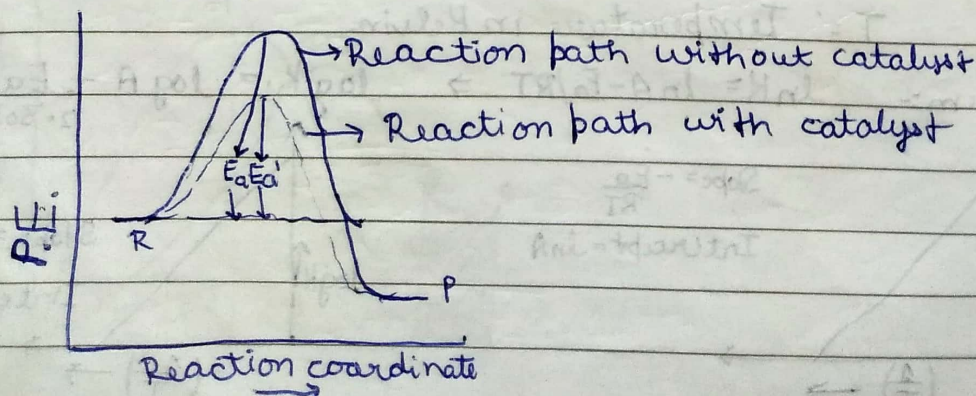
activation energy
with catalyst.

Effect of catalyst on rate of reaction or rate constant

According to intermediate complex formation theory, the reactants first combined with catalyst to form intermediate complex which is unstable and decompose to form the product and regenerate the catalyst.



The intermediate complex form as much lower potential energy than the intermediate complex form between the reactants in the absence of catalyst. Therefore catalyst decrease the activation energy of the reaction and the reaction becomes faster.



The no. of collision that take place per second per unit volume of the reaction mixture is called collision frequency.

Collision Theory of chemical reaction

According to collision theory, the rate of a reaction depends upon the no. of effective collision which depends upon the following two factors:

Energy factor:- The colliding molecule must have energy greater than threshold energy.

Orientation factor:- The colliding molecule must have proper orientation at the time of collision.

1. Can a reaction have zero activation energy (E_a)
 If $E_a = 0$, then according to Arrhenius equation,

$$k = A e^{-E_a/RT} = A e^0 = A$$
 This means every collision results into a chemical reaction, which can not be true hence activation energy cannot be zero.

2. Can a reaction have negative activation energy.
 If E_a is negative, then according to Arrhenius equation,

$$k = A e^{-E_a/RT}$$

$$k = A e^{+E_a/RT} \quad \text{i.e. } k \gg A$$
 which is impossible. Hence E_a cannot be negative.

3. Why equilibrium constant of a reaction does not change in the presence of a catalyst?
 The catalyst increase the speed of forward

reaction as well as backward reaction to a same extent. Hence equilibrium is not disturbed. But it stabilize quickly.

Formula (Arrhenius equation)

1. $k = A e^{-E_a/RT}$

2. $\log k = \log A - \frac{E_a}{RT \times 2.303}$

3. At two different temperatures,

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

4. In case of catalyst,

$$\log \frac{k_2}{k_1} = \frac{\Delta E_a}{2.303RT}$$

where $\Delta E_a = E_a - E'_a$
 $\begin{matrix} \downarrow & & \downarrow \\ E_a \text{ without} & & E_a \text{ with} \\ \text{catalyst} & & \text{catalyst} \end{matrix}$

* (a) Arrhenius equation \Rightarrow First order

(b) Use proper units: $T, T_1, T_2 \Rightarrow$ in Kelvin.

$A, k, k_1, k_2 \Rightarrow$ in sec^{-1}

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \text{ or } 8.3 \times 10^{-3} \text{ K J K}^{-1} \text{ mol}^{-1}$$

$$E_a, E'_a \Rightarrow \text{J mol}^{-1} \text{ or } \text{KJ mol}^{-1}$$

(c) Boltzmann factor or fraction of molecule having energy equal or greater than $E_a(z) =$

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

$$\ln Z = \frac{-E_a}{RT}$$

$$\log Z = \frac{-E_a}{2.303RT}$$

Problems

1. The rate of a reaction triples when temperature change from 50°C to 100°C . Calculate E_a ?

$$\text{Given: } \frac{k_2}{k_1} = 3$$

$$T_1 = 50 + 273 = 323\text{K}$$

$$T_2 = 100 + 273 = 373\text{K}$$

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

$$\log 3 = \frac{E_a}{19.15 \times 10^{-3}} \left(\frac{373 - 323}{373 \times 323} \right)$$

$$0.4771 = \frac{E_a}{19.15 \times 10^{-3}} \left(\frac{50}{373 \times 323} \right)$$

$$E_a =$$

$$E_a = 22.01 \text{ kJ mol}^{-1}$$

2. The rate constant of a first order reaction becomes 6 times when the temperature is increase from 350K to 410K . Calculate the E_a ?

$$\frac{k_2}{k_1} = 6$$

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

$$\log 6 = \frac{E_a}{2.303 \times 8.314 \times 10^{-3}} \left[\frac{410 - 350}{410 \times 350} \right]$$

$$0.7781 = \frac{E_a}{19.15 \times 10^{-3}} \times \frac{60}{350 \times 410}$$

$$E_a = 35.64 \text{ kJ mol}^{-1}$$

3. The activation energy of a first order reaction at 300 K each is 60 kJ mol^{-1} . In the presence of a catalyst, the activation energy is reduced to 50 kJ mol^{-1} at the same temperature. How many times the rate of reaction will change

$$\Delta E_a = E_a - E_a' = 60 - 50 = 10 \text{ kJ mol}^{-1}$$

$$\log \frac{K_2}{K_1} = \frac{\Delta E_a}{2.303RT}$$

$$\log \frac{K_2}{K_1} = \frac{10}{2.303 \times 8.314 \times 10^{-3} \times 300}$$

$$\log \frac{K_2}{K_1} = \frac{100}{6.909 \times 8.314}$$

$$\log \frac{K_2}{K_1} = 1.7401$$

$$\frac{K_2}{K_1} = 5.5 \times 10^1 = 55$$

4. The activation energy for the reaction:-

$2\text{HI(g)} \rightarrow \text{H}_2\text{(g)} + \text{I}_2\text{(g)}$ is $209.5 \text{ kJ mol}^{-1}$ at 581 K. Calculate the fraction of molecules of reactant having energy equal to or greater than activation energy (Z).

Fraction of molecules having energy equal to or greater than activation energy = Z

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

$$\ln Z = \frac{-E_a}{RT}$$

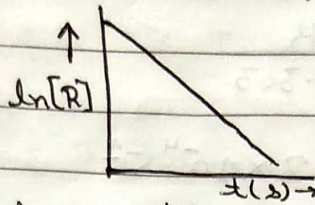
$$2.303 \log Z = \frac{-E_a}{RT}$$

$$\log Z = \frac{-E_a}{RT \times 2.303} = \frac{-209.5}{8.314 \times 10^{-3} \times 581 \times 2.303} = -19.1677$$

$$\log Z = \overline{19.1677}$$

$$Z = 1.471 \times 10^{-19}$$

5. For a certain chemical reaction, the following curve is obtained.



- What is the order of reaction?
- What is the unit of rate constant?
- What is the slope of line indicate?
- Give the relation between half life and rate constant.

(i) Ans → First order reaction.

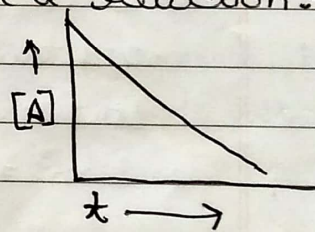
(ii) Ans → Unit of $K = s^{-1}$

(iii) Ans → Slope = $-K$

(iv) Ans → $t_{1/2} = \frac{0.693}{K}$

6. The following graph is obtained for a reaction:-

- What is the order of reaction?
- Derive the expression for the time require for the completion of the reaction.



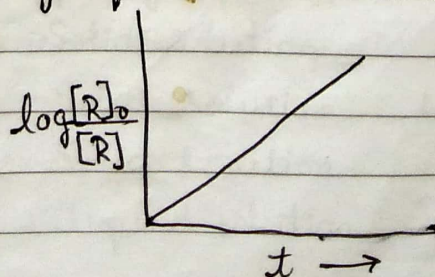
(i) Zero order reaction.

(ii) At completion of reaction $[R] = 0$

$$K = \frac{[R]_0 - [R]}{t} = \frac{[R]_0 - 0}{t}$$

$$K = \frac{[R]_0}{t} \Rightarrow t = \frac{[R]_0}{K}$$

7. Answer the following question on the basis of following graph.



- (i) What is the slope of line indicate?
 (ii) Calculate the rate constant if the slope is $2 \times 10^{-4} \text{ s}^{-1}$.

(i) $\text{Slope} = \frac{k}{2.303}$

(ii) $\text{Slope} = 2 \times 10^{-4} \text{ s}^{-1}$

$k = 2.303 \times \text{Slope}$

$k = 2.303 \times 2 \times 10^{-4} \text{ s}^{-1}$

$k = 4.606 \times 10^{-4} \text{ s}^{-1}$

SBG STUDY

