Chemical kinetics.

It is a branch of physical chemistry It deals with the rate of reaction is called the "chemical kinetics".

The study of chemical kinetcs used to know the followings:

i) The rate of reaction and rate laws.

ii) The facters temperature, pressure, concentration and catalyst influence.

The Machanism or the sequence of the steps by which a reaction occurs.

The knowledge of the rate of reactions is very valuble to understand the chemical of reactions. It is also great importance in selecting optimum conditions for an industrial process to proceeds as maximum yield.

Reaction Rate:

The rate of reaction tell us to what speed reaction occurs.

Let us consider simple reaction

$A \rightarrow B$ The concentration of reactant A decreases and B increases as time passes.

$$\text{rate} = -\frac{d[A]}{dt} \quad \text{(or)} \quad \text{rate} = +\frac{d[B]}{dt}$$

where [ ] represent concentration in moles per litre.

d -> infenetesionally small

It is defined as the change in concentrat
of any of reactant (or) products per unit
time.

For a given reaction, the rate of reaction
may be equal to the rate of disappeara
of A is equal to the rate of appearance
of B.

The Negative sign source the concentration
of the reactant A decreases, The positive
sirgn indicates the increasing concentration
of B.

~~UNIT~~

Rate
Units of concentration:

The Reactions rate has unit of
Concentrations divide by time.

mole / litre sec (or) mol $l^{-1} s^{-1}$

mole / litre min (or) mol $l^{-1} min^{-1}$

mole / Litre hour (or) mol $l^{-1} h^{-1}$ and so on.

They are two type of rate of reaction
measured for chemical reaction.

i) Average Rate of Reaction

ii) Instentaneous Rate of Reaction

i) **Average rate of reaction:**
These depends on chemical and Nature of
reaction.

As the reaction Proceeds, the consentrat
of reactant A

Conc of CO:

0.100	0.067	0.050	0.040	0.033
(0)	(10)	(20)	(30)	(40)

Time seconds

$CO_{(g)} + NO_{2(g)} \rightarrow CO_{2(g)} + NO_{(g)}$

$$\boxed{rate = \frac{-\Delta[CO]}{\Delta t} = -\frac{d[CO]}{dt}}$$

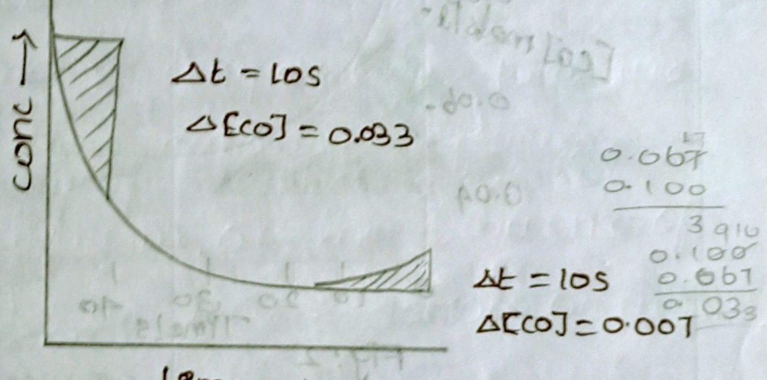

fig-1

over the 10sec average rate,

$$-\frac{d[CO]}{dt} = \frac{-(0.067-0.100)}{(10-0)} = \frac{0.033}{10} = 0.0033 \text{ mol } l^{-1} s^{-1}$$

The results are shown in graphycally in figure 1.

As a reaction proceeds, where conc. of CO decreases rapidly the inital stage of reaction. Then the conc. of CO decreases more and more slowly. The rate of reaction is a function of time. The reaction is slowing down with time. As indicatted the experimental data.

The Average rate are not always useful because they cover a large time interwel during which the rate of reaction changes significantly. So the better way to estimate the rate of the reaction, we need to make the time interwel as small as possible.

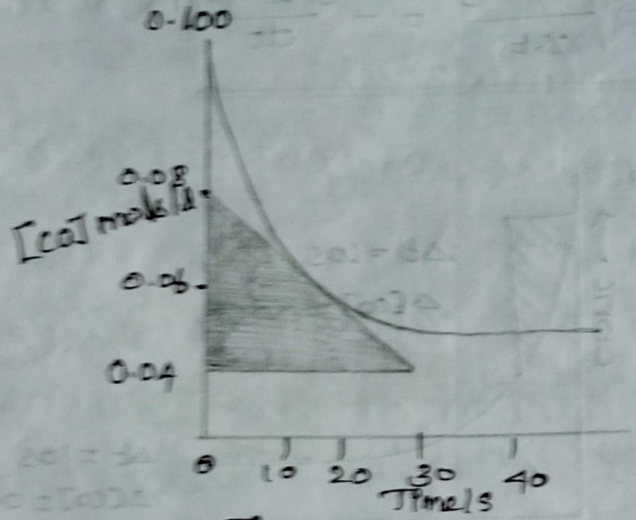

Fig: 2

The slope of tangerd at 10s is equal to the instantaneous rate.

Instantaneous Rate of reaction:

The Average rates not useful, the better way to estimate the rate of reaction is to make the time interwel as small as possible. If the time interwel is infinitesimally small (very very small) (Δt approches to 0), The rate is reffered to as the instantaneous rate and is written calculas as equation(1)

$$\text{rate} = \frac{d[\ ]_t}{dt} \longrightarrow ①$$

$$\text{Instantaneous rate} = -\frac{d[CO]}{dt} - ①$$

where $[\ ]_t$ is conc. at time t.

conc → concentration

Therefore, The Instantaneous rate at any time is equal to the slope of a straight line drawn of tangend curve at a time.

for example, In figure 2. The Instantaneous rate at 10s is found to be 0.0022 mol/l/sec^{-1}

Rate laws (or) Rate equation

At a fixed temperature, the rate of a given reaction depends on conc. of reactants. To the relation between conc. and rate is determined by measuring the reaction rate with different initial reactant conc.

By a study of numarous reactions Its shown that: The rate of a reaction directly proposiral to reactant conc., each conc. is rised to some power.

For a Substance A under going reaction

For a reaction,

$$A \longrightarrow pdt$$ (product)

$$rate \propto [A]^n$$

(or)

$$rate = k[A]^n \quad — ①$$

For a reaction:

$$2A + B \longrightarrow products$$

$$rate = k[A]^m[B]^n \rightarrow ②$$

The rate of a reaction may be expressed as eqn (1) and e(2). indicates, the relation between the rate of a reaction and reactant [ ].

An equation which sources how the reaction rate is relat~~ion~~ted to concentration is called "rate law con rate equation"

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order of a Reaction:

Reaction	Rate law (rate=$k[A]^m[B]^n$)	Reaction order m+n
① $2N_2O_5 \rightarrow 4NO_2 + O_2$	rate = $k[N_2O_5]$	1 (First order)
② $H_2 + I_2 \rightarrow 2HI$	rate = $k[H_2][I_2]$	1+1=2 [second]
③ $2NO_2 \rightarrow 2NO + O_2$	rate = $k[NO_2]^2$	2
④ $2NO + 2H_2 \rightarrow N_2 + 2H_2O$	rate = $k[H_2][NO_2]^2$	1+2=3 (Third order)
⑤ $NO_2 + CO \rightarrow NO + CO_2$	rate = $k[NO_2]^2[CO]^0$	2+0 (second and 0 (zero) CO

The rate law for a reaction must be determinate ~~it can't be~~ by experiment It can't be return by no the equation with knowledge of law of mass action. However, for some elementry reaction The power in the rate law may correspont to co-efficient in the chemical equation. But usually The powers of concentration in the rate law are different from co-efficient.

"The order of reaction of defend as the Sum of the power of concentration in the rate law."

Let us consider the example of reaction has the rate law.

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

The order of such a reaction $(m+n)$

The order of reaction also bee defined to a single reactant.

Thus the reaction order with respect to A is m and with respect to B is n.

The over all order of reaction $m+n$

The over all order of reaction can be have range from 1 to 3 and can be fractional

Zero order reaction:

Def:

The Zero order reaction is one whose rate is independent of concentration and does not affect the reaction rate, not include in the rate law.

Such reactant power 0 (zero)

The example,

$$NO_2 + CO \xrightarrow[\Delta]{200°C} NO + CO_2$$

$$\text{rate} = k\,[NO_2]^0\,[CO]^0$$

respect to $[NO_2]$. The overall
tion

lecularity of reaction:

Chemical reaction classified into
types :
1) Elementary reaction
2) Complex reaction

Elementary reaction:-

Elementary reaction is a simple
ction. with occurs. in a single steps
A complex reaction is occurs
wo (or) more steps

ecularity of elementary reactions:

It is defined as the number of
tant
ions molecules involved in a reaction
The molecularity of an elementary
on is one, 2, 3... etc. according to
or) 3 reactant molecules are
cipiding in the reaction are
d unimolecular (or) bimolecular and
molecular reaction respectively.

Ex:

Unimalecular reaction: (1)

Malic acid → feumaric acid

$Br_2 \longrightarrow 2Br$

Bimolecular reaction: (2)

Ethyl acitate + water

$CH_3COOH + H_2O \longrightarrow CH_3COOH + CH_2CH_3OH$

Ter molecular reaction: (3)

$2NO + O_2 \longrightarrow 2NO_2$

Molecularity of a complex reaction:

Most of the reactions are complex reactions occurs in a series of steps. Each step is an elementary reaction. Thus step wise sequence of elementary reactions is called the mechanism of the reaction. ~~hede~~ sum of stem will be fast others will be slow. Thus the slowest stem is a rate determining step of the reaction.

Ex:

$2N_2O_5 \rightarrow 4NO_2 + O_2$

Step : 1 : $2N_2O_5 \longrightarrow 2NO_2 + 2NO_3$ (slow)

2 : $NO_2 + NO_3 \rightarrow NO + NO_2 + O_2$ (Slow)

3 : $NO + NO_3 \longrightarrow 2NO_2$ (fast)

overall reaction $2N_2O_5 \longrightarrow 4NO_2 + O_2$

pd

Each elementary reaction has its own molecularity equal to the number of molecules or atoms participating.

The molecularity of the over all reaction is different with different steps, is the best molecularity of reaction is the number of molecules (or) atoms taking part in the rate determining step.

Difference between order and molecularity.

	Order of a Reaction:	Molecularity of Reaction:
1)	It is the some of powers of the concentration terms in the rate law equation.	It is the number of reacting species under going simultaneous collision in the simple reaction.
2)	Experimentally determined value	It is a theoritical concept.
3)	It can have fractional values.	It is always whole number val.
4)	It can assume zero value.	It can't have zero value.
5)	It can change by change the condition, pressure, Temperature and concentration.	It is invarient for a chemical equation.

✓ Derivation of rate constant of a zero order reaction:-

rate is independed of the reactions.

Ex: photoelectric reaction

$A \rightarrow$ products

Initial conc. a $\quad$ 0

final conc. $a-x$ $\quad$ x

Rate of reaction $= -\frac{d[A]}{dt} = k_0[A]^0$.

(or)

$$\frac{dx}{dt} = \frac{-d(a-x)}{dt}$$ conc of reaction.

$$= k_0(a-x)^0$$

$$\frac{dx}{dt} = k_0$$

on intergration we get

$$\int dx = k_0 \int dt$$

$$x = k_0 t$$

$$\boxed{\frac{x}{t} = k_0} \rightarrow \boxed{\text{rate constant} = k}$$

is equal to all conc of reaction.

When k_0 is a rate constant of a zero order oreaction, the unite is the conc. per unit time. In zero order reaction the rate constant is equal to the rate of reation at all concentrations.

Derivation of rate constant of a first order reactions:

Let us consider the first order reactions

$A \rightarrow$ products,

$$-\frac{dx}{dt} = k(a-x)$$

(or)

$$-\frac{dx}{(a-x)} = k\,dt \rightarrow \textcircled{1}$$

Intergration of the equ ①, we get

$$-\int \frac{dx}{a-x} = \int k\,dt$$

$$-\ln(a-x) = kt + I$$

The constant k evaluated by putting

$t=0,\ x=0,$

They $I = -\ln a$

Sub. for I in equ ②

$$-\ln(a-x) = kt - \ln a$$

$$\ln a - \ln(a-x) = kt$$

$$\ln\left(\frac{a}{a-x}\right) = kt \rightarrow \textcircled{3}$$

(or) $$k = \frac{1}{t}\ln\left(\frac{a}{a-x}\right)$$

Change into common log

$$k = \frac{2.303}{t}\log\left(\frac{a}{a-x}\right) \rightarrow \textcircled{4}$$

Ex:

Some common reactions ~~its~~ which follows first order kinetics ~~are~~ following:

1. decomposition of N_2O_5 in CCl_4 solution:

$$N_2O_5 \longrightarrow 2NO_2 + 1 O_2$$

Nitrogen pentoxide in CCl_4 solution decomposes to form oxygen gas ~~decomposition of H~~

decomposition of H_2O_2 in accquous solution:

$$H_2O_2 \xrightarrow{Pt} H_2O + O$$

Hydrogen peroxide in the presence of Pt as catalyst is a first order reaction

The progress of the reaction titrating equal valume of the mixture against standared $KMnO_4$ soln. at different time intervels.

Problem: 1

A solution of H_2O when titrated against $KMnO_4$ soln. at different time intervels gave the following results.

t (minites)	0	10	20
valume $KMnO_4$ used for 10ml H_2SO_4	23.8 ml	14.7 ml	9.1 ml

Show that the decomposition of H_2O_2 is a first order reaction

$$H_2O_2 \xrightarrow{Pt} H_2O + O$$

Answer:

The Intergrated rate equation for the first order is

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

Since the volume of $KMnO_4$ used in the titration is measure of conc. of H_2O_2 in solution.

Initial conc of react — $a = 23.8$ ml

$(a-x) = 14.7$ ml when $t = 10$ mts

$(a-x) = 9.1$ ml when $t = 20$ mts

i) $k = \frac{2.303}{10} \log \frac{23.8}{14.7}$

$= 0.2303 (\log 23.8 - \log 14.7)$

$= 0.2303 (1.3766 - 1.1673)$

$= \underline{0.04820}$

ii) $k = \frac{2.303}{20} \log \frac{23.8}{9.1}$

$= 2.10165 (\log 23.8 - \log 9.1)$

$= 2.10165 (1.3766 - 0.9595)$

$= \underline{0.0423}$

Problem 2:

Hydrolysis of an Ester:

Hydrolysis of Ethyl acetate (or) methyl acetate in the presence of a mineral acid as catalyst is a first order reaction.

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+/HCl} CH_3COOH + C_2H_5OH$$

For studying a kinetics of the reaction, a known volume of ethyl acetate is mixt mixed with a relatively a large quantity of acid soln. at varies intervels of time a known volum of the ~~rec~~ mixture is titrated against a std. Alkali soln.

Hydrolysis of the Ester Produceses acetic acid. therefore as a reaction proceeds, The valume of alkali required for titration those on Increasing

t (sec	0	4500	7140	∞
volume of alkali used	24.36	29.32	31.72	47.15

The following about data was obtained on hydralysis of Ethyl acetate 25°c in 0.35N HCl established that its a first order reaction.

Answer:

for a ~~Sodn~~. first order reaction

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

$a = 47.15 - 24.36 = 22.79$ ml

$(a-x)$ after 4500 sec

$= 47.15 - 29.32 = 17.83$ ml

$(a-x)$ after 7140 sec

$= 47.15 - 31.72 = 15.43$ ml

$$k = \frac{2.303}{4500} \log \frac{22.79}{17.83}$$

$= 0.00005455$

~~Since the~~

$$k = \frac{2.303}{7140} \log \frac{22.79}{15.43}$$

$= 0.00005446$

Since the values of t in the two experiments and fairly constant the reaction is of the first order.

For a Second order reaction derivation:

$2A \rightarrow$ products

$$-\frac{dx}{dt} = k(a-x)^2 \rightarrow ①$$

Suppose the initial concentration a is a moles per litre.

After time t the x moles of

we known that for second order reactions the rate of reaction is propositional to Sequere of the conc. of the reactant.

k is the rate constant

Rearranging equ(1), we get:

$$-\frac{dx}{(a-x)^2} = k\,dt$$

On intervation the equation two it gives,

$$-\int \frac{dx}{(a-x)^2} = k\int dt$$

$$-\int (a-x)^{-2}dx = k\int dt$$

$$-\frac{(a-x)^{-2+1}}{-2+1} = kt + I$$

$$-\frac{(a-x)^{-1}}{-1} = kt + I$$

$$+(a-x)^{-1} = kt + I$$

$$\frac{1}{(a-x)} = kt + I \rightarrow ③$$

I is the Intergrated constant.

putting $x=0$ and $t=0$,

$$I = \frac{1}{a} \rightarrow ④$$

Substituting for I in eqn (3)

$$\frac{1}{a-x} = kt + \frac{1}{a}$$

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

Thus,

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

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

Ex of second order reaction

1. Hydralysis of an Ester by NaOH :

$CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH$

Units of zero order rate constant:

Thus the units of $K = \frac{mol}{\cancel{time}\ lit} \times \frac{1}{time}$

Time may be mole^{-1} time^{-1}

Units of First order rate constant:

$K =$ time^{-1}

Units of second order rate constant:

K = mole

Half life of a first order reaction:

$t_{1/2}$

Reaction rates can also expersed in terms of half life

It is defined as the time requier ~~one~~ for concenctrated of a reactant required to decrease to half its initial value.

In other words, half life is time required of one half of the reaction to be completed. It is repersented by the symbol $\boxed{t_{1/2}}$ (or) $\boxed{t_{0.5}}$

Half-life of a Reaction

The Integrated first order rate eqn;

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

where, $[A]_0$ = initial concentration of reactant A.

$[A]$ = concentration of reactant A at any time t.

Half life, $t_{1/2}$ of $[A] = \frac{1}{2}[A]_0$

Substituting values in Eqn(1) we have,

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

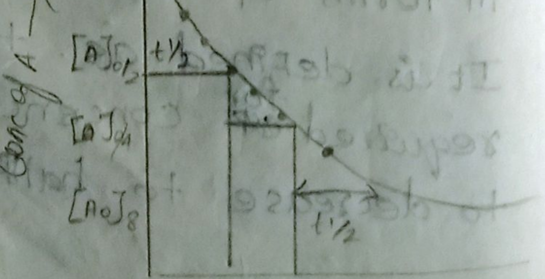
$$\text{(or)} \quad t_{1/2} = \frac{2.303}{k} \log 2$$

$$= \frac{2.303}{k} \times 0.3010$$

$$\text{(or)} \quad t_{1/2} = \frac{0.693}{k}$$

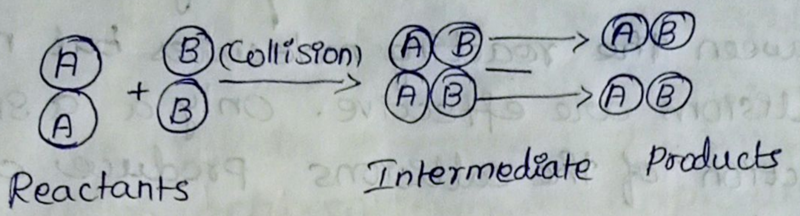
$t_{1/2}$ $\Rightarrow$ Independent of Inial concn.

$t_{1/2} \quad \frac{1}{\alpha} k$



Collision theory of Reaction rates

$A_2 + B_2 \longrightarrow 2AB$



(i) Collision rate $\propto [A][B]$

Collision, $CR = Z[A_2][B_2] \longrightarrow$ ① $10^9 s$

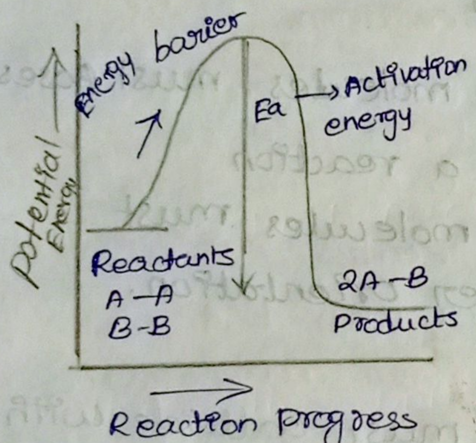


fig:1. Ⓐ

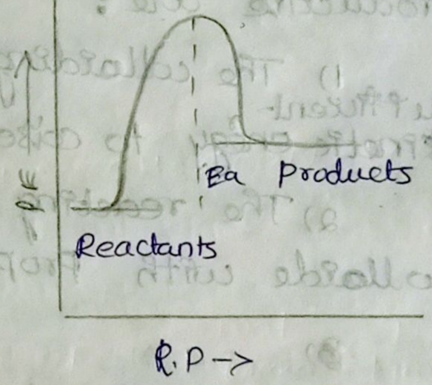


fig:1. Ⓑ

(ii) $\boxed{\text{Rate} \propto f}$

$$f = e^{-Ea/Rt}$$

$$f = e^{-\frac{[100\times10^3]}{8.314\times300}}$$

$$f = e^{-40}$$

$$f = 4\times10^{-8} = \frac{4}{10^8}$$

$$f = \frac{4}{1000000000000000000}$$

According to this theory the chemical reaction takes place only by collision between the reacting molecules but not all collisions are effective. Only a a small fraction of the collisions produce a reaction.

The two main conditions for a collision between the reacting molecules to be productive are:

1) The colloiding molecules must poseses sufficient kinetic enrgy to coise a reaction

2) The reacting molecules must colloide with proper orientation.

1) The molecule must colloide with sufficient .

Let us consider a reaction

$$A-A + B-B \longrightarrow 2A-B$$

A chemical reaction occurs by breaking bonds between the atoms of the reacting molecules and forming a new bonds in the product molecules. The energy for the breaking of bonds comes from the kinetic energy (activation energy) possesed by the reacting molecules before the collision. fig 1 (a) (b) shows the energy of molecules A_2 and B_2 as the reaction progreses.

The fig a and b also shows the activation energy [Ea] is the minimum energy necessary to cause a reaction between the colloiding molecules. only the molecules colloide with a kinetic energy grater than activation energy are able to get over the barrier and react. The molecules colloide with kinetic energy less than ~~Ea~~ Ea fail to surmount the barrier the collision between them are unproductive and the molecules simply bounce off.

$$\text{collision rate} \propto [A_2][B_2]$$

collision rate is directly proposional to the number of molecules per litre per second.

$$CR = z[A_2][B_2] \longrightarrow ①$$

where z is collision proposinality factor.

② Rate directly proportional to f

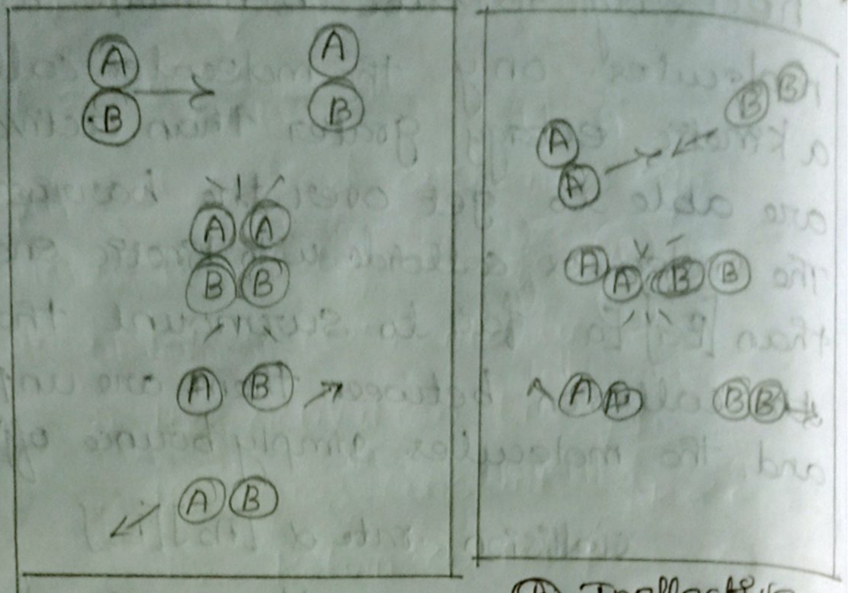
where f <u>fraction of the effective collision</u> with correct activation energy

$$\text{Rate} \propto F \longrightarrow ②$$

$$f = \frac{-Ea}{RT}$$

2) The molecules must colloide with proper orientation:

The reactant must colloide with favarable orientation. The correct orientation is ensure direct contact between the atom involves with breaking and forming.



ⓐ Effective collision ⓑ Ineffective collision

Fig:2 orientation of reactive molecules A_2 & B_2 leads to ⓐ & ⓑ

from the above discusion of collision theory, only the molecules colloiding with kinetic energy grater then E_a and with correct oriendation can casuse reaction.

Therefore, the rate of reaction depends on orientation of reacting molecules A_2 and B_2 with effective collision

ie, $\boxed{\text{Rate} \propto P}$ — ③

where P = steric factor
depends on correct
orientation of A_2 & B_2

from equation ① ② and ③ the rate of reaction from the collision theory

$\boxed{\text{Rate} = P \times f \times CR}$ — ④

Substituting equation ①,②,③ to ④

$$\boxed{\text{Rate} = P \times e^{-\left(\frac{E_a}{RT}\right)} \times z\,[A_2][B_2]}$$

From rate law

$$\boxed{Rate = k[A_2][B_2]} \quad - ⑤$$

from eqn (4) and (5);

final form $$\boxed{k = Pe^{-\left(\frac{Ea}{RT}\right)}Z} \quad - ⑥$$

Eqn (6) is the rate constant of the bimolecular reaction from the collision theory.

Effect of Increase of Temperature on Reaction Rate:

Temperature depends of reaction rate and arhenius equation:

It is formed that the rate of reaction increases with increase of Temp. As a rule, an increase of Temp. by 10°C doubles the reaction rate, generally the increase of temp. leads to ↑ the kinetic energy of colliding molecules.

Arhenius Equation:

we know that the K.E of a gas is ∝ to its temp. As the Temp of the system is ↑, more and more molecules will ~~acquire~~ ~~occur and~~ acquire and necessary energy grater then Ea to ~~called~~ ~~as~~ productive collision This increase the rate of reaction.

In 1889, Arhenius suggested simple relationship between the rate constant k for a reaction and the temp. of the system.

Arrhenius Equation :-

$$K = A e^{\frac{-Ea}{RT}} \quad \text{—} ①$$

The eqn ① is called arhenius eqn where a is the frequency factor, are determined by experimentally.

Ea is the Activation Energy.

R is the Gas constant

T is the Kelvin ~~co~~ Temp.

$$k \propto e^{\left(-\frac{Ea}{RT}\right)}$$

$$k = A e^{-\left(\frac{Ea}{RT}\right)}$$

Equ ① is Arhenius equ

Taking natural logs each side of Arhenius eqn ①

$$\ln k = \ln \left[A \cdot e^{\left(-\frac{Ea}{RT}\right)} \right]$$

$$\ln k = \ln A + \ln e^{\left(\frac{-Ea}{RT}\right)}$$

$$\ln k = \ln A - \frac{Ea}{RT} \log_e e^{\left(\frac{-Ea}{RT}\right)}$$

Arrhenius Equ

$$\ln k = \ln A - \frac{Ea}{RT} (\log_e e)$$

$$\ln k = \ln A - \frac{Ea}{RT} \left(\frac{1}{T}\right) \rightarrow ②$$

At two different Temperature

(i) At $T = T_1$, $k = K_1$;

$$\ln k_1 = \ln A - \frac{Ea}{R} \left(\frac{1}{T_1}\right) \rightarrow ③$$

(ii) At $T = T_2$, $k = K_2$;

$$\ln K_2 = \ln A - \frac{Ea}{RT} \left(\frac{1}{T_2}\right) \rightarrow ④$$

Equ ④ - ③ :

$$\ln k_2 = \cancel{\ln A} - \frac{E_a}{R}\left(\frac{1}{T_2}\right)$$

$$\ln k_1 = \underset{(-)}{\cancel{\ln A}} \underset{(+)}{-} \frac{E_a}{R}\left(\frac{1}{T_1}\right)$$

$$\ln k_2 - \ln k_1 = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$2.303 \log\left(\frac{k_2}{k_1}\right) \Rightarrow$

$$\boxed{\log\left(\frac{k_2}{k_1}\right) = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]} \rightarrow ⑤$$

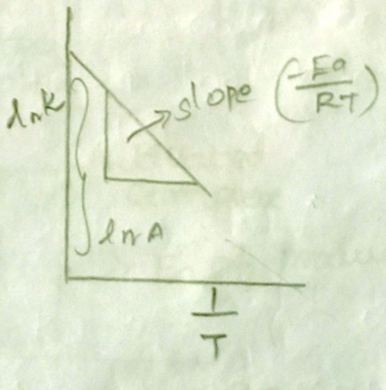
Equ ⑤ is Arrhenius equ for two diff Temp.

From graph: Equ ② - slightly modified in the form of $y = mx + c$ (straight line)

$$\ln k = \ln A - \frac{E_a}{R}\left(\frac{1}{T}\right)$$

$$\ln k = \left(\frac{-E_a}{R}\right)\frac{1}{T} + \ln A$$

$$y = mx + c$$



$$\text{slope} = \frac{-E_a}{R}$$

$$\text{Intercept} = \ln A$$

Note: $\ln = \log_e$ $\quad\therefore \log_e e = 1$

$\log = \log_{10}$

very important theory

ARRT (Absolute Reaction Rate theory)

Activated complex theory (or) Transition State theory

Energy barrier

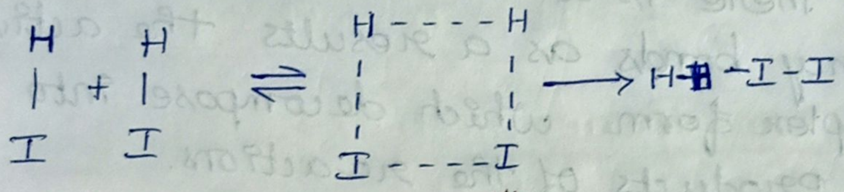
redistrib

$$A+B \rightleftharpoons X^{\neq} \longrightarrow \text{Products}$$

Reactants   Activated complex

Ie., examples:

(Dissociation of HI & formation of products)



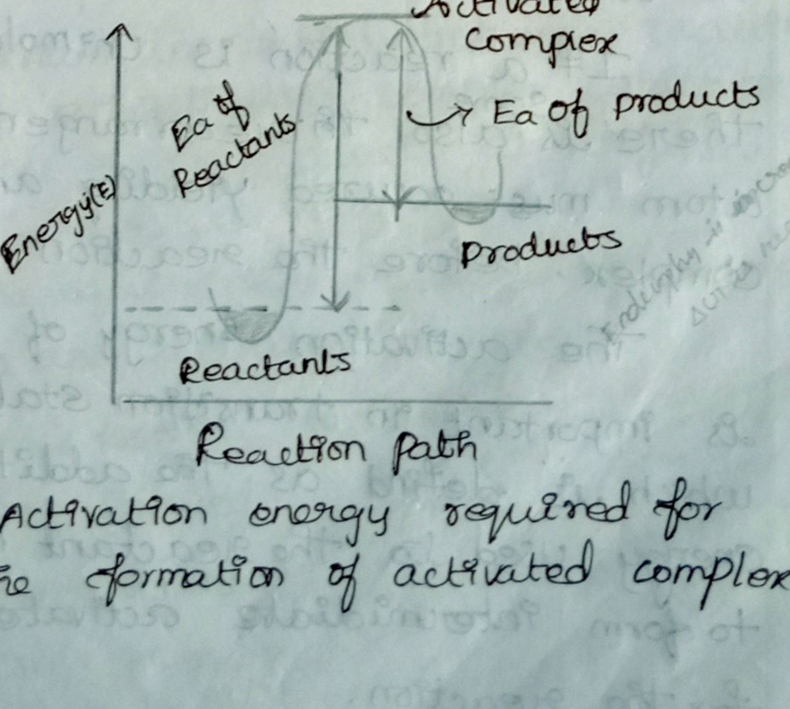
(Two molecules with sufficient energy come close to each other)

Redistribution of bonds and energy

The reactant to cross the energy barrier to form a products

Reactants   Activated complex

Activation energy is calculated from the activated complex



Free energy

Spontaneous reaction

Endothermic is increase ΔG is negative

Eg: Activation energy required for the formation of activated complex.

By a Bimolecular reaction between a molecule a and b the ~~sp~~ Steps involved are reporsented below. :

$$\underset{\text{Reactants}}{A+B} \rightleftharpoons \underset{\text{Activated complex.}}{x^{\#}} \longrightarrow \text{Products}$$

The reacting molecules Possesing sufficient energy approache each other and there is a redistribution of valency bonds as a results the activated complex form which decompose into the products of the reactions.

for example,

The dissociation of HI in to H_2 and I_2, the formation of the activated complex and it decomposes in to products are reporsented by The above

If a reaction is unimolecular there is also some ~~th~~ rearrangement of atom must ocured yielding and activated complex, before the reaction is proceed.

The activation energy of a reaction is important in transition state theory which is defind as the additional energy used to the reactant molecule to form intermidiate activated complex for the reaction.

The small initial fall in the potensial energy is due to approche of reactant molecules closed to one another. befor reacting to form the activatated complex similarly, the small final rises in energy of the products is due to falling apart of the products From the graph the energy of products higher then the reactants, the reaction is Endothermic. However, the products have less Then enery then the reactant, the reaction is Exothermic.

Derevation of rate constant: (ARRT)

A bimolecular Second order reaction consider to occur the following manner.

$$A + B \rightleftharpoons X^{\neq} \longrightarrow \text{products}$$

Reactants Activated complex

In this repersentation, It is assumed that an equlibrium an exbits between reacting molecules an activated complex which tern de composes to give Products at definite rate. The rate is very slow does't affect the equilibrium between the reacting molecules and activated complex.

Applying Stastical Mechanics: relation betw Temp dibel and Kinetic Energy difference

Erying showed;

The rate constant k of a given reaction given by

$$K = \frac{RT}{Nh} K^{*} \text{ —— ①}$$

k^* → equilibrium Constant for reactant convert into activated complex.

rate of reaction depent on the formation of activated complex.

N_0 avagatro Number

h Plank constant → energy of [illegible] is calculated

Where R = gas constant.

T = Absalute Temperature

N_0 = Avagatro Number

h = Plank constant

From thermodynamics:

standard state $\Delta G^\circ = -RT \ln k \longrightarrow$ ② → Third law of thermodynamics

$\ln$ → Natural log.

and $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \longrightarrow$ ③

where ΔG°, ΔS°, ΔH° are the Standard free energy changing, Standard Entropy chang, Standard Enthalphy change.

k = Equilibrium constant.

Eqn(2) may also written as,

$$K = e^{-\frac{\Delta G}{RT}} \longrightarrow ④$$

Sub. ΔG° from Eqn ③ in Eqn ④:

we get Eqn ⑤

$$k = e^{-\Delta G^\circ/RT}\, e^{\Delta S^\circ/R} \text{ --- } ⑤$$

Eqn ⑤ written as:

$$k^* = e^{-\Delta G^*/RT} \text{ --- } ⑥$$

or

$$k^* = e^{-\Delta H^*/RT}\, e^{-\Delta S^*/R} \text{ --- } ⑦$$

in eqn ⑥ and ⑦, ΔG^*, ΔH^* and ΔS^* are Standard energy of activation. Standard enthalphy activation and Standard Entrophy of activation. respectively all are repersent thermodynamics function for activated complex different from reactant at standard State of unit activity.

Sub. the value of K^* from eqn ⑤ in eqn ①

we get,

$$k = \frac{RT}{Noh}\left[e^{-\Delta G^*/RT}\right] \quad — ⑧$$

desorder of the system is calculated by Entrophy

$$= \frac{RT}{Noh}\left[e^{-\Delta H^*/RT}\, e^{\Delta S^*/R}\right] - ⑨$$

Since, $\frac{R}{N_0} = k_B$ (Boltzmann constanst),

→ Average kinetic energy of gas is calculated by KB

Eqn ⑨ written as follows:

$$k = \frac{k_BT}{h}\left[e^{-\Delta H^*/RT}\, e^{\Delta S^*/R}\right] — ⑩$$

from eqn ⑨ and ⑩ ; RT/Noh and k_BT/h are constant independents of reactants and products.

if ΔH^* is close to energy of activation (E_a) ; ∴ eqn ⑩ written as fallows:

$$k = \frac{k_BT}{h}\left[e^{\cancel{\Delta H^*}-E_a/RT}\, e^{\Delta S^*/R}\right] — ⑪$$

An comparing eqn ⑪ with Arhenius eqn.

$$K = Ae^{-E_a/RT} \quad — ⑫$$

The eqn ⑪ and ⑫ are Identical

number of molecules involved in collision

if the frequency factor A put as

$$A = \frac{k_B T}{h} e^{\Delta S^{*}/R} \quad — ⑬$$

Eqn ⑪ compare with eqn of the collision theory.

$$k = PZe^{-E_a/RT} \quad — ⑭$$

Its follows that

$$PZ = \frac{k_B T}{h} e^{\Delta S^{*}/R} \quad — ⑮$$

collision theory

bimolecular reacn

complex reaction apply

(or)

$$P = \frac{k_B T}{Zh} e^{\Delta S^{*}/R} \quad — ⑯$$

important

measured the entrophy

In eqn ⑯ The P is probabality factor introduced as a correction term in the rate constant eqn. derived from collision theory. is related to the entrophy of activation, ΔS^{*}.

Comparision of collision theory and Transition state theory:

In collision theory equation the factor A found to be retated to Z, the number of collision taking Place per unit volume per second. that is ie, $A = Z$.

Where as in the activated complex theory, A is different meaning which is connected to entrophy of activation.

However, the reaction involving ~~sy~~ simple molecules the value of A found to be same.

as z. Therefore the reactions involving simple molecules, The two theory is are identical

However for the reaction involving complex molecules where the collision theory fails, The transition state theory is useable and yields statisfactory results in agreement with experiments. The transition state theory is superior to the simple collision theory. The reason is that when the reacting molecules are complex ie, they contain large number of atoms. the formation of Ea activated. complex is accompained a large decrease in Entrophy. The quantity $e^{\Delta S^{*}/R}$ in eqn ⑩ is small in all such cases. but the q/ K_BT/h is universal constant remainds same for all reactions. It follows that the frequency factor A in eqn ⑪ is much smaller in complex reactions. which is also less then the value of z by a factor as large as $\boxed{10^6}$. The probability factor P introduced derived from collision theory of reactions rate.

Em.

Lindemann's Hypothesis (or) Collision theory and Unimolecular reactions

The decomposion of Nitrogen pentoxide;

$$N_2O_5 \rightarrow N_2O_4 + \frac{1}{2}O_2$$

which is some deficulties in applying in collision theory to a truely unimolecular reactions.

For collision to occur atleast two molecu of the same gases (or) different gases, the reaction can't be truly unimolecular so the collision theory can't applied to unimolecular b reactions.

In order to explain anomaly of the unimolecular reactions

Lindamann's proposed a new hypothesis, according to which there is a time-lag between activation by collisions and substitu reaction. During this time lag, the activat mollecule are also likely to lose the exce energy and not react. However if they do not lose the excess energy and they will react.

Consider a unimoleular reaction of the type

$$\boxed{A \rightarrow \text{products}}$$

According to lindemann's, its will takes place in the folloing stage:

$$A + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} A^* + A$$

$$A^* \xrightarrow{k_3} \text{products}$$

The first stage involving collision of molecules. The formation of a few activationate molecules represented by A^* molecules.

k_1 -> is the rate constant of this reaction.

Then there is some time-lag, during this interwel the activated molecules may lose the excess energy and revert to the original state, k_2 is the rate constant of this reverse process as shown.

Alternatively, the activated molecules may react and decompose into the products k_3 is the rate constant of these reaction. Which is follows from the above eqn.

- Rate of formation of activated molecules = $k_1[A]^2$ and
- Rate of disappearance of activated molecules = $k_2[A^*][A] + k_3[A^*]$

Heare, we may applay to "Study state approximation": According to this, whenever a short lived reaction-Intermidiate occurs in a system, its rate of formation can be taken us equal to it rate of disappearance.

Applying this approximation

$$k_1[A]^2 = k_2[A^*][A] + k_3[A^*]$$

$$= [A^*](k_2[A] + k_3) \quad \text{—} ①$$

Therefore,

$$[A^*] = \frac{k_1[A]^2}{k_3[A] + k_3} \quad \text{—} ②$$

Since the rate of reaction is proporsinal to the $\overset{\text{conc.}}{[\ ]}$ of ~~a~~ the activated molecules, It follows that

$$\boxed{r = -\frac{d[A]}{dt} = k_3[A^*]}$$

Then substitute the value of A^* form in eqn ② in eqn ③ we get, ④ eqn.

$$-\frac{d[A]}{dt} = \frac{k_1 k_3 [A]^2}{k_2[A]+k_3} \longrightarrow ④$$

Condition :1 $k_3 << k_2[A]$

When k_2 is very small in comparission to.

If the conc. of A is very high

$$-\frac{d[A]}{dt} = \frac{k_1 k_3 [A]^2}{k_2 [A]}$$

$$= k'[A] \quad — ⑤$$

$$k' = k_1 k_3 / k_2$$

from eqn.⑤ indicate reaction follows 1 order

Condition :2

If [A] is high $k_3 >> k_2[A]$

If k_2 is very much grater than.

Then eqn ④ converted into eqn ⑥

$$-\frac{d[A]}{dt} = \frac{k_1 \cancel{k_3} [A]^2}{\cancel{k_3}}$$

$$-\frac{d[A]}{dt} = k_1 [A]^2 \quad — ⑥$$

from the eqn⑥ The reaction follows Second order If the conc. is low.