

Chemical kinetics

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Contents

- ✓ *Introduction*
- ✓ *Molecularity*
- ✓ *Order of reaction*
- ✓ *Difference between order of reaction and molecularity*
- ✓ *Zero order reaction*
- ✓ *Pseudo order reaction*
- ✓ *First order reaction*
- ✓ *Second order reaction*

Introduction

REACTION: CHANGE IN STATE

REACTANTS



PRODUCTS

TYPES OF REACTION

1. PHYSICAL REACTION:

CHANGE IN PHYSICAL STATE

Eg:

SUBLIMATION, VAPORISATION,
CONDENSATION

2. CHEMICAL REACTION:

CHANGE IN CHEMICAL COMPOSITION

Eg: ACID-BASE REACTION,
REDOX REACTION, ETC.

IMPORTANCE OF THERMODYNAMICS

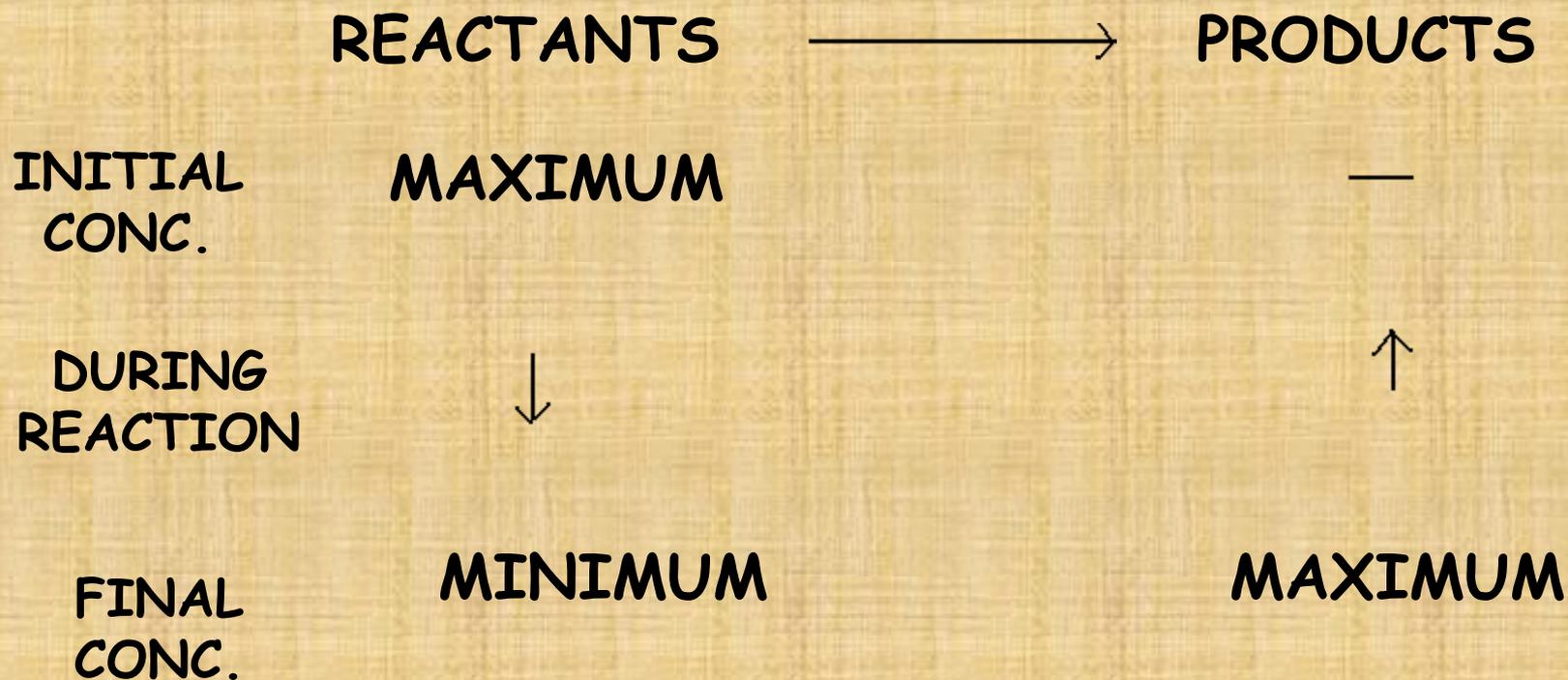
1. A REACTION WILL OCCUR SPONTANEOUSLY OR NOT
2. A REACTION IS EXOTHERMIC OR ENDOTHERMIC

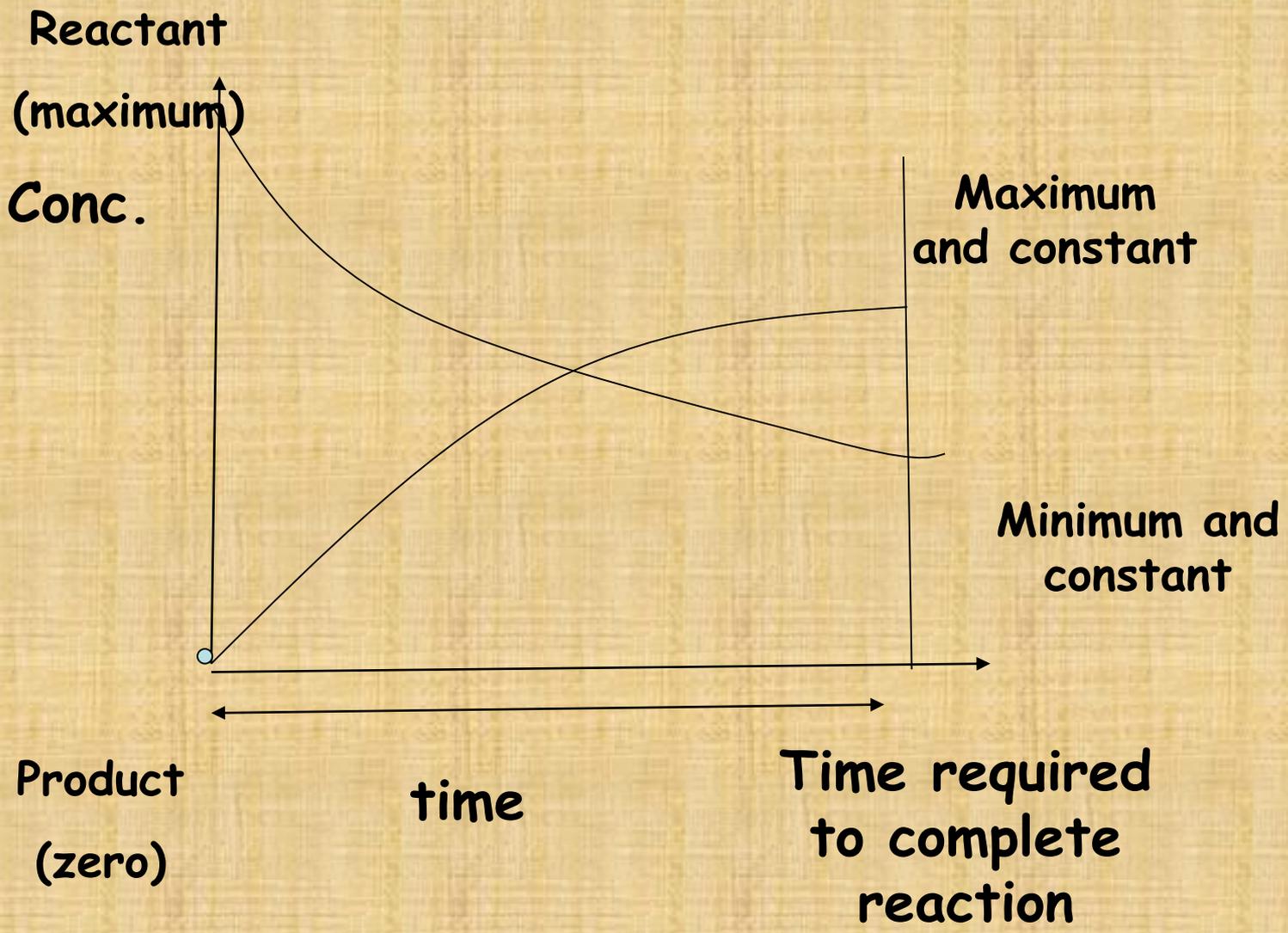
LIMITATION OF THERMODYNAMICS

IT DOES NOT GIVE INFORMATION ABOUT THE TIME IN WHICH IT WILL TAKE PLACE.

RATE OF REACTION:

RELATION BETWEEN REACTION AND TIME.





$$\text{RATE OF REACTION} = \frac{\text{DECREASE IN CONC. OF REACTANT}}{\text{TIME}}$$

$$= \frac{\text{INCREASE IN CONC. OF PRODUCT}}{\text{TIME}}$$

RATE OF FORWARD REACTION = V_F

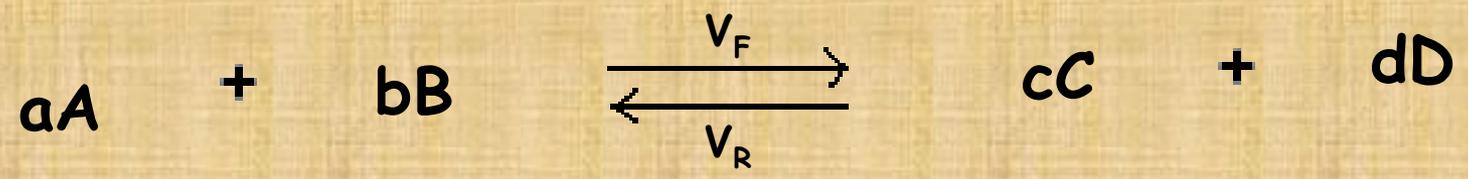
RATE OF REVERSE REACTION = V_R

- WHEN $V_F = V_R$ THE EQUILIBRIUM IS ESTABLISHED
- AT EQUILIBRIUM
 - CONC. OF REACTANTS: MINIMUM & CONSTANT
 - CONC. OF PRODUCTS: MAXIMUM & CONSTANT
 - TEMP. OF THE SYSTEM: CONSTANT
 - PRESSURE OF THE SYSTEM: CONSTANT

LAW OF MASS ACTION

- ON THE BASIS OF EXPERIMENTAL STUDIES OF MANY REVERSIBLE REACTIONS, THE NORWEGIAN CHEMISTS GULDBERG AND WAAGE PROPOSED IN 1864 THAT LAW OF MASS ACTION.

'THE DRIVING FORCE OF REACTION IS PROPORTIONAL TO THE PRODUCT OF ACTIVE MASSES OF REACTANTS.'



ACC. TO LAW OF MASS ACTION

$$V_F \propto [A]^a[B]^b$$

$$V_F = K_F[A]^a[B]^b$$

$$V_R \propto [C]^c[D]^d$$

$$V_R = K_R[C]^c[D]^d$$

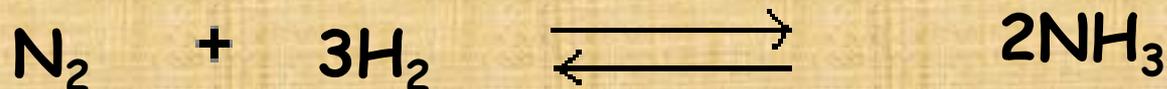
Molarity

MOLECULARITY

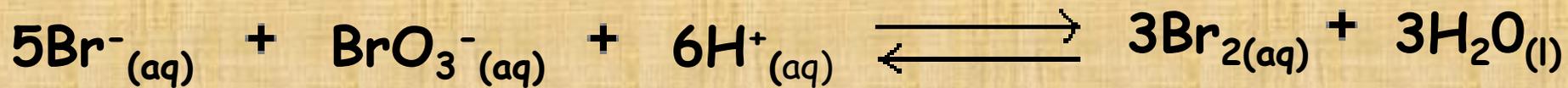
- ✓ "The number of atoms, ions or molecules of the reactant that take part in the reaction and which experience collision with each other so that reaction results, it is called molecularity
- ✓ MOLECULARITY IS THEORETICAL PHENOMENA.
- ✓ IT IS POSSIBLE TO FIND OUT MOLECULARITY FROM STOICHIOMETRIC RELATION ONLY.



$$\text{MOLECULARITY} = n_1 + n_2$$



$$\text{MOLECULARITY} = 1 + 3 = 4$$

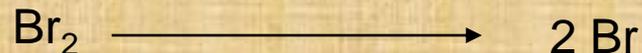


$$\text{MOLECULARITY} = 5 + 1 + 6 = 12$$

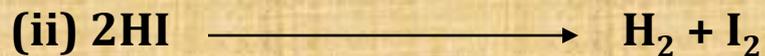


$$\text{MOLECULARITY} = 1 + 1 = 2$$

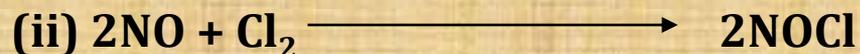
(a) Unimolecular reaction



(b) Bimolecular reaction



(c) Termolecular reaction



Why high molecularity reactions are rare ?

- ✓ Most of the reactions involve one, two or the most three molecules. The reactions involving four or more molecules are very rare.
- ✓ The rarity of reactions with high molecularity can be explained on the basis of the kinetic molecular theory.
- ✓ According to this theory, the rate of a chemical reaction is proportional to the number of collisions taking place between the reacting molecules.
- ✓ The chances of simultaneous collision of reacting molecules will go on decreasing with increase in number of molecules.
- ✓ Thus, the possibility of three molecules colliding is much less than in case of bimolecular collision.

Order of reaction

ORDER OF REACTION

- ✓ "THE NUMBER OF MOLECULES OF REACTANT WHICH CAN ALTER THE RATE OF REACTION."
- ✓ ORDER OF REACTION IS EXPERIMENTAL PHENOMENA.
- ✓ IT IS POSSIBLE TO FIND OUT ORDER OF REACTION ONLY THROUGH EXPERIMENT.
- ✓ FOR ELEMENTARY REACTION THE MOLECULARITY IS THE ORDER OF REACTION.
- ✓ THE ORDER OF REACTION AND MOLECULARITY FOR BIMOLECULAR AND TRIMOLECULAR REACTIONS ARE THE SAME.

Difference between order of reaction and molecularity

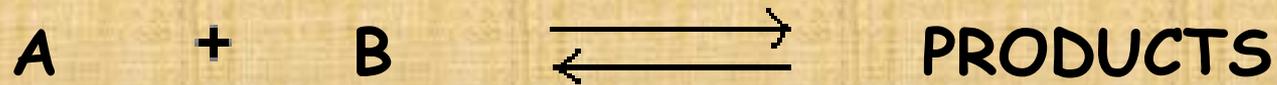
Order of reaction

- ❑ It is the sum of powers of the concentration term in the rate law expression
- ❑ It is an experimentally determined value
- ❑ It can have fraction value
- ❑ It can assume zero value
- ❑ Order of reaction can change with the conditions such as pressure, temperature and concentration

Molecularity of a reaction

- ❑ It is the number of reacting species undergoing simultaneous collision in elementary or simple reaction
- ❑ It is theoretical concept
- ❑ It is always a whole number
- ❑ It can not have zero value
- ❑ Molecularity is invariant for chemical equation

UNIT OF RATE CONSTANT



DIFFERENTIAL RATE LAW

$$\frac{-d[A]}{dt} = K [A]^a [B]^b$$

INITIAL RATE OF REACTION = RATE CONSTANT × INITIAL CONCENTRATION

$$\frac{\text{mole}}{\text{lit}} \times \frac{1}{\text{time}} = K \left[\frac{\text{mole}}{\text{lit}} \right]^a \left[\frac{\text{mole}}{\text{lit}} \right]^b$$
$$= K \left[\frac{\text{mole}}{\text{lit}} \right]^{a+b}$$
$$K = \left[\frac{\text{lit}}{\text{mole}} \right]^{a+b} \times \left[\frac{\text{mole}}{\text{lit}} \right] \times \frac{1}{\text{time}}$$

$$k = \left[\frac{\text{lit}}{\text{mole}} \right]^{a+b-1} \times \frac{1}{\text{time}}$$

$a+b$ = net order of reaction

$a+b$		UNIT OF K
0	ZERO ORDER REACTION	$\text{mol lit}^{-1} \text{time}^{-1}$
1	FIRST ORDER REACTION	time^{-1}
2	SECOND ORDER REACTION	$\text{lit mol}^{-1} \text{time}^{-1}$
3	THIRD ORDER REACTION	$\text{lit}^2 \text{mol}^{-2} \text{time}^{-1}$
n	n^{TH} ORDER REACTION	$\text{lit}^{n-1} \text{mol}^{1-n} \text{time}^{-1}$

ELEMENTARY REACTION



MOLECULARITY OF REACTION = 1 + 1 = 2

IT IS BIMOLECULAR REACTION.

DIFFERENTIAL RATE LAW

$$\text{RATE} = k [\text{H}_2] [\text{I}_2]$$

NET ORDER OF REACTION = 1 + 1 = 2

COMPLEX REACTIONS



MOLECULARITY OF REACTION = 1 + 1 = 2

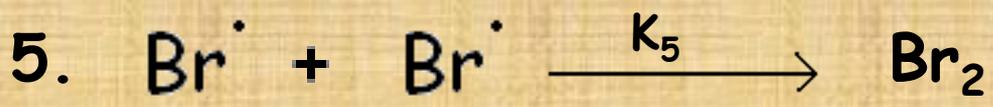
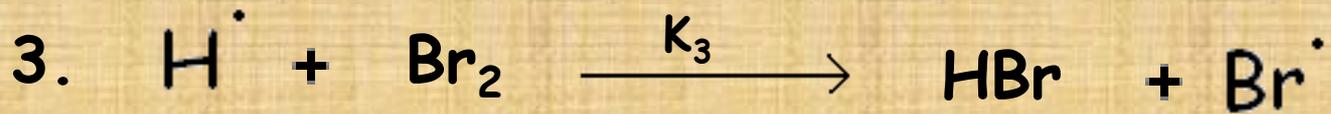
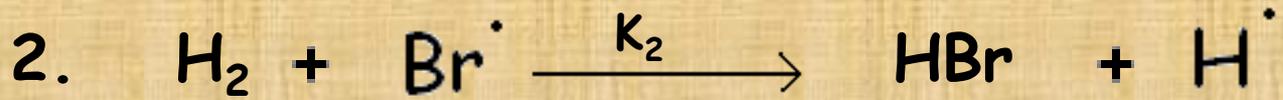
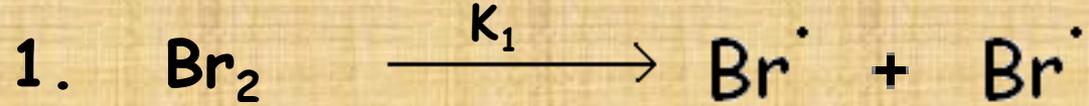
IN ABSENCE OF HBr

DIFFERENTIAL RATE LAW

$$\text{INITIAL RATE} = k [\text{H}_2] [\text{Br}_2]^{\frac{1}{2}}$$

NET ORDER OF REACTION = 1 + $\frac{1}{2}$ = 1.5

✓ ONCE THE REACTION STARTS THE ORDER OF THE REACTION CHANGES BECAUSE THIS REACTION OCCUR IN FIVE STEPS.



$$\frac{d[\text{HBr}]}{dt} = K_2[\text{H}_2][\text{Br}^\cdot] + K_3[\text{H}^\cdot][\text{Br}_2] - \underline{K_4[\text{H}^\cdot][\text{HBr}]} \quad (1)$$

$$\begin{aligned} \frac{d[\text{Br}^\cdot]}{dt} &= K_1[\text{Br}_2] + K_3[\text{H}^\cdot][\text{Br}_2] + K_4[\text{H}^\cdot][\text{HBr}] \\ &\quad - K_2[\text{H}_2][\text{Br}^\cdot] - \underline{K_5[\text{Br}^\cdot]^2} \\ &= 0 \end{aligned} \quad (2)$$

ZERO ORDER REACTION:



$$\text{RATE} = \frac{-d[R]}{dt} = K[R]^a$$

$a = 0$ for zero order reaction.

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

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

On integration we get,

$$[R] = -Kt + c \quad (1)$$

$c =$ integration constant

For determination of c

$$t = 0 \quad [R] = [R]_0$$

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

Substitute this value in eq. (1)

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

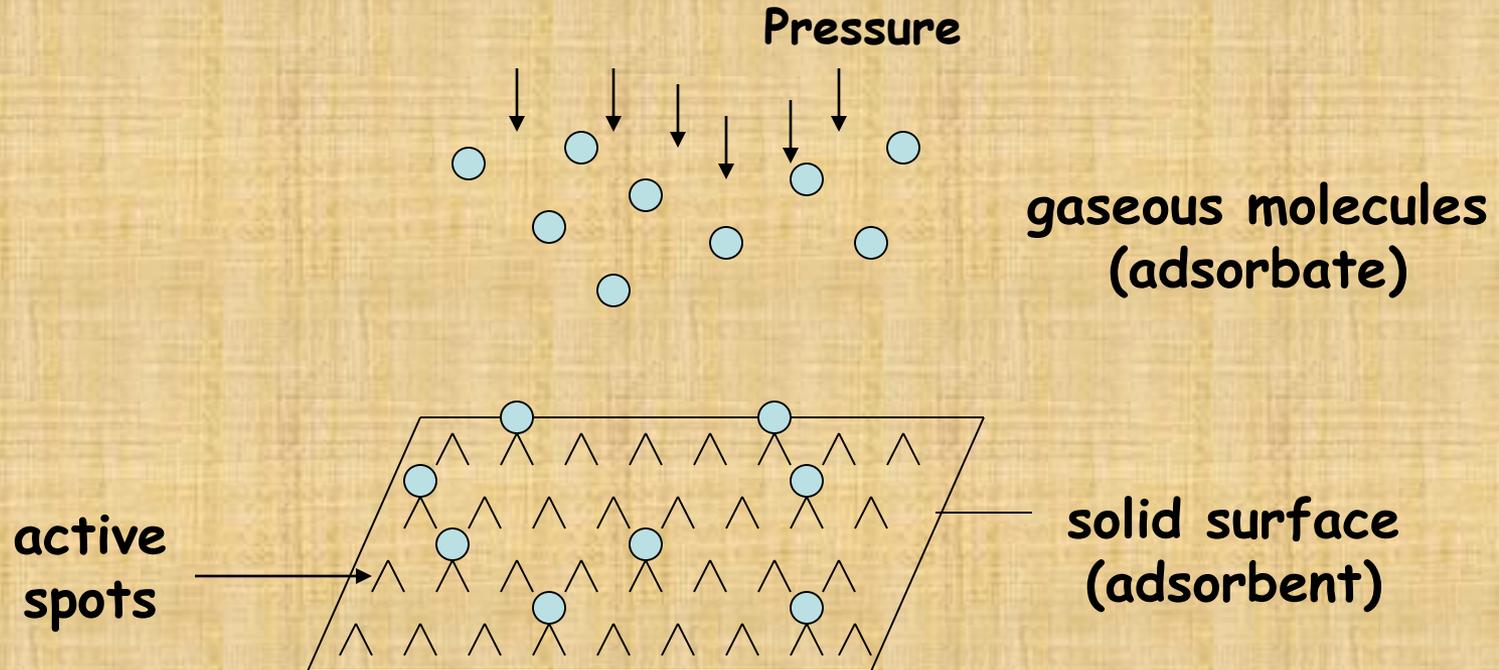
$$-kt = [R] - [R]_0$$

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

$$k = \frac{[R]_0 - [R]}{t} \quad (2)$$

Integrated rate law for zero order

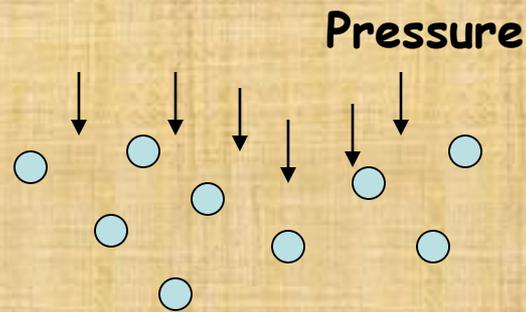
o Zero order reaction takes place mostly in heterogenous systems. Eg. The adsorption of reactant on the surface of solid adsorbent.



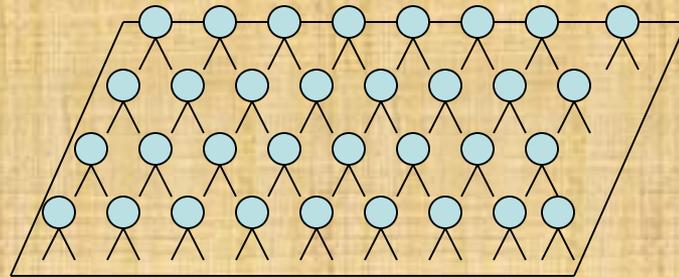
Initial stage of adsorption

o Initially if more pressure is applied the rate of adsorption increases. i.e. the rate of adsorption is proportional to concentration.

o Hence it becomes first order reaction.

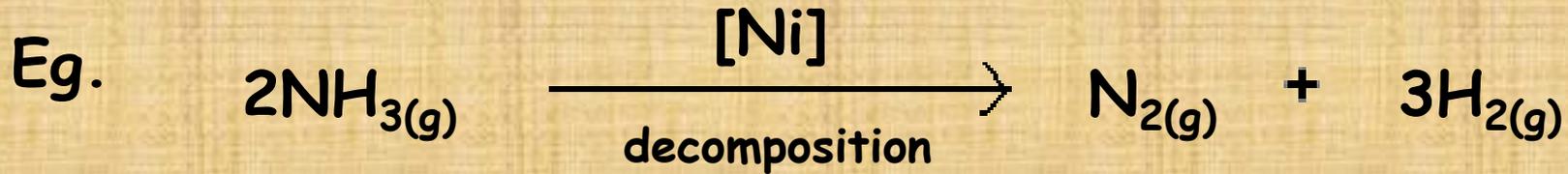


Reflected molecules
from the surface of
catalyst



Final stage of adsorption
(At saturation point)

- o At higher pressures or concentrations the surface of catalyst is completely covered and further adsorption is not possible.
- o Therefore there is no effect of increasing pressure or concentration at this point and the reaction becomes **zero** order reaction.



$$\text{RATE} = \frac{K_1[\text{NH}_3]}{1 + K_2[\text{NH}_3]}$$

At low conc. or low pressure, $[\text{NH}_3]$ is very less, therefore $1 \gg K_2[\text{NH}_3]$

$$\text{RATE} = \frac{K_1[\text{NH}_3]}{1}$$

Thus the reaction will be of first order.

At higher concentration or pressure of ammonia

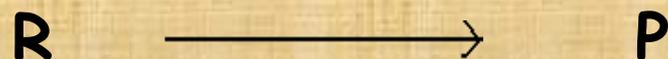
$$1 \ll K_2[\text{NH}_3]$$

$$\begin{aligned} \text{RATE} &= \frac{K_1[\text{NH}_3]}{K_2[\text{NH}_3]} &= \frac{K_1}{K_2} \\ & &= K \end{aligned}$$

Thus the reaction will be of zero order.

K is known as specific rate constant.

INTEGRATED RATE LAW FOR FIRST ORDER



$$\text{RATE} = \frac{-d[R]}{dt} = K[R]^a$$

$a = 1$ for first order reaction.

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

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

On integration we get,

$$\ln[R] = -Kt + c \quad (1)$$

$c =$ integration constant

For determination of c

$$t = 0 \quad [R] = [R]_0$$

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

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

Substitute this value in eq. (1)

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

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

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

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

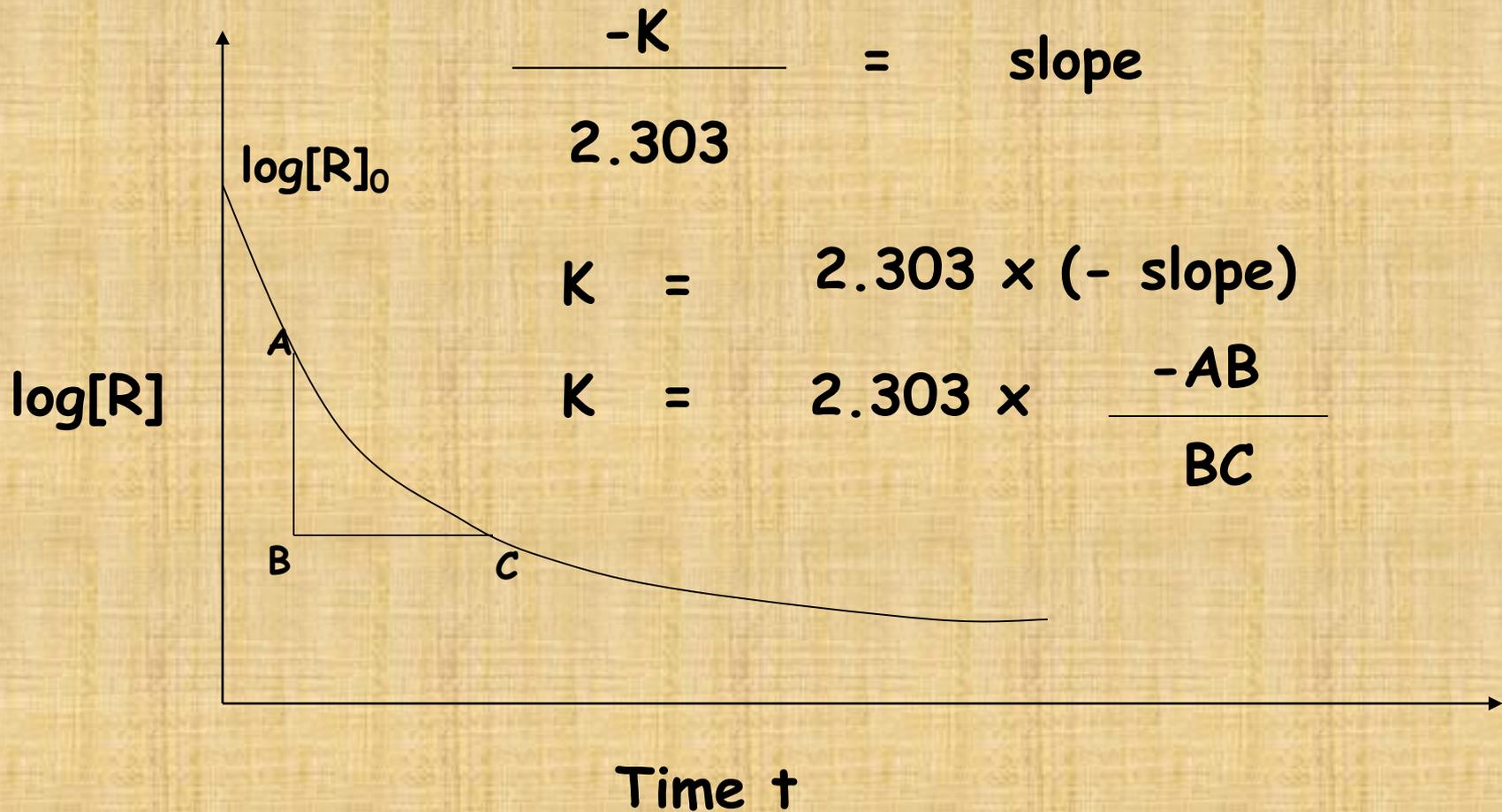
$$K = \frac{2.303}{t} \log \frac{[R]_0}{[R]} \quad (2)$$

Determination of rate constant for first order reaction.

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

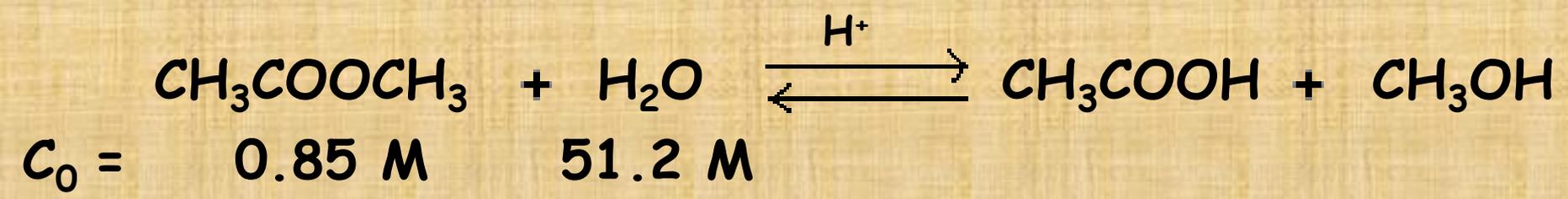
$$2.303 \log[R] = -Kt + 2.303 \log[R]_0$$

$$\log[R] = \frac{-Kt}{2.303} + \log[R]_0$$



- ❖ The concentration of B does not change significantly even on the completion of the reaction.
- ❖ Thus $[B]=\text{constant}$.
- ❖ Therefore Rate = $K_0[A]^a$ where $K_0 = K[B]$
- ✓ If $a=1$, this reaction will act as first order reaction. Such reactions are called pseudo first order reaction.

Eg. Hydrolysis of ester.



Prove that hydrolysis of methylacetate follows first order.

Time in min	t_0	t_1	t_2	t_3
	0	30	60	90
$[\text{CH}_3\text{COOCH}_3]$	0.85 M	0.8004 M	0.7538 M	0.7096 M
	C	C_1	C_2	C_3

Exercise

1) The initial concentration of N_2O_5 in the first order reaction $\text{N}_2\text{O}_{5(g)} \rightarrow 2\text{NO}_{2(g)} + \frac{1}{2}\text{O}_{2(g)}$ is $1.24 \times 10^{-2} \text{ mol lit}^{-1}$ at 318 K temperature. The concentration of N_2O_5 decreases to $0.20 \times 10^{-2} \text{ mol lit}^{-1}$ after 1 hour. Calculate the rate constant of this reaction at this temperature.

For a first order reaction,
 $\log R_1/R_2 = k(t_2 - t_1)/2.303$

$$k = (2.303/t_2 - t_1) \log R_1/R_2$$

$$k = (2.303/60) \log(1.24 \times 10^{-2} \text{ mol l}^{-1} / 0.20 \times 10^{-2} \text{ mol l}^{-1})$$

$$k = (2.303/60) \log 6.2 \text{ min}^{-1}$$

$$K = 0.0304 \text{ min}^{-1}$$

2) The rate constant of a first order reaction is $1.20 \times 10^{-3} \text{ s}^{-1}$. What time it will take to have reactant 3 gram from 5 gram?

For a first order reaction,

$$k = (2.303/t) \log R_1/R_2$$

$$1.20 \times 10^{-3} \text{ s}^{-1} = (2.303/t) \log 5/3$$

$$\therefore t = (2.303/1.2 \times 10^{-3}) \log 1.6666$$

$$\therefore t = 1.919 \times 10^3 (0.2219)$$

$$\therefore t = 0.42586 \times 10^3 \text{ sec}$$

$$\therefore t = 425.86 \text{ sec}$$

3) During decomposition of SO_2Cl_2 , its concentration becomes half of its initial concentration in 60 minutes. What will be the rate constant of this reaction?

Concentration becomes half of its initial concentration means half life time

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

$$\therefore k = 0.693/60$$

$$\therefore k = 0.01155 \text{ min}^{-1}$$

Or

$$\therefore k = 0.693 \text{ sec}^{-1}$$

4) The following results are obtained in one pseudo first order reaction:

Time (second)	0	30	60	90
Concentration of reactant mol lit ⁻¹	0.551	0.312	0.173	0.085

- (i) Calculate average rate of reaction between 30 and 60 seconds (ii) Calculate the rate constant of this first order reaction.

$$[\text{reactant}]_{30} = 0.312 \text{ mol l}^{-1}$$

$$[\text{reactant}]_{60} = 0.173 \text{ mol l}^{-1}$$

$$\begin{aligned} R_{\text{av}} &= -\Delta[\text{reactant}]/\Delta t \\ &= -(0.173 - 0.312)/60-30 \\ &= 0.139/30 \\ &= 0.004633 \text{ mol l}^{-1} \text{ s}^{-1} \end{aligned}$$

$$\therefore R_{\text{av}} = 4.633 \times 10^{-3} \text{ mol l}^{-1} \text{ s}^{-1}$$

5) Prove for the first order reaction that the time required for completion of 99% reaction is double than the time required for completion of 90% reaction.

Its is assumed that the reaction is of first order(the order of reaction is not given here), then

$$t = 2.303/k \log(a/a-x) \\ = 2.303/k \log(1/1-(x/a))$$

When $x/a = 90\% = 0.9$,

$$t_{90} = 2.303/k \log(1/1-0.9)$$

$$t_{90} = 2.303/k \log(10)$$

When $x/a = 99\% = 0.99$

$$t_{99} = 2.303/k \log(1/1-0.99)$$

$$t_{99} = 2.303/k \log(100)$$

$$\text{This gives } t_{99}/t_{90} = \log 100/10$$

$$\therefore t_{99}/t_{90} = 1$$

6) Sucrose is converted to glucose and fructose in presence of acidic solution which is first order reaction. The half reaction time of this reaction is $t_{1/2} = 3$ hours. How many times the initial concentration becomes less after 9 hours?

For a first order reaction,

$$k = 0.693/t_{1/2} = 0.693/3 = -2.303/t \log [R]_t/[R]_0$$

$$0.693/3 = -2.303/9 \log [R]_t/[R]_0$$

$$0.693 \times 9 / 3 \times 2.303 = -\log [R]_t/[R]_0$$

$$0.9027 = -\log [R]_t/[R]_0$$

$$[R]_t/[R]_0 = -\text{antilog } 0.9027$$

$$[R]_t/[R]_0 = 0.1253$$

$$\text{This gives, } [R]_t/[R]_0 = 0.1253$$

So, after 9 hours, 0.1253 of the initial concentration remains unreacted.

7) The decomposition of NH_3 on the platinum surface is zero order reaction. If $k = 2.5 \times 10^{-4} \text{ ms}^{-1}$, what will be the rate of production of N_2 and H_2 ?

For the reaction,



$$\begin{aligned}\text{Reaction rate} &= -1/2 \frac{d[\text{NH}_3]}{dt} \\ &= \frac{d[\text{N}_2]}{dt} \\ &= 1/3 \frac{d[\text{H}_2]}{dt} \\ &= k [\text{NH}_3]^0 \\ &= k\end{aligned}$$

Then from this relationship,

$$\begin{aligned}\text{Rate of production of } \text{N}_2 &= \frac{d[\text{N}_2]}{dt} = k \\ &= 2.5 \times 10^{-4} \text{ ms}^{-1}\end{aligned}$$

$$\begin{aligned}\text{Rate of production of } \text{H}_2 &= \frac{d[\text{H}_2]}{dt} = 3k \\ &= 3 \times 2.5 \times 10^{-4} \\ &= 7.5 \times 10^{-4} \text{ ms}^{-1}\end{aligned}$$

8) If the rate of reaction is doubled by increasing the temperature from 298 K to 308 K, then calculate the energy of activation of the reaction.

$$T_1 = 298 \text{ K}$$

$$T_2 = 308 \text{ K}$$

$$\therefore k_2/k_1 = 2$$

$$\log k_2/k_1 = E_a/2.303R[T_2-T_1/T_2T_1]$$

$$\log 2 = E_a (10)/2.303 \times 1.987 \times 298 \times 308$$

$$E_a = 12642.27 \text{ cal}$$

$$\therefore E_a = 12.642 \text{ kcal}$$

9) The half life period of ^{14}C is 5370 years. In a sample of dead tree, the proportion of ^{14}C is found to be 60% in comparison to living tree. Calculate the age of the sample.

$$t_{1/2} = 5370 \text{ years}$$

If a is the initial ^{14}C activity in a living tree, then

Activity in the dead tree, $a_t = (60/100)a$

The nuclear/radioactive decay follows the first order kinetics.

$$\text{so, } t = 2.303/k \log a/a_t$$

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

$$\therefore t = 2.303/(0.693/t_{1/2}) \log a/((60/100)a)$$

$$t = (2.303 \times 5370)/0.693 \log 100/60$$

$$= 17845.75 \log 1.6666$$

$$= 17845.75(0.2219)$$

$$t = 3959.97 \text{ years}$$

10) The radioactive ^{90}Sr that is formed due to nuclear explosion has half life period of 28.1 years. In the body of a child born at this time ^{90}Sr is found to be $1\mu\text{g}$ (10^{-6} gram), then what will be ^{90}Sr left in the body of the child when (a) the age of the child will be 20 years and (b) when the age of child will be 70 years. (^{90}Sr is not lost in any other way).

$$t_{1/2} (^{90}\text{Sr}) = 28.1 \text{ year}$$

Initial amount of ^{90}Sr absorbed, $a = 1\mu\text{g}$

Final amount of ^{90}Sr left in the body, $a_t = ?$

(a) Time = 20 years

(b) Time = 70 years

For this reaction,

$$(a) \quad k = 0.693/t_{1/2} = 0.693/28.1$$

$$\text{and } k = (2.303/t)\log a/a_t$$

When $t=20$ years

$$0.693/28.1 = (2.303/20)\log 1\mu\text{g}/a_t$$

$$\therefore \log 1\mu\text{g}/a_t = (0.693 \times 20) / (28.1 \times 2.303)$$

$$\log 1\mu\text{g}/a_t = 0.21417$$

$$\therefore 1\mu\text{g}/a_t = \text{antilog } 0.21417$$

$$1\mu\text{g}/a_t = 1.638$$

$$\therefore a_t = 1/1.638 \mu\text{g}$$

$$\therefore a_t = 0.6104 \mu\text{g}$$

(b) When, $t = 70$ years

$$0.693/28.1 = (2.303/70) \log 1\mu\text{g}/a_t$$

$$\therefore \log 1\mu\text{g}/a_t = (0.693 \times 70) / (28.1 \times 2.303)$$

$$\log 1\mu\text{g}/a_t = 0.7496$$

$$\therefore 1\mu\text{g}/a_t = \text{antilog } 0.7496$$

$$= 5.618$$

$$\therefore a_t = 1/5.618 \mu\text{g}$$

$$\therefore a_t = 0.1780 \mu\text{g}$$

11) The rate constant of a reaction is $2 \times 10^{-3} \text{ min}^{-1}$ at 300 K temperature. By increase in temperature by 20 K, its value becomes three time; then calculate the energy of activation of the reaction. What will be its rate constant at 310 K temperature?

$$k_1 = 2 \times 10^{-3} \text{ min}^{-1}$$

$$T_1 = 300 \text{ K}$$

$$k_2 = 6 \times 10^{-3} \text{ min}^{-1}$$

$$T_2 = 320 \text{ K}$$

$$\log k_2/k_1 = E_a/2.303R[T_2-T_1/T_2T_1]$$

$$\log 6 \times 10^{-3}/2 \times 10^{-3} = E_a/2.303 \times 1.987 [320-300/(320)(300)]$$

$$\log 3 = E_a/2.303 \times 1.987 [20/(300)(320)]$$

$$0.4771 = E_a/2.303 \times 1.987 [20/(300)(320)]$$

$$\therefore E_a = 0.4771 \times 2.303 \times 1.987 \times 300 \times 320 / 20$$

$$= 10480 \text{ cal}$$

$$\therefore E_a = 10.480 \text{ kcal}$$

$$T_1 = 300 \text{ K}$$

$$T_3 = 310 \text{ K}$$

$$k_1 = 2 \times 10^{-3}$$

$$k_3 = ?$$

$$\log k_3/k_1 = Ea/2.303R [T_3 - T_1/T_3 T_1]$$

$$\log k_3/2 \times 10^{-3} = 10480/2.303 \times 1.987 [310 - 300/310 \times 300]$$

$$\log k_3/2 \times 10^{-3} = 0.2462$$

$$k_3/2 \times 10^{-3} = 1.763$$

$$\therefore k_3 = 3.526 \times 10^{-3} \text{ min}^{-1}$$

12) In a reaction $R \rightarrow P$ the concentration $[M]$ obtained at different times (t) are shown in the following table, calculate the average rate r_{av} of the reaction.

Time (t) (second)	0	5	10	20	30
Concentration $[M]$	160×10^{-3}	80×10^{-3}	40×10^{-3}	10×10^{-3}	3.5×10^{-3}

Sr	Time t_1 (sec)	Time t_2 (sec)	Conc. at t_1 $[R_1]$ M	Conc. at t_2 $[R_2]$ M	$t_2 - t_1$	$R_2 - R_1 = \Delta[R]$	Avg. $r_{av} = -\Delta[R]/\Delta t$ (mol/lit sec)
1	0	5	160×10^{-3}	80×10^{-3}	5	-80×10^{-3}	8×10^{-3}
2	5	10	80×10^{-3}	40×10^{-3}	5	-40×10^{-3}	4×10^{-3}
3	10	20	40×10^{-3}	10×10^{-3}	10	-30×10^{-3}	3×10^{-3}
4	20	30	10×10^{-3}	3.5×10^{-3}	10	-6.5×10^{-3}	0.65×10^{-3}

Its is apparent from the above results that the average rate (r_{av}) decreases from 8×10^{-3} to $0.65 \times 10^{-3} \text{ ms}^{-1}$ in 0 to 30 sec

13) The rate constant of a reaction of first order is 70 sec^{-1} . what time will be taken to have the concentration $1/18$ part of the initial concentration?

$$k = 70 \text{ s}^{-1}$$

Let , Initial conc. of the reactant = a

$$\text{Final conc. of the reactant} = (1/18)a = a/18$$

For a first order reaction,

$$t = (2.303/k) \log a/a/18$$

$$= (2.303/70) \log 18$$

$$= 0.0329(1.2553)$$

$$= 0.04130 \text{ sec}$$

14) The decomposition rate constant of hydrocarbon is $2.428 \times 10^{-5} \text{ sec}^{-1}$ at 550 K and activation energy is 197.7 k joule mol^{-1} , then calculate Arrhenius constant.

The Arrhenius equation is,

$$k = A \exp(-E_a/RT)$$

where A is the pre-exponential factor

$$A = k / \exp(-E_a/RT) = 2.428 \times 10^{-5} / \exp(-197.7 / 8.3 \times 550)$$

$$A = 2.428 \times 10^{-5} / \exp(-43.307)$$

this gives,

$$A = 1.550 \times 10^{14} \text{ s}^{-1}$$

15) In the reaction of decomposition of reactant A into product, the rate constant is $4.5 \times 10^3 \text{ sec}^{-1}$ at 283 K temperature and energy of activation is 60 kJ mol^{-1} . at which temperature, the value of rate constant K will be $3 \times 10^{10} \text{ sec}^{-1}$?

$$k_{283} = 4.5 \times 10^3 \text{ s}^{-1}$$

$$k_T = 3 \times 10^{10} \text{ s}^{-1}$$

$$E_a = 60 \text{ kJ mol}^{-1} = 60000 \text{ J mol}^{-1}$$

$$T = ?$$

Using Arrhenius equation, one can write

$$\log k_T/k_{283} = E_a/2.303R [T-283/(T)(283)]$$

$$\log 3 \times 10^{10}/4.5 \times 10^3 = 60000/2.303 \times 8.314 [T-283/283T]$$

$$\log 0.6666 \times 10^7 = 60000$$

$$(7 + 0.8239) = 3133.62[T - 283/283T]$$

$$7.8239/3133.62 = T - 283/283T$$

$$0.70658T = T - 283$$

$$283 = T - 0.70658 T$$

$$283 = 0.2934 T$$

$$\therefore T = 964.55 \text{ K}$$