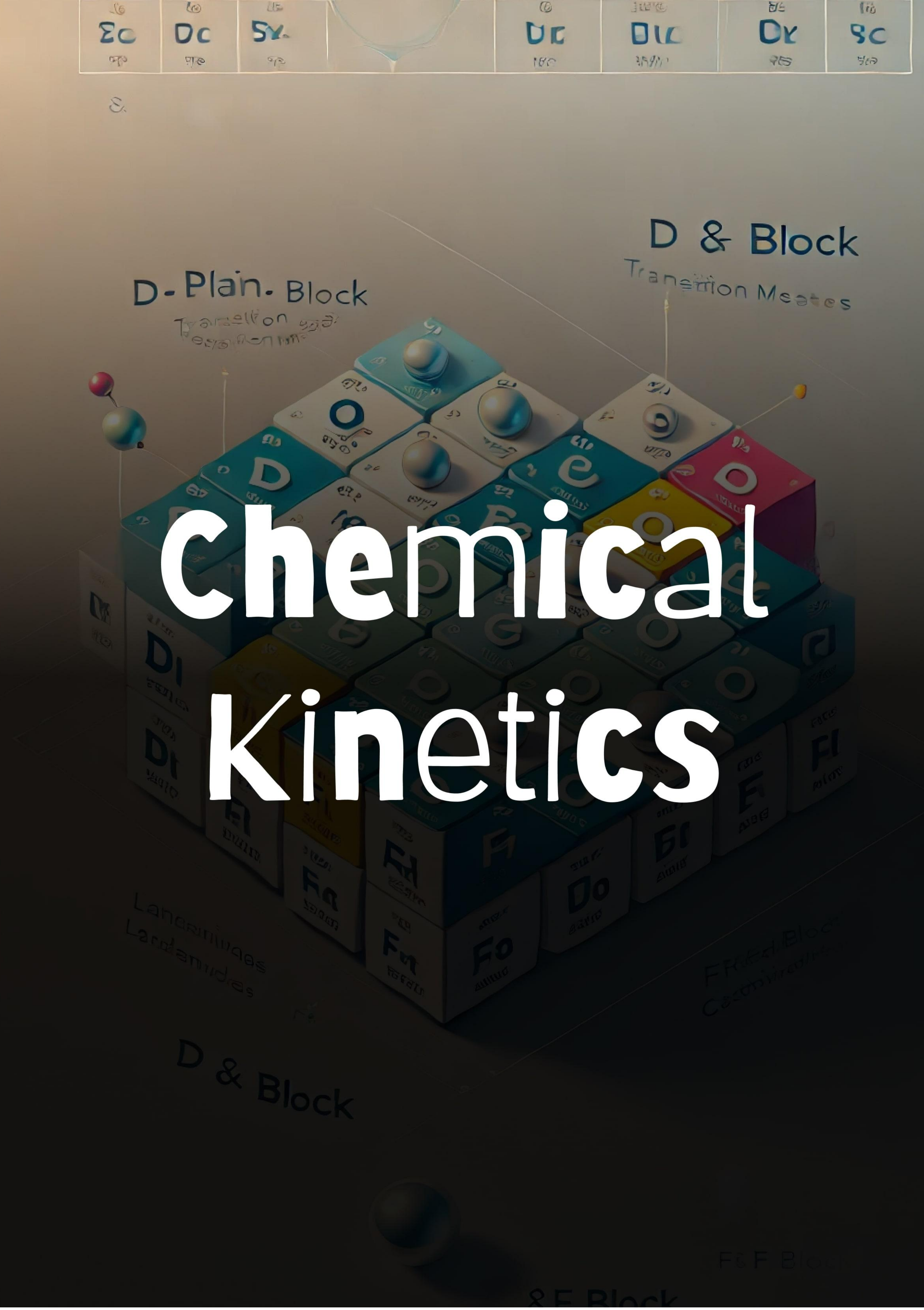


Chemical Kinetics

Chemical kinetics

- Rate of Reaction, factors affecting rate of reaction and mechanism of reaction

- Rate of Reaction = $-\dfrac{(\text{decrease in conc}^n \text{ of Reactant})}{\text{time interval}}$

always +ve = $\dfrac{(\text{increase in conc of product})}{\text{time interval}}$

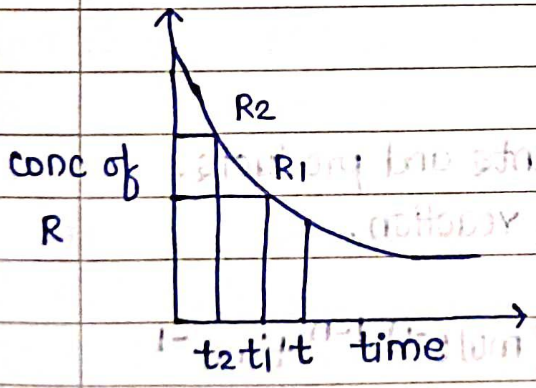
Unit of Rate of Reaction = $\dfrac{M}{\text{time}}$ = $\text{Mol L}^{-1}\text{ time}$

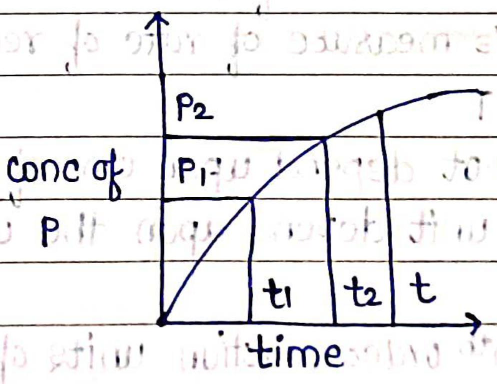
In Gaseous state, conc = Pressure

Unit = atm time^{-1}, mm time^{-1}

- Types of Rate of Reaction:

	Instantaneous rate (r_{inst})	Average rate (r_{av})
①	time interval – very small	① time interval – Big
	$r_{inst} = \dfrac{-d[R]}{dt} = \dfrac{+d[P]}{dt}$	$r_{avg} = \dfrac{-\Delta[R]}{\Delta t} = \dfrac{+\Delta[P]}{\Delta t}$





$r_{avg} = \dfrac{-\Delta[R]}{\Delta t} = \dfrac{[R_1]-[R_2]}{t_1-t_2}$

$r_{avg} = \dfrac{+\Delta[P]}{\Delta t} = \dfrac{[P_2]-[P_1]}{t_2-t_1}$

r_{inst} = – slope of tangent

r_{inst} = + slope of tangent

- For a general reaction $aA + bB \rightarrow cC + dD$

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

① $\frac{-d[A]}{dt}$ = rate of dissappearance or decomposition or consumption of A.

② $\frac{-d[B]}{dt}$ = ,,

③ $\frac{+d[C]}{dt}$ = rate of appearance or production or Formation of c

④ $\frac{+d[D]}{dt}$ = ,,

- Rate law : For a general Reaction $aA + bB \longrightarrow P$

rate $\propto [A]^x [B]^y$ — x and y are determined experimentally and they may or may not be equal to a and b.

rate $= K[A]^x [B]^y$

rate = K when [A] = 1, [B] = 2

— K is called rate constant

- Characteristics of K:

① It is measure of rate of reaction

② $K \propto T$

③ Do not depend upon conc of reactants and products.

④ Its unit depend upon the order of reaction.

- For n^{th} order reaction units of $K = (mol\,L^{-1})^{1-n}\, time^{-1}$
$= (atm)^{1-n}\, time^{-1}$

- Order of Reaction :

x+y — order of reaction

x — order of reaction w.r.t A

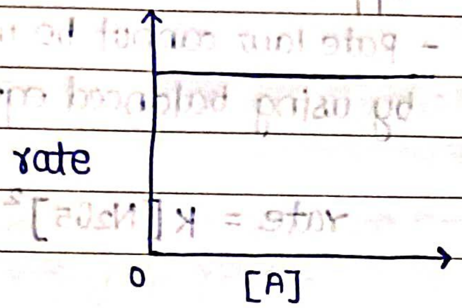
y — order of reaction w.r.t B

① Zero order Reaction

$rate = K[A]^0$

$rate = K$

rate of reaction is constant throughout i.e. rate do not depend on the conc of reactant

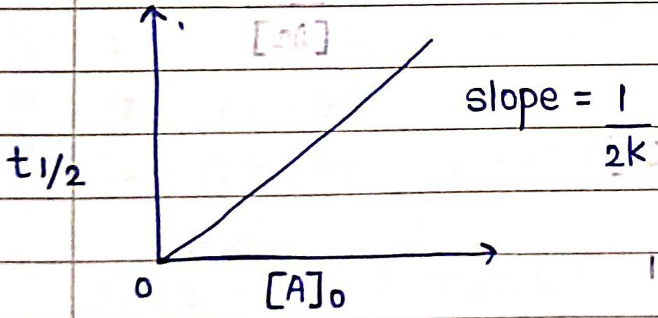


- Integrated rate eqn:

$$K = \frac{[A]_0 - [A]_t}{t}$$

- $t_{1/2}$ or 50% $= \frac{[A]_0}{2K}$

$\therefore t_{1/2} \propto [A]_0$

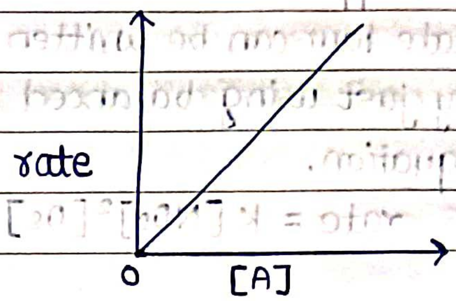


- $t_{100\%} = \frac{[A]_0}{K}$

② First order Reaction

$rate = K[A]^1$

rate $\propto$ [A]

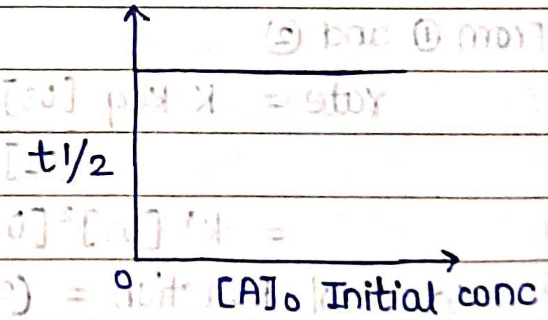


- Integrated rate eqn:

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

- $t_{1/2}$ or 50% $\doteq \frac{0.693}{K}$ ←

$t_{1/2}$ is independent upon initial conc. of reactants



- $t_{100\%} = \infty$

- Order of Reaction from the mechanism:

Two types of Reaction on the basis of number of steps.

① Elementary Reaction	② complex Reaction
completes in single step	completes in more than one step
ex : $2NO + O_2 \rightarrow 2NO_2$	ex : $2N_2O_5 \rightarrow 4NO_2 + O_2$
- mechanism concept is not applicable.	- mechanism concept is applicable
- Rate law can be written by just using balanced equation.	- Rate law cannot be written by using balanced equation
$rate = K[NO_2]^2[O_2]^1$	$rate = K[N_2O_5]^2$

Q. The chemical reaction $2O_3 \longrightarrow 3O_2$ proceeds as

step I : $O_3 \rightleftharpoons O_2 + O$ (Fast)

step II : $O + O_3 \rightleftharpoons 2O_2$ (slow)

Find the order of the Reaction :

→ step II is RDS (slow)

$\therefore Rate = K[O]^1[O_3]^1$ —— ①

O is intermediate

From step I $\quad Keq = \dfrac{[O_2][O]}{[O_3]} \qquad [O] = Keq\dfrac{[O_3]}{[O_2]}$ —— ②

From ① and ②

$$rate = K\,Keq\,\frac{[O_3]}{[O_2]}[O_3]$$

$$= k'[O_3]^2[O_2]^{-1}$$

$\therefore$ Order of Reaction = (2) + (-1)

= 1

- Methods to determine order of Reaction :

① Half life method :

For nth order reaction :

$t_{1/2} \propto (a_0)^{1-n}$

① For zero order reaction $n=0$

$t_{1/2} \propto a_0^{1-0}$

$t_{1/2} \propto a_0$

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

② For Second order reaction $n=1$

$t_{1/2} \propto (a_0)^{1-1}$

$\therefore t_{1/2} \propto (a_0)^0$

$t_{1/2}$ is independent upon initial concenteration

$t_{1/2} = 0.693 / K$

③ For second order reaction $n=2$

$t_{1/2} \propto (a_0)^{1-2}$

$t_{1/2} \propto a_0^{-1}$

$t_{1/2} \propto \frac{1}{a_0}$

- Initial Rate method : Q. During the kinetic study of the Reaction $2A+B \longrightarrow C+D$ Following results were obtained.

Run	[A]	[B]	Initial Rate
I	0.1	0.1	6×10^{-3}
II	0.3	0.2	7.2×10^{-2}
III	0.3	0.4	2.88×10^{-1}
IV	0.4	0.1	2.40×10^{-2}

Find the order of Reaction ?.

① w.r.t A

I and II consider

On increasing conc A 4 times rate also increases 4 times

$\therefore$ rate $\propto [A]^1$

② w.r.t B

II and III consider

On increasing conc B 2 times rate increased 4 times

$\therefore$ rate $\propto [B]^2$

$\therefore$ Rate law – Rate $= K[A]^1[B]^2$

Order of Reaction $= 1+2 = 3$

- Effect of Temperature on the rate of Reaction :

Rate of Reaction $\propto T$

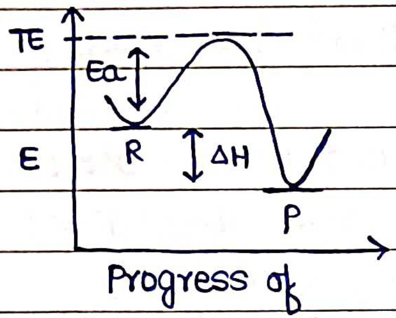
$K \propto T$

- Temperature coefficient (μ or η)

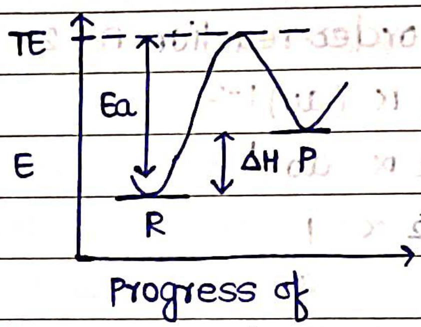
$$\mu = \frac{K \text{ at } (T+10)^\circ}{K \text{ at } T^\circ} \qquad 2 \leqslant \mu \leqslant 3$$

$$\frac{K_2}{K_1} = \mu^{(T_2-T_1)/10}$$

- Concept of Activation energy (Ea):

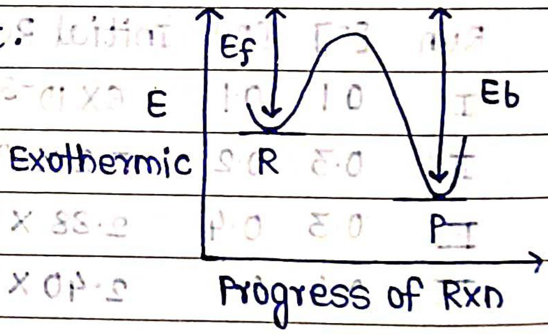


ΔH-ve Reaction
(For exothermic reaction)



Reaction ΔH+ve
(For endothermic Reaction)

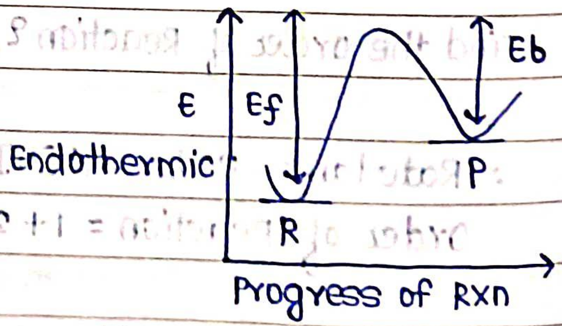
- Ea = TE − energy passed by reactant.
- In exothermic Ef < Eb
- In endothermic Eb < Ef



- Arrhenius Equation

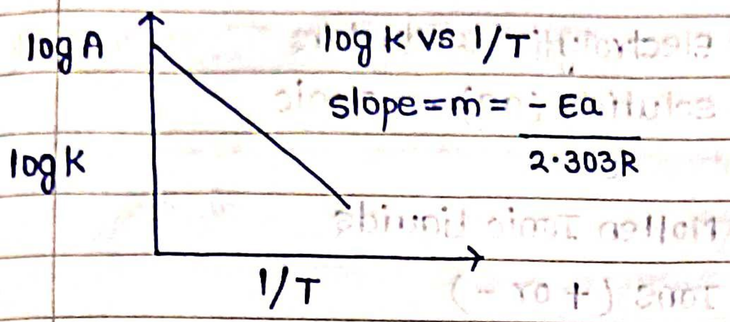
$K = Ae^{-Ea/RT}$

A → pre exponential Factor
or Frequency factor

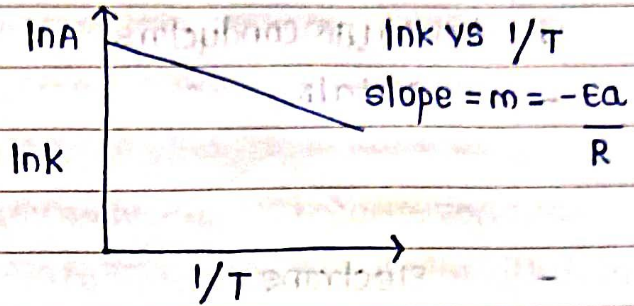


① $\ln k = \ln A - \frac{Ea}{RT}$

② $\log K = \log A - \frac{Ea}{2.303RT}$ Rate of Reaction $\propto \frac{1}{Ea}$



slope $= m = \dfrac{-E_a}{2.303R}$



slope $= m = \dfrac{-E_a}{R}$

- $\log \dfrac{K_2}{K_1} = \dfrac{E_a}{2.303R}\left(\dfrac{T_2 - T_1}{T_2 T_1}\right)$

- $E_a = J\,mol^{-1}$ $R = 8.314$ $(25/3)$
  $E_a = KJ\,mol^{-1}$ $R = 8.314 \times 10^{-3}$
  $E_a = cal\,mol^{-1}$ $R = 2$
  $E_a = Kcal\,mol^{-1}$ $R = 2 \times 10^{-3}$
  $E_a = ergs$ $R = 8.314 \times 10^{7}$