

Methods for determination of order of Rxn :-

① Hit and Trial Method :-

Given \rightarrow

Time	0	t_1	t_2	t_3
Concentration of Reactant	A_0	A_1	A_2	A_3

Assume 1st order

$$k_1 = \frac{1}{t_1} \ln \frac{(A_0)}{(A_1)}$$

$$k_2 = \frac{1}{t_2} \ln \frac{(A_0)}{(A_2)}$$

$$k_3 = \frac{1}{t_3} \ln \frac{(A_0)}{(A_3)}$$

If $k_1 = k_2 = k_3 \Rightarrow$ 1st order

but if $k_1 \neq k_2 \neq k_3$

Assume zero order

$$(A_0) - (A_1) = k_1 t_1$$

$$(A_0) - (A_2) = k_2 t_2$$

$$(A_0) - (A_3) = k_3 t_3$$

If $k_1 = k_2 = k_3 \Rightarrow$ zero order

But if $k_1 \neq k_2 \neq k_3$

Assume 2nd order

check first for zero order

if $k_1 \neq k_2$ then assume 1st order

Q. Catalytic decomposition of N_2O shows that 50% decomposition in 53 minutes and 73% decomposition reaction in 100 minutes. Predict order of reaction.

Sol

Assume 1st order

$$k_1 = \frac{2.303}{53} \log \frac{100}{50} = \frac{2.303}{53} \log 2$$

$$k_2 = \frac{2.303}{100} \log \frac{100}{27} = \frac{2.303}{100} (2 - 3 \log 3)$$

$$\text{As } k_1 = k_2$$

\Rightarrow 1st order

Arrhenius Equation :-

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

$K \rightarrow$ Rate constant

$E_a \rightarrow$ Activation Energy

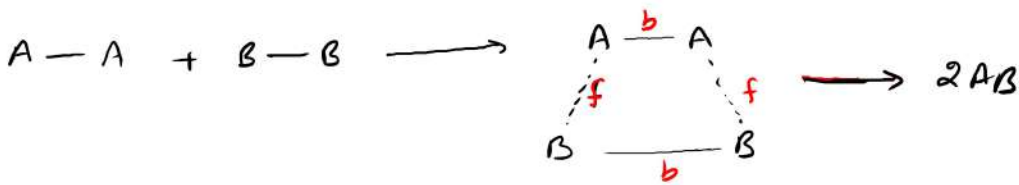
$T \rightarrow$ Temperature in Kelvin

$A \rightarrow$ Pre-exponential factor
or

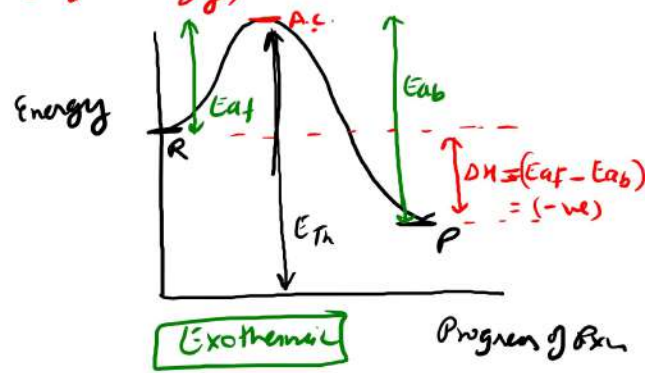
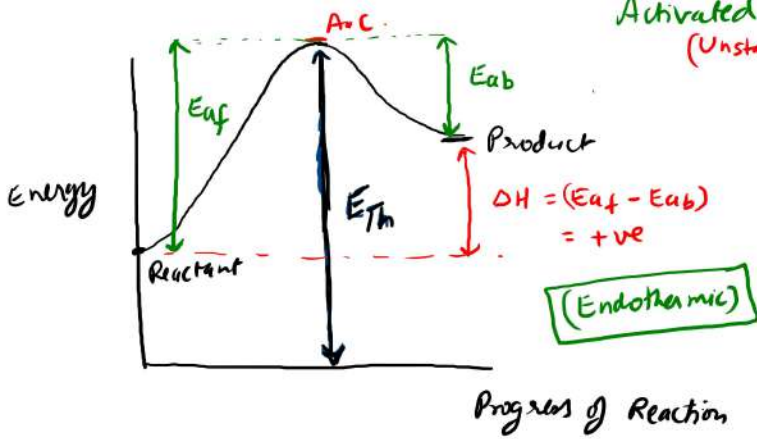
Arrhenius parameter
or

frequency factor.

Activation Energy :-



Activated Complex
(Unstable) (High Energy)



Q. For a reaction at (-73°C) , half life of 1st order reaction is found to be 5 minutes. Whereas at (27°C) , half life of same reaction is found to be 2.5 min.
Calculate Activation Energy in Calorie $[\ln 2 = 0.7]$

Sol.

$$T_1 = 200\text{K}$$

$$k_1 = \frac{\ln 2}{5}$$

$$T_2 = 300\text{K}$$

$$k_2 = \frac{\ln 2}{2.5}$$

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

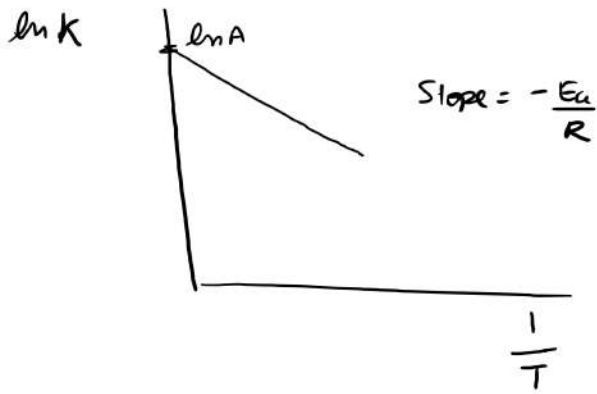
$$\ln \left(\frac{\ln 2 / 2.5}{\ln 2 / 5} \right) = \frac{E_a}{2} \left(\frac{1}{200} - \frac{1}{300} \right)$$

$$\ln 2 = \frac{E_a}{2} \left(\frac{100}{200 \times 300} \right)$$

$$E_a = 0.7 \times 2 \times 2 \times 300$$
$$= 840 \text{ Cal.}$$

Graphs -

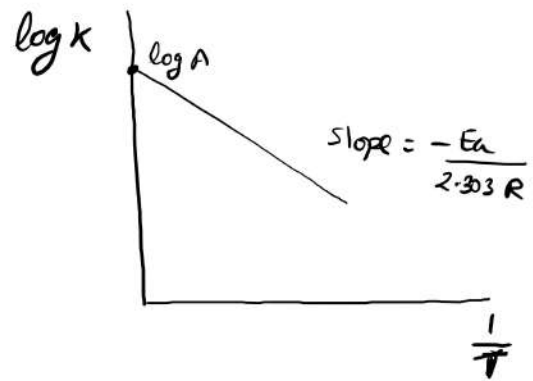
①



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

Annotations: $\ln k$ is circled in red with a 'y' below it. $\ln A$ has a red underline. $-\frac{E_a}{R}$ has a red 'm' below it. $\frac{1}{T}$ is circled in red with an 'x' to its right.

②



$$\log k = \log A - \frac{E_a}{2.303 R} \left(\frac{1}{T} \right)$$

Annotations: $\log k$ is circled in red with a 'y' below it. $\frac{1}{T}$ is circled in red with an 'x' to its right.

M.W.

S-I → 51, 52, 55, 56

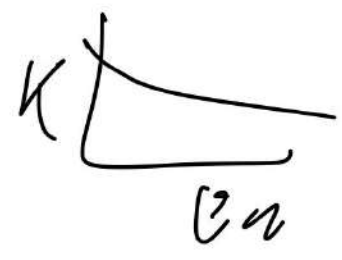
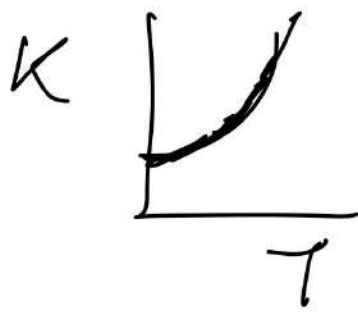
O-I → (34, 35, 36, 37, 38) &

(49, 50, 51, 52, 53, 54)

J.M. → 6, 10, 11, 18, 20, 21

J-Adv. → 3

J.M/18



(21)

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

$$-\frac{E_a}{R} = -4606$$

$$T_1 = 400K \longrightarrow 10^{-5} = k_1$$

$$T_2 = 500K \longrightarrow k_2 = ?$$

$$\ln \frac{k_2}{10^{-5}} = 4606 \left(\frac{1}{400} - \frac{1}{500} \right)$$

J.M
(6)

$$\frac{E_{af}}{E_{ab}} = \frac{2}{3}$$

$$-40 \pm (E_{af} - E_{ab})$$

~~(7)~~

0-I/07

$$(t_m)_1 = 235$$

$$P_1 = 500$$

$$(t_m)_2 = 950$$

$$P_2 = 250$$

$$\frac{(t_m)_2}{(t_m)_1} = \left(\frac{P_1}{P_2}\right)^{n-1}$$

$$\frac{950}{235} = \left(\frac{500}{250}\right)^{n-1}$$

$$4 = 2^{n-1} \Rightarrow (n-1) = 2$$

0-I/35

Use Hit & Trial

I-A/3

$$R = K [P]^1 [Q]^0$$

At 75% = 2 x 75% Graph.

0-1

(54)

$$T_1 = 300K$$

$$K_1 = \frac{\ln 2}{20}$$

$$T_2 = 320K$$

$$K_2 = \frac{\ln 2}{5}$$

(55)

$$T \rightarrow \infty$$

$$K \rightarrow A$$

(51)

$$\frac{K_2}{K_1} = 2$$

$$T_1 = 298K$$

$$T_2 = 308K$$

$$\Rightarrow K_a = ?$$

$$\ln K_w = \ln A - \frac{E_{aw}}{RT_w} \quad \text{--- (1)}$$

$$\ln K_c = \ln A - \frac{E_{ac}}{RT_c} \quad \text{--- (2)}$$

(2) - (1)

$$\ln \frac{K_c}{K_w} = \frac{E_{aw}}{RT_w} - \frac{E_{ac}}{RT_c}$$

Q. A catalyst increases rate constant of reaction by four times at 500K. If activation Energy of Catalysed rxn is 10 kcal/mole. Find " " " " Uncatalysed rxn? ($\ln 2 = 0.7$)

Sol.

Without catalyst

$$\ln k_w = \ln A - \frac{(E_a)_w}{R \times 500} \quad \text{--- (1)}$$

With catalyst

$$\ln k_c = \ln A - \frac{(E_a)_c = (10 \text{ kcal})}{R \times 500} \quad \text{--- (2)}$$

$$\frac{k_c}{k_w} = 4$$

$$(2) - (1)$$

$$\ln \left(\frac{k_c}{k_w} \right) = \frac{(E_a)_w - E_{ac}}{R \times 500}$$

$$\ln 4 = \frac{(E_a)_w - 10}{\frac{2 \times 500}{1000}}$$

$$\rightarrow 2 \times 0.7 = (E_a)_w - 10$$

(11.4 kcal)

Reaction Mechanism :-

Rate Law of a reaction can be written with the help of reaction mechanism.

① For elementary/simple rxn :- Single step rxn.



$$R = k[A]^2[B]^1$$

② For complex rxn :- Multiple step.

Step-I :- Write Rate law using RDS. (elementary)

Step-II :- Rate law should hold reactant / product but it should not have Intermediate.

Step-III :- Intermediate is removed using given equilibrium reaction.

EX-1

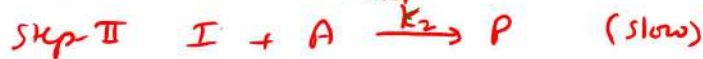


} Given

Sol.

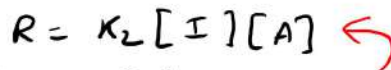


EX-2



} Given

Sol.



$$\frac{k_1}{k_{-1}} = \frac{[I]}{[A][B]} \Rightarrow [I] = \frac{k_1}{k_{-1}} [A][B]$$

$$R = \frac{k_2 k_1}{k_{-1}} [A]^2 [B]$$

$$K_{eq} = \frac{k_1}{k_{-1}}$$

↑
Chemical Eq.

57

At 300K

$$e^{-E_a/RT} = \frac{50}{100}$$

$$\ln e^{-E_a/RT} = \ln\left(\frac{1}{2}\right)$$

$$-\frac{E_a}{RT} = \ln\left(\frac{1}{2}\right) \quad \text{--- (1)}$$

At T_1

$$e^{-E_a/RT_1} = \frac{25}{100}$$

$$-\frac{E_a}{RT_1} = \ln\left(\frac{1}{4}\right) \quad \text{--- (2)}$$

①/②

$$\Rightarrow T_1 = ?$$

60
59

$$\log k = -2000 \cdot \frac{1}{T} + 6 \quad \text{--- (1) (Given)}$$

$$\log k = \frac{-E_a}{2.303 R} \left(\frac{1}{T} \right) + \log A \quad \text{--- (2)}$$

Compare

$$-2000 = \frac{-E_a}{2.303 R}$$

$$k = \frac{k_1 \sqrt{k_3}}{k_2}$$

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

$$= \frac{A_1 e^{-E_{a1}/RT} \cdot (A_3 e^{-E_{a3}/RT})^{1/2}}{A_2 e^{-E_{a2}/RT}}$$

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

$$= \frac{A_1 A_3^{1/2}}{A_2} e^{-\frac{1}{RT} (E_{a1} + \frac{E_{a3}}{2} - E_{a2})}$$

$$\Rightarrow \boxed{A = \frac{A_1 A_3^{1/2}}{A_2}}$$

$$E_a = (E_{a1} + \frac{E_{a3}}{2} - E_{a2})$$

$$= (40 + \frac{20}{2} - 30)$$

$$= (40 + 10 - 30) = 20$$

60
Good

Case-2



time	0	t
Pressure (Total)	P_0	P_t

Cal. 'k' for 1st order

Sol.



t=0	P_0	—	—
t=t	$P_0 - p$	p	p

$$k = \frac{1}{t} \ln \left(\frac{P_0}{P_0 - p} \right)$$

$$(P_0 - p) + p + p = P_t$$
$$p = (P_t - P_0)$$

$$k = \frac{1}{t} \ln \frac{P_0}{P_0 - (P_t - P_0)}$$

$$k = \frac{1}{t} \ln \frac{P_0}{2P_0 - P_t}$$

Case - 3



time	t	∞
Total Press.	P_t	P_{∞}

Cal. 'k'

Sol.



$$t=0 \quad P_0 \text{ (assume)}$$

$$t=t \quad P_0 - p \qquad p \qquad p$$

$$t=\infty \quad - \qquad P_0 \qquad P_0$$

$$k = \frac{1}{t} \ln \frac{P_0}{P_0 - p}$$

$$\text{At time 't'} \quad (P_0 - p) + p + p = P_t \quad \text{--- (1)}$$

$$\text{At time '\infty'} \quad P_0 + P_0 = P_{\infty} \quad \text{--- (2)}$$
$$P_0 = \frac{P_{\infty}}{2}$$

Using (1)

$$\frac{P_{\infty}}{2} + p = P_t$$
$$p = \left(P_t - \frac{P_{\infty}}{2} \right)$$

$$k = \frac{1}{t} \ln \frac{P_{\infty}/2}{\frac{P_{\infty}}{2} - \left(P_t - \frac{P_{\infty}}{2} \right)}$$

$$k = \frac{1}{t} \ln \frac{P_{\infty}}{2(P_{\infty} - P_t)} \quad \checkmark$$