Chemical Kinetics

on basis of Rate

- Slow Rxn ⇓ Rusting
- Moderate Rxn ⇓ Molecular Rxn
- Fast Rxn ⇓ ionic Rxn

C·K deals with these Rxn

C·K deals about

* Rate of Rxn
* Mechanism of Rxn
* factors affecting Rate of rxn.

Rate:

change in Concentration per unit time.

$$Rate = \frac{\Delta [c]}{\Delta t}$$

For Gases:

$$Rate = \frac{\Delta P}{\Delta t}$$

For mole:

$$Rate = \frac{\Delta \text{mole}}{\Delta t}$$

For gases volume

$$Rate = \frac{\Delta \text{Volume}}{\Delta t}$$

Units:

* $Rate = mol \cdot dm^3 \cdot sec^{-1}$
* $Rate = Molarity \cdot sec^{-1}$
* $= atm \cdot sec^{-1}$
* $Rate = mol \cdot sec^{-1}$
* $Rate = dm^3 \cdot sec^{-1}$

Note:

Rate Can be defined for one mole.

Types

(#) Average Rate:

Rate b/w two interval.

$$Rate_{(avg)} = \frac{\Delta[c]}{\Delta t}$$

(#) Instantaneous Rate:

$$Rate_{(inst)} = \frac{d[\Delta t]}{dt}$$

At start of rxn:

inst Rate > avg rate

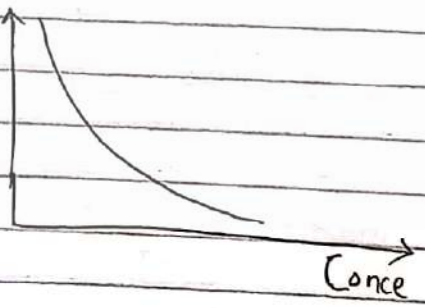
At end of rxn:

inst Rate < avg rate

Note:

Rate is variable for a rxn.

Rate - Con graph:



Rate in a chemical rxn:

$$\text{Rate} = \frac{\text{Rate}}{\text{co-efficient}}$$

$$\text{Rate} = \frac{1}{\text{co-efficient}} \times \frac{\Delta[C]}{\Delta t}$$

MCQs

$$3H_2 + N_2 \rightleftharpoons 2NH_3$$

$$R_{H_2} = \frac{1}{3}\frac{\Delta[H_2]}{\Delta t} = \text{one mole} \qquad R_{N_2} = \frac{1}{1}\frac{\Delta[N_2]}{\Delta t} = \text{one mole}$$

$$R_{NH_3} = \frac{1}{2}\frac{\Delta[NH_3]}{\Delta t} = \text{one mole}$$

So

$$R_{H_2} = R_{N_2} = R_{NH_3}$$

$$\frac{1}{3}\frac{\Delta[H_2]}{\Delta t} = \frac{1}{1}\frac{\Delta[N_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[NH_3]}{\Delta t}$$

MCQs

$$3H_2 + N_2 \rightleftharpoons 2NH_3$$

Q rate of appearence of NH_3 is how much that of rate of disappearance of H_2:

$$\frac{R_{NH_3}}{2} = \frac{R_{H_2}}{3}$$

$$R_{NH_3} = \frac{2}{3} R_{H_2} \Rightarrow R_{NH_3} = 0.6\, R_{H_2}$$

Rate of formation of NH_3 is 0.6 time that of H_2.

Q#

$3H_2 + N_2 \rightleftharpoons 2NH_3$

if rate of disappearance of H_2 is 6×10^{-2} $M \cdot sec^{-1}$ then rate of appearance of N_2 is:

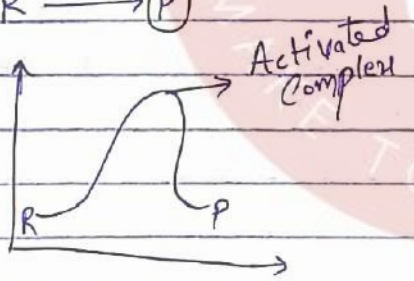
$$\frac{R_{N_2}}{1} = \frac{R_{NH_3}}{3}$$

$$R_{N_2} = \frac{6 \times 10^{-2}}{3} \qquad \boxed{R_{N_2} = 2 \times 10^{-2}}$$

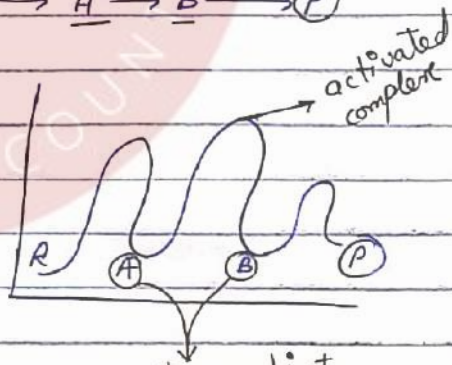
New Lec

=> on Basis of Mechanism

elementary Rxn
⇓
which occur in 1 step
$R \longrightarrow (P)$



Complex Rxn
⇓
which occur in more than 1 step.
$R \rightarrow \underline{A} \rightarrow \underline{B} \rightarrow (P)$



* Single step Rxn
* 1 activated Complex
* No intermediate
* 1st step = R.D.S
* Molecularity define for each step determined

* More step Rxn
* more than 1 activated complex
* having intermediate
* slow step = R.D.S
* Molecularity Cannot find

Elementary Rxn | Complex Rxn

* Order defined (↓ No# molecules in R.D.S (#)) | * order defined.

Rate determining Step

* Slowest step in the Rxn.
* define rate of Rxn.
* A.E of R.D.S is high.
* R.D.S is always endothermic
* Order can be written from → R.D.S
* Rate Law ~ ~ ~ → R.D.S
* R.D.S may include
  - => Reactant => Catalyst
  - => Product => intermediate (↓ Cannot be counted while finding order.)

-ve order Rxn

~~A+B → D~~

intermediate: A → B (fast)

B+C → XY (slow)

X+C → D (fast)

order: 1 order

$A + B + C \longrightarrow X$

-ve order

A+B → D (fast)

R ← B+X → Y (slow)

P ← A+C → X (fast)

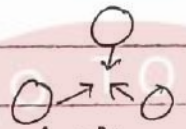
Molecularity

No # Reacting molecules in rxn.

$A + B \longrightarrow C$

which

Collide at Same time, same place, Same extent



* Max Molecularity ⟶ possible (3)
* Min ⟶ ⟶ ⟶ 1

$CaCO_3 \longrightarrow CaO + CO_2$

start vibration ↳ break

* M ⟶ always be +ve

not be zero, -ve ↳ fraction.

* Molecularity ⟶ Theoritical term.
* independant of Rxn.
* define for elementary Rxn.

MCQs:

$A + B \longrightarrow C \quad (M=2)$

MCQs: $A + \frac{1}{2}B \longrightarrow C \quad (M=3)$

$2 \times A + \frac{1}{2} \times B$ multiply with n. comes w.n.

$2A + 1B \longrightarrow C$

MCQs → M=5 → not possible

$2A + 3B \longrightarrow 5C$

⇓

Complex Rxn (M => not defines)

Order of Reaction

* No # molecules in rate determining step.
* Sum of power in Rate Law.
* Not Consider intermediate
* Order Can never exceed from 03
* Order => +ve, Fraction, -ve, Zero.
* define for both elementary & Complex Rxn.
* depend on Condition.

Rate Law

(Rate ∝ Concentration) => Law of mass action

(Rate Law) ← Rate → Concentration ⇓ order => No # molecules in rate determining step.

* Experimental Law.
* only define for chemical System.

$H_2O_{(l)} \longrightarrow H_2O_{(ice)}$ → No order (Physical change)

$Rate = K[A]^x$

K = Rate constant / velocity constant / specific rate constant.

* K ∝ rate
* K ∝ I

K → not depen on T, P & V

different for rxn. due to different A.E

depend on Nature of Reactant + A.E

$K \propto \frac{1}{A.E}$

1st order Rxn

Rate $\propto [A]^1$

$\text{Rate} = K[A]^1$ → simple rate equation

$\text{Rate} = K\left[\frac{n}{V}\right]^1$

Nuclear decay are 1st order.

$\frac{-dx}{dt} = K[A]^1$ → differential rate equation.

unit of K

$K = (\text{mol} \cdot \text{dm}^{-3})^{1-n}\ \text{sec}^{-1}$

=> Rate of 1st order rxn depends upon:

* 1st power of Concentration.
* Temperature.
* K value.
* Time (half life)

unit of K:

$K = (\text{mol} \cdot \text{dm}^{-3})^{1-1}\ \text{sec}^{-1}$

$K = \text{sec}^{-1}$

Q# $\text{Rate} = K[A]^1$

if volume is increase 4 time & no # moles ⇑ 2 time then rate of rxn becomes

$\text{Rate} = K\left[\frac{2V}{4n}\right]^1 \qquad K = \left[\frac{c}{2}\right]^1$

Q# For a rxn K is $2 \times 10^{-3}\ sec^{-1}$. if rate can increase 4 times then rate increase.

(a) 4 times

* 2nd order Rxn

rate ↓ with time

$Rate \propto [A]^2 \qquad R = K[A]^2$

$-\frac{dx}{dt} = [A]^2$

unit of K:

$K = (mol \cdot dm^{-3})^{1-2}\ sec^{-1}$

$K = mol^{-1} \cdot dm^3\ sec^{-1}$

=> Rate depends upon

* 2nd power of Conce
* K * Temperature * Time (half life)

* 3rd order Rxn

$Rate = K[A]^3$

$-\frac{dx}{dt} = [A]^3$

unit of K:

$K = mol^{-2} \cdot dm^6 \cdot sec^{-1}$

=> Rate depen On:

* 3rd power of Con
* K * Tempe * Time.

Q# Rate = $K[A]^x[B]^y$

Conc. of A & B is same if Conc of A & B ⇑ from 0.2×10^{-2} to 0.4×10^{-2}. Rate increase from 0.1×10^{-1} to 0.2×10^{-1} Msec^{-1}

A	0.2	0.4	0.1	0.2
B	0.2	0.4		
	(concen)			(rate)

Zero Order Rxn

Rate = $K[A]^0$

not depend on Concentration.

$= \frac{-dx}{dt} = K[A]^0$

unit: $K = mol\cdot dm^{-3} sec^{-1}$ → same as unit of rate

* light induced Rxn ⇓ (photochemical Rxn)

* Catalytic rxn.

Rate depend → not depend on Concentration.

depend on ⇓

* Temperature (Rate $\propto$ T)
* Time * K value.

* Fractional Order Rxn

* $Rate = K[A]^{1/x}$ $\quad \frac{1}{x} = \frac{1}{2}, \frac{1}{3}, \frac{2}{3}, \frac{3}{2}$

* only possible in Complex Rxn

* $Rate = K[2]^{2/3} = 0.6$ $Rate = K[2]^{3/2} = 1.5$

⇓

Conc 2↑ => 0.6

* **$Rate \propto \frac{1}{Concentration}$**

Q# $Rate = K[A]^{1/2}[B]^{1/2}$

unit of K

$order = \frac{1}{2} + \frac{1}{1} = \frac{3}{2}$

$K = (mol \cdot dm^{-3})^{1-n} sec^{-1}$

$K = (mol \cdot dm^{-3})^{1-3/2} sec^{-1}$

$K = (mol \cdot dm^{3})^{-1/2}$ **$K = mol^{-1/2} \cdot dm^{3/2} sec^{-1}$**

Q# ~~$Rate = K[A]^{2/3}[B]^{1/2}$~~

~~order~~

$Rate = K[A]^{1/2}[B]^{1/2}$

if conc of A & B is double then rate becomes.

$order = \frac{1}{2} + \frac{1}{2} = 1$

Rate = doubles.

$\frac{5}{4} + \frac{3}{3} = (3)$

Q#

$$Rate = K[A]^{5/3}[B]^{4/3}$$

if A & B doubles the rate

order = 3

$$Rate = [A]^3 = [2]^3$$

$$\boxed{Rate = 8 \uparrow\uparrow}$$

News Lec

* Negative Order Rxn

$$Rate \propto \frac{1}{[A]}$$

* in Rate Law = product present
* Complex Rxn.
* if one Component becomes -ve = Negative order.
* Overall order = undefined.

$$2O_3 \rightleftharpoons 3O_2$$

$$Rate = K[O_3]^2[O_2]^{-1}$$

(-1) → experimentally Come.

order = 2 - 1 = 1 ✗

units

$$Rate = K[A]^{-1}$$

$$(mol \cdot dm^{-3})^{1-(-1)} \; sec^{-1}$$

$$\boxed{mol^2 \cdot dm^{-6} \; sec^{-1}}$$

* Rate $\propto \frac{1}{conce}$
* Rate $\propto$ Temp
* K
* Time.

* Pseudo order Rxn:

* One Component is in excess.
* Look like Zero order.
* Molecularity > Order. → Sometimes equal

*	Molecularity = order	=>	possible
*	Molecul > Order	=>	possible
*	Molecul < Order	=>	Not possible

MCQs

* $A + B_{(excess)} \longrightarrow C$

M = 2, order = 1 → Pseudo first order.

* $A + B + C_{(excess)} \longrightarrow C$

M = 3 order = 1 → Pseudo Second order

Methods To find Order

* Differential rate Method
* Half life method
* integrated rate method
* Method of Large excess.
* Initial rate method.

Integrated Equation

Zero → $[A_0] - [A]_t = kt$

First → $\ln[A_0] - \ln[A]_t = kt$

Second → $\frac{1}{[A]_t} - \frac{1}{[A_0]_t} = kt$

Third → $\frac{1}{2[A]_t^2} - \frac{1}{2[A_0]^2} = kt$

Initial rate Method

Q#

$A + B \longrightarrow C$

A	B	Rate
0.1	0.2	2×10^{-2} M sec^{-1}
0.1	0.4	4×10^{-2} M sec^{-1}
0.2	0.4	16×10^{-2} M sec^{-1}

(A: 0.1 → 0.1 → 0.2, ×2; B: 0.2 → 0.4 → 0.4, double; Rate: 2×10^{-2} → 4×10^{-2} → 16×10^{-2}, double, ×4)

Rate $= [A]^2 [B]^1$

overall order = 3

Q#

$A + B \longrightarrow C$

A	B	Rate
0.4	0.8	10×10^{-2} M sec^{-1}
0.8	0.8	20×10^{-2} M sec^{-1}
0.8	0.4	10×10^{-2} M sec^{-1}

(A: 0.4 → 0.8 double, 0.8 → 0.8 same; B: 0.8 → 0.8, 0.8 → 0.4 half; Rate: 10×10^{-2} → 20×10^{-2} double, 20×10^{-2} → 10×10^{-2} half)

→ when con half rate half

Rate = $[A]^1[B]^1$

order = 2nd

Q#: $A + B \longrightarrow C$

A	B	Rate
0.02	0.2	2×10^{-2}
↓2	↓2	↓2
0.04	0.4	4×10^{-2}
↓2	↓2	↓2
0.08	0.8	8×10^{-2}

Rate = $[A]^{1/2}[B]^{1/2}$ $\quad \frac{1}{2} + \frac{1}{2} = 1$

order = 1

Half life

50% Conversion to product that time called half life.

zero $t_{1/2} = \frac{[A_0]}{2K}$ → $t_{1/2} \propto [A_0]$, $t_{1/2} \propto \frac{1}{K}$

1st $t_{1/2} = \frac{\ln 2}{K} = \frac{0.693}{K}$ → $t_{1/2} \propto [A_0]^0$, $t_{1/2} \propto \frac{1}{K}$

2nd $t_{1/2} = \frac{1}{K[A_0]}$ → $t_{1/2} \propto \frac{1}{[A_0]^1}$, $t_{1/2} \propto \frac{1}{K}$

3rd $t_{1/2} = \frac{3}{2K[A_0]^2}$ → $t_{1/2} \propto \frac{1}{[A_0]^2}$, $t_{1/2} \propto \frac{1}{K}$

$t_{1/2} \propto a^{1-n}$ (a = initial Concentration)

Zero order ← $t_{1/2} \propto a$ | $t_{1/2} \propto a^0$ → 1st order.

2nd order ← $t_{1/2} \propto a^{-1}$ | $t_{1/2} \propto \frac{1}{a}$ | $t_{1/2} \propto a^{-2}$ → 3rd order

Numericals

$$t_{1/2} = \frac{\text{total time taken}}{n}$$

Q#
If a rxn is completed 75% then how much time it will take if its half life is 10 min.

$100\% \xrightarrow{n_1} 50\% \xrightarrow{n_2} 25\%$

50 25 → 75%

$t_{1/2} = \frac{t}{2} = 10 = \frac{t}{2}$ $t = 20$ min

Q#
What is the half life of a reaction if 12.5g of Reactant is left in 60min.

$100 \xrightarrow{n_1} 50 \xrightarrow{n_2} 25 \xrightarrow{n_3} 12.5$

$t_{1/2} = \frac{t}{n}$ $t_{1/2} = \frac{60}{3}$ $t_{1/2} = 20$ min

Q#
How much reactant is left in 40 min if half life of rxn is 10 min.

$n = \frac{t}{t_{1/2}}$

$n = \frac{40}{10} = 4$

Reac left

$100 \xrightarrow{n_1} 50 \xrightarrow{n_2} 25 \xrightarrow{n_3} 12.5 \xrightarrow{n_4} 6.25$

React = decompose $100 - 6.25 = 94$

Factors affecting Rate

Rate $\propto \frac{1}{A \cdot E}$

Rate $\propto \frac{1}{\text{stability of Rxn}}$

Rate $\propto \frac{1}{\text{particle size}}$

Rate $\propto$ S.Area

either exo or endo

Rate $\propto$ conce (1, 2, 3)

Rate $\propto T$

Rate $\propto \frac{1}{\text{conc.}}$ (frac, -ve)

Rate $\propto [\text{con}]^0$ (zero)

$A \cdot E \leftarrow \xrightarrow{-Ea/RT} \rightarrow$ gen $\sigma \cdot E$.

$K = Ae^{-Ea/RT}$ → Tem

↓ rate cons ↓ A·con

$K \propto T$

Rate $\propto K$ so Rate $\propto T$

T increases the rate of

* endothermic rxn
* exothermic rxn
* Reversible rxn.
* Irreversible rxn

→ forward ↑ backward ↑

→ Rate of any order rxn.

$\frac{T_1}{T_2} = \Delta T = 0$

Experimentally:

* T ↑ or ↓ => Rate ⇑ or ⇓ by 2 times

* 10°C ⇑ ⟶ Rate → 2 double.

$$\boxed{\text{Rate} = (2)^n}$$

Q# $A + B \longrightarrow C$ 60 → 100 (40)

if Temper ⇑ from 60°c to 100°c

then How much Rate ⇑

$$\text{Rate} = (2)^4 = (16 \text{ time})$$

④ Temperature Co-efficient

Ratio of Temperature which have 10°c difference in Temperature.

T ↑ 10° ⇑ then rate ⇑ (Co)

$$T°C = \frac{T1 + 10°C}{T_1} \qquad \frac{T_1 + 10°C}{T_1} = 2$$

* unitless

Q# Which one is Temperature Co-efficient?

(a) ✓ $\frac{35°C}{25°C}$ - (10) b) $\frac{25°C}{20°C}$ c) $\frac{45°C}{30°C}$ d) All.

⑤ Catalyst effect

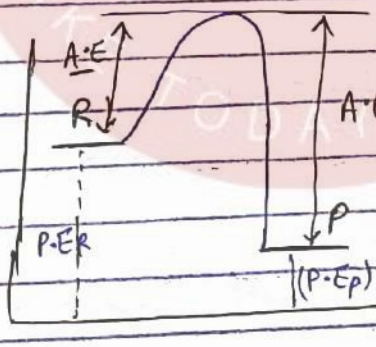
Rate ∝ Catalyst → +ve

Rate ∝ $\frac{1}{\text{Catalyst}}$ → -ve

Activation Energy

* Energy required to start a rxn.
* external energy
* always endothermic → exothermic rxn / endothermic rxn.
* Ea always Positive
* unit = KJ/mol
* depend on Nature of Reactant
  - depend on K ($K \propto \frac{1}{Ea}$)
  - ($Ea \propto \frac{1}{rate}$)
  - not depend upon Temperature. b/c barrier of Eq same.
  - P, V, conc.

(#) For Exothermic Rxn



Threshold E = A·E + P·E

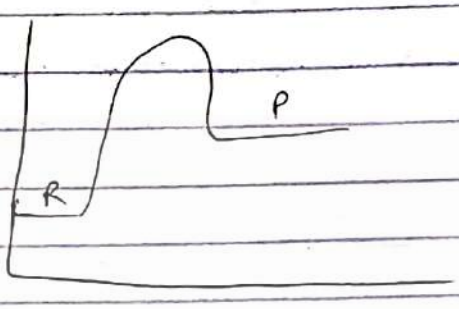
* $P \cdot E_{(R)} > P \cdot E_{(P)}$
* $Stab_{(P)} > Stab_{(R)}$
* $T \cdot E_{(R)} = T \cdot E_{(P)}$
* $A \cdot E_{(back)} > A \cdot E_{(forw)}$
* $A \cdot E_{(P)} > A \cdot E_{(R)}$

$\Delta H = A \cdot E_{(f)} - A \cdot E_{(b)}$

$\Delta H = -ve$

New Lec

Endothermic:



* Threshold E of R = P

* P.E of P > R

* stabil R > P

* A.E R > P

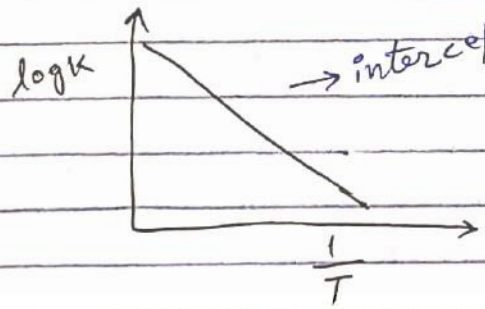
* A.E (7) > A.E (b)

* ΔH = A.E (7) - A.E (b)

* ΔH = +ve

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

$\log K = \frac{-Eq}{2.303RT} + \log A$



→ intercep = $\log A$ = +ve

slop = $\frac{-Eq}{2.303R}$

* unit of slope b/w log K & $\frac{1}{T}$ =

slope = $\frac{KJ/mol}{KJ/molK}$ ← $\frac{-Eq}{-2.303R}$ $R = \frac{PV}{nT}$

slope = K^{-1} So slope = Temper

slope = $T = \frac{-E_a}{2.303R}$ Kelvin

$E_a = -2.303RT$

Collision Theory

For gas but Concept extend to liquid & Solid

* Mathematically:

Z = collision frequency = no # collision per unit volume per unit time

P = Orientational factor = proper orientation.

$f = e^{-E_a/RT}$ => frictional factor = Fraction of molecules having energy = to $A \cdot E$ or greater than $A \cdot E$

Rxn rate ← $K \propto Z$

$K \propto P$

$K \propto f$

$K \propto Zpf$

$K = Zpf$

Arhenius constant ← $A = Z \times p$

$K = Af$

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

Points:

* Molecules 1st Comes Close to each other

Single specie → isolate → stable

intermediate is not T·state → not stable

* must be collision

effective Collision ⇓ $A \geq A \cdot E$ ⇓ Formed product

ineffective collision ⇓ $E < A \cdot E$ ⇓ will not form product

* effective Collision:
  * $E_{mol} \geq A \cdot E$
  * proper orientation is needed.

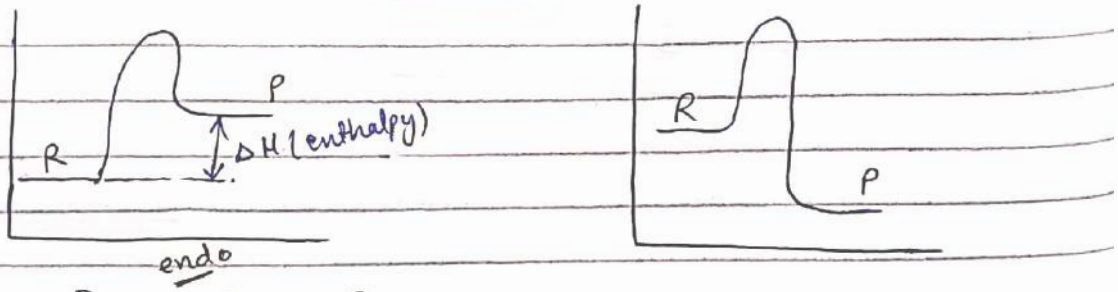
× ——— × ———

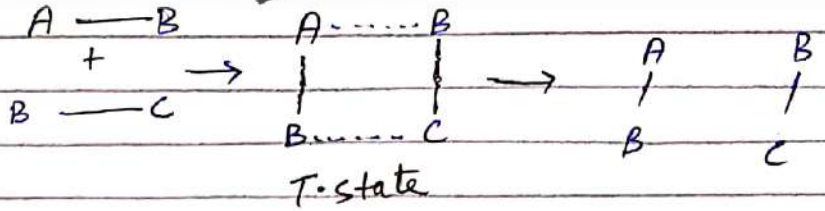
Rate $\propto K$ ↑

Rate $\propto T$ → b/c many molecules gain more energy.

$Z \propto T$ Rate $\propto Z$ Rate $\propto P$ Rate $\propto Z$

(#) Transition State Theory





* Molecules present at T. state called (activated Complex)

⊛ Transition state:

⊛ It is high energy zone
⊛ unstable molecules
⊛ loose bonds.
⊛ Molecular geometry present.
⊛ Molecular mass present
⊛ Enthalpy present
⊛ Cannot be isolated.
⊛ Short life.
⊛ 50% tendency
- to convert ⇓ Reactant
- to convert ⇓ product.

⊛ 50% bonds
- Formed
- Break

For endo:

A.Com > P > Reac

For exo:

A.Com > R > P

catalyst ↑ Fe + Mo

⊛ Catalysis ↓ study of Catalyst
- → +ve ⇒ Rate ⇑
- → promoter ⇒ ⇑ catalytic behavior.
- → -ve ⇒ Rate ⇓

* Catalyst ⇑ or ⇓ Rate of Rxn.
* Use in Small amount.
* specific in action.
* donot change the A.E
* change mechanism of Rxn.
* not change enthalpy of Rxn.
* auto catalyst → produced during Rxn.
  - mostly +ve
  - + product → (act as a catalyst)

Rate of Rxn ⇑ with time