CHEMICAL KINETICS

1. Rate of rxn
2. Order of rxn
3. Molecularity of rxn
4. Method to find order of rxn.
5. Theory related with rate of rxn → collision theory, activation energy theory.
6. Factors affecting rate of rxn
7. Factors affecting rate constant → Temp, Catalyst

- **Rate in chemistry:—**

$$\text{Rate} = \frac{\text{change in concentration/pressure}}{\text{change in time.}}$$

unit → mol L^{-1} $time^{-1}$.

atm $time^{-1}$.

e.g.-- $A \longrightarrow B$

$t=0$ a 0

$t=t$(sec) conc. $a-y$ (dissociate conc.) $\frac{1}{1} \times y = y$ (conc.)

- Rate of disappearance of A $= -\frac{\Delta(A)}{\Delta t}$ or $\frac{-d(A)}{dt}$

$= \frac{a-(a-y)}{t-0}$

$= \frac{y}{t}$ M/s. (Molarity/sec.)

Rate of appearance of B $= +\frac{\Delta(B)}{\Delta t}$ or $\frac{d(B)}{dt}$

$= \frac{y-0}{t-0} = y/t$ M/s.

Q. $2A \longrightarrow B$

$t=0$ a 0

$t=t$(sec) $a-y$ $\frac{1}{2} \times y = y/2$

- Rate of disappearence of A $= -\frac{\Delta(A)}{\Delta t}$

$= \frac{a-(a-y)}{t-0}$

$= y/t$.

- Rate of appearence of B $= +\frac{\Delta(B)}{\Delta t} = \frac{y/2}{t} = \frac{y}{2t}$.

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Q. $2A \longrightarrow 3B$

$t=0$ a 0

$t=t_{sec}$ $(a-y)$ $\frac{y \times 3}{2}$

Rate of disappearence of $A = \frac{-\Delta A}{\Delta t} = \frac{a-(a-y)}{t}$

$= y/t$

rate of appearence of $B = +\frac{\Delta B}{\Delta t} = \frac{3/2\, y}{t} = \frac{3y}{2t}$.

Q. $2A \longrightarrow 3B + 4C$

$t=0$ a 0 0

$t=t_{sec}$ $a-y$ $\frac{3}{2} \times y$ $\frac{4}{2} \times y = 2y$

Rate of disappearence of $A = -\frac{\Delta A}{\Delta t} = \frac{a-(a-y)}{t}$

$= y/t$

Rate of formation of $C = \frac{2y}{t}$.

Rate of formation of $B = \frac{3y}{2t}$

Q. $3Z \longrightarrow 2P + 5Y$

$t=0$ a 0 0

$t=t_{sec}$ $a-2y$ $\frac{2y \times 2}{3}$ $\frac{2y \times 5}{3}$

Rate of disap. of $Z = -\frac{\Delta A}{\Delta t} = \frac{a-(a-2y)}{t}$

$= \frac{2y}{t}$.

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Rate of disappearance of $P = \frac{4y}{3t}$

rate of appearance of $y = \frac{10y}{3t}$

Q. $2A \longrightarrow 3B$

	a	0
t=0		
t=tsec	$2x$ $(a-y)$	$\frac{y \times 3}{2}$

rate of disappearence of $A = \frac{y}{t}$ mol L^{-1} sec^{-1}.

$\rightarrow$ So,

$$\frac{-\Delta A}{\Delta t} = \frac{y}{t}$$

$$\frac{a-(x)}{t} = \frac{y}{t}$$

$x = a-y$

$a - x = y$

$\therefore$ rate of formation of $B = \frac{3y}{2t}$

Rate Relate

Condition : ① Rxn must be balanced.

② Unit of rate not in terms of gram-mole.

Q. $2A \longrightarrow 3B$.

$$\frac{\text{Rate of Dis. of A}}{2} = \frac{\text{Rate of B formation of B}}{3}$$

$$\frac{-\Delta A/\Delta t}{2} = \frac{\Delta B/\Delta t}{3}$$

Q. $aA + bB \longrightarrow cC + dD$

$$\text{Rate of rxn} \Rightarrow \left(\frac{-\Delta A/\Delta t}{a}\right) = \left(\frac{-\Delta B/\Delta t}{b}\right) = \frac{+\Delta C/\Delta t}{c} = \frac{+\Delta D/\Delta t}{d}$$

rate of A, rate of B, rate of C, rate of D

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Q. $2A \longrightarrow 3B + C$. No. of moles of B increased by 6×10^{-3} mole in 10 sec in 10 L container. Find Rate of disap of A & Rate of rxn.

→

$2A \longrightarrow 3B + C$.

rate of formation of B $= \dfrac{+\Delta(B)}{\Delta t}$

$= \dfrac{\frac{6 \times 10^{-3}}{10}}{10}$ (mole, conc, volume, time) $= 6 \times 10^{-5}$ Mol/Ls.

$RoR = \dfrac{\frac{\Delta(B)}{\Delta t}}{3} = \dfrac{6 \times 10^{-5}}{3} = 2 \times 10^{-5}$ mole

$RoR = \dfrac{\frac{-\Delta(A)}{\Delta t}}{2}$

$2 \times 2 \times 10^{-5} = \dfrac{-\Delta A}{\Delta t}$ $\therefore \boxed{\dfrac{-\Delta A}{\Delta t} = 4 \times 10^{-5}}$

Q. $2N_2O_5 \longrightarrow 4NO_2 + O_2$. Initial concentration of N_2O_5 is 7.2 mol/L and after 20 min $[NO_2]$ is 2.4 mol L^{-1}. Then what will be ROD of N_2O_5 in M min^{-1}?

(a) 0.06 (b) 0.03 (c) 1.3 (d) 2.4.

$2N_2O_5 \longrightarrow 4NO_2 + O_2$

t=0 7.2 0 0

t=20, 2.4

$7.2 - \frac{2.4}{2}$

$= 6$.

Rate of Dis. of $N_2O_5 = \dfrac{-\Delta N_2O_5}{\Delta t}$

$= \dfrac{7.2 - 6}{20 - 0}$

$= \dfrac{1.2}{20}$

$= 0.06$ M/min.

rate of formation of $NO_2 = \dfrac{2.4 - 0}{20 - 0}$

$= 12 \times 10^{-2}$.

rate of rxn $= \dfrac{12 \times 10^{-2}}{} = 3 \times 10^{-2}$.

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Q. $2A + 3B \longrightarrow 4C + 5D$. Rate of disap. of B is 0.06 mol/L min.
Then find out :-

(a) Rate of rxn.

$$r = \frac{-\frac{d[B]}{dt}}{3} = \frac{0.06}{3} = 0.02$$

(rate of disp. / coeff of B)

(b) ROR of A.

$$ROR = \frac{ROD \text{ of } A}{2}$$

$$0.02 = \frac{ROD \text{ of } A}{2}$$

$$\therefore ROD \text{ of } A = 0.04.$$

(c) Rate of formation of C

$$ROR = \frac{ROF \text{ of } C}{4}$$

$$4 \times 0.02 = ROF \text{ of } C$$

$$\therefore ROF \text{ of } C = 0.08.$$

(d) Rate of Formation of D.

$$ROF \text{ of } D = ROR \times 5$$
$$= 0.02 \times 5$$
$$= 0.1.$$

Q. $2NO_2 \longrightarrow 2NO + O_2$. Rate of formation of NO is 6gm/min. Calculate ROD of NO_2 in gm/min.

→ $2NO_2 \longrightarrow 2NO + O_2$

ROF of NO = $\frac{6}{30}$ mol/min

$$ROR = \frac{ROF \text{ of } NO_2}{2} = \frac{6}{30} = \frac{6}{30} = \frac{1}{5}$$

$$ROR = \frac{ROD \text{ of } NO_2}{2} \quad \therefore ROD \text{ of } NO_2 = \frac{1}{5} \text{ mol/min}$$
$$= \frac{1}{5} \times 46 \text{ gm/min}$$
$$= 9.2 \text{ gm/min}.$$

Q. $aA + bB \longrightarrow cC$. If $-\frac{dA}{dt} = 2\left(\frac{dB}{dt}\right) = 1.5 \times \frac{dC}{dt}$

Then a : b : c.

(a) 3 : 2 : 1 (b) 6 : 3 : 1 (c) 6 : 3 : 4 (d) 1 : 4 : 3

$a = \frac{1}{2}$, $b = \frac{1}{2}$, $c = \frac{1}{1.5}$

$a : b : c = 6 : 3 : 4$.

→ $\frac{\frac{1}{2}\frac{dB}{dt}}{a} = \frac{\frac{dB}{dt}}{b} = \frac{\frac{dB}{dt} \times \frac{1.5}{2}}{c}$

$\frac{1}{2a} = \frac{1}{b} = \frac{3}{4c}$ ⇒ $a : b : c = 6 : 3 : 4$.

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Q. $\frac{5}{4}A + \frac{3}{2}B \longrightarrow \frac{10}{7}D$.

$$ROR = \frac{4}{5} \times \frac{dA}{dt} = \frac{2}{3} \times -\frac{dB}{dt} = \frac{7}{10} \times \frac{d(D)}{dt}.$$

Q. $3A + B \longrightarrow 4C + D$, rate of rxn is 0.3 mole/L sec. Find out:—
(a) rate of disappearence of B.

$$ROR = \frac{ROD \text{ of } B}{1}$$

$$0.3 = ROD \text{ of } B.$$

(b) Rate of appearence of C.

$$ROR = \frac{ROA \text{ of } C}{4}$$

$$4 \times 0.3 = ROA \text{ of } C$$

$$\therefore ROA \text{ of } C = 1.2 \text{ M/s}$$

Q. In haber's process of formation of NH_3, conc. of NH_3 increases from 0.5 M to 1M in 5 min. Calculate:
(a) ROF of NH_3. (b) ROD of N_2.

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

Sol

(a) $ROF \text{ of } NH_3 = \frac{1 - 0.5}{5 - 0} = \frac{0.5}{5}$

$= 0.1$ M/min.

(b) $ROD \text{ of } N_2 = \frac{0.5}{5} = 0.1$ M/min

$$= \frac{ROF \text{ of } NH_3}{2}$$

$$= \frac{0.1}{2} = 0.05 \text{ M/min}.$$

(c) $ROR = \frac{ROF \text{ of } NH_3}{2} = \frac{0.1}{2} = 0.05.$

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Q. $\frac{1}{2}A + \frac{2}{5}B \longrightarrow \frac{1}{4}C + \frac{4}{5}D$. if ROF of D is 4 atm/sec. Then find out :-

(a) ROR.

Sol^n

$$ROR = 2 \times \frac{-d(A)}{dt} = \frac{5}{2} \times \frac{-d(B)}{dt} = +4 \times \frac{d(C)}{dt} = \frac{5}{4} \times \frac{d(D)}{dt}.$$

$$ROR = \frac{5}{4} \times 4$$

$$\therefore \boxed{ROR = 5 \text{ atm/sec}}$$

ROF of C → ~~ROR~~

$$ROR = 4 \times \frac{d(C)}{dt}$$

$$\therefore \frac{d(C)}{dt} = \frac{5}{4} = 1.25.$$

Q. $2CO_{(g)} + O_{2(g)} \longrightarrow 2CO_{2(g)}$ – In this rxn, 1.6 gm/Lit O_2 disappear in 10sec. Find rate of appearence of CO_2 in (gm/Lit/sec).

(balance the eq.)

→ $2CO_2 + O_2 \longrightarrow 2CO_2$.

Mole of $O_2 = \frac{1.6}{32} =$

ROD of $O_2 = \frac{1.6}{32} \times \frac{1}{10} = 5 \times 10^{-3}$ mole/Lit/sec.

~~ROF of CO_2~~ $= \frac{\text{ROF of } CO_2}{2} = \text{ROD of } O_2$

$\therefore$ ROF of $CO_2 = 2 \times 5 \times 10^{-3}$

$= 10 \times 10^{-3}$ mole/Lit/sec.

$= 10^{-2}$

for gm/Lit/s. $= 10^{-2} \times 44$

Q. $2A \longrightarrow 3B$. Initial conc of A is 10 mol/lit. After 10min total conc. of mixture is 12 mol/lit. Then find out ROR at this time.

(a) 0.8 (b) 0.4 (c) 0.2 (d) 0.1

Sol.

	$2A$	$\longrightarrow$	$3B$
$t=0$	10		0
$t=10$min	$10-2x$		$3x$

$$10-2x+3x = 12$$

$$x = 2.$$

$$\frac{-2x+3x}{2} = 2$$

$$x = 4.$$

$$\text{ROD of A} = \frac{10-(10-2\times 2)}{10}$$

$$= \frac{4}{10} = 0.4$$

$$\text{ROF of B} = \frac{3\times 2}{10}$$

$$= \frac{6}{10}$$

$$= 0.6.$$

$$\therefore \text{ROR} = \frac{0.4}{2} = 0.2.$$

$$\text{ROR} = \frac{0.6}{3} = 0.2$$

Q. $2A \longrightarrow B + 3C$. Initial concentration of A is 10mol/Lt. After 10 min 4 mol/lit of reactant A remaining. Then find ROR.

$\rightarrow$

	$2A$	$\longrightarrow$	B	$+$	$3C$
$t=0$	10		0		0
$t=10$,	$10-6$ $=4$.		$\frac{6\times 1}{2}$ $=3$		$\frac{3\times 3}{2}$ $=9$.

$$\text{ROD of A} = \frac{10-4}{10}$$

$$= \frac{6}{10}$$

$$= 0.6.$$

$$\therefore \text{ROF of B} = \frac{3}{10} = 0.3.$$

$$\therefore \text{ROR} = \frac{0.3}{1} = 0.3.$$

$$\therefore \text{ROR} = \frac{0.6}{2}$$

Q. $2N_2O_5 \longrightarrow 4NO_2 + O_2$. Initial 1 mole of N_2O_5 were heated in a 100 mL vessel. After 10 min 2.24 litre of O_2 obtained at NTP. Find ROR

(0.1 mole)

→

	$2N_2O_5$	$\longrightarrow$	$4NO_2$	$+O_2$
$t=0$,	1		0	0
$t=10$ min	$1-2x$		$4x$	x (0.1 mole)

$$ROR = \frac{0.1-0}{10 \times \left(\frac{100}{mL}\right)} \times \left(\frac{1000\ mL}{L}\right)$$

$$= 0.1\ mol\ (Lit\ min.$$

Q. $2H_2O_2 \longrightarrow 2H_2O + O_2$. Initial 1.7g of H_2O_2 were heated in a 100 mL vessel. If after 10 min 3.4g H_2O_2 remain. Then find ROR.

$\frac{3.4}{34} = 0.1$ mole.

Mole of $H_2O_2 = \frac{17}{34} = 0.5$ mole.

$= \frac{1}{10}$

~~ROR = 0.1~~

	$2H_2O_2$	$\longrightarrow$	$2H_2O$	$+O_2$
$t=0$,	0.5		0	0
$t=10$ min.	$0.5-2x$ (0.1)		$2x$	x.

$\therefore 0.5 - 2x = 0.1$

$\therefore x = 0.2$.

$$\therefore ROR = \frac{0.5(0.5-2\times0.2)}{2 \times 100 \times 10} \times 1000$$

$$= \frac{(0.5-0.1)\times10}{2}$$

$$= \frac{0.4}{2} = 0.2.$$

ROD of H_2O_2 = 0.4

Q. $2SO_3 \rightarrow 2SO_2 + O_2$. Initial 80g SO_3 were heated in 100mL vessel. Then after 10min total 1.25 mol of mix is obtained?

(a) 1.25 mol/lit min (b) 0.25 mol/lit min

(c) 2.5 mol/lit min (d) 0.125 mol/lit min

SO_3 mole $= \frac{80}{80}$

$= 1$ mole.

	$2SO_3$	$\rightarrow$ $2SO_2$	$+ O_2$
$t=0$,	1	0	0
$t=10$ min	$1-2x$	$2x$	x

$\because 1-2x+2x+x = 1.25$

$\therefore x = 0.25.$

$\because 2x = 2 \times 0.25$

$= 0.5.$

Rate of for of $O_2 = \frac{0.25}{10 \times 100} \times 1000$

time vol.

$= 0.25.$

Rate of Rxn $= \frac{0.25}{1} = 0.25$

Rate law:-

Law of mass action:- Theoretical law.

↳ rate को expression

$2A + B \rightleftharpoons C.$

$r = K[A]^2[B]^2.$

rate of rxn. — rate const. or vel. const. or sp. rate. — conc of reactivity sps.

$\boxed{r = P_A^2 P_B^2}$

↳ for gaseous only.

→ $2A + B \rightleftharpoons 3C.$

rate $= [A]^p [B]^q$

Rate law → experimental law.

$2A + B \longrightarrow 3C$.

- We can't write rate expression of any rxn by just using stiochiometric coefficient because power of conc./pressure of reacting species depend on experimental result.

$r = K[A]^p[B]^q$ → rate law

p & q can be +ve, -ve, fraction or zero.

→ All reversible reactions are elementary.

Q. For rxn: $A + 2B \longrightarrow 3C$.

Rate expr of rxn is:-

(a) $r = K[A]^1[B]^2$ → for elementary ≈ reversible (b) $r = K[A][B]$

(c) $r = K[A]^0[B]^2$ (d) ~~cannot predict~~.

Q. For a elementary rxn, rate expression of

$A + 2B \longrightarrow 3C$.

(a) $r = K[A][B]^2$ (b) $r = K[A][B]$ (c) can't predict

Q. For a rxn, $A + 2B \longrightarrow 3C$. Rate expression is:-

(a) $r = K[A][B]^2$ (b) $r = K[A][\theta]$

(c) $r = K[A]^0[B]^2$ (d) $r = K[A]^2[B]^2$.

Q. for a rxn, $A + 2B \longrightarrow 3C$. $r = K[A]^1[B]^2$. Which of the following is correct.

(a) Rxn is complex (b) LOMA (law of mass action) is not valid.

(c) Rxn is elementary (d) Rxn occurs in multiple step.

Meaning of rate expression:-

(1) Dependency of Rate of rxn / rate of disappearence / rate of appearence conc or Pressure of reacting species.

eg.: $2A + B \longrightarrow 3C$. , $r = K[A][B]^2$.

ROR | ROD | ROD → all.

- If conc. of A double → ROR = double.
- If conc of B double → ROR → 4 times.
- If conc. of A & B double → 8 times.

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Q. $2A + 3B \longrightarrow 4C$. $r = K[A][B]^2$. If conc. of B double. rate of rxn → 4 times.

RoD of A → 4 times.

RoD of B → 4 times.

RoA of C → 4 times.

Q. $2A + B \longrightarrow 3C$. $r = K[A]^1[B]^1$. If volume of container becomes half by ↑ing pressure on piston. Rate of rxn = ?

→ volume half then conc. will double.
└A & B दुवैको

∴ RoR = 2 × 2 = 4 times.

Q. $2x + 3y \longrightarrow 4z$.

rate law →

$r = K(x)^p(y)^q$.

for elementary. $r = K(x)^2(y)^3$.

for rate law, $r = K(x)^3(y)^5$.

जति नि हुन्
पर्यो -

Q. Rate of formation of O_2 is $3.2\,g\,L^{-1}sec^{-1}$. write RoF of O_2 in $kg\,ml^{-1}\,hr^{-1}$.

→ O_2 of RoF = $3.2\,g\,L^{-1}sec^{-1}$

$$= \frac{3.2}{1 \times 1} = \frac{3.2 \times \frac{1}{1000} \times 60 \times 60}{1000 \times \cancel{60 \times 60}}$$

$$= \cancel{\frac{3.2}{3600}} \quad \frac{3.2 \times 3600}{1000 \times 1000}\ kg\,ml^{-1}hr^{-1}$$

=

Q. ROF of NH_3 is 1.7 g l^{-1} min^{-1} at 27°C. Write ROF of NH_3 in atm min^{-1}.

Sol:

ROF of NH_3 = $\frac{1.7}{17}$ mol l^{-1} min^{-1}.

(Conc)

$\because PV = nRT$

$P = \frac{n}{V}RT$.

$P = CRT$

(C = Conc)

$\therefore P = \frac{1.7}{17} \times 0.0821 \times 300$ min^{-1}

atm.

$= 0.0821 L \times 30$ atm / min.

- **Rate law:-**

$aA + bB \longrightarrow cC + dD$

$\text{Rate} \propto [A]^p [B]^q$

order w.r.t A = p

order w.r.t B = q.

overall order = p+q.

$2A + B \longrightarrow 2C$.

$\text{rate} = K[A][B]^2$.

order w.r.t A = 1

order w.r.t B = 2.

overall order = 3.

- **unit of K =**

$r = K[\ ]^n$

$A \longrightarrow B$

$\text{rate} = K[A]^n$ (n = order of rxn)

$K = \frac{\text{rate}}{[A]^n} = \frac{\text{mol } l^{-1} \text{ time}^{-1}}{(\text{mol } l^{-1})^n}$

$K = (\text{mol } l^{-1})^{1-n} \text{ time}^{-1}$

$\therefore K = (\text{mol } L^{-1})^{1-n} \text{ time}^{-1}$

n = order of rxn

$K = (\text{atm})^{1-n} \text{ time}^{-1}$.

for n=0 (zero order)

$K = \text{mol } L^{-1} \text{ time}^{-1}$.

for n=1 (first order)

$K = s^{-1}$.

For n=2, (2nd order).

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

If unit of K is given, & order = ?

order = L-power of mol.

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Q. For 1st order rxn, the unit of rate is :- (rate = equal for all.)

(a) mol $L^{-1}sec^{-1}$ (b) sec^{-1} : rate constant.

(c) mol^{-1} lit sec^{-1} (d) mol^{-1} lit^{-1} sec^{-1}

Q. $2A + B \rightarrow 3C$. $r = \frac{K[A]}{[B]^{1/2}}$. Find the unit of rate constant.

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

order of rxn = $1 + (-1/2) = 1/2$.

Unit of K = $(mol\ l^{-1})^{1-1/2}\ sec^{-1}$.

= $mol^{1/2}\ lit^{-1/2}\ sec^{-1}$.

Q. For reaction, $2A + B \rightarrow 3C$. $r = K[A]^2[B]^0$. Which is correct?

(a) If conc of A is doubled then rate of disappearence of A becomes 8 times.

(b) If conc. of B is doubled, then rate of disap. of A becomes four times.

(c) If conc. of A & B both doubled then rate of app. of C becomes 4 times. ($2^2 = 4$, C^0)

Q. For a rxn :- $2P + 3Q \rightarrow 4R$.

$r = K[P]^2[Q]^1$. Which is incorrect?

(a) rate of ap. of R is twice of rate of disp. of P — Right.

$\frac{\text{rate of disp of P}}{2} = \frac{\text{rate of ap of R}}{4}$

(b)

(c) Order of over all rxn is greater than 2.

(d) Unit of rate constant is $mol^{-2}\ lit^2\ sec^{-1}$. ($n = 1+2 = 3$; $K = (mol\ l^{-1})^2\ sec^{-1}$.)

(d) If conc. of P double then rate of ap. of R becomes 16 times. → 4 times.

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How to write rate expression if experimental details are given:—

Type-I:- experimental detial given in theory format.

e.g. for Rxn, $2A + B \longrightarrow 3C$. If conc. of A double then rate also doubled but if conc of A & B both doubles then rate becames 4 times. Find rate law.

Sol. $r = K[A]^p[B]^q$.

$\therefore (p+q) \times 2 = 4$

$p = 1$. $\quad \therefore q = 1$.

$\therefore \boxed{r = K[A][B]}$ $\quad$ order = 1+1 = 2

Type-2 :- Experimental detail given in table format.

e.g. $2A + B \longrightarrow 3C$. Find rate law.

expt.	[A]	[B]	Rate.
1.	0.01	0.02	2×10^{-2}
	×2	same.	rate ×2.
2.	0.02	0.02	4×10^{-2}
	×2	not depend.	rate ×2.
3.	0.04	0.08	8×10^{-2}.

$\text{rate} = K[A]^p[B]^q$.

$\therefore p = 1$. (rate double when [A] double.)

$\therefore q = 0$.

$\therefore \boxed{\text{rate} = K[A]^1[B]^0}$

Q. $2A + B \longrightarrow 3C$

expt.	[A]	[B]	Rate
1.	0.1	0.2	2×10^{-3}
	same	×2	rate ×2.
2.	0.1	0.4	4×10^{-3}
	×2	×2	↑ ½
3.	0.2	0.8	2×10^{-3}.

$r = K[A]^p[B]^q$

$\therefore q = 1$. (rate double, when [B] double.)

$\therefore \left(\frac{1}{2}\right)_{\text{rate}} = \left(\frac{2}{2}\right)^p_A \left(\frac{2}{2}\right)^q_B$.

$\therefore 2^p = 1$

Q.

expt.	[A]	[B]	Rate
1.	0.012	0.035	0.1
2.	0.024	0.070	1.6
3.	0.024	0.035	0.2
4.	0.012	0.07	0.8

×2 same ×2 ×8 ×2.

$r = K[A]^p[B]^q$

$\therefore p = 1.$ from ① & ③.

$\because q = 3.$ B double conc 8 times. from ② & ③

$\therefore 2^3 = 8.$

$\therefore q = 3.$

$\therefore \boxed{r = K[A]^1[B]^3}$

Q. ~~expt.~~ $x + 3y \longrightarrow xy_3$.

x	y	rate
0.1	0.1	0.002
0.2	0.1	0.002
0.3	0.2	0.008
0.4	0.3	0.018

×2 ×1. ×1 ×2 ×4.

ⓐ $r = K(x)(y)^3$ ⓑ $r = K(x)(y)$ ~~ⓒ~~ $r = K(x)^0(y)^2$

ⓓ $r = K(x)^0(y)^3$.

$\therefore p = 0.$

x^0 – dont dep. on con. of x.

y^2 $\because q = 2$ (y को dou हुआ rate ×4).

so, $2^2 = 4$.

Q.

expt	[A]	[B]	Rate
1.	0.05	0.05	0.0012
2.	0.1	0.05	0.0024
3.	0.05	0.10	0.0012

(a) 1, 0 (b) 1, 1 (c) 0, 1 (d) None

$r = K[A]^p[B]^q$.

$\therefore p = 1$. (A due rate d). B को rate ×2 if conc same (1 & 3)

so, $q = 0$.

Q. $2A + B \longrightarrow C + D$.

expt	[A]	[B]	Rate
1.	0.1	0.1	0.0075
2.	0.3	0.2	0.09
3.	0.3	0.4	0.36
4.	0.4	0.1	0.09

$\therefore q = 2$. (from 2 & 3).

$\therefore p = 1$. (from 1 & 4).

Q. $2A + B \longrightarrow C$. Write rate law if conc of A is doubled then rate of rxn becomes 4 times. But if conc. of A & B both doubled then rate of rxn becomes 2 times.

→ $r = K[A]^x[B]^y$.

$\boxed{x = 2.}$

$\because$ ~~x+y=2~~ $2^2 \times 2^y = 2$

$\frac{1}{2} = 2^y$

$\therefore \boxed{y = -1.}$

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Q. In rxn. $P + 2Q + R \longrightarrow$ product. when conc. of P & Q doubled then ROR = 4 times. When conc. of Q ↑ by 1.5 times then ROR becomes 2.25 times. When conc of both Q & R doubled rate doubled.

$$r = K[P]^x [Q]^y [R]^z$$

→

Q. $2P + Q \longrightarrow 3R$.

exp.	[P]	[Q]	ROD of P
1.	0.1	0.2	3×10^{-2}
2.	0.3	0.2	9×10^{-2}
3.	0.6	0.4	360×10^{-3}

① Rate law ② Order of rxn ③ unit of rate cont

④ value of rate constant ⑤ find ROR of R in expt 2.

→

Zero order reaction

→ $A \longrightarrow B$

$r = K[A]^0 = K.$

→ zero order is always complex.

$\boxed{r = K}$

→ rate will be constant throughout the rxn.

→ for zero order rxn, rate of rxn doesnot depend on the concentration of reactant.

Integrated rate equation

$A_0 = a$ = initial conc of reactant.

$A_t = a - x$ = conc. of reactant remain after time 't'.

$A_0 - A_t = x$ = decomposed conc. of reactant in time 't'.

$\frac{x}{a}$ → fraction decomposed in time 't'.

$\frac{a-x}{a}$ → fraction remain after time 't'.

$A \longrightarrow B$

$t=0$, $[A_0] = a$. 0

$t = t_1$ $a - x$

A_t

$r = K[A]^0$

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

$$\int_{A_0}^{A_t} -d[A] = K\int_0^t dt$$

$$\boxed{K = \frac{A_0 - A_t}{t} = \frac{x}{t}}$$

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• Half Life:- 50% decompose.

$x = a/2$

$K = \frac{x}{t}$

$x = Kt_{1/2}$

$\therefore \frac{a}{2} = Kt_{1/2}$

$\boxed{t_{1/2} = \frac{a}{2K}}$

• 20% decompose → $x = a/5$

→ For zero order rxn, unit and volue of rate constant and rate of rxn will same.

→

$t_{100\%} \rightarrow x = a.$

$\therefore K = \frac{x}{t} = \frac{a}{t}$

$\therefore \boxed{t_{100\%} = \frac{a}{K}}$

$\boxed{t_{50\%} = \frac{t_{100\%}}{2}}$

$\boxed{x = Kt \quad A_0 - A_t = Kt \quad K = \frac{A_0 - A_t}{t}}$

Q. Initial 10^{-2} mole of an acid are present in 100ml solution. Then for the ionisation rxn of an acid rate constant 10^{-2} mole lit^{-1} sec^{-1} Then calculate $t_{1/4}$ for the ionisation rxn of acid.

(a) 3.5×10^{-4} (b) 1.5×10^{-4}

(c) 4.1×10^{-4} (d) 2.5×10^{-4}.

→ ~~$A_0 = 10^{-2}$~~ $a = M = \frac{10^{-2}}{100} \times 1000 = 0.1$ mol/lit.

$x = Kt$

$x = a/4$, for $t_{1/4}$.

$\therefore x = \frac{a}{4}$

$\boxed{a = A_0}$

$t_{1/4} = \frac{x}{K} = \frac{a/4}{K} = \frac{0.1}{4 \times 10^8}$

$= 2.5 \times 10^{-4}$.

Q. Rate const for zero order rxn is :- 3×10^{-2} mol L^{-1} sec^{-1}. If after 25 sec conc. of reactant is 0.5 M (A_t). Find out initial conc of reactant.

$\rightarrow x = Kt$

$= 3 \times 10^{-2} \times 25$

$\therefore x = 75 \times 10^{-2}$

$= 0.75$.

$\because a - x = 0.5$

$a = 0.5 + 0.75$

$\boxed{A_0 = a = 1.25 \text{ Ans}}$.

Q. 3.4 g NH_3 heated in a 100 mL vessel. for dissociation of NH_3 rate constant is 10^{-2} mol L^{-1} sec^{-1}. Calculate $t_{40\%}$.

Sol

$a = M = \frac{3.4}{17 \times 100} \times 1000$

$a = A_0 = M = 2$.

$t_{40\%} = \frac{x}{K}$

$\boxed{x = 0.4a}$

$= \frac{0.4 \times 2}{10^{-2}} = 80$.

Q. Volume of 1 drop diluted solution is 0.05 mL. In this solution 3×10^{-6} mole H^+ ion present. If rate constant for disap. rxn of H^+ ion is 10^7 mol L^{-1} sec^{-1}. Then find time required for complete disappearence of H^+.

$\longrightarrow x = a$.

$a = M = \frac{3 \times 10^{-6}}{0.05} \times 1000$

$= 0.06$.

$t = \frac{x}{K}$

$= \frac{a}{K} = \frac{0.06}{10^7} = 6 \times 10^{-9}$.

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Relation between 2 different time interval for same reaction (K same)

$t_{60\%}$ | $t_{80\%}$

$$t_{60\%} = \frac{x}{K} = \frac{0.6a}{K} \quad -(I)$$

$$t_{80\%} = \frac{x}{K} = \frac{0.8a}{K} \quad -(II)$$

$$\therefore \frac{t_{80\%}}{t_{60\%}} = \frac{0.6a}{K} \times \frac{K}{0.8a} = \frac{6}{8}$$

$$\therefore \boxed{t_{60\%} = \frac{6}{8} \times t_{80\%}}$$

Trick

$$\frac{t_{60\%}}{t_{80\%}} = \frac{60}{80} = \frac{6}{8}$$

Q. $t_{25\%}$ & $t_{75\%}$

$$\frac{t_{25\%}}{t_{75\%}} = \frac{25}{75} = \frac{1}{3}$$

Q. $t_{3/8}$ & $t_{3/4}$

$$\frac{t_{3/8}}{t_{3/4}} = \frac{3/8}{3/4} = \frac{1}{2}$$

First order rxn

$$A \longrightarrow B$$

$$r = K[A]^1$$

$t=0$	a		0
$t=t_1$	$(a-x)$		x

$$r = K[A]^1$$

$$-\frac{d(A)}{dt} = K(A)^1$$

$$\int_{A_0}^{A_t} \frac{-d(A)}{dt} = -K\int_0^t dt$$

$$K = \frac{1}{t} \ln \frac{A_0}{A_t}$$

$$K = \frac{2.303}{t} \log \frac{[A_0]}{[A_t]} \quad \text{or} \quad A_t = A_0 e^{-Kt}$$

$$K = \frac{2.303}{t} \log \frac{a}{a-x}$$

- Calculation of $t_{50\%}$ or $t_{1/2}$.

$$K = \frac{2.303}{t_{1/2}} \log \frac{a}{a - a/2}$$

$$K = \frac{2.303}{t_{1/2}} \log 2$$

$$t_{1/2} = \frac{2.303 \log 2}{K} \Rightarrow \frac{0.693}{K}$$

General:

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

→ $\frac{t_{80\%}}{t_{60\%}} = ?$

$$t_{80\%} = \frac{2.303}{K} \log \frac{a}{a - 0.8a}$$

$$= \frac{2.303}{K} \log \frac{x}{0.2x} \quad -(1)$$

$$t_{60\%} = \frac{2.303}{K} \log \frac{x}{0.4x} \quad -(2)$$

$$\therefore \frac{t_{80\%}}{t_{60\%}} = \frac{\log \frac{1}{0.2}}{\log \frac{1}{0.4}} = \frac{\log \frac{100}{20}}{\log \frac{100}{40}}$$

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Q. $t_{7/8}$ & $t_{15/16}$.

$7/8 = (1 - 7/8)$

$$\frac{t_{7/8}}{t_{15/16}} = \frac{\log \frac{1}{1/8}}{\log \frac{1}{1/16}}$$

$$= \frac{\log 8}{\log 16} \quad \text{Ans}$$

Q. $t_{99\%}$ & $t_{90\%}$.

$$\frac{t_{99\%}}{t_{90\%}} = \frac{\log \frac{100}{1}}{\log \frac{100}{10}} = \frac{2}{1} = 2.$$

Q. $t_{99.9\%}$ & $t_{90\%}$

$$\frac{t_{99.9\%}}{t_{90\%}} = \frac{3}{1} = 3.$$

Q. $t_{99.9\%}$ & $t_{99\%}$.

↳ 3/2.

Q. $t_{99.99\%}$ & $t_{99\%}$.

$$\frac{t_{99.99\%}}{t_{99\%}} = \frac{4}{2} = 2.$$

Q. A 1st order rxn complete 99% in 32 min. In what time the rxn will complete?

(a) 32 (b) 48 (c) 80 (d) 64.

→ $t = \frac{2.303}{K} \log \frac{a}{a-x}$

$$99\% = 32 = \frac{2.303}{K} \log \frac{100}{1} \quad -(1)$$

$$99.99\% = t = \frac{2.303}{K} \log \frac{100}{} \quad -(2)$$

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$$\therefore \frac{32}{t} = \frac{\log 100}{\log 10000} = \frac{2}{4}$$

$$t = \frac{32 \times 4}{2} = 64.$$

Q. Rate constant for a rxn 7×10^{-3} sec^{-1}. Calculate $t_{1/2}$.
1st order

→

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

$$= \frac{0.693}{7 \times 10^{-3}} = \frac{0.693 \times 10^{3}}{7}$$

$$= 99.$$

Q. Rate constant for a rxn 10^{-4} sec^{-1}. ~~Calculate $t_{1/2}$~~ Initial log of reactant is heated then in what time it will reduce to 2gm.
a.
(a-x).

→

$$t = \frac{2.303}{K} \log \frac{a}{a-x}$$

$$t = \frac{2.303}{K} \log \frac{10}{2}$$

$$= \frac{2.303}{10^{-4}} \log 5$$

$$= \frac{2.303 \times 0.7}{10^{-4}} = 1.6 \times 10^{4}$$

Q. Rate constant for 1st order rxn is 6×10^{-12} sec^{-1}. Then calculate 2/3rd life period.
drive

$a - x = \frac{a}{3}$
बाकी

Sol

$$t_{2/3} = \frac{2.303}{K} \log \frac{a}{a-x}$$

$$t_{2/3} = \frac{2.303}{K} \log \frac{a}{a/3}$$

$$t_{2/3} = \frac{2.303}{6 \times 10^{-12}} \log 3 = \frac{2.303}{6 \times 10^{-12}} \times 0.48 = 18.4 \times 10^{10}$$

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Q. A radioactive (1st order) substance dissociate 60%. in 20 min. Then in what time 90% dissociate:-

$$\frac{t_{60\%}}{t_{90\%}} = \frac{\log \frac{100}{40}}{\log \frac{100}{10}}$$

$$\frac{20}{t_{90\%}} = \frac{\log \frac{10}{4}}{1}$$

$$\frac{20}{t_{90\%}} = \log 10 - \log 4 \quad (\log 10 = 1,\ \log 4 \to 0.6)$$

$$t_{90\%} = \frac{20}{0.4} = 50 \text{ min.}$$

Q. A radioactive substance dissociate 20%. in 10 min. If initial no. of molecules are 10^{20}. Then in what time no. of molecules will remain 10^{10}.

(a) 150 min (b) 200 min (c) 250 min (d) 400 min.

$$\frac{t_{20\%}}{t_{x\%}} = \frac{\log \frac{100}{80}}{\log \frac{100}{x}}$$

$$K = \frac{2.303}{t=10\text{min}} \log \frac{100}{80}$$

$$= \frac{2.303}{10} \times 0.1$$

$$= 2.303 \times 10^{-2}.$$

$$t = \frac{2.303}{K} \log \frac{10^{20}}{10^{10}}$$

$$t = \frac{2.303}{2.303 \times 10^{-2}} \log 100$$

$$= 100 \log \times 2$$

$$= 200 \text{ min.}$$

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Q. Ratio of half life of two different 2nd order reaction 3:2 then calculate t_1/t_2. Where t_1 is the time period for 50% completion of 1st rxn & t_2 is the time period for 75% completion of 2nd reaction?

(a) 2/3 (b) 4/3 (c) 3/2 (d) 3/4

→ (c)

$$\frac{(t_{1/2})_1}{(t_{1/2})_2} = \frac{3}{2}$$

$$\frac{(t_{1/2})_1}{(t_{1/2})_2} : \frac{k_2}{k_1} = 3/2$$

$$t = \frac{2.303}{k} \log \frac{a}{a-x}$$

$$t_1 = \frac{2.303}{k_1} \log \frac{100}{50} \quad -(1)$$

$$t_2 = \frac{2.303}{k_2} \log \frac{100}{25} \quad -(11)$$

$$\frac{t_1}{t_2} = \frac{k_2}{k_1} \frac{\log 2}{\log 4}$$

$$= \frac{3}{2} \times \frac{0.3}{0.6} 2.$$

$$= \frac{3}{4}.$$

Q. Half life of a 1st order rxn is 120 min, then find out the % remaining quantity of reactant after 480 min.

(a) 5.62%. (b) 6.25%. (c) 7.65%. (d) 4.25%.

$t_{1/2} = 120 \text{ min}$

$\frac{0.693}{k} = 120 \text{ min}$

$k = \frac{0.693}{120}.$

100 —120 min→ 50% —120 min→ 25% —120 min→ 12.5%

120 + 120 + 120 + 120 = 480 min

300 min – 12.5

6.25%.

Q. Elementary rxn $A \rightarrow B + C$, $t_{1/2} = 20 \text{ min}$, then in what time 90% of reactant will dissociate?

(a) 66.6 min (b) 56.25 min (c) 76.5 min (d) 70.6 min

$r = k[A]^2$ $\quad k = \frac{0.693}{20} = \frac{2.303 \log 2}{20}$

$t = \frac{2.303}{2.303 \times \log 2} \times 20 \log \frac{100}{10}$

$\frac{t_{90\%}}{t_{40\%}} = \frac{\log 10}{\log \frac{100}{70}}$

$= \frac{\log 2}{1}$

$= \frac{20}{0.3} \times 1 = 66.6 \text{ min}$

Q. In 1st order rxn, the concentration of the reactant, decreases from 0.8 M to 0.4 M in 15 min. ~~The~~ Time taken for the concentration to change from 0.1 M to 0.025 M is:-

(a) 30 min (b) 15 min (c) 7.5 min (d) 60 min.

$0.8M \xrightarrow[\text{(15 min) half life}]{} 0.4M$

$0.1 \xrightarrow[15 \times 2 \to 30 min]{} 0.025$

Q. The half life period for catalytic decomposition of AB_3 at 50 mm is found to be 4 hrs and at 100 mm it is 2 hrs. The order of reaction is:-

(a) 3 (b) 1 (c) 2 (d) 0

indepen.

directly $\propto$.

conc ↑ – half life ↓ eo.

$t_{1/2} \propto a^{1-n}$

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

$t_{1/2} \propto a^{-1} = \frac{1}{a}$.

Q. If the half life of a reaction ↑es as the initial concentration of substance increases, the order of rxn is:-

(a) zero (b) 1st (c) 2nd (d) 3rd.

$t_{1/2} \propto a^{1-n} \to 0$.

Q. When the concentration of a particular reactant is tripled, the initial rate of rxn ↑es by a factor of nine, what is the order of the reaction with respect to this reactant?

(a) zero (b) one (b) two (c) three

$9 = 3^p$

$\therefore p = 2$.

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Q. For a reaction $A + B \longrightarrow$ product, the rate of the reaction was doubled when the concentration of A alone was reduced to half. Half life of reaction is doubled when concentration of B is reduced to half keeping concentration of A constant. Then order of rxn with respect to A & B are:-

(a) 2, 2 (b) 2, 3 (c) $\frac{1}{2}, \frac{1}{2}$ (d) -1, 2

$2 = \left(\frac{1}{2}\right)^p$

B — conc. decl. rxn half → 2nd order rxn.

$\left(\frac{1}{2}\right)^{-1} = \left(\frac{1}{2}\right)^p \quad \therefore p = -1.$

↳ rate of rxn for A.

Q. Consider the rxn: $2ICl_{(g)} + H_{2(g)} \longrightarrow 2HCl_{(g)} + I_{2(g)}$

At certain temp^r, the rate constant is found to be 1.63×10^{-6} L/mol-s, what is the overall order of rxn?

↳ 2nd order (unit)

(a) zero (b) one (c) two (d) three

Q. In a 1st order rxn, the reacting substance has half life period of ten minutes. What fraction of the substance will be left after an hour the rxn has occured?

↳ 60 min.

(a) $\frac{1}{6}$ of initial concentration

(b) $\frac{1}{64}$ of initial conc.

(c) $\frac{1}{12}$ of initial conc.

(d) $\frac{1}{32}$ of initial conc.

1 $\xrightarrow{10m}$ $\frac{1}{2}$ $\xrightarrow{10m}$ $\frac{1}{4}$ $\xrightarrow{10m}$ $\frac{1}{8}$ $\xrightarrow{10m}$ $\frac{1}{16}$ $\xrightarrow{10m}$ $\frac{1}{32}$ $\xrightarrow{10min}$ $\frac{1}{64}$

$\therefore \frac{A_t}{A_0} = \left(\frac{1}{2}\right)^6$

$= \frac{1}{64}.$

Q. In a zero order reaction, half life is 100sec. After how much time 7/8 fraction of reactant will be reacted?

(a) 300sec. (b) 200sec (c) 175sec. (d) 25 sec.

$\frac{(t_{1/2})}{(t_{7/8})} = \frac{1/2}{7/8} = \frac{1}{2} \times \frac{8}{7}$

$= \frac{4}{7} \times 100$

$t_{7/8} = 175$ sec.

1st order → 300 sec.

Q. For a 1st order rxn :-

$A \longrightarrow B$. The rate of rxn at conc of $A = 0.1\,M$ is 10^{-2} M/min. Then half life of rxn is :-

(a) 0.699 sec (b) 69.3 sec (c) 6.93 sec (d) 415.8 sec.

Sol $r = K[A]^1$

$$K = \frac{10^{-2}}{0.1} = 10^{-1}\ \text{min}^{-1}$$

$$t_{1/2} = \frac{0.693}{K} = \frac{0.693}{10^{-1}} = 6.93\ \text{min}$$

$$= 6.93 \times 60\ \text{sec}$$

$$= 415.8\ \text{sec}$$

Q. For zero order rxn :-

$A \longrightarrow B$. Half life is 20 min. How much time it will take till conc. of reactant remain 2 M from 16 M.

Sol $x = Kt$

$$t = \frac{x}{K} = \frac{16-2}{K} = \frac{14}{K}$$

$\because t_{1/2} = \frac{a}{2K}$

$$K = \frac{a}{2 \times t_{1/2}} = \frac{16}{2 \times 20} = \frac{16}{40}$$

$$t = \frac{14}{\frac{16}{40}} = \frac{14}{1} \times \frac{40}{16}$$

$$= 35\ \text{min}$$

For 1st order

16 → (20 min) 8 → (20 min) 4 → (20 min) 2

$= 60\ \text{min}$.

For zero order

16 → (20 M) 8 → (10 M) 4 → (5 M) 2

Collision theory of chemical rxn

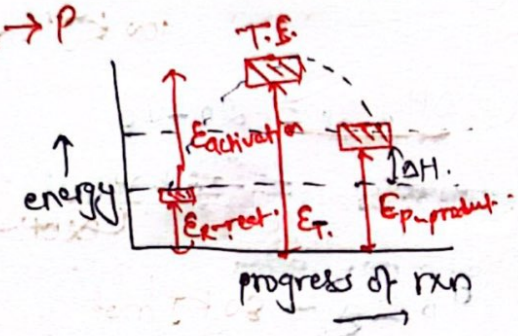
- Trautz and William lewis.
- Based on kinetic theory of gas.
- After collision betw reactant molecules product is formed.
- No. of collision per sec per unit volume – it is called collision frequency
- only a fraction of total collision will convert into product
  ↳ (effective collision)

• condition for effective collision

(i) Sufficient energy
(ii) proper orientation.

Energy – Profile diagram

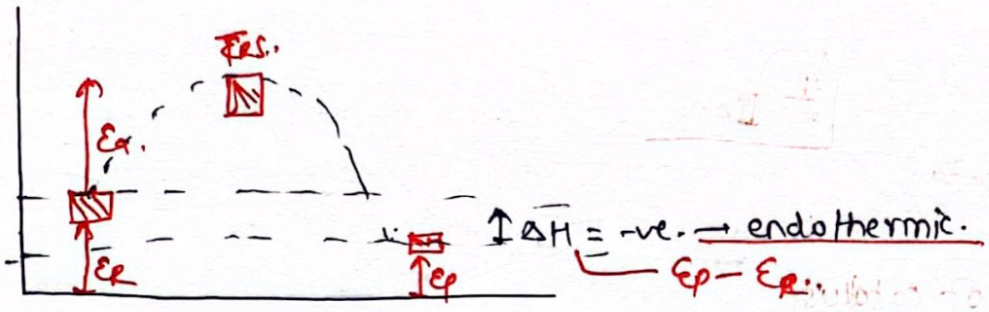
① R → P



E_R → internal energy of reactant
E_P = " " of product
E_a → activation energy or extra amt of energy
E_T → Threshold energy = $E_R + E_a$.

$$\Delta H = E_p - E_R$$
$$= +ve.$$
→ endothermic.

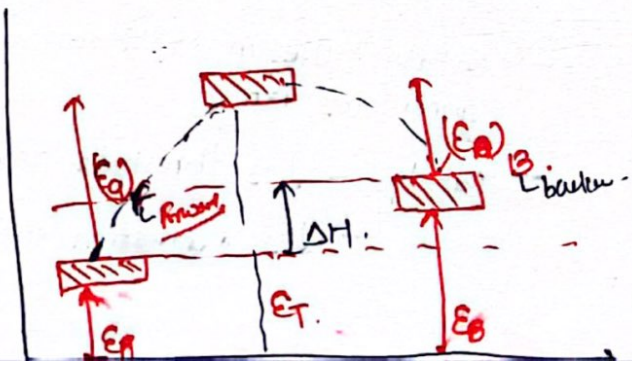
→



ΔH = -ve. → endothermic.
$E_p - E_R$.

→

A ⇌ B



$\Delta H = E_B - E_A$ (A → B).

$\Delta H = E_A - E_B$ (B → A).

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Q. If forword activation energy is 70 kJ/mol. find backward activation energy.

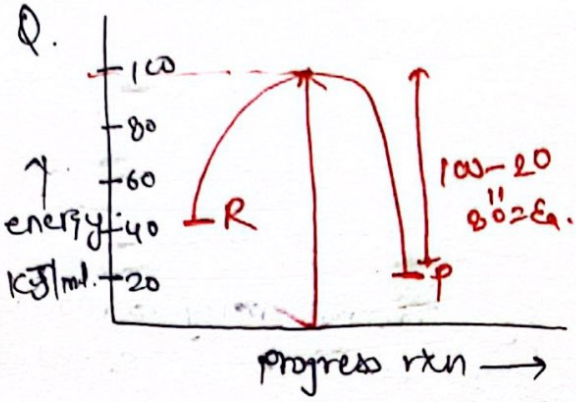
$R \rightarrow P \rightleftharpoons Q$. , $\Delta H = -50$ kJ/mol.

$\rightarrow \Delta H = (E_a)_F - (E_a)_B$

$-50 = 70 - (E_a)_B$

$\therefore (E_a)_B = 120$ kJ/mol.

Q.



Calculate :-

(a) Threshold energy :- 100 KJ/mol.

(b) $\Delta H_{R \rightarrow P} = 20 - 40$

$= -20$ kJ/mol. Exother

(c) $E_a{}_{P \rightarrow R} \rightarrow 80$ kJ/mol

Q. For endothermic rxn :

(a) $E_a > \Delta H$ (b) $E_a < \Delta H$ (c) $E_a = \Delta H$ (d) ΔU.

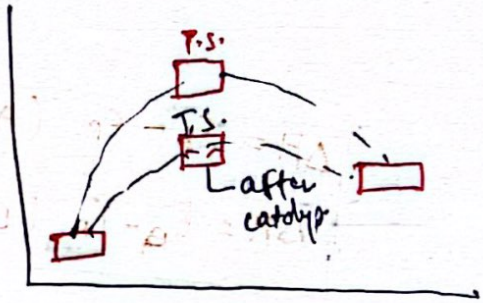


exothermic →



$\Delta H > E_a$.

Effect of catalyst



→ catalyst changes path.

→ Catalyst use in small amt & for spontaneous rxn.

→ Catalyst – les threshold energy
└ les activation energy.

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- catalyst ↓es $(E_a)_f$ & $(E_a)_b$ by equal value.
- catalyst ↑es (K_f) (forward rate constant) & K_b (Backword Rate const) by equal amount

$P \rightarrow Q$, $\Delta H = -50$ → exothermic.

$P \rightarrow Q$, $Q = -50$ → endothermic.

$\Delta H \rightarrow -ve$ — exo.
$Q \rightarrow -ve \rightarrow$ endo

$P \rightarrow Q$, $\Delta H = -50$, $Q = +150$, $x = +50$ } exothermic.

Factors affecting rate of rxn

① Conc. of reactant

$R \propto [A]^n$.

Rate ∝ conc. of reactant.

Note:- For zero order rxn, ROR does not depend on the conc of reactant.

② Effect of surface area of reactant

As surface area ↑es collision freq ↑es then ROR also ↑es.

③ Catalyst

In presence of catalyst a short intermediate path is obtained so that the value of E_a ↓es, so ROR ↑es.

④ Effect of Light radiation

In few rxn, reactant does not have sufficient energy so rxn does not proceed but when these rxns are carried in presence of light, radiation, reactant molecule absorb the radiation & cross the energy barrier hence ROR ↑es.

⑤ Temperature:-

tempr ↑es, ROR ↑es — for both endo & exo,
└ collision freq ↑es, so no of molecules activated ↑es.

⑥ Nature of reactant:-

- In ionic reactant, electrostatic attraction is present so value of activation energy is very low, so ROR is high.
- In covalent compound, energy is reqr to break the d.t bond means activation energy is high, so ROR is low.

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4) Nature of solvent:-

Polar solvent → high rate of rxn.
Non-polar solvent → low rate of rxn.

Factors affecting rate constant

① Catalyst:- Catalyst doesnot take part in rxn. means doesn't show effect on concentration.

$r = K(A)^n$ conc.

$\therefore r \propto K$

→ catalyst show same effect on rate constant as rate of r

② Temperature:-

Arrhenious eqn

$$K = Ae^{-\frac{E_a}{RT}}$$

K = Rate constant
A → Arrhenius parameter
" factor or freq. factor or pre-expotential factor

E_a → Activation energy
T → temp in Kelvin.
R - Gas constant = 8.314 J/mol K = $\frac{8.314}{1000}$ KJ/
= 2 cal / mol K.

$e^{-\frac{E_a}{RT}}$ → fraction of molecules having energy ≥ E_a.
or effective collision.

$\therefore$ T ↑es $\frac{E_a}{RT}$ ↓es but $e^{-\frac{E_a}{RT}}$ ↑es.
unitless.

unit of A = unit of K.

→ Take log on both sides,

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

$$\log K_1 = \log A - \frac{E_a}{2.303RT_1} \quad -(1)$$

$$\log K_2 = \log A - \frac{E_a}{2.303RT_2} \quad -(II)$$

from (I) & (II)

$$\therefore \log \frac{K_1}{K_2} = \frac{E_a}{2.303R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad -(III)$$

$$\log \frac{K_2}{K_1} = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad -(IV)$$

Q. At 550K temp^r, rate constant is 3.5×10^{-7} sec^{-1} and 560 K temp rate constant is 7×10^{-7} sec^{-1} Then find out E_a in KJ/mol.

(a) 177 KJ (b) 197 KJ (c) 167 KJ (d) 187 KJ.

$$\therefore \log \frac{K_1}{K_2} = \frac{E_a}{2.303R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\therefore \log \frac{3.5 \times 10^{-7}}{7 \times 10^{-7}} = \frac{E_a}{2.303 \times 8.314}\left(\frac{1}{560} - \frac{1}{550}\right)$$

$$\therefore \log \frac{1}{2} = E_a \cdot \frac{1}{0.3}$$

$$\therefore E_a = 177 \text{ KJ}.$$

$$\rightarrow \log \frac{(t_{1/2})_1}{(t_{1/2})_2} = \frac{E_a}{2.303}\left(\frac{1}{T_1} - \frac{1}{T_2}\right). \qquad T_{1/2} \propto \frac{1}{K}$$

Q. for the decomposition of hydrocarbon $K = 4.5 \times 10^{11}\ \text{sec}^{-1} \cdot e^{-\frac{2000}{T}}$. find :-

(a) value of orhenious constant :- $K = Ae^{-\frac{E_a}{RT}}$.

↳ $4.5 \times 10^{11}\ \text{sec}^{-1}$

(b) order of rxn :- 1st order. — unit ($\frac{1}{\text{sec}}$)

(c) value of activation energy in Kcal →

$$\frac{E_a}{RT} = \frac{2000}{T}$$

$$\frac{E_a}{R} = 2000 \qquad \therefore E_a = \frac{2000 \times R}{1000} \text{ cal.} = \frac{2000 \times 2}{1000} = 4 \text{ Kcal.}$$

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Temperature coefficient (μ)

When tempr of a rxn ↑es by 10°C then rate of rxn or rate const almost becomes double.

→ let at tempr 'T' rate constant is K_1 & at tempr (T+10) rate constant is K_2 then :-

$$\mu = \frac{K_2}{K_1} = \frac{2}{1}.$$

Q. Calculate rate at tempr 47°C. If rate at 27°C is 2×10^{-3} m

→

27°C → 37°C → 47°C
r 2r 4r.

$4\times2\times10^{-3}$
$= 8\times10^{-3}$ m/sec.

Q. For a rxn, rate of rxn at 10°C is r_1, how many times rate of rxn will change if tempr increases by 60°C.
final tempr 70°C.

→

10 → 20°C → 30 → 40°C → 50°C → 60°C → 70°C.
r_1 2r $4r_1$ $8r_1$ $16r_1$ $32r_1$ $64r_1$

Molecularity of reaction

→ Molecularity always defined for simple and elementary, not defined for complex rxn.

→ It is theoretical concept.

→ Molecularity will always a whole no. (never zero, -ve, fra

→ No. of molecules collide, simultaneously = Molecularity.

Elementary rxn	Molecularity
① $A \rightarrow B$	1
② $2A \rightarrow C$	2
③ $A+B \rightarrow 2D+P$	2
④ $2A+B \rightarrow 4C+Q$	3.

→ for elementary rxn + Rxn balanced in least whole no. ratio.

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- $2A \rightarrow C$
  - ↳ Molecularity - 2

- $A \longrightarrow \frac{C}{2} \times 2$
  - ↳ $2A \longrightarrow C$
    - ↳ Molecularity → 2

- probability of Molecularity > 3 is very less.

- $2A \longrightarrow B$ (Multistep rxn)
  - ↳ can't say Molecularity.

- $A \longrightarrow C$ (Slow) $\boxed{M = 1}$

- $A + B \longrightarrow C$ (fast) $\boxed{M = 2}$

Q. $2P + Q \longrightarrow 3R$,
Molecularity of rxn is:-

(a) 1 (b) 3 (c) 2 ~~(d)~~ Not defined.
↳ can't said that rxn is elementary

if elementary.

$\boxed{r = K(P)^2(Q)}$ (experiment ग्रहण)

Q. $A + 2B \longrightarrow C$.

$r = K(A)(B)^2$.

Molecularity of rxn is:-

(a) 1 ~~(b)~~ 3 (c) 2 (d) not defined

Q. $2P + Q \longrightarrow 4D$. $\boxed{r = K(P)^1(Q)^1}$ rate doesn't matched with rxn. Molecularity of rxn is:-
complex rxn

(a) 1 (b) 2 (c) 3 ~~(d)~~ Not defined.

Q. $2A + \frac{1}{2}B \longrightarrow C$. , elementary rxn.

order → $\left(2 + \frac{1}{2}\right) = \frac{5}{2}$.

Molecularity → $4A + B \longrightarrow 2C$.
↓
5.

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Pseudo 1st order rxn

- order = 1.
- Molecularity > 1.

e.g. Hydrolysis of ester in acidic medium

$$CH_3-\overset{O}{\overset{\|}{C}}-O-C_2H_5 + \underset{(excess)}{H_2O} \xrightarrow{H^+} CH_3COOH + C_2H_5OH.$$

$$rate = \underset{const.}{K}(CH_3COOC_2H_5)\underset{const.}{(H_2O)}$$

Water is in excess, so its conc. remain constant during the rxn.

$$\therefore rate = K(H_2O)(CH_3COOC_2H_5)$$

$K' \rightarrow$ pseudo rate const.

$$\therefore \boxed{rate = K'(CH_3COOC_2H_5)}$$

$$K' = K(H_2O).$$

constant.

Q. $\underset{(excess)}{2A} + B \longrightarrow 3C$ (elementary).

$$r = K(A)^2(B)^1$$

A is in excess

$$\therefore \boxed{r = K'(B)^1}$$

if B is in excess, then

$$r = K'(A)^2.$$

pseudo 2nd order rxn.

Inversion of cane sugar (Hydrolysis)

$$C_{12}H_{22}O_{11} + \underset{(excess)}{H_2O} \xrightarrow{H^+} \underset{glucose}{C_6H_{12}O_6} + \underset{fructose}{C_6H_{12}O_6}.$$

$$rate = \underset{con}{K}(C_{12}H_{22}O_{11})\underset{ex.}{(H_2O)}\ \text{con.}$$

$$\therefore \boxed{Rate = K'(C_{12}H_{22}O_{11})}$$ pseudo 1st order

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Q. For the acidic hydrolysis of sugar, rate constant is 2×10^{-3} mol^{-1} (min^{-1}). Determine pseudo rate const.

Sol. $K' = K(H_2O)$ (conc. 55.5).

$= 2 \times 10^{-3} \times 55.5$

$= 1.11 \times 10^{-1}$ min^{-1}.

Q. For $A + 2B \longrightarrow C$ rate law : $r = K(A)(B)^2$. find order of rxn if A is taken in excess.

$r = K(A)(B)^2$.

$r = K'(B)^2$

$\therefore$ 2nd order rxn.

Q. $CH_3COOCH_3 + H_2O \xrightarrow{H^+} CH_3COOH + CH_3OH$.

(excess).

$r = K(CH_3COOCH_3)(H_2O)$

$r = K'(CH_3COOCH_3)$. If $K' = 2.004 \times 10^{-3}$ min^{-1}. Then find the value of K.

$\because K' = K(H_2O)$

$K = \frac{K'}{H_2O} = \frac{2.004 \times 10^{-3}}{55.5}$ Ans