Q:21 Find order of reaction:

(1.) $A_2 + 2B \longrightarrow A_2B_2$ ...(1)

mechanism:

$A_2 \rightleftharpoons 2A$ (2A → intermediate b'coz it is not there in parent rxn)

$2A + 2B \longrightarrow A_2B_2$ (slow)

$\Rightarrow$ Rate $= K[A]^2[B]^2$ ——— eq(1)

here,

A is an intermediate [as it's not there in parent rxn]

$\therefore K_{eq} = \dfrac{[A]^2}{[A_2]}$

$\Rightarrow [A]^2 = K_{eq} \cdot [A_2]$ ——— eq(11)

putting eq(11) in eq(1)

$$\text{Rate} = K\left[K_{eq}^{1/2}[A_2]^{1/2}\right]^2[B]^2$$

$\therefore$ Rate $= K \cdot (K_{eq})^{1/2}[A_2]^{1}[B]^2$ (1+2=3)

Order of rxn is 3.

Q:22. (1.) $A_2 + 2B \longrightarrow A_2B_2$

mechanism:

- $A_2 \longrightarrow 2A$ (slow)
- $2A + 2B \longrightarrow A_2B_2$ (fast)

$\Rightarrow$ Rate $= [A_2]^1$

$\therefore$ Order of reaction is 1st order.

[2A wouldn't be considered an intermediate as it is a product of slow step rxn].

Q:23 Find out the order of reaction:

$$X_2 + Y_2 \longrightarrow 2XY$$

mechanism: (2 intermediates)

- $X_2 \rightleftharpoons X + X$ (fast)
- $X + Y_2 \longrightarrow XY + Y$ (slow)
- $X + Y \longrightarrow XY$ (fast).

$\Longrightarrow$ $\text{Rate} = K[X][Y_2]^1$ ——— eq(1).

here,

X is an intermediate

$\therefore$, $K_{eq} = \dfrac{[X]^2}{[X_2]}$ ... since $(X+X)$.

$\therefore$, $[X]^2 = K_{eq} \cdot [X_2]$.

$[X] = K_{eq}^{1/2} [X_2]^{1/2}$ ——— eq(11)

$\therefore$, $\text{Rate} = K [K_{eq}]^{1/2} [X_2]^{1/2} [Y_2]^1$

$=$ ↓eq.

$\therefore$, $\text{Rate} = 1.5$

* Pseudo FOR:

- chemical reaction in which value of order of reaction is one but molecularity is more than one is known as pseudo unimolecular / pseudo first order reaction.

eg: inversion of cane sugar is bimolecular reaction but it is first order reaction.

disaccharide hydrolysis →

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$$

[cane sugar] — [Glucose] [Fructose]

- $Rate = K'[C_{12}H_{12}O_{11}][H_2O]$
- As the water is excess then its concentration remain constant during reaction so $[H_2O]$ is taken as constant therefore rate eq is

$Rate = K[C_{12}H_{22}O_{11}]$ where $K = K'[H_2O]$

* Integrated rate eqn for Gaseous System:

- consider a typical first order gas phase rxn

$$A_{(g)} \longrightarrow B_{(g)} + C_{(g)}$$

- let P_i be the initial pressure of A and P_t is the total pressure at time 't' while P_A, P_B and P_C are partial pressure of A, B and C respectively at time 't'.

Total pressure: $P_t = P_A + P_B + P_C$.

- if 'x' atm be decrease in pressure of A at time 't' and one mole of B and C is being formed, increase in pressure of B and C will also be 'x' atm each.

	$A_{(g)} \longrightarrow$	$B_{(g)}$ +	$C_{(g)}$
at t=0	p_i atm	0 atm	0 atm
at t time	$(p_i - x)$ atm	x atm	x atm.

where, p_i is initial pressure at time $t = 0$.

$$P(t) = (p_i - x) + x + x$$
$$= p_i + x$$

$$x = (p_t - p_i)$$

where, $p_A = p_i - x = p_i - (p_t - p_i)$

$$p_A = 2p_i - p_t$$

$$K = \left[\frac{2.303}{t}\right]\left[\log \frac{p_i^\circ}{p_A}\right]$$

$$\boxed{K = \frac{2.303}{t} \log \frac{p_i}{(2p_i - p_t)}}$$

Q.24 for a 'EOR' $A(g) \longrightarrow 2B(g) + C(g)$; initial press is 90 mmHg ; pressure after 10 minutes 180 mmHg. Find out the rate constant

$\Longrightarrow$

	$A(g)$	$\longrightarrow$	$2B(g)$	+	$C(g)$
$t=0$	p_i°		0		0
$t=10$ min	$p_i^\circ - x$		$2x$		x

$P_t = p_i^\circ - x + 2x + x$

$P_t = p_i^\circ + 2x$

$180 = 90 + 2x \longrightarrow x = 45$

$\therefore K = \frac{2.303}{t} \log \frac{p_i^\circ}{p_i^\circ - x}$

$= \frac{2303 \times 10^{-3}}{6 \times 10^2} \log \frac{90}{90-45}$

$\longrightarrow K = 383.83 \times 10^{-5} \times \log(2)$

$= 383.83 \times 10^{-5} \times 301 \times 10^{-3}$

$= 115532.83 \times 10^{-8}$

$K = \underline{0.1155}$

Q:25 following data were obtained during FOR thermal decomposition of $N_2O_5(g)$ at constant vol.

$$2N_2O_5(g) \longrightarrow 2N_2O_4(g) + O_2(g)$$

	time (sec)	Pt (atm)
1.)	0	0.5
2.)	100	0.512

$\Longrightarrow$

	$2N_2O_5$	$\longrightarrow$	$2N_2O_4$	+	O_2
t=0 s	P_i°		0		0
t=100s	$P_i^\circ - 2x$		$2x$		x

$P_t = P_i^\circ - 2x + 2x + x$

$\therefore P_t = P_i^\circ + x$

$0.512 = 0.5 + x \quad \therefore x = 0.012$

$\therefore K = \frac{2.303}{t} \log \frac{P_i^\circ}{P_i^\circ - x}$

$= \frac{2.303}{100} \cdot \log \left[\frac{0.5}{0.5 - 0.024}\right]$

$= 2303 \times 10^{-1} \cdot \log \left(\frac{0.5}{0.476}\right)^{1.050}$

$= 230.3 \cdot 0.0216$

$= \underline{4.98 \times 10^{-4} \text{ sec}^{-1}}$

Q:26 Reaction $A(s) \longrightarrow 2B(g) + C(g)$ is FOR. Pressure after 20 min and after very long time are 150 mmHg and 225 mmHg. K = ? P = ? after 40 min.

$\longrightarrow$

	$A(s)$	$\longrightarrow$	$2B(g)$	+	$C(g)$
t=0	150		0		0
t=T	150 − x		2x		x

$$K = \frac{2.303}{20} \cdot \log\left(\frac{225}{225-150}\right)$$

$$K = \frac{1}{20} \ln 3 \ \text{min}^{-1}$$

$\therefore$ $K = 0.05 \ln(3) \ \text{min}^{-1}$

$\therefore$ (extra (150 mm Hg))

$$K = \frac{2.303}{20} \times \log(3)$$

$$= \frac{2.303 \times 0.4717}{20}$$

$$= \frac{0.9212}{20} \quad \therefore K = 0.046 06$$

$\therefore$ $Kt = \frac{2.303}{} \log \frac{P_t}{P - P^\circ}$

$$\frac{2.303}{20} \times \log(3) \times (40) = \frac{2.303}{} \cdot \log \frac{225}{225 - P_{40}}$$

$$0.05 \times \log(3) \times 40 = \log 225 - \log 225 + \log P_{40}.$$

$$0.05 \times 0.4717 \times 40 = \log 225 - \log 225 + \log P_{40}.$$

$\therefore$ 0.9434

* Example of Fractional Order of Reaction:

Reaction	Order
- $H_2 + Br_2 \longrightarrow 2HBr$	1.5
- $CO + Cl_2 \longrightarrow COCl_2$	2.5
- $COCl_2 \longrightarrow CO + Cl_2$	1.5

* Example of Second Order of Reaction:

Reaction	Order
- $2NO_2 \longrightarrow 2NO + O_2$	2
- $CH_3COOC_2H_5 + NaOH \longrightarrow CH_3COONa + C_2H_5OH$ (ester)	
- $2NO_2 + F_2 \longrightarrow 2NO_2F$	

* Example of Third Order of Reaction:

- $2NO + O_2 \longrightarrow 2NO_2$
- $2NO + Cl_2 \longrightarrow 2NOCl$
- $2FeCl_3 + SnCl_2 \longrightarrow 2FeCl_2 + SnCl_4$