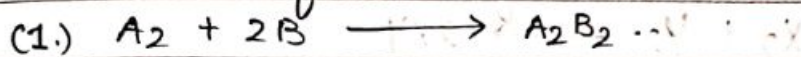
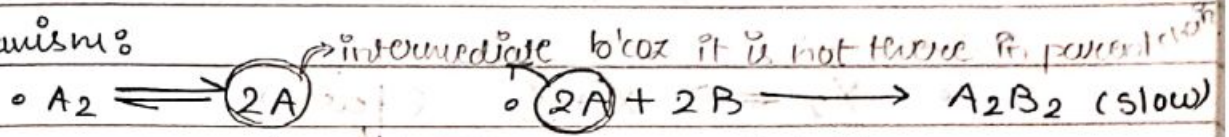


Q21 Find order of reaction:



mechanism:



$$\Rightarrow \text{Rate} = k [A]^2 [B]^2 \text{ --- eq(1)}$$

here,

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

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

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

putting eq(11) in eq(1)

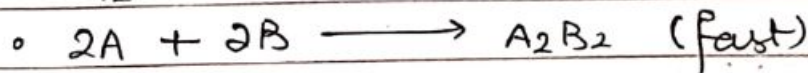
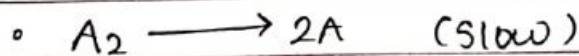
$$\text{Rate} = k [K_{eq}^{1/2} [A_2]^{1/2}]^2 [B]^2$$

$$\therefore, \text{Rate} = k \cdot (K_{eq})^{1/2} [A_2] [B]^2$$

Order of rxn is 3. (1+2=3)

Q22. (1.)  $A_2 + 2B \longrightarrow A_2B_2$

mechanism:

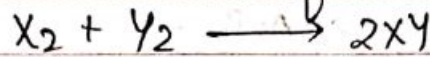


$$\Rightarrow \text{Rate} = [A_2]^1$$

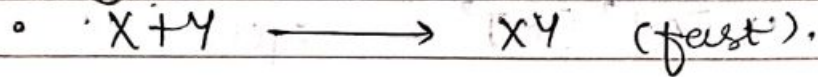
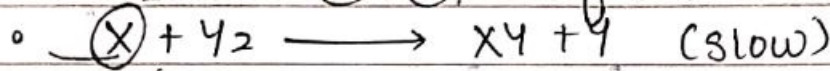
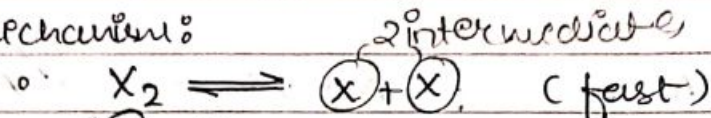
$\therefore$ , Order of reaction is 1<sup>st</sup> order.

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

Q 23 Find out the order of reaction:



mechanism:



$$\implies \text{Rate} = k [X] [Y_2] \quad \text{--- eq (I)}$$

here,

X is an intermediate

$$\bullet \bullet, K_{eq} = \frac{[X]^2}{[X_2]} \quad \text{--- due to } (X + X)$$

$$\bullet \bullet, [X]^2 = K_{eq} [X_2]$$

$$[X] = K_{eq}^{1/2} [X_2]^{1/2} \quad \text{--- eq (II)}$$

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

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

\* 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.

Q: inversion of cane sugar is bimolecular reaction but it is first order reaction,



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

$$p(t) = (p_i - x) + x + x \\ = p_i + x$$

$$x = (p_t - p_i)$$

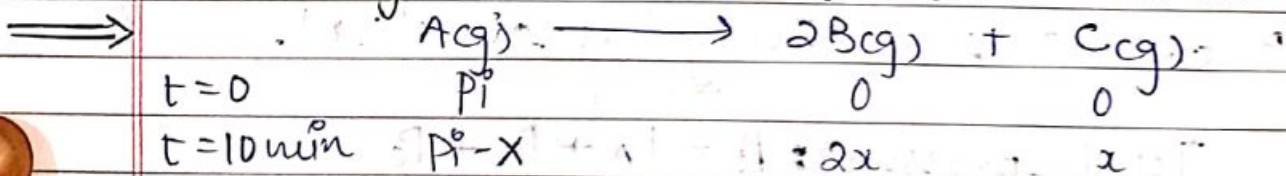
where,  $p_A = p_i - x = p_i - (p_t - p_i)$

$$p_A = 2p_i - p_t$$

$$k = \left[ \frac{2.303}{t} \right] \left[ \log \frac{p_i}{p_A} \right]$$

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

Q24 for a 'FOR'  $A(g) \rightarrow 2B(g) + C(g)$ ; initial press is 90 mmHg; pressure after 10 minutes is 180 mmHg. Find out the rate constant



$$p_t = p_i - x + 2x + x$$

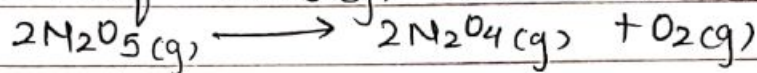
$$p_t = p_i + 2x$$

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

$$\therefore k = \frac{2.303}{t} \log \frac{p_i}{p_i - x} \\ = \frac{2.303 \times 10^{-3}}{6 \times 10^2} \log \frac{90}{90 - 45}$$

$$\begin{aligned} \rightarrow K &= 383.83 \times 10^{-5} \times \log(2) \\ &= 383.83 \times 10^{-5} \times 301 \times 10^{-3} \\ &= 11553283 \times 10^{-8} \\ K &= \underline{0.1155} \end{aligned}$$

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



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

 $\Rightarrow$ 

 $t=0s$ 
 $P_i = 0.5$ 
 $0$ 
 $0$ 
 $t=100s$ 
 $P_i - 2x$ 
 $2x$ 
 $x$ 

$$P_t = P_i - 2x + 2x + x$$

$$\therefore P_t = P_i + x$$

$$0.512 = 0.5 + x$$

$$\therefore x = 0.012$$

$$\therefore K = \frac{2.303}{t} \log \frac{P_i}{P_i - 2x}$$

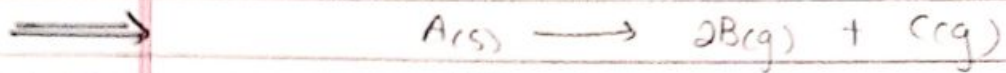
$$= \frac{2.303}{100} \cdot \log \left[ \frac{0.5}{0.5 - 0.024} \right]$$

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

$$= 230.3 \cdot 0.0216$$

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

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



$$t=0 \quad 150 \quad 0 \quad 0$$

$$t=T \quad 150-x \quad 2x \quad x$$

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

$$K = \frac{1}{20} \ln 3 \text{ min}^{-1} \quad \text{or} \quad K = 0.05 \ln(3) \text{ min}^{-1}$$

Exitog (No. of)

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

$$= \frac{2.303 \times 0.4771}{20}$$

$$= \frac{0.9212}{20} \quad \text{or} \quad K = 0.004606$$

$$\text{or} \quad Kt = \frac{2.303}{A-P} \log \frac{P}{A-P}$$

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

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

$$0.05 \times 0.4771 \times 40 = \log 225 - \log 225 + \log P_{40}$$

$$\text{or} \quad 0.9434$$

### \* Example of Fractional Order of Reaction:

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

### \* Example of Second Order of Reaction:

<u>Reaction</u>	<u>Order</u>
- $2NO_2 \longrightarrow 2NO + O_2$	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:

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