



**EXERCISE # O-II**  
**SOLUTION**

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1. For 2<sup>nd</sup> order reaction

$$\frac{1}{[A]_t} = \frac{1}{[A]_0} + kt$$

Curve between  $\frac{1}{[A]_t}$  vs t is straight line with slope k and intercept  $\frac{1}{[A]_0}$

2.  $-\frac{d[A]}{dt} = k[A]^{\frac{1}{2}}$

On solving

$$k = \frac{2}{t} [A_0^{\frac{1}{2}} - A^{\frac{1}{2}}]$$

3.  $\frac{d[C]}{dt} = k[A]^1 [B]^{-1}$

$$\therefore \frac{[A]}{[B]} = \frac{1}{2}$$

$$\therefore \frac{d[C]}{dt} = k [A] \left[ \frac{A}{2} \right]^{-1} = 2k$$

$$\therefore [C] = 2kt$$



t = 0	P°	0	0
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t = 20 min	P° - x	$\frac{2}{3}x$	$\frac{2}{3}x$
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t = ∞	0	$\frac{2}{3}P°$	$\frac{2}{3}P°$
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At t = ∞ : Total pressure =  $\frac{2P°}{3} + \frac{2}{3}P° = \frac{4}{3}P° = 4 \Rightarrow P° = 3$

At t = 20 min : Total pressure =  $P° - x + \frac{2}{3}x + \frac{2}{3}x = 3.5 \Rightarrow x = 1.5$

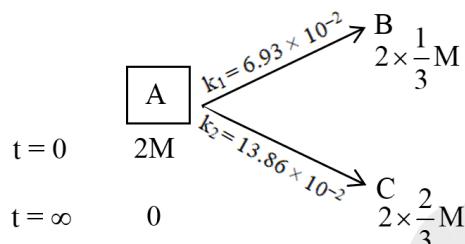


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$$\therefore \text{At } t = 20 \text{ min.} \quad x = \frac{P^o}{2}$$

$$\therefore t_{1/2} = 20 \text{ min.}$$

5.

At  $t = \infty$ :

$$\begin{aligned} \text{Rotation} &= \frac{2}{3} \times (-72) + \frac{4}{3} \times (42) \\ &= 8 \end{aligned}$$

$$\text{Half life} = \frac{0.693}{k_1 + k_2} = \frac{10}{3} \text{ min.}$$

6. 
$$\frac{d[\text{CH}_3\text{Br}]}{dt} = \frac{k_1[\text{CH}_4][\text{Br}_2]}{1 + k_2 \frac{[\text{HBr}]}{[\text{Br}_2]}}$$

(B) If  $[\text{HBr}] \neq 0$ 

$$\frac{d[\text{CH}_3\text{Br}]}{dt} = k_1 [\text{CH}_4] [\text{Br}_2]$$

(C) If  $[\text{Br}_2] \neq 0$ 

$$\frac{d}{dt} [\text{CH}_3\text{Br}] = \frac{k_1 [\text{CH}_4][\text{Br}_2]}{1 + k_2 \frac{[\text{HBr}]}{[\text{Br}_2]}}$$

$$= \frac{k_1 [\text{CH}_4][\text{Br}_2]^2}{[\text{Br}_2] + k_2 [\text{HBr}]} = \frac{k_1 [\text{CH}_4][\text{Br}_2]^2}{k_2 [\text{HBr}]}$$

7. (A) Order of reaction is experimentally decided.

(B)  $r = K[A]^{\circ} \Rightarrow r = K$ 

(C) Zero order reaction does not depend on conc. of reactant

(D) Zero order reaction is always complex reaction



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8. (A) Unit of A = Unit of  $k_1$   
 (B) Because molecularity can't be zero.  
 (C) For complex reaction molecularity is not defined.  
 (D)  $k$  increases with increase in temperature.
  
9. (A) For elementary reaction order must be equal to molecularity but reverse is not valid.  
 (B) Same as (A)  
 (C) Order can be found experimentally.

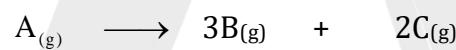
10.  $k = A e^{-E_a/RT}$

At  $T \rightarrow \infty$  :  $k = A$

When  $E_a = 0$  :  $k = A$

11. Since reaction is occurring at constant pressure it means volume of the contains is variable.

$$\therefore t_{1/2} = \frac{0.693}{1.386 \times 10^{-2}} = 50 \text{ min}$$



$$t = 0 \quad 2 \text{ mole} \quad 0 \quad 0$$

$$t = 100 \text{ min.} \quad \frac{2}{2^2} = 0.5 \text{ mole} \quad 3 \times 1.5 \quad 2 \times 1.5 \text{ mole}$$

$$\text{Total moles} = 0.5 + 4.5 + 3 = 8 \text{ mole}$$

$$\therefore \frac{V_2}{V_1} = \frac{n_2}{n_1} \quad \text{at constant pressure.}$$

$$\therefore V_2 = 12.5 \times \frac{8}{2} = 50 \ell t$$

$$\therefore [B] = \frac{4.5}{50} = 0.09 \text{ M}$$

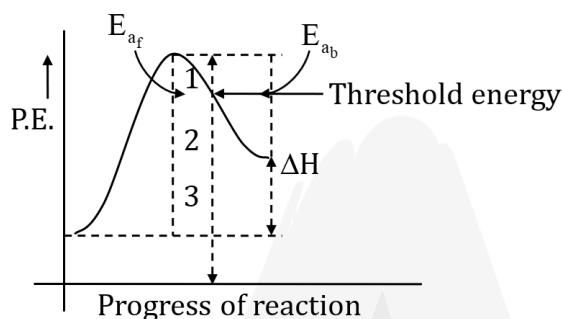
### ASSERTION & REASONING TYPE QUESTIONS



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12. For reaction of the order one or greater rate depends upon concentration of reactant and as the concentration of reactant decreases its rate also decreases so it take infinite time for completion.

13. For endothermic reaction :



14. Presence of catalyst changes the mechanism of reaction.

15. Integrated expression for rate law =  $-\ln(1-f) = kt$

$$k = -\frac{\ln(1-f)}{t} = -\left(-\frac{3}{200}\right) \text{ hr}^{-1}$$

$$t_{1/2} = \frac{0.693}{3} \times 200 = 46.2 \text{ hrs}$$

16.  $\ln(1-f) = -Rt$

$$1 - f = e^{-Rt}$$

$$f = 1 - e^{-Rt}$$

$$17. t_{\max} = \frac{\ell n(k_2 / k_1)}{(k_2 - k_1)}$$

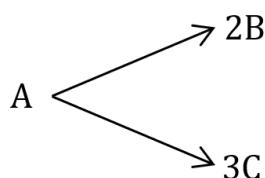
18.  $\therefore k_1 \ggg k_2$

Option (C) will be correct.



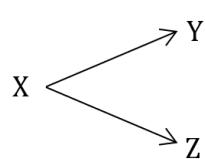
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19.



$$[A]_0 = [A]_t + \frac{[B]_+}{2} + \frac{[C]_+}{3}$$

20.

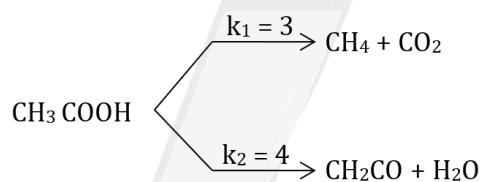


$$[X]_t = a_0 \times e^{-(k_1+k_2)t}$$

$$[Y]_t = \frac{k_1}{k_1 + k_2} a_0 [1 - e^{-(k_1+k_2)t}]$$

$$[Z] = \frac{k_2}{k_1 + k_2} a_0 [1 - e^{-(k_1+k_2)t}]$$

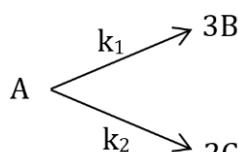
21.



Fraction of  $\text{CH}_3\text{COOH}$  reacting as per reaction (i)

$$= \frac{k_1}{k_1 + k_2} = \frac{3}{3+4} = \frac{3}{7}$$

22.



$$\frac{dB}{dt} = 3k_1 [A]$$

$$\frac{dC}{dt} = 2k_2 [A]$$