

- $\frac{1}{4} \frac{d[A]}{dt} = \frac{-d[B]}{dt}$
- **B-2.** Sol. Order of reaction is experimentally determined.
- **B-3.** Sol. Overall order = sum of individual orders.

Overall order = 
$$\frac{1}{2} + \frac{1}{3} + \frac{1}{4} = \frac{13}{12}$$
.

- B-4. Sol. Rate of reaction is independent of concentration of reactant for zero order reaction. B-5. Sol.
- B-6. Sol. R K [A] [B] Order wrt. A = 1 & above wr.t B = 1 k depends on temperature
- $2NO + 2H_2 \longrightarrow N_2 + 2H_2O$ B-7. Sol. 1 d[H<sub>2</sub>] -1 d[NO]  $d[N_2]$  $1 \, d[H_2O]$ 2 dt = -2 dt dt = 2dt = Rate \_  $k_1$ "  $k_1'$ k  $k_1 = 2 = 2 = 2$ 2

1

- $A + B \longrightarrow Products$ B-9. Sol.  $R = k [A]^2 [B]^3$  $R' = R.2^2 [A]^2 2^3 [B]^3 = 2^5 R = 32R$
- B-10. Sol.  $R = k [A]^{m} [B]^{n}$  $2R = k 2^{m} [A]^{m} [B]^{n}$  $2R = k 2 [A]^m 2^n [B]^n$ m = 1 n = 0.

### Section (C) : The integrated rate laws

- C-1. Sol. Unit of k is L mol<sup>-1</sup> sec<sup>-1</sup> so order is 2.
- Co 2.303 2.303 Ct t= K log Κ C-2.  $[\log C_{\circ} - \log C_{t}]$ Sol. ⇒ t = Κ Kt 2.303  $2.303 = \log C_0 - \log C_t$  $\log C_t =$ t + log Co ⇒ – K` 2.303 So (vr%), slope (<+ky) =
- C-3. Sol. Amount decayed = a - (a / 8) = 7a / 8
- C-4. Sol. According to graph given it would be zero order reaction so rate independent of time.

C-5. Sol. 
$$N_2O_5 \rightarrow 2NO_2 + \frac{1}{2}O_2$$
  
 $R = K [N_2O_5]$   
 $R = 6.2 \times 10^{-4} S^{-1} \times 1.25 \text{ mole } L^{-1} = 7.75 \times 10^{-4} \text{ mole } L^{-1} s^{-1}$   
C-6. Sol. As per unit, zero orde reaction  
 $Co - Ct = kt$   
 $Co - 0.5 = 2 \times 10^{-2} \times 25$   
 $Co = 1.0 \text{ m}$   
C-7. Sol.  $log(a-x)$  vs time t is straight line  
 $log(a - x) = kt$  (k & k' are some constants)  
 $ln(a - x) = K't$   
 $\frac{1}{a - x} - \frac{-dx}{dt} = K.$  (on differenciating)

ln2

-dx

dt = K (a - x)' shows a first order reaction.

- **C-8.** Sol. Equal amount of Rxn completed in equal time property as zero order Rxn, and unit as Rate constant mole Litre<sup>-1</sup> sec<sup>-1</sup>
- **C-9.** Sol.  $t_1 = 2 \times t_{1/2}$ ;  $t_2 = t_{1/2}$
- **C-10. Sol.** Unit of rate constant is (time)<sup>-1</sup>. Hence first order reaction.

Time required to change concentration 1 M to 0.25 M =  $2 \times t_{1/2} = 2 \times k = 20$  min.

C-11. Sol.  $C_t = Co \ kt \Rightarrow kt = Ct \ / \ Co$  $\frac{kt \ 75\% \ = 0.75co}{\frac{t75\%}{t50\%} \ = \frac{75}{50}} \ . \ f \ \frac{kt \ 50\% \ = 0.5co}{1.5.}$ 

C-12. Sol.  $K = \frac{2.303}{80} \log \left(\frac{100}{6.25}\right) = 3.465 \times 10^{-2} \text{ min}^{-1}$ Then  $3.465 \times 10^{-2} = \frac{2.303}{100} \log \left(\frac{.2}{a_t}\right)$   $a_t = 0.006265$ Rate (nj) =  $K \times [a_t] = 0.006265 \times 3.465 \times 10^{-2}$  $= 2.166 \times 10^{-4} \text{ sec}^{-1}$ 

### Section (D) : Methods to determine the rate law

D-1. Sol.  $A + B \rightarrow C$  $R = k [A]^m [B]^n$ compere exp. (1) & (2) (O;atd 1 o 2 dh rqyuk djus ij)  $\frac{0.1}{0.8} = \left(\frac{1}{2}\right)^{m} \Rightarrow m = 3$ compere exp. (2) & (4) (O;atd 2 o 4 dh rqyuk djus ij)  $\frac{0.8}{0.8} = \left(\frac{1}{2}\right)^n n = 0$  so. R = K[A]<sup>3</sup> D-3. dx  $\log \frac{dx}{dt}$   $\log [A]$  $dt = K[A]^2$ Sol. dx  $\log dt = 2\log[A] + \log k$ compare with y = m x + c graph obtained Sol. D-4.  $A \longrightarrow Product$ а a – x Since equal interval of time equal conc. decreased then reaction zero order  $\frac{\Delta A}{\Delta A} = \frac{20-12}{8} = \frac{8}{100}$ 20 20 = 0.4Rate (nj) =  $\Delta t$ 

**D-7.** Sol. A (s) 
$$\longrightarrow 2 \text{ B }(g) + C (g)$$
  

$$K = \frac{1}{t} \ln \left( \frac{P_{\infty} - P_{0}}{P_{\infty} - P_{t}} \right) \qquad P_{0} = 0 \qquad P_{t} = 150 \qquad P_{\infty} = 225$$

$$\frac{1}{20} \ln \left[ \frac{225}{225 - 150} \right] \qquad \Rightarrow \qquad \frac{1}{20} \ln \left( \frac{225}{75} \right) = 0.05 \ln 3$$

$$\frac{1}{20} \ln \left( \frac{225}{75} \right) = \frac{1}{20} \ln \left( \frac{225}{225 \times P_{40}} \right) \qquad \Rightarrow \qquad \left( \frac{225}{75} \right)^{2} = \frac{225}{225 \times P_{40}}$$

$$\frac{225}{75 \times 75} = \frac{1}{225 - P_{40}} \qquad \Rightarrow \qquad P_{40} = 200$$

Section (E) : Methods to monitor the progress of the reaction E-1.

 $\begin{array}{ccc} 2 \text{ A } (g) & \longrightarrow & 3 \text{ B } (g) + \text{ C } (g) \\ P^0 & 0 & 0 \end{array}$ Sol. t = 0  $\frac{3x}{2}$  $\left(\frac{x}{2}\right)$  $(P^0 - x)$ t = 3 hour $(P^0 + x) = 2 P^0$  $\dot{\mathbf{x}} = \mathbf{P}^0$ 

Reaction is completed in limited time so reaction is zero order reaction.

E-2. А —  $\rightarrow$  2 B + C Sol. 0 t = 0 P<sub>0</sub> 0 Ρo (P₀ − x) 2x t = t х  $P_0 + 2x = 176$  $\mathbf{P}_0$ 0 2 Po  $3 P_0 = 270$  $P_0 = 90$ 2 x = 176 - 90 = 86x = 43 Pressure of A after 10 minute = 90 - 43 = 47

E-3. Ans. 
$$k = \frac{1}{t} \ln \left( \frac{P_0}{P_t} \right)$$
  
Sol.  $A \rightarrow B + C$   
 $t = 0, Po \quad 0 \quad 0$   
 $t = t, P_0 -x \quad x \quad x$ 

E-4.

C(g) + 0 Px Sol. A (g) B (g) + D(g) Initially Pi 0 0  $(P_i - P_x)$   $P_x$ Px At time t total pressure at time t =  $(P_i + 2P_x) = P_t$  $P_{x} = \begin{pmatrix} \frac{P_{t} - P_{i}}{2} \end{pmatrix}$ So  $\begin{aligned} P_{x} &= \\ K &= \frac{2.303}{t} \log \left( \frac{P_{i}}{P_{i} - P_{x}} \right) = \frac{2.303}{t} \log \left( \frac{2P_{i}}{3P_{i} - P_{t}} \right) \end{aligned}$ E-5. Sol. Initial pressure 65 105 185 y 290 670 820 Half life х Initial pressure of gas a Initial moles of gas in above question.

#### Half life a Initial pressure So, it must be zero order reaction $P_{O}$ 65 Co 65 $t_{1/2} = 2k = 2k 290 = 2k$ $k = \overline{2 \times 290} = 0.112 \text{ mm of Hg/sec}$ ⇒ $105 \times 2 \times 290$ $y \times 2 \times 290$ $2 \times 64$ 2 × 65 = 468 sec 670 = y = 150 mm of Hgx = ⇒

E-6.

Sol. 
$$NH_4NO_2 \text{ (aq)} \longrightarrow N_2 \text{ (g)} + 2H_2O (\ell)$$
  
 $K = \frac{2.303}{t} \log \left( \frac{V_{\infty} - V_0}{V_{\infty} - V_t} \right) \Rightarrow V_0 = 0 \Rightarrow K = \frac{2.303}{20} \log \left( \frac{70 - 0}{70 - 40} \right)$   
 $= \frac{2.303}{20} \log \left( \frac{70}{30} \right) \Rightarrow K = \frac{2.303}{1200} \log \frac{7}{3}.$ 

E-7. Sol. V<sub>0</sub> become zero.

### Section (F) : Effect of Temperature

- F-1. Sol. Rate of reaction increases as temp increases.
- F-2. Sol. Rate increases as temperature increases.
- **F-3.** Sol.  $K = A \times e^{-Ea/RT} = A \times e^{-Ea/R} \times = A = 6.0 \times 10^{14} \text{ s}^{-1.}$
- **F-6.** Sol.  $\Delta H = Eat Eab 20 = 60 Eab so Eab = so .$

F-8. Sol. 
$$k = \frac{1}{t} \ln \left(\frac{a}{a-x}\right)$$
  
 $V_{\infty} \propto a$   
 $V_{t} \propto x$   
 $\left(\frac{a}{a-x}\right)_{=} \left(\frac{V_{\infty}}{V_{\infty} - V_{t}}\right)$ 

**F-9. Sol.** log k = 15.0 – T

compair this relation with  $\log k = \log A - \frac{1}{2}$ we find  $A = 10^{15}$ .  $E = 1.9 \times 10^4$  KJ

 $E = \log A - 2.303RT$ 

**F-10.** Sol.  $\Delta H = E_f - E_b$   $-40 = 80 - E_b$   $E_b = 120 \text{ kJ/mole},$ catalyst lower the  $E_f$  To 20 kJ/ mole for forward Rxn then  $E_f = 20 \text{ kJ/mol}$ we know catalyst decreases the Activation energy equal amount in both direction  $E_b = (120 - 60) = 60 \text{ kj/mol}$  $\frac{E_b}{E'_b} = \frac{120}{60} = 2.0$ 

### Section (G) : Mechanism of reactions

 $\begin{array}{ll} \textbf{G-1.} & \textbf{Sol.} & H_2\left(g\right) + Br_2\left(g\right) \rightarrow 2HBr\left(g\right) \\ r = k[H_2] \ [Br_2]^{1/2} \\ & \text{Molecularity is defined for one step reactions only.} \end{array}$ 

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

G-2. Sol. Slowesr step is rate determining step.

**G-3.** Sol. Slow step is :  $\begin{array}{ccc}
\frac{1}{2} \\
\chi_2 + \gamma_2 & \longrightarrow & \chi\gamma_2 \\
\text{Hence} \\
r = k[X_2]^{1/2}[Y_2] \\
\text{OR} = & \frac{1}{2} + 1 = 1 \\
\begin{array}{c}
\frac{1}{2}
\end{array}$ 

## Exercise-2

### PART - I : OBJECTIVE QUESTIONS

- 1. Sol. Total time for drop to dissapear  $(a_0 - a_t) = kt$  $a_t = 0$  $3.0\times10^{-6}$  $\overline{(0.05\times10^{-3})\times1.0\times10^{7}} = t_{100\%} \Rightarrow$ t100% = 6 × 10<sup>-9</sup> sec  $\left(\frac{50}{50-10}\right)_{=}\frac{2.303}{10}$ 2.303 10 log 1.25 min<sup>-1</sup> K = 2. Sol. log
- 3. Sol. Rate constant depends on temperature.
- 4. Sol. Unit of K is mole  $L^{-1}$  Sc<sup>-1</sup> So order is 0.
- 5.  $r = K [A]^{1} [B]^{2}$   $r_{1} = K [1]^{1} [1]^{2} = 1 \times 10^{-2}$  (K = 1 × 10<sup>-2</sup>)  $r_{1} = K \begin{bmatrix} \frac{1}{2} \end{bmatrix} \begin{bmatrix} \frac{1}{2} \end{bmatrix}^{2}$  $= 1 \times 10^{-2} \times \frac{1}{8} = 1.25 \times 10^{-3}$
- 7. Sol. As given, it is an elementary reaction.
- 8. Sol. As  $t_{50\%}$  is constant. Hence order of reaction is 1.  $t_{50\%} = \frac{0.693}{K}$   $n = 1, t_{1/2} = \frac{0.693}{K}$
- 9. Sol.  $K = \frac{1}{t} \left[ \ln \frac{a}{a-x} \right] = \frac{2.303}{t} \log \frac{a}{a-x}$

2.303

1

4

2.303  $K = \frac{20}{100} \log \frac{0.25}{0.25} = \frac{20}{100} \log \frac{1}{1} = 0.0693 \text{ min}^{-1}$ 10. Sol. by graph we can say  $\log t_{1/2} = \log a$  $t_{1/2} = a$ ....(1) а  $k \times t_{1/2} = 2$ .....(2)  $t_{1/2} \propto a$  for zero order Rxn 1 then k = 2 $k = \frac{1}{t} \frac{a}{\ln a - x}$ Sol. 11. а =  $\overline{1.388 \times 3600}$  In 0.25a  $= 2.77 \times 10^{-4} \text{ sec}^{-1}$ . **Sol.**  $r_1 = K[0.01]^a [0.01]^b = 6.93 \times 10^{-6}$ 12.  $r_2 = K[0.02]^a [0.01]^b = 1.386 \times 10^{-5}$  $r_3 = K[0.02]^a [0.02]^b = 1.386 \times 10^{-5}$ From data a = 1, b = 0Overall order = 1 ;  $K = 6.93 \times 10^{-4} \text{ sec}^{-1}$ 1  $A_0$  $6.93 \times 10^{-4} = \overline{50 \times 60} \ln A_t$  $A_0$  $0.693 = \ln \overline{A_t}$  $A_t = 0.0625$ rate of reaction =  $6.93 \times 10^{-4} \times 0.0625 = 4.33 \times 10^{-5} \text{ Ms}^{-1}$ . 13.  $E_{af} - E_{ab} = \Delta_r H \Rightarrow 15 - E_{ab} = 5 \Rightarrow E_{ab} = 15 - 5 = 10$ Sol. 14. Sol.  $2NO_2(g) + F_2(g)$  $\rightarrow$  $2NO_2F(g)$ Ρo  $2P_0 + P_0 = 3$  atm t = 0 2Po t = 0 2 atm 1 atm 0  $P_0 = 1$  atm t = t0 0 2 atm  $K = Ae^{-E/RT}$ 15. Sol.  $K_1 = A_1 e^{-E_1/RT}$  and  $K_2 = A_2 e^{-E_2/RT}$ 16. Sol.  $K_1$  $\frac{1}{K_2} = \frac{1}{A_2} = e^{(E_2 - E_1)/RT}$ ; A<sub>1</sub> and A<sub>2</sub> are not given.  $\log K = \begin{bmatrix} - E_a \\ 2.303 R \end{bmatrix}_x \frac{1}{T}$  $\begin{bmatrix} \frac{1}{T} \end{bmatrix}_{=0} \qquad T = \infty$  $\frac{E_a}{R \ln A}_{=T}$ + log A at Y axies 17. Sol.  $\frac{-E_a}{2.303 R_x} \frac{1}{T} = -\log A$ at x axis  $\log k = 0$ For reaction,  $A \longrightarrow B$ . 18. Sol.  $E_a = 10 \text{ kJ/mole}$ ,  $\Delta H = 5 \text{ kJ/mole}$ Rxn endothermic because  $\Delta H$  (+)  $\Delta H = E_{\rm a} - E_{\rm b}$  $5=~10-E_{\rm b}$ 

 $E_{ab} = 10 - 5 = 5 \text{ kJ/mole}.$ Then [B]. Clearly,  $t_{1/2} \propto a^{1-n}$ 19. Sol. Now ln k = ln A -  $\frac{E_a}{R} \times \frac{1}{T}$ Sol. 20. Slope =  $-\frac{E_a}{R} = \frac{-8.3 \times 10^3}{8.3} = 1000$ **Sol.**  $\log k = -\frac{E_a}{2.303} - \frac{1}{T} + \text{constant}$ 21. 10<sup>3</sup> Ea  $=-\frac{2.303}{2.303}$  R  $\times 10^{-3}$  x T + constant  $E_a \times 10^{-3}$ 4 thus, slope of graph will be  $-\frac{1}{2.303}$  R  $= -\frac{1}{0.4}$  $\Rightarrow$  E<sub>a</sub> = 2.303 × 1.98 × 10<sup>4</sup> = 45600 cal 23. **Sol.** Rate =  $K[X][Y_2]$  $[X]^2$  $K_{eq} = \overline{[X_2]}$  $[X] = \sqrt{K_{eq}} \times [X_2]^{1/2}$ Rate = K ×  $\sqrt{K_{eq}}$  [X<sub>2</sub>]<sup>1/2</sup> [Y<sub>2</sub>] So the order of overall reaction is 1.5  $[X]^2$  $K_{eq} = \overline{[X_2]}$  $[X] = \sqrt{K_{eq}} \times [X_2]^{1/2}$  $= K \times \sqrt{K_{eq}} [X_2]^{1/2} [Y_2]$ 

25.

**Sol.** Half life is not depend upon initial concentration.

26. Sol. 
$$C_3 = \frac{C_0}{2^3} = \frac{C_0}{8}$$
  
 $\frac{C_3}{C_0} = \frac{1}{8}$   
27. Sol.  $N = N_0 \left(\frac{1}{2}\right)^n$   
 $\left(\frac{xv}{22}\right) \qquad \left(\frac{1}{2}\right)^4$ 

 $\left(\frac{1}{20}\right)^{2} = (x) \times 200$ V = 250 ml. So added volume of water = 50 ml.

# Exercise-3 PART - I : JEE (MAIN) / AIEEE PROBLEMS (PREVIOUS YEARS)

**OFFLINE JEE-MAIN** 

- **1. Sol.**  $K = (mol L^{-1})^{1-n} sec^{-1}, n = 0, 1.$
- **2.** Sol. Order is the sum of the power of the concentrations terms in rate law expression.  $R = [A] \cdot [B]^2$

Thus, order of reaction = 1 + 2 = 3.

Ratio between new and earlier rate.

3. Sol.  $H_2 + I_2 \rightarrow 2HI$ When 1 mole of  $H_2$  and 1 mole of  $I_2$  reacts, 2 moles of HI are formed in the same time interval.  $-\Delta[H_2] - \Delta[I_2] = 1 \Delta[HI]$ 

Thus the rate may be expressed as 
$$\Delta t = \frac{1}{\Delta t} = \frac{1}{2} \frac{1}{\Delta t}$$
  
The negative sign signifies a decrease in concentration of the reactant with increase of time.

Sol. Rate1 = k [A]<sup>n</sup> [B]<sup>m</sup>
 On doubling the concentration of A and halving the concentration of B
 Rate2 = k [2A]<sup>n</sup> [B/2]<sup>m</sup>

 $\frac{k \quad \left[2A\right]^n \ \left[B/2\right]^m}{k \ \left[A\right]^n \ \left[B\right]^m} = 2^n \times \left(\frac{1}{2}\right)^m = 2^{n-m}$ 

 Sol. Rate<sub>1</sub> = k [NO]<sup>2</sup> [O<sub>2</sub>] When volume is reduced to 1/2, concentration become two times,

> Rate<sub>2</sub> = k [2NO]<sup>2</sup> [2O<sub>2</sub>]  $\therefore$  Rate<sub>2</sub> = 8 Rate<sub>1</sub>.  $\frac{Rate_1}{Rate_2} = \frac{k [NO]^2 [O_2]}{k [2NO]^2 [2O_2]} \text{ or } \frac{Rate_1}{Rate_2} = \frac{1}{8}$

- 6. Sol. In Arrhenius equation, k = Ae -Ea/RT
   k = rate constant, A = frequency factor
   T = temperature, R = gas constant, Ea = energy of activation.
   This equation can be used for calculation of energy of activation.
- 7. Sol. The concentration fo the reactant decreases from 0.8 M to 0.4 M in 15 minutes, i.e.,  $t_{1/2} = 15$  minute. Therefore, the concentration of reactant will fall from 0.1 M to 0.025 in two half live. i.e.,  $2t_{1/2} = 2 \times 15 = 30$  minutes.
- 8. Sol. 2 A + B → C rate = k [A] [B] The value of k (velocity constant) is always independent of the concentration of reactant and it is a function of temperature only.

9. Sol.  $t_{1/2} = 4$  hours  $n = \frac{T}{t_{1/2}} = \frac{24}{4} = 6;$   $N = N_0 \left(\frac{1}{2}\right)^N$ or,  $N = 200 \times \left(\frac{1}{2}\right)^6 = 200 \times \frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} = 3.125g.$ 

### **Chemical Kinetics**

**10.** Sol. For endothermic reaction,  $\Delta H = + ve$ 

 $\Delta H = E_f - E_b$ , it means  $E_b < E_f$ .

- **11. Sol.** Generally, molecularity of simple reactions is equal to the sum of the number of molecules of reactants involved in the balanced stoichiometric equation. Thus, a reaction involving two different reactants can never be unimolecular.
- 12. Sol. Given rate = k [CO]<sup>2</sup> Thus, according to the rate law expression doubling the concentration of CO increases the rate by a factor of 4.
- **13. Sol.** NO(g) + Br<sub>2</sub>(g)  $\overrightarrow{}$  NOBr<sub>2</sub>(g)

 $\begin{array}{l} \text{NOBr}_2(g) \ + \ \text{NO}(g) \ \overrightarrow{} 2 \text{NOBr}(g) \ [rate determining step]} \\ \text{Rate of the reaction} \ (r) = k \ [\text{NOBr}_2] \ [\text{NO}] \\ \text{where} \ [\text{NOBr}_2] = K_c \ [\text{NO}] \ [\text{Br}_2] \\ r = k. \ \text{Kc.} \ [\text{NO}] \ [\text{Br}_2] \ [\text{NO}] \\ r = k' \ [\text{NO}]^2 \ [\text{Br}_2]. \\ \end{array}$ The order of the reaction with respect to NO(g) = 2.

- **14.** Sol.  $\Delta H_R = E_f E_b = 180 200 = -20 \text{ kJ mol}^{-1}$ The correct answer for this question should be  $-20 \text{kJ mol}^{-1}$ . But no option given is correct. Hence we can ignore sign and select option
- **15. Sol.** Let A be the activity for safe working.

Given = 10 AAo x No and A x N 2.303 No 2.303 A<sub>o</sub>  $\lambda \log N = \lambda$ log A t = 2.303 2.303 imes 30 $2.303 \times 30$ 0.693 10A  $\log A =$  $0.693 \log 10 = 0.693 = 99.69 \text{ days}$ = 30

16. Sol. 
$$\frac{1}{2}A \longrightarrow 2B$$
  
 $-\frac{1}{1/2}\frac{d(A)}{dt} = \frac{1}{2}\frac{d(B)}{dt}$   
 $-\frac{d(A)}{dt} = \frac{1}{4}\frac{d(B)}{dt}$ 

17. Sol. In first order reaction for X% complation

$$\frac{2.303}{t} \int_{\log}^{100} \left(\frac{100}{100 - x\%}\right)$$

$$\frac{0.693}{t_{1/2}} = \frac{2.303}{t} \int_{\log}^{100} \left(\frac{100}{100 - 99}\right)$$

$$\frac{0.693}{6.93} = \frac{2.303 \times 2}{t}$$
So, t = 46.06 min.

**18.** Sol. A  $\longrightarrow$  product For zero order reaction  $\frac{1}{t_{1/2} \propto a^{n-1}} \qquad a = \text{initial concentration of reactant}$  $t_{1/2} \propto a$  19.

$$\frac{(t_{1/2})_{1}}{(t_{1/2})_{2}} = \frac{a_{1}}{a_{2}} ; \frac{1}{(t_{1/2})_{2}} = \frac{2}{0.50}$$

$$\frac{0.5}{2} = 0.25 \text{ h.}$$
19.
Sol. Mechanism (1) rate = K [Cl<sub>2</sub>] [H<sub>2</sub>S]  
Mechanism (2) rate = K\_{1} [Cl<sub>2</sub>] [HS<sup>-</sup>]  
$$K_{eq} = \frac{\frac{[H^{+}][HS^{-}]}{[H_{2}S]}}{K_{eq}[H_{2}S]}$$

$$[HS^{-}] = \frac{\frac{K_{eq}[H_{2}S]}{[H^{+}]}}{[Cl_{2}][H_{2}S]}$$

Rate = 
$$K_1 K_{Eq.}$$
 [H<sup>+</sup>]

Mechanism (1) is consistent with this rate equation. *:*.

50

**20.** Sol. 
$$\frac{\text{Rate at } 50^{\circ}\text{C}}{\text{Rate at } T_{1} \circ \text{C}} = (2)^{\frac{\Delta T}{T_{1}}} = (2)^{\frac{50}{10}} = 2^{5} = 32 \text{ times}$$

21. Sol. 
$$K_1 = \frac{A_1 e^{-Ea_1/RT}}{K_2 = \frac{A_2 e^{-Ea_2/RT}}{\frac{K_1}{K_2} = \frac{A_1}{A_2} e^{(E_{a_2} - E_{a_1})/RT}}$$
  
 $K_1 = \frac{K_2 A \times e^{E_{a_1}/RT}}{K_1 = K_2 A \times e^{E_{a_1}/RT}}$ 

22. Sol. 
$$K = \frac{1}{40} \ln \frac{0.1}{0.025} = \frac{1}{40} \ln 4$$
  
 $R = K[A]^{1} = \frac{1}{40} \ln 4(.01) = \frac{2\ln 2}{40}(.01) = 3.47 \times 10^{-4}$ 

$$\log \frac{K_2}{K_1} = \frac{-E_a}{2.030R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$
  
Sol.  

$$\frac{K_2}{K_1} = 2$$
  
;  $T_2 = 310 \text{ K}$   

$$\Rightarrow \log 2 = \frac{-E_a}{2.303 \times 8.134} \left( \frac{1}{310} - \frac{1}{300} \right)$$
  

$$\Rightarrow E_1 = 52598 \text{ for } 1/\text{mol}$$

$$\Rightarrow E_a = 53598.6 \text{ J/mol} = 53.6 \text{ KJ/mol}$$
  
Ans is (1)

- 24. **Sol.**  $1.2 \times 10^{-3} = K (0.1)^{x} (0.1)^{y}$  $1.2 \times 10^{-3} = K (0.1)^{\times} (0.2)^{y}$  $2.4 \times 10^{-3} = K (0.2)^{x} (0.1)^{y}$  $R = K [A]^1 [B]^0$
- 25. Sol. Higher order (> 3) reactions are rare due to low probability of simultaneous collision of all the reacting species.

23.

1 In 50 minutes, concentration of H<sub>2</sub>O<sub>2</sub> becomes 4 of initial. 26. Sol.  $2 \times t_{1/2} = 50$  minutes ⇒  $t_{1/2} = 25$  minutes . 0.693 25 per minute K = 0.693  $r_{H_2O_2} = 25 \times 0.05 = 1.386 \times 10^{-3}$  $2H_2O_2 \rightarrow 2H_2O + O_2$ 1  $r_{O_2} = \overline{2} \times r_{H_2O_2}$  $r_{O_2} = 0.693 \times 10^{-3}$ :  $r_{O_2} = 6.93 \times 10^{-4}$  mol/minute × litre  $k_1 = Ae^{-Ea_1/RT}$  .  $k_2 = Ae^{-(Ea_1-10)/RT}$ Sol. 27.  $\left(\frac{k_2}{k_1}\right) = \frac{10}{RT} = \frac{10}{8.314 \times 10^{-3} \times 300} = 4$ **ONLINE JEE-MAIN**  $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$ 6. Sol. t = 0 50 0 0  $t = 30 \quad 50 - 2x$ 4x х  $\Rightarrow 87.5 = 50 + 3x$  $\Rightarrow$  3x = 37.5  $\Rightarrow$  x = 12.5  $\Rightarrow P_{N_2O_5}$  after 30 min = 50 – 25 = 25  $\Rightarrow$  t<sub>1/2</sub> = 30 min. 50 Hence afer 60 min, (two half lives),  $P_{N_2O_5}$  remaining =  $\frac{4}{4}$  = 12.5 torr.  $\Rightarrow$  Hence decrease in  $P_{N_2O_5} = 50 - 12.5 = 37.5$  torr.  $\Rightarrow P_{N_2O_5} = 2 \times 37.5 = 75 \text{ torr.}$ 37.5  $P_{O_2} = 2 = 18.75$  torr

- **7. Sol.** Rate is first order with respect to B. So it doubles on doubling concentration of B. While keeping concentration of A as same.
- 8. Sol.  $\Delta H = E_{af} E_{ab}$   $\Rightarrow -40 = 2x - 3x$  $\Rightarrow E_{ab} = 80 \text{ kJ/mol}$ ;  $E_{ab} = 120 \text{ kJ/mol}$

 $\Rightarrow$  P<sub>total</sub> = 12.5 + 75 + 18.75 = 106.25 torr.

9.

 $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$ Sol. t = 0 50 0 0  $t = 30 \quad 50 - 2x$ 4x Х 87.5 = 50 + 3x⇒ x = 12.5 3x = 37.5 $\Rightarrow$ ⇒  $P_{N_2O_5}$  after 30 min = 50 – 25 = 25 ⇒

 $\Rightarrow$   $t_{1/2} = 30$  min.

Hence after 60 min, (two half lives),  $P_{N_2O_5}$  remaining =  $\frac{50}{4}$  = 12.5 torr.

 $\Rightarrow$  Hence decrease in  $P_{N_2O_5} = 50 - 12.5 = 37.5$  torr.

 $\Rightarrow \qquad P_{NO_2} = 2 \times 37.5 = 75 \text{ torr} \\ P_{O_2} = \frac{37.5}{2} = 18.75 \text{ torr}$ 

- $\Rightarrow$  P<sub>total</sub> = 12.5 + 75 + 18.75 = 106.25 torr.
- **10. Sol.** Rate is first order with respect to B. So it doubles on doubling concentration of B, while keeping concentration of A as same.
- 11. Sol.  $\Delta H = E_{af} E_{ab}$   $\Rightarrow -40 = 2x - 3x$   $\Rightarrow E_{af} = 80 \text{ kJ/mol}$  $E_{ab} = 120 \text{ kJ/mol}$
- **12. Sol.** The rate constant of overall reaction depends slowest step. Hence equation(i) is slowest step. Option(2) is correct.

14. Sol. 
$$\log \frac{K_1}{K_2} = \frac{\varepsilon_a}{2.303 \text{ R}} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$
  
for A log 2 =  $\frac{\varepsilon_{aA}}{2.303 \text{ R}} \left(\frac{1}{300} - \frac{1}{310}\right)$  ....(1)  
for B log 2 =  $\frac{\varepsilon_{a\theta}}{2.303 \text{ R}} \left(\frac{1}{300} - \frac{1}{T_2}\right)$  ....(2)  
On dividing (2) by (1) T\_2 = 304.92 K

15.

Sol. Form arthenius equation

$$\ell n \qquad \left(\frac{k_2}{k_1}\right)_{=} \qquad \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$
$$\therefore 4 = \frac{E_a}{8.314} \left(\frac{1}{300} - \frac{1}{310}\right)$$
$$\therefore E_A \approx 107166 \text{ J} \approx 107.2 \text{ kJ}$$

### PART - II : JEE (ADVANCED) / IIT-JEE PROBLEMS (PREVIOUS YEARS)

- **1. Sol.** r = k [A]
- $2.4 \times 10^{-5} = 3 \times 10^{-5} \times [A] \qquad \Rightarrow \qquad [A] = 0.8 \text{ M}$
- 2. Sol. Rate of formation of AB will depend upon intensity of absorbed light and it will directly proportional to intensity

3.

- Sol. For a chemical reaction,
  - $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$

⇒

Concentration of  $N_2$  and  $H_2$  are decreased so negative sign is represented in expression, while concentration of  $NH_3$  is increased. So +ve. sign is represented in expression. Also, from stoichiometry it can be said that the time during which 1 mole of  $N_2$  will be consumed in the same time 3 moles of  $H_2$  is consumed and 2 moles of  $NH_3$  is formed.

4. Sol. For Ist order Rxn

 $[A] = [A_0]^{n} \qquad n \rightarrow \text{No. of Half life.}$   $50 = 800 \qquad \left(\frac{1}{2}\right)^{n}$  n = 4.Then, Half life =  $\frac{2 \times 10^4}{4} = 5 \times 10^3 \text{ sec.}$   $\frac{0.6932}{5 \times 10^3} = 1.38 \times 10^{-4} \text{ sec}^{-1}.$ 

**5. Sol.** Since 0.01 M of X changes to 0.0025 M in 40 minutes,  $t_{1/2}$  of reaction = 40/2 = 20 minutes Rate of reaction of

$$\mathbf{r} = \mathbf{k}[\mathbf{X}] = \frac{0.693}{t_{1/2}} \times [\mathbf{X}] = \frac{0.693}{20} \times 0.01 = 3.47 \times 10^{-4} \,\mathrm{M \,min^{-1}}.$$

- 6. Sol. Rate of exchange of <sup>14</sup>C between atmosphere and living organism is so fast that an equilibrium is set up between the intake of <sup>14</sup>C by organism and its exponential decay.
- 7. Sol. Fossil has 6000 year age for the determination of the age of old organism.

**Sol.** 
$$\lambda = \frac{1}{T_1 - T_2} \frac{C_1}{\ln C_2}$$

8.

- 9. Sol.  $aG + bH \longrightarrow products$   $Rate = k[G]^{x} [H]^{y} \Rightarrow$   $R = K [G]_{0^{x}} [H]_{0^{y}}$  (Let initial conc. are  $[G]_{0} \& [H]_{0}$ )  $8R = K[2G]_{0^{x}} [2H]_{0^{y}} = K2^{x}.2^{y}R$ so  $2^{x+y} = 8 \Rightarrow x+y = 3$
- **10.** Sol. For I<sup>st</sup> order reaction  $k_{1} = \frac{ln2}{t_{1/2}} = \frac{0.693}{40} \operatorname{second}^{-1}$ For zero order reaction  $k_{0} = \frac{ln2}{2} = \frac{1.386}{2 \times 20}$ For zero order reaction  $k_{0} = \frac{ln2}{2} = \frac{1.386}{2 \times 20}$ For zero order reaction
- 11. Sol. From Arrhenius equation  $K = Ae^{-Ea/RT}$   $\frac{Ea}{\ell nk} = \ell nA - \frac{Ea}{RT}$ 2.303 log K = 2.303 log A -  $\frac{Ea}{RT}$   $\log K = \frac{-Ea}{2.303 \text{ R}} \times \frac{1}{T} + \log A \qquad \dots (A)$   $\log K = -(2000) \frac{1}{T} + 6 \qquad \dots (B)$



**13. Sol.** For P, if  $t_{50\%} = x$ then  $t_{75\%} = 2x$ This bappens only in first

This happens only in first order reaction. So, order with respect to P is 1. For Q, the graph shows that concentration of Q decreases linearly with time. So rate, with respect to Q, remains constant. Hence, it is zero order wrt Q. So, overall order is  $0 + 1 = 1 \rightarrow Ans$ . is D

14. Sol. As ester hydrolysis is first order with respect to [H<sup>+</sup>].

$$\frac{R_{HA}}{R_{HX}} = \frac{[H^+]_{HA}}{[H^+]_{HX}}$$

$$\frac{1}{100} = [H^+]_{HA}$$

$$HA \qquad \qquad H^+ + A^-$$

$$1 - 0.01 \qquad 0.01 \qquad 0.01$$

$$\approx 1$$

$$K_a = \frac{0.01 \times 0.01}{1} = 10^{-4}$$

15. Sol. M  $\longrightarrow$  N  $r = K [M]^{x}$ as [M] is doubled, rate increases by a factor of 8. i.e.  $8r = K [2M]^{x} \Rightarrow 8 = (2)^{x}$ x = 3

**16. Sol.** Initially on increasing temperature rate of reaction will increase, so % yield will also increase with time. But at equilibrium % yield at high temperature (T<sub>2</sub>) would be less than at T<sub>1</sub> as reaction is exothermic so the graph is :



### Additional Problems For Self Practice (APSP)

### **PART - I : PRACTICE TEST PAPER**

1. 2B(g) Sol. A(g) +  $\rightarrow$ C(g) 0 atm t = 00.4 atm 1 atm t = t(0.4 - 0.3) atm (1 - 0.6) atm 0.3 atm Since reaction is elementary. So, Rate of reaction w.r.t. A & B will be of order equal to stoichiometric coefficient Rate = K [A]  $[B]^2$ Rate(Initial) = K [0.4]  $[1]^2$  $Rate_{(aftar t = t)} = K [0.1][0.4]^2$  $R_{(t=t)}$  K[0.1] [0.4]<sup>2</sup> 1  $\overline{R_{(t=o)}} = K[0.4]$  [1] <sub>=</sub> 25

**2. Sol.** Rate constant change on changing temperature.

5. Ans. 
$$k = \frac{1}{t} \ln \left( \frac{P_0}{2P_0 - P_t} \right)$$
  
Sol.  $A \rightarrow B + C$   
 $t = 0 Po$   
 $t = f Po \cdot x \cdot x$   $pt = Po + x$ .  
 $k = t rm \frac{P_0}{P_0 - x} = \frac{P_0}{P_0 - P_t - Pt}$ 

10. Sol. 
$$K_{eq} = \frac{k_f}{k_b} = \frac{[CH_3]^2}{[C_2H_6]}$$

$$\therefore \qquad [CH_3] = \frac{10^{-4}}{10} = 10^{-5} M$$
$$\frac{1.57 \times 10^{-3}}{k_b} = \frac{(10^{-5})^2}{1}$$

$$\Rightarrow$$
 k<sub>b</sub> = 1.57 × 10<sup>7</sup> L mol<sup>-1</sup>s<sup>-1</sup>

11.

$$k = \frac{2.303}{t} \log\left(\frac{C_{A_0}}{C_A}\right)$$
Sol.  

$$log\left(\frac{C_{A_0}}{C_A}\right)$$

$$2.303 \times 1 = 2.303$$

$$\frac{\log\left(\frac{C_{A_0}}{C_A}\right)}{C_A}$$

$$= 10$$

$$C_A \Rightarrow \frac{1}{10} = 0.1$$

$$\therefore$$
rate after 1 min r<sub>1</sub> = k.C<sub>A</sub>  

$$\Rightarrow 2.0303 \times 0.1 \Rightarrow 0.2303 \text{ min}^{-1}$$

12.  $r_1 = k[A]^2 [B]; r_2 = k[2A]^2 [2B] = 8 r_1$ Sol.  $K = Ae^{-E_a/RT}$ 13. Sol.  $\mathsf{E}_{\mathsf{a}}$ When T = infinite, then -RT = 0Or  $e^{-E_a/RT} = 1$  $K_{max} = A$ 0.2 M  $\xrightarrow{t_{1/2}=5 \text{ hr}}$  0.1 M  $t_{1/2}=5 \text{ hr}$ 0.05 M 14. Sol. t = 10 hr 0.05 M From 0.2 M So t<sub>1/2</sub> is constant which is characteristic of first order reaction. Hence,  $t_{1/2} \propto (a)^0$ . 15. Sol. First step is slow (require large activation energy) second step is fast (less activation energy) and overall reaction exothermic, so product energy level should be less as compare to reactants. 17.  $r_1 = k[A] [B]^2 = k[0.6] [0.80]^2$ Sol. After reaction 2B С D А + 0.6 - 0.20.8 - 0.40.2 0.2 0.4 0.4 0.2 0.2  $\frac{r_2}{r_2} = \frac{k(0.4)(0.4)^2}{r_2}$ 1  $(0.6)(0.8)^2$ 6 r<sub>1</sub>  $\frac{d(BrO_{3}^{-})}{dt} = -\frac{1}{5} \frac{d(Br^{-})}{dt} = -\frac{1}{6} \frac{d(H^{+})}{dt} = +\frac{1}{6} \frac{d(H^{+})}{$  $d(Br_2)$ dt 18. Sol. We know  $d(Br_2)$ 3 d(Br<sup>-</sup>) dt 5 dt Then by this relation \_ \_ 19. Sol. Rate = k [conc]<sup>n</sup>  $\longrightarrow$  Independent of conc. of A. 20. Sol. More is the activation energy less is the rate of reaction.  $t_{1/2} = \frac{t}{4} \ ; \ t_{1/2} = T \ ln \ 2$ 21. Sol. so  $4 = T \ln 2$ ; t = 4T ln 2 22. Sol. it is a parabolic graph dC dt of  $y = x^2$ С So This is the graph of second order





9. **Sol.**  $A + B \rightarrow C$  $R = K [A]^{m} [B]^{n}$ compere exp. (1) (3) 0.2 0.1 = [2]<sup>m</sup> m = 1 compere exp. (2) & (3) $\frac{1.6}{0.2} = \left(\frac{0.07}{0.035}\right)^n$ n = 3  $R = k A [B]^{3}$  $\left(\frac{K_2}{K_1}\right) = \frac{E_a}{2.303R} \frac{E_a}{2.303R} = \frac{65 \times 10^3 \times (298 - 273)}{2.303 \times 8.3 \times 298 \times 273}$ loa 10. Sol.  $\frac{K_2}{K_1} = 11$ calculation we find  $\Delta H = Eaf - Eab < 0$  (for exothermic) 11. Sol. 50 – Eab < 0 So Eab > 50 12. Sol. – 20 = 30 – Eab Eab = 50.14. Rate =  $k_1$  [M] [Z] Sol. .....(1) [M] from equation (1)  $K_{eq} = [x][y]$ .  $M = k_{eq} [x] [y]$ .....(2) put the value of M from (2) to (1) Rate =  $k_1$  keq [x] [y] [z] Rate = k [x] [y] [z]100 d  $\frac{dt}{dt}$  [SO<sub>3</sub>] = 100 gram / min =  $\frac{80}{80}$  mole / min = 1.25 mole/min 17. Sol. -1 d -d 1 d 2 dt [SO<sub>2</sub>] = dt [O<sub>2</sub>] = 2 dt [SO<sub>3</sub>] -d 1.25 1.25 dt  $[O_2] = 2$  mole/min = 2 x 32 gram/min = 20 gram/min 18. Sol. Rate wrt A is 2 and wrt B is zero. Rate wrt RCI is 1. 19. Sol. **Sol.**  $4A + B \longrightarrow 2C + 2D$ 20. 1 d[A] d[B] 1 d[C] 1 d[D] \_ 4 dt \_\_ dt \_+ 2 dt \_ 2 dt 21. Sol.  $0.4 \longrightarrow 0.2 \longrightarrow 0.1$  $t_{1/2} = 1hr.$ 1hr. t<sub>1/2</sub> is censtant, so I<sup>st</sup> asder. : a  $\xrightarrow{5\text{min}}$  2a  $\xrightarrow{5\text{min}}$  a  $\xrightarrow{5\text{min}}$  a/2 22. Sol. А 5min →a/2 :a — В So time is 15 mintes. 23. Sol. A is in excess, so Rate will be independent of change in concentration.

$$R = k [B]^{n}$$

$$R = R 4^{n} [B]^{n} \qquad n = \frac{1}{2}.$$
24. Sol. For zero order  $t_{1/2} = \frac{a_{0}}{2k}$ , so  $\frac{t_{1/2} \times a_{0}}{2k} = \frac{a^{2}}{2k}$  is not a constant.  
For 1<sup>st</sup> order  $t_{1/2}$  is constant so  $\frac{t_{1/2} \times a_{0}}{k}$  is not constant.  
For 2<sup>nd</sup> order  $t_{1/2} = \frac{1}{a_{0}k}$  so  $\frac{t_{1/2} \times c_{0} = k}{k}$  is constant.  
26. Sol.  $2A + B \xrightarrow{k} C + D$   
 $r = K [A]^{1} [B]^{2} \qquad r_{0} = K (C_{0})^{1} (2C_{0})^{2} = 4 K (C_{0})^{3} \qquad .....(1)$   
 $t = 0 \qquad C_{0} \qquad 2C_{0} \qquad 0 \qquad 0$   
 $(C_{0} - 2x) (2C_{0} - x) \qquad x \qquad x$   
 $x = \frac{\left(\frac{C_{0}}{4}\right)}{(A] = C_{0} - \frac{C_{0}}{2} = \frac{C_{0}}{2}} \qquad [B] = 2C_{0} - \frac{T}{4} = \frac{T}{4}$   
 $r = K \left(\frac{C_{0}}{2}\right) \left(\frac{T}{2} \frac{C_{0}}{7}\right)^{2} = \frac{49K(C_{0})^{3}}{32}$ 

- **28.** Sol. From the given graph it is clear that the concentration decrease linearly with time then zero order Reaction and  $A \rightarrow 3B$  type.

**30.** Sol. 
$$E_a = 41570 \times R = 41570 \times 8.31 = 345446.70 J$$

31. Sol. For Rxn rate determining step is slowest step Then in 1st mechanism Rate = k [NO<sub>2</sub>] [O<sub>3</sub>] .....(i) But in 2nd mechanism  $k_a \text{ fast}$  (1)

$$O_{3} \xrightarrow{k_{b}} O_{2} + [O] \qquad \dots (1)$$

$$NO_{2} + O \xrightarrow{slow} NO_{3} \qquad \dots (2)$$

NO<sub>3</sub> + NO<sub>2</sub> 
$$\xrightarrow{\text{fast}}$$
 N<sub>2</sub>O<sub>5</sub> ....(3)  
Then for Rxn (1)

$$\frac{k_{a}}{k_{b}} = \frac{[O_{2}] \ [O]}{[O_{3}]} = k_{eq} \qquad \dots (4)$$

....(ii)

by Rxn (2) Rate = k [NO<sub>2</sub>] [O] put value of [O] from (4) to (ii)  $k_{og}$  [O<sub>2</sub>]

Rate = k 
$$\frac{k_{eq} [O_3]}{[O_2]} \times [NO_2]$$
$$\frac{k_1 [NO_2] [O_3]}{[O_2]}$$

- 33. Sol. N<sub>2</sub>(g) + 3H<sub>2</sub>(g) → 2NH<sub>3</sub>(g)  $\frac{-d[N_2]}{dt} = -\frac{1}{3}\frac{d[H_2]}{dt} = +\frac{1}{2}\frac{d[NH_3]}{dt}$   $\frac{-d[H_2]}{dt} = \frac{3}{2}\frac{d[NH_3]}{dt} = \frac{3}{2} \times 0.001 = 0.0015 \text{ mole h}^{-1}$
- **35. Sol.**  $t_{1/2} \propto a^{1-n}$ here  $t_{1/2} \propto a^{-1}$  $-1 = 1-n \Rightarrow n = 2$