

CHEMICAL KINETICS (SOLUTION)

1. (B) Rate law = $r = k_1 [O][O_3]$

$$K = \frac{[O_2][O]}{[O_3]} \Rightarrow r = k_1 K \frac{[O_3]^2}{[O_2]}$$

Since it is given $r = \frac{k[O_3]^2}{[O_2]}$

$$k = Kk_1$$

2. (B) Using $\frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{p_2}{p_1}\right)^{n-1}$

Where p_2, p_1 are the initial pressures

We get

$$\frac{80}{113} = \left(\frac{0.8}{1.6}\right)^{n-1}$$

Taking logarithms.

$$\log 0.7 = (n-1)\log 0.5$$

$$\Rightarrow n = 1.5$$

3. (A) $\frac{n_{CH_4} + n_{CO_2}}{n_{CH_2CO} + n_{H_2O}} = \frac{k_1}{k_2}$

$$\Rightarrow \frac{n_{CH_4} + n_{CO_2}}{n_{CH_4} + n_{CO_2} + n_{CH_2CO} + n_{H_2O}} = \frac{k_1}{k_1 + k_2}$$

$$\Rightarrow \frac{2n_{CH_4}}{n_{total}} = \frac{k_1}{(k_1 + k_2)} \Rightarrow \frac{n_{CH_4}}{n_{total}} = \frac{k_1}{2(k_1 + k_2)}$$

$$\Rightarrow \frac{n_{CH_4}}{n_{total}} \times 100 = \frac{50k_1}{(k_1 + k_2)}$$

4. (B) Let the reaction is of 1st order.

$$k = \frac{2.303}{t} \log \frac{(A_0)}{[A]}$$

From 1st data, $k = \frac{2.303}{480} \log \frac{100}{100-80} = 3.35 \times 10^{-3}$

2nd data $k = \frac{2.303}{18 \times 60} \log \frac{100}{100-90} = 2.132 \times 10^{-3}$

Now try for 2nd order.

$$K = \frac{1}{t} \left[\frac{1}{[A]} - \frac{1}{[A_0]} \right]$$

From 1st data, $k = \frac{1}{480} \left[\frac{1}{1 \times \frac{20}{100}} - \frac{1}{1} \right] = 8.33 \times 10^{-3}$

$$2^{\text{nd}} \text{ data } k = \frac{1}{18 \times 60} \left[\frac{1}{1 \times \frac{10}{100}} - \frac{1}{1} \right] = 8.33 \times 10^{-3}$$

Since, data is following 2nd order kinematics, the reaction is of 2nd order.

5. (C) This is a gaseous phase reaction. One mole of gaseous ether decomposes to give three moles of gaseous products.

p_i = initial pressure of ether

x = decreases in pressure of ether after time t

$3x$ = pressure of three gaseous products after time t

\therefore Total pressure at time $t = (p_i - x) + 3x = p_i + 2x$

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

$$3.2 \times 10^{-4} \text{ s}^{-1} = \frac{2.303}{(8 \times 60)} \log \left(\frac{0.350}{0.350 - x} \right)$$

$$\frac{3.2 \times 10^{-4} \times 480}{2.303} = \log \left(\frac{0.350}{0.350 - x} \right)$$

$$\log \left(\frac{0.350}{0.350 - x} \right) = 0.0667$$

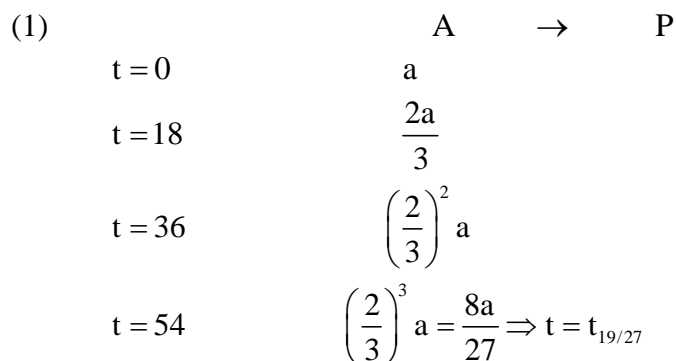
$$\left(\frac{0.350}{0.350 - x} \right) = 1.166 \Rightarrow x = 0.05$$

$$P_{\text{total}} = p_i + 2x = 0.35 + 2 \times 0.05 = 0.45 \text{ atm}$$

6. (B) For a zero order reaction, $t_{1/2} = [A_0] / 2K$.

7. (A) Rate expression $\frac{dx}{dt} = k[A]^m[B]^n$ shows that the total order of reaction is $m + n + 0 = m + n$ as the rate of reaction is independent of concentration of C, i.e., the order with respect to C is zero. This is the reaction that C does not figure in the rate expression.

8. (A)



$$(2) \quad \begin{array}{l} A \rightarrow P \\ t=0 \quad a \\ t=16 \quad \frac{3a}{4} \\ t=32 \quad \left(\frac{3}{4}\right)^2 a = \frac{9}{16}a \Rightarrow t = t_{7/16} \end{array}$$

$$(3) \quad \begin{array}{l} A \rightarrow P \\ k = \frac{1}{4} \left[\frac{3}{2a} - \frac{1}{a} \right] = \frac{1}{8a}; \frac{1}{8a} = \frac{1}{56} \left[\frac{1}{[A]_t} - \frac{1}{a} \right] \\ [A]_t = \frac{a}{8} \Rightarrow t = t_{7/8} \end{array}$$

$$(4) \quad \begin{array}{l} A \rightarrow P \\ t=0 \quad a \\ t=6 \quad a-x \\ t=18 \quad a-3x = 2a/3 \Rightarrow x = a/9 \\ t=30 \quad a-5x \Rightarrow t = t_{5/9} \end{array}$$

$$(5) \quad \begin{array}{l} A \rightarrow P \\ t=0 \quad a \\ t=4 \quad a-x \\ t=16 \quad a-4x = a/2 \Rightarrow x = a/8 \\ t=28 \quad a-7x \Rightarrow a - (7a/8) \Rightarrow t = t_{7/8} \end{array}$$

9. (B)

(p) When concentration of B is maximum

$$t_{\max} = \frac{1}{(k_2 - k_1)} \ln \left(\frac{k_2}{k_1} \right)$$

(q) When $t = t_{1/2}$ of A = $\frac{\ln 2}{k_1}$ and $k_2 = 2k_1$

$$[B]_t = \frac{k_1 [A_0]}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) = [A_0] (e^{-\ln 2} - e^{-2 \ln 2}) = [A_0] \left(\frac{1}{2} - \frac{1}{4} \right) = \frac{[A_0]}{4}$$

$$[C]_t = [A_0] - [A] - [B] = [A_0] - \frac{[A_0]}{2} - \frac{[A_0]}{4} = \frac{[A_0]}{4}$$

$$\Rightarrow [B]_t = [C]_t$$

(r) $[A]_t = [B]_t$

$$\text{Or } [A]_0 e^{-k_1 t} = \frac{k_1 [A_0]}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t})$$

$$\text{Or } \frac{k_2 - k_1}{k_1} = 1 - e^{-(k_2 - k_1)t}$$

$$\text{Or } e^{(k_1 - k_2)t} = 1 - \frac{k_2 - k_1}{k_1} = \frac{2k_1 - k_2}{k_1} = 2 - \frac{k_2}{k_1}$$

$$\therefore t = \frac{\ln(2 - k_2/k_1)}{k_1 - k_2}$$

10. (A) For first order reaction

$$k = \frac{1}{t} \log \frac{a}{a-x} = \frac{1}{t} \ln \frac{(P_f - P_0)}{(P_f - P_t)}$$

$$\begin{aligned} k(\text{hr}^{-1}) &= \frac{1}{70/3600} \ln \frac{500-200}{350-200} \\ &= \frac{3600}{70} \ln \frac{300}{150} = \frac{3600}{70} \ln 2 \\ &= \frac{3600}{700} \times 0.7 = 36 \end{aligned}$$

$$\text{Hence, } x = \frac{36}{9} = 4$$

11. (C) In first order reactions, equal fraction completes in equal time intervals. So, it does not depend on initial concentration of the reactant.

12. (B) Since B is in large excess, rate law will become

$$\text{Rate} = k'[A]^2 \text{ where } k' = k[B]$$

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = k't; \quad \frac{1}{[A]_0 k'} = t_{1/2};$$

$$t_{1/2} = \frac{1}{0.2 \times 5 \times 10^{-5} \times 2 \times 10^3} = 50 \text{ minutes}$$

13. (A) $1.5 \times 10^{-4} \times \frac{1}{100} = e^{-E_a/RT} \cdot 1.5$

$$\Rightarrow 1.5 \times 10^{-6} = e^{-E_a/R \times 300}$$

$$\therefore E_a = 33.43 \text{ kJ mole}^{-1};$$

Using $k = e^{-E_a/RT}$, we get

$$\frac{dk}{dT} = \frac{E_a}{RT^2} k$$

$$\begin{aligned} k &= 0.2 \times \frac{8.314 \times 325 \times 325}{33.45 \times 1000} = 5.25 \text{ s}^{-1} = 315 \text{ min}^{-1} \\ &= 3.15 \times 10^2 \text{ min}^{-1} \end{aligned}$$

14. (B) Let the equation of straight line is $P = mV + c$

Now putting the values, we get $P + V = 12$

From the ideal gas equation,

$$T = \frac{PV}{nR} = \frac{PV}{R}; \quad T = \frac{(12-V)V}{R}$$

For T to be maximum $\frac{dT}{dV} = 0$

$$V = 6 \text{ lt.}, P = 6 \text{ atm}$$

$$\text{Value of } T_{\max} = \frac{36}{0.082} = 439\text{K}$$

Now putting the values of $A = 20\text{sec}^{-1}$

$$E_a = 40 \times 10^3 \text{ J mole}^{-1}$$

We get, $k = A e^{-E_a/RT}$

$$k = 20 e^{\frac{10 \times 10^3}{8.314 \times 439}} = 3.4788 \times 10^{-4} \text{ sec}^{-1} \text{ or } 3.48 \times 10^{-4} \text{ sec}^{-1}$$

15. (C) $\frac{d \ln K}{dT} = \frac{E_a}{RT^2} \therefore \frac{dK}{K} = \frac{E_a}{RT^2} dT$

$$\frac{dK}{K} = \frac{11.11}{100}; dT = 1^\circ\text{C}; T = 27^\circ\text{C} = 300\text{K}$$

$$\therefore 0.1111 = \frac{E_a \times 1}{1.987 \times 300 \times 300},$$

$$\therefore E_a = 0.1111 \times 1.987 \times [300]^2$$

At 127°C ,

$$\frac{dK}{K} = \frac{E_a}{1.987} \times (400)^2 = \frac{0.1111 \times 1.987 \times (300)^2}{1.987 \times (400)^2}$$

$$= 0.1111 \times \left(\frac{3}{4}\right)^2 = 0.06249$$

$$\therefore \% \text{ increase} = 6.25$$

16. (AD) In first order reaction, if α is the degree of dissociation therefore

$$kt = \log_e \frac{1}{(1-\alpha)} = -\log_e (1-\alpha) \text{ or } e^{-kt} = 1-\alpha$$

$$\therefore \alpha = 1 - e^{-kt}$$

The Arrhenius equation is, $k = A e^{-E_a/RT}$

Dimensions of pre-exponential factor 'A' are equivalent to dimensions of k, which is $T^{-1}(\text{time}^{-1})$ for a first order reaction.

17. (BC) Arrhenius equation is given by

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

Where $e^{-E_a/RT}$ is a dimensionless quantity and A has units as that of rate constant (k).

18. (BCD) According to activated complex theory for a reaction to occur the reactant molecules and having sufficient energy must approach each other to form activated complex. This intermediate product has partially formed bonds and the energy of this complex is higher than that of reactants and products. Transition states although has no independent existence but it has more vibrational character than unstable intermediate because in the formation of unstable intermediate one vibrational degree of freedom changes into translational degree of freedom.