

Daily Tutorial Sheet 1

JEE Advanced (Archive)

- 1.(A) It is a constant of a particular reaction at a given temperature. It does not depend upon initial concentration of the reactants, time of reaction and extent of reaction.

2. (i) $A = 1, B = 0$ (ii) $t_{1/2} = 1.386 \text{ min}$

Looking at the rate data of experiment number 1 and 2 indicates that rate is doubled on doubling concentration of A while concentration of B is constant. Therefore, order with respect to A is 1. Similarly, comparing data of experiment number 1 and 3, doubling concentration of B, while concentration of A is constant, has no effect on rate.

Therefore, order with respect to B is zero.

$$\Rightarrow \text{Rate} = k[A] \quad \Rightarrow \quad k = \frac{0.005}{0.010} = 0.5 \text{ min}^{-1} = \frac{0.693}{t_{1/2}} \quad \Rightarrow \quad t_{1/2} = \frac{0.693}{0.5} = 1.386 \text{ min}$$

3. (i) $k = 0.023 \text{ min}^{-1}$, (ii) 60 min

For a first order reaction,

$$kt = \ln \frac{[A]_0}{[A]}$$

Where $[A]_0$ = Initial concentration of reactant

$[A]$ = Concentration of reactant remaining unreacted at time t

$$(i) \quad k = \frac{1}{t} \ln \frac{[A]_0}{[A]} = \frac{1}{10} \ln \frac{100}{100 - 20} = \frac{1}{10} \ln \frac{5}{4} = \frac{2.303(\log 5 - 2 \log 2)}{10} \text{ min}^{-1} = 0.023 \text{ min}^{-1}$$

$$(ii) \quad t = \frac{1}{k} \ln \frac{100}{25} = \frac{2 \ln 2}{k} = \frac{2 \times 0.693}{0.023} = 60 \text{ min}$$

- 4.(D) It is characteristic constant of a particle reaction at a given temperature. It does not depend upon initial concentration of the reactants, time of reaction and extent of reaction.

- 5.(C) A catalyst does not change the position of equilibrium, through it helps in reaching the equilibrium faster.

- 6.(BC) A catalyst decreases the activation energy by altering the mechanism.

7. Decomposition of N_2O_5 follows first order kinetics

$$\text{For a first order process : } \ln \frac{[A]_0}{[A]} = kt$$

$$\Rightarrow \ln[A] = \ln[A]_0 - kt$$

If the reactant is in gaseous state

$$\ln p = \ln p_0 - kt \quad \dots (i)$$

Where p is the partial pressure of reactant remaining unreacted at instant ' t ' and p_0 is its initial partial pressure.

Also, from equation (i), $\ln p$ vs t would give a straight line. Therefore, decomposition of N_2O_5 following first order kinetics.

8. Concentration of reactant(s) at that instant

$$9.(T) \quad \frac{(2[A])^1}{[A]^1} \text{ for } A \rightarrow \text{products.}$$

10. Acidic, first or basic, second

- 11.(128.33 hr)

$$k = 1.5 \times 10^{-6} \text{ s}^{-1}$$

$$kt = \ln \frac{100}{100 - x}$$

$$\Rightarrow \ln \frac{100}{100-x} = 1.5 \times 10^{-6} \text{ s}^{-1} \times 10 \times 60 \times 60 \text{ s} = 0.0054$$

$$\Rightarrow \frac{100}{100-x} = 1.055$$

$\Rightarrow x = 5.25\%$ reactant is converted into product.

$$\text{Half-life} = \frac{\ln 2}{k} = \frac{0.693}{1.5 \times 10^{-6}} = 462000 \text{ s} = 128.33 \text{ h}$$

12. $k = 0.0231 \text{ min}^{-1}$, $43.848 \text{ kJ mol}^{-1}$

$$k = \frac{0.693}{t_{1/2}}; \frac{k_2}{k_1} = \frac{E_a}{2.303} \left[\frac{T_2 - T_1}{T_1 \cdot T_2} \right]$$

Substituting the value at the two given conditions

$$k_1 = k_{300} = \frac{0.693}{30} = 0.0231 \text{ min}^{-1} \quad \Rightarrow \quad k_2 = k_{320} = \frac{0.693}{10} = 0.0693 \text{ min}^{-1}$$

$$\text{We also know that } \log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \times \frac{T_2 - T_1}{T_1 \times T_2}$$

$$\text{or } E_a = \frac{2.303R \times T_1 \times T_2}{T_2 - T_1} \log \frac{k_2}{k_1} = \frac{2.303 \times 8.314 \times 10^{-3} \times 300 \times 320}{320 - 300} \times \log \frac{0.0693}{0.0231} = 43.848 \text{ kJ mol}^{-1}$$

13.(311.34 K)

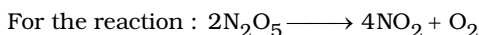
$$\text{Arrhenius equation is: } \log k = \log A - \frac{E_a}{2.303 RT}$$

$$\text{When } t_{1/2} = 10 \text{ min}, k = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{10 \times 60} = 1.15 \times 10^{-3} \text{ s}^{-1}$$

$$\frac{E_a}{2.303RT} = \log A - \log k = \log \frac{A}{k} = 16.54$$

$$T = \frac{E_a}{2.303R \times 16.54} = \frac{98.6 \times 1000}{2.303 \times 16.54 \times 8.314} = 311.34 \text{ K}$$

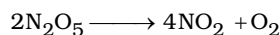
14. $5.2 \times 10^{-3} \text{ min}^{-1}$



If p_0 is the initial pressure, the total pressure after completion of reaction would be $\frac{5}{2}p_0$

$$\Rightarrow 584.5 = \frac{5}{2}p_0 \Rightarrow p_0 = 233.8 \text{ mm}$$

Let the pressure of N_2O_5 decreases by 'p' amount after 30 min. Therefore,

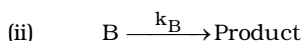
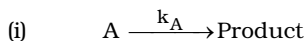


$$\text{At 30 min: } \quad p_0 - p \quad \quad 2p \quad \quad \frac{p}{2}$$

$$\text{Total pressure} = p_0 + \frac{3}{2}p = 284.5 = p = \frac{2}{3}(284.5 - 233.8) = 33.8$$

$$\text{Now, } kt = \ln \frac{p_0}{p_0 - p} \quad \Rightarrow \quad k = \frac{1}{30} \ln \frac{233.8}{233.8 - 33.8} \text{ min}^{-1} = 5.2 \times 10^{-3} \text{ min}^{-1}$$

15. $t_{1/2} = 21.2 \text{ min}$, $k = 3.26 \times 10^{-2} \text{ min}^{-1}$



$$\text{For (i)} \quad \frac{E_a}{R} \left(\frac{10}{300 \times 310} \right) = \ln 2$$

$$\Rightarrow E_a(\text{i}) = 9300 \ln 2 = 53.6 \text{ kJ} \quad \Rightarrow E_a(\text{ii}) = \frac{E_a(\text{i})}{2} = 26.8 \text{ kJ}$$

At 310 K $t_{1/2}(\text{i}) = 30 \text{ min}$

$$\therefore \text{Rate of (ii)} = 2 \text{ rate of (i)} \Rightarrow t_{1/2}(\text{ii}) = 15 \text{ min}$$

Now for reaction (ii):

$$\ln \left\{ \frac{k_B(310)}{k_B(300)} \right\} = \ln \left\{ \frac{t_{1/2}(300)}{t_{1/2}(310)} \right\} = \frac{E_a(\text{ii})}{R} \left(\frac{10}{300 \times 310} \right)$$

$$\Rightarrow \ln \left\{ \frac{t_{1/2}(300)}{15} \right\} = \frac{\ln 2}{2} \quad \Rightarrow t_{1/2}(300) = 21.2 \text{ min}$$

$$\Rightarrow k_B(300) = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{21.2} = 3.26 \times 10^{-2} \text{ min}^{-1}$$