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 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.

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

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

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

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

For a first order process : $\ln\frac{[A]_2}{[A]} = kt$

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

If the reactant is in gaseous state

$\ln p = \ln p_0 - kt$ **... (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) $\frac{(2[A])^1}{[A]^1}$ for A → products.

10. Acidic, first or basic, second

11.(128.33 hr)

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

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

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

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

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

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

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

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

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

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)

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

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

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

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

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

For the reaction : $2N_2O_5 \longrightarrow 4NO_2 + O_2$

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

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

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

$$2N_2O_5 \longrightarrow 4NO_2 + O_2$$

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

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

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

(i) $A \xrightarrow{k_A} \text{Product}$

(ii) $B \xrightarrow{k_B} \text{Product}$

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

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

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

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

Now for reaction (ii):

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

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

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