# IMPORTANT QUESTIONS CLASS – 127<9A=GHFM CHAPTER – 3 CHEMICAL KINETICS

## Question 1.

# What is meant by rate of a reaction? Differentiate between average rate and instantaneous rate of a reaction.

# Answer:

**Rate of reaction:** It is the change in concentration of the reactants or products in a unit time. Average rate : Average rate depends upon the change in concentration of reactants or products and the time taken for the change to occur.  $R \rightarrow P$ 

Average rate = 
$$-\frac{\Delta[R]}{\Delta t}$$
  
or Average rate =  $+\frac{\Delta[P]}{\Delta t}$ 

**Instantaneous rate:** It is defined as the rate of change in concentration of any one of the reactant or product at a particular moment of time.

$$\lim_{\Delta t \to 0} \left[ \frac{-\Delta[\mathbf{R}]}{\Delta t} \right] = \frac{-d[\mathbf{R}]}{dt}$$

# Question 2.

(a) What is the physical significance of energy of

activation ? Explain with diagram.

(b) In general, it is observed that the rate of a chemical

reaction doubles with every 10 degree rise in

temperature. If the generalization holds good for the reaction in the temperature range of 295 K to 305 K, what would be the value of activation energy for this reaction ?

# [R = 8.314 J mol<sup>-1</sup> K<sup>-1</sup>]

# Answer:

(a) The minimum extra amount of energy absorbed by the reactant molecules so that their energy becomes equal to threshold value is called activation energy. Less is the activation energy, faster is the reaction or greater is the activation energy, slower is the reaction

(b) Since



Question 3.

(a) A reaction is second order in A and first order in B.

(i) Write the differential rate equation,

(ii) How is the rate affected on

increasing the concentration of A three

$$\begin{split} \log \frac{K_2}{K_3} &= \frac{E_a}{2.303R} = \left\lfloor \frac{T_3 - T_1}{T_1 T_2} \right\rfloor \\ \log 2 &= \frac{E_a}{2.303 \times 8.314} \approx \left\lfloor \frac{305 - 295}{305 \times 295} \right\rfloor \\ 3010 &= \frac{E_a}{2.303 \times 8.314} \times \frac{10}{305 \times 295} \\ E_g &= \frac{0.3010 \times 2.303 \times 8.314 \times 305 \times 295}{10} \\ \therefore E_a &= 51855.19 \text{ J/mol} = 51.86 \text{ kJ/mol} \end{split}$$

times?

(iii) How is the rate affected when the concentrations of both A and B are doubled?

(b) A first order reaction takes 40 minutes for 30% decomposition. Calculate  $t_{1/2}$  for this reaction. (Given log 1.428 = 0.1548)

#### Answer:

(a) (i) Differential rate equation : dxdt = K [A]<sup>2</sup>[B]
(ii) When concentration of A is increased to three times, the rate of reaction becomes 9 times

 $r = K[3A]^2B \therefore r = 9KA^2B \text{ i.e.} = 9 \text{ times}$ (iii)  $r = K[2A]^2[2B] \therefore r = 8KA^2B \text{ i.e.} = 8 \text{ times}$ 

(b) Given : Time, t = 40 minutes, t =? Let a = 100,  $\therefore$  x = 30% of 100 = 30 Using the formula :

#### **Question 4.**

(a) For a first order reaction, show that time required for 99% completion is twice the time required for the completion of 90% of reaction.
(b) Rate constant 'k' of a reaction varies with temperature 'T' according to the equation:

 $\log k = \log A - Ea2.303R(1T)$ 

where  $E_a$  is the activation energy. When a graph is plotted for log k vs. 1T<sup>----</sup>, a straight line with a slope of – 4250 K is obtained. Calculate ' $E_a$ ' for the reaction. (R = 8.314 JK<sup>-1</sup> mol<sup>-1</sup>) Answer:

$$\label{eq:eq:energy} \begin{split} & \div \ E_a = 2.303 \times 8.314 \ (JK^{\text{-1}} \ mol^{\text{-1}}) \times 4250 \ K \\ & = 81.375 \ J \ mol^{\text{-1}} \ or \ 81.375 \ kJ \ mol^{\text{-1}} \end{split}$$

 $t = \frac{2.303}{K} \log \frac{a}{a-x}$ or  $40 = \frac{2.303}{K} \log \frac{100}{100-30}$ or  $K = \frac{2.303}{40} \log \frac{100}{70}$ or  $K = \frac{2.303}{40} (\log 10 - \log 7)$ or  $K = \frac{2.303}{40} (1 - 0.8451)$ or  $K = \frac{2.303}{40} \times 0.1549$ or  $K = \frac{0.2567}{40} = 0.0089 \text{ min}$  $\therefore t_{1/2} = \frac{0.693}{K} = \frac{0.693}{0.0089} = 77.86 \text{ min.}$ 

$$\therefore \quad t_{99\%} = \frac{2.303}{K} \log \frac{a}{a - 0.99a} \\ = \frac{2.303}{K} \log 10^2 = 2 \times \frac{2.303}{K} \\ 90\% \text{ completion means that } x \\ = 90\% \text{ of } a = 0.90a \\ \therefore \quad t_{90\%} = \frac{2.303}{K} \log \frac{a}{a - 0.90a} \\ = \frac{2.303}{K} \log 10 = \frac{2.303}{K} \\ \therefore \quad \frac{t_{99\%}}{t_{90\%}} = \frac{\left(\frac{2 \times 2.303}{K}\right)}{\left(\frac{2.303}{K}\right)} = 2 \\ \therefore \quad t_{99\%} = 2 \times t_{90\%} \\ \text{Slope of the line } = \frac{-E_a}{-E_a} = -4250 \text{ I}$$

(b) Slope of the line =  $\frac{-E_a}{2.303 \text{ R}} = -4250 \text{ K}$ 

Question 5. (a) The decomposition of A into products has a value of K as 4.5 × 10<sup>3</sup> s<sup>-1</sup> at 10°C and energy of activation 60 kj mol-1. At what temperature would K be 1.5 × 10<sup>4</sup> s<sup>-1</sup>?

(b) (i) If half life period of a first order reaction is x and 3/4,<sup>th</sup> life period of the same reaction is y, how are x and y related to each other? (ii) In some cases it is found that a large number of colliding molecules have energy more than threshold energy, yet the reaction is slow. Why?

#### Answer:

(a) Given :  $K_1 = 4.5 \times 10^3 \text{ s}^{-1}$ ,  $T_1 = 10\text{K} + 273\text{K} = 283\text{K}$   $K_2 = 1.5 \times 10^4 \text{ s}^{-1}$ ,  $T_2 = ?$   $E_a = 60 \text{ KJ mol}^{-1}$ Using formula :

 $\therefore$  Temperature, T<sub>2</sub> will be = 297° - 273° = 24° C

(b) (i)  $t_{1/2} = 0.693$ K (For first order reaction)

 $t_{3/4} = K \Rightarrow t_{3/4} = 1.3864K$ According to condition (The value 1.3864 is double of 0.693) From the above equation it is clear that  $t_{3/4} = 2t_{1/2} \therefore y = 2X$ (ii) It is due to improper orientation of the colliding molecules at the time of collision.

# Question 6.

(a) A first order reaction takes 100 minutes for completion of 60% of the reaction. Find the time when 90% of the reaction will be completed.(b) With the help of diagram explain the role of activated complex in a reaction.

$$\log : \frac{K_2}{K_1} = \frac{E_a}{2.303R} \left( \frac{T_2 - T_1}{T_1 T_2} \right)$$
  

$$\log \frac{1.5 \times 10^4}{4.5 \times 10^3} = \frac{60000 \text{ Jmol}^{-1}}{2.303 \times 8.314 \text{ JK}^{-1} \text{mol}^{-1}} \left( \frac{T_2 - 283}{283 T_2} \right)$$
  

$$\log 3.333 = 3133.63 \left( \frac{T_2 - 283}{283 T_2} \right)$$
  

$$\frac{0.5228}{3133.63} = \frac{T_2 - 283}{283 T_2}$$
  

$$0.0472 \text{ T}_2 = T_2 - 283$$
  

$$0.9528 \text{ T}_2 = 283$$
  

$$T_2 = \frac{283}{0.9528} = 297 \text{ K}$$

# (Comptt. Delhi 2013) Answer:

(a) For the first order reaction,

(b) In order that the reactants may change into products, they have to cross an energy barrier as shown in the diagram



This diagram is obained by plotting potential energy vs. reaction coordinate. It is believed that when the reactant molecules absorb energy, their bonds are loosened and new bonds are formed between them. The intermediate complex thus formed is called activated complex. It is unstable and immediately dissociates to form the stable products.

# Question 7.

For the hydrolysis of methyl acetate in aqueous solution, the following results were obtained :

 t/s
 0
 30
 60

 [CH<sub>3</sub>COOCH<sub>3</sub>]/mol L<sup>-1</sup>
 0.60
 0.30
 0.15

(i) Show that it follows pseudo first order reaction, as the concentration of water remains constant.

(ii) Calculate the average rate of reactionbetween the time interval 30 to 60 seconds.(Given log 2 = 0.3010, log 4 = 0.6021)Answer:

is 60% complete = 0.6a, 100 100 min (Given) 2.303 100 .30 100 2.303 log 2.5 ...(i) 100 = ?, when reaction is 90% complete = 0.9a2.303 logthen k 2.303 log 10 Taking equations (i) and (ii), we get  $\frac{2.303}{100}\log 2.5 = \frac{2.303}{100}\log 10$ 0.3979 100 0.397 = 251.31 minutes

(i) 
$$k = \frac{2.303}{t} \log \frac{[A_0]}{[A]}$$
  
 $k_1 = \frac{2.303}{30} \log \frac{0.60}{0.30}$   
 $k_1 = \frac{2.303}{30} \times \log 2$   
 $k_1 = \frac{2.303}{30} \times 0.3010 \text{ sec}^{-1}$   
 $k_1 = 2.31 \times 10^{-2} \text{ sec}^{-1}$   
 $k_2 = \frac{2.303}{60} \log \frac{0.60}{0.15}$   
 $k_2 = \frac{2.303}{60} \times \log 4$   
 $k_2 = \frac{2.303}{60} \times 2 \log 2$   
 $k_2 = \frac{2.303}{60} \times 2 \log 2$   
 $k_2 = \frac{2.303 \times 2 \times 0.3010}{60}$ 

As k is constant in both the readings, hence it is a pseudo first order reaction.

(ii) Rate =  $-\Delta[R] / \Delta t$ , Average rate between 30 to 60 seconds

= -(0.15-0.30)60-30=0.1530

 $= 0.5 \times 10^{-2} \text{ mol } \text{L}^{-1} \text{ sec}^{-1}$ 

#### **Question 8.**

(a) For a reaction A + B → P, the rate is given by Rate = k[A] [B]<sup>2</sup>
(i) How is the rate of reaction affected if the concentration of B is doubled?
(ii) What is the overall order of reaction if A is present in large excess?
(b) A first order reaction takes 30 minutes for 50% completion. Calculate the time required for 90% completion of this reaction.

#### $(\log 2 = 0.3010)$

#### Answer:

(a) For the reaction  $A + B \rightarrow P$  rate is given by Rate =  $k[A]^{1}[B]^{2}$ (i)  $r_{1} = k[A]1 [B]2$  $r_{2} = k[A]^{1}[2B]^{2} =$  $r_{2} = k[A]^{1} [2B]^{2} = 4k[A]^{1} [B]^{2}$  $r_{1} = 4r_{2}$ , rate will increase four times of actual rate.

(b) 
$$t_1 = 30$$
 minutes,  $t_1 = \frac{0.693}{k}$   
 $\Rightarrow 30 \text{ min} = \frac{0.693}{k}$   
 $\Rightarrow k = \frac{0.693}{30} \text{ min}^{-1} \Rightarrow k = 0.0231 \text{ min}^{-1}$ 

(ii) When A is present in large amount, order w.r.t. A is zero. Hence overall order = 0 + 2 = 2, second order reaction.

Question 9. For the hydrolysis of methyl acetate in aqueous solution, the following results were obtained:

t/s	0	10	20
[CH <sub>3</sub> COOCH <sub>3</sub> ]/mol L <sup>-1</sup>	0.10	0.05	0.025

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

$$t = \frac{2.303}{0.0231} \log \frac{100}{10} \implies t = \frac{2.303}{0.0231} \min$$
  

$$\therefore \quad t = 99.7 \text{ minutes}$$

(i) Show that it follows pseudo first order

reaction, as the concentration of water remains constant.

(ii) Calculate the average rate of reaction between the time interval 10 to 20 seconds. (Given :  $\log 2 = 0.3010$ ,  $\log 4 = 0.6021$ )

Answer:

$$\begin{array}{ll} (i) \ [A]_0 = 0.10 \ \mathrm{mol/L}, \ [A] = 0.5 \ \mathrm{mol/L}, \ t = 10s \\ [A]_0 = 0.10 \ \mathrm{mol/L}, \ [A] = 0.25 \ \mathrm{mol/L}, \ t = 20s \\ k = \frac{2.303}{t} \log \frac{[A_0]}{[A]} \\ k_1 = \frac{2.303}{10} \log \frac{0.1}{0.05} \\ k_1 \stackrel{*}{=} \frac{2.303}{10} \times \log 2 \\ k_1 = \frac{2.303 \times 0.3010}{10} \\ k_1 = \frac{0.693}{10} = 0.0693 \ \mathrm{sec^{-1}} \end{array} \right| \begin{array}{l} k = \frac{2.303}{t} \log \frac{[A_0]}{[A]} \\ k_2 = \frac{2.303}{20} \log \frac{0.1}{0.025} \\ k_2 = \frac{2.303 \times 2\log 2}{20} \\ k_2 = \frac{2.303 \times 0.3010 \times 2}{20} \\ k_2 = \frac{2.303 \times 0.3010 \times 2}{20} \\ k_3 = 0.0693 \ \mathrm{sec^{-1}} \end{array}$$

As  $k_1$  and  $k_2$  are equal, hence pseudo rate constant is same.

It follows the pseudo first order reaction.

(ii) Average rate of reaction between 10 to 20 seconds

 $= -\Delta[R]\Delta t = -(0.025 - 0.05)(20 - 10) = 0.02510$ 

= 0.0025 mol lit<sup>-1</sup> sec<sup>-1</sup>

# Question 10.

(a) For a reaction  $A + B \rightarrow P$ , the rate is given by Rate = k[A] [B]<sup>2</sup>

(i) How is the rate of reaction affected if the concentration of B is doubled?

(ii) What is the overall order of reaction if A is present in large excess?

(b) A first order reaction takes 30 minutes for 50% completion. Calculate the time required for 90% completion of this reaction.

# Answer:

(a) For the reaction  $A + B \rightarrow P$ rate is given by Rate =  $k[A]^{1}[B]^{2}$  (i)  $r_1 = k[A]^1 [B]^2$   $r_2 = k[A]^1 [2B]^2 = 4k[A]^1 [B]^2$  $r_1 = 4r_2$  (rate of reaction becomes 4 times)

(ii) When A is present in large amounts, order w.r.t. A is zero. Hence overall order = 0 + 2 = 2

(b) 
$$t_{\frac{1}{2}} = \frac{3.693}{k} t_{\frac{1}{2}} = 30 \text{ minutes } k = \frac{0.693}{30} \text{ min}^{-1}$$
  
 $k = 0.0231 \text{ min}^{-1}$   
 $k = \frac{2.303}{t} \log \frac{[A_0]}{[A]}$   
 $t = \frac{2.303}{0.0231} \log \frac{100}{10}$   $t = \frac{2.303}{0.0231} \text{ min}$   
 $\therefore t = 99.7 \text{ min}$