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### **CHEMICAL KINETICS**

Chemical Kinetics: (Study of reaction rates and their mechanisms.)

**Rate of Reaction :** The change in concentration of reactant or product per unit time .(SI unit molL<sup>-1</sup>s<sup>-1</sup>).

Let a reaction :  $aA + bB \rightarrow cC + dD$ .

Average rate of reaction: The rate of reaction measured over a long period of time.

 $R_{av} = \frac{-1}{a} \frac{\Delta[A]}{\Delta t} = \frac{-1}{b} \frac{\Delta[B]}{\Delta t} = \frac{1}{c} \frac{\Delta[C]}{\Delta t} = \frac{1}{d} \frac{\Delta[D]}{\Delta t}$ 

**Instantaneous rate of reaction:** The rate of reaction at a particular instant of time i.e.(△T approaches zero)

$$R_{inst} = \frac{-1}{a} \frac{d[A]}{dt} = \frac{-1}{b} \frac{d[B]}{bt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{-1}{d} \frac{d[D]}{dt}$$

#### Factors affecting rate of reaction:

1.	Rate of reaction	$\infty$ Conc. of reactants	
2.		∞ Temperature	
3.		$\infty$ Surface area of reactants	
4.		<sup>∞</sup> Bond dissociation energy of reactants	
5.		Increases in the presence of catalyst	
6.		Depends on pressure in case of gases.	

#### Rate law or rate equation:

The mathematical expression which denotes the experimentally observed rate of a reaction in terms of the concentration of the reactants which influences the rate of reaction.

Rate =  $k[A]^{\times}[B]^{\vee}$ 

k = rate constant and x  $\leq$  a , y  $\leq$  b.

### Order of a reaction :

The sum of powers of the concentration of the reactants in the rate law expression.

Order = x + y

eq. Rate =  $k[A]^{1/2} [B]^{3/2}$ 

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

- \* Order of a reaction can be 0, 1, 2, 3 and even a fraction .
- (k) **Rate constant :** It is defined as the rate of reaction, when the conc. of each of the reactants is unity.

The unit of rate constant for  $n^{th}$  order =  $(molL^{-1})^{l-n}s^{-1}$ 

- <u>Reaction</u> <u>n</u> <u>Units of rate constant</u>
- zero order 0 mol  $L^{-1}s^{-1}$
- $1^{st}$  Order  $1 s^{-1}$
- $2^{nd}$  Order 2 mol<sup>-1</sup>L s<sup>-1</sup>

#### Molecularity of a reaction :

The number of reacting species which collide simultaneously to bring about a chemical reaction. Molecularity = a + b

eg.  $NH_4NO_2 \rightarrow N_2 + 2H_2O$  (Unimolecular reaction)  $2HI \rightarrow H_2 + I_2$  (Bimolecular reaction)  $2NO + O_2 \rightarrow 2NO_2$  (Tri or termolecular)

Elementary reactions : The reactions taking place in one step

#### **Complex reactions :**

When a sequence of elementary reactions gives us a products, the reactions are called complex reactions.

\* Molecularity is applicable only for elementary reactions. For complex reactions it has no meaning

\* For complex reactions, order is given by the slowest step (i.e. rate determining step) and generally, molecularity of the slowest step is same as the order of the over all reaction.

#### **Integerted rate equations:**

#### Zero order reactions:

Let a reaction : 
$$R \rightarrow P.$$
 (Product)  
So. Rate  $= \frac{-d[R]}{dt} = k[R]^{0}$   
Thus  $k = \frac{[R]_{0} - [R]}{t}$  [R]<sub>0</sub> = Initial conc. of reactant  
[R] = Conc. of reactant after trums  
eg.  $2NH_{3}(g) \xrightarrow{Pt} N_{2}(g) + 3H_{2}(g)$   
Rate  $= k[NH_{3}]^{0} = k$   
First order reaction:  $R \rightarrow P$   
So. Rate  $= \frac{-d[R]}{dt} = k[R]$   
Thus  $k = \frac{2.303}{t} log \frac{[R]_{0}}{[R]}$   
eg.1  $C_{2}H_{4}(g) + H_{2}(g) \rightarrow C_{2}H_{6}(g)$   
Rate  $= k[C_{2}H_{4}]$ 

eg.2 All natural and artificial radioactive decay of unstable nuclei

 $^{226}_{88}$ Ra  $\rightarrow^{4}_{2}$ He  $+^{22}_{86}$ Rn

**eg.3** Decomposition of  $N_2O_5$  and  $N_2O$ .

### Half life of reaction $(t_{1/2})$ :

The time in which the concentration of a reactant is reduced to one half of its initial concentration.

eg. For a Zero Order reaction 
$$t_{1/2} = \frac{l^{n} J_0}{2k}$$

eg. For a first order reaction : 
$$t_{1/2} = \frac{2.303}{k}$$
  $\log 2 = \frac{0.693}{k}$ 

#### **Psendo First Order reaction :**

A reaction which behaves as a first order reaction even when there is more than one concentration involved. It is because the other concentration is in large excess or present as a catalyst for which the concentration does not change.

eg.1 Hydrolysis of cane sugar.

 $C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$ (excess) Glucose Fructose

eg.2 Hydrolysis of ester

t = 0 0.01 mol

t

 $CH_3COOC_2H_5 +$  $H_2O \rightarrow$ CH<sub>3</sub>COOH C<sub>2</sub>H<sub>2</sub>OH +10 mol 0 mol 0 mol

[ص]

0 mol 9.9 mol 0.01 mol Rate =  $k'[H_2O][CH_3COOC_2H_5]$ 

[H<sub>2</sub>O] taken as constant as it does not altered much.

Thus. Rate = 
$$k[CH_3COOC_2H_5]$$

Where  $k = k' [H_2O]$ 

#### $\mathbf{k} = \mathbf{A}\mathbf{e}^{-\mathbf{E}\mathbf{a}/\mathbf{R}\mathbf{T}}$ **Arrhenius equation :**

\* The temperature dependence of the rate of chemical reaction can be accurately explained by Arrhenius equation

0.01 mol

A = Arrhenius factor or frequency factor

R = Gas constant, Ea = Activation energy

\*It has been found that for a chemical reaction with rise in temperature by 10°, the rate constant is nearly doubled.

Reaction 
$$H_2(g) + I_2(g) \rightarrow 2HI$$



**Reaction Co-ordinate** 

### Diagram showing plot of P.E v/s reaction co-ordinate.

The energy required to form this intermediate, called activated complex (C) is known as **Activation Energy (Ea).** 



\*Peak of the curve correspond to the most probable K.E.

\* If rate constants of a reaction at  $T_1$  and  $T_2$  are  $K_1$  and  $K_2$ ,

$K_2$	Ea	1	1
$\frac{109}{K_1}$	2.303R	$T_1$	T <sub>2</sub>

Collision Theory : By Max Trautz and william Lewis. According to it

- (a) For a chemical reaction to occur, there must be collisions between the reactants molecules.
- (b) Only a certain fraction of the total number of collisions are effective in forming the products.
- (c) For effective collisions, the molecules should have sufficient energy as well as orientation. A + B  $\rightarrow$  Products.

Rate =  $Z_{AB}e^{-Ea/RT}$ 

**Z**<sub>AB</sub> = **Collision frequency :** No. of collisions per second per unit volume of the reaction mixture.

#### **Effective collistion :**

The collisions in which molecules collide with sufficient K.E. (Called threshold energy) and proper orientation, so as to facilitate breaking of bonds between reacting species and formation of new bonds to form products are called as effective collisions.

Threshold Energy =  $E_a$  + energy possesed by reacting species.

To account for effective collisions another factor 'P' called steric factor was introduced.







 $[ester]/mole L^{-1} 0.55 0.31 0.17 0.085$ 

#### (i) Calculate the average rate of reaction between the time interval 30 to 60 seconds (ii) Calculate the pseudo first order rate constant for the hydrolysis of ester.

**Sol.** (i) Average rate of reaction

$$= \frac{\text{Change in concentration}}{\text{Change in time}} = \frac{(0.31 - 0.17)}{(60 - 30)}$$
  
= 4.67 × 10<sup>-3</sup>L<sup>-1</sup>s<sup>-1</sup>

(ii)  $k = \frac{2.505}{t} \log \frac{[\Lambda_0]}{[\Lambda]}$ 

Where  $[A_0] = 0.55$  M is initial concentration of ester ( t = 0 ) and [A] is the concentration of ester at time t.

At 30 sec :  

$$k_{1} = \frac{2.303}{30} \log \frac{0.55}{0.31} = 1.91 \times 10^{-2} \text{ s}^{-1}.$$
At 60 sec :  

$$k_{2} = \frac{2.303}{60} \log \frac{0.55}{0.17} = 1.96 \times 10^{-2} \text{ s}^{-1}.$$
At 90 sec :  

$$k_{3} = \frac{2.303}{90} \log \frac{0.55}{0.85} = 2.07 \times 10^{-2} \text{ s}^{-1}.$$
Thus, Average  

$$k = \frac{k_{1} + k_{2} + k_{3}}{3} = \frac{1.91 \times 10^{-2} + 1.96 \times 10^{-2} + 2.07 \times 10^{-2}}{3}$$

$$k = 1.98 \times 10^{-2} \text{ s}^{-1}.$$

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#### Q.4 A reaction is first order in A and second order in B. (i) Write differential rate equation.

(ii) How is the rate affected on increasing the concentration of B three times?

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(iii) How is the rate affected when the concentration of both A and B are doubled?
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Sol. (i)

(ii)

Rate =  $k [A]^{1}[B]^{2}$  $= k [A]^{1}[B]^{2}$ r<sub>o</sub> = k [A]<sup>1</sup>[3B]<sup>2</sup> = 9 k [A]<sup>1</sup>[B]<sup>2</sup> = 9 ×  $r_0$ r<sub>1</sub> The rate is increased by 9 times.  $= k [A]^{1}[B]^{2}$  $r_0$  $= k [2A]^{1}[2B]^{2} = 8 k [A]^{1}[B]^{2} = 8 \times r_{0}$ r,

The rate is increased by 8 times.

#### In a reaction between A and B, the initial rate of reaction (r<sub>o</sub>) was measured for different initial Q.5 concentration of A and B as given below:

$[A]/mol L^{-1}$	0.20	0.20	0.40	
[B]/mol L <sup>−1</sup>	0.30	0.10	0.05	
Rate( $r_0$ )/mol L <sup>-1</sup> S <sup>-1</sup>	$5.07 \times 10^{-5}$	$5.07 \times 10^{-5}$	$1.43 \times 10^{-4}$	

#### What is the order of reaction with respect to A and B? Let the rate of reaction, $r = k [A]^m [B]^n$ Sol. $(r_1) 5.07 \times 10^{-5} = k [0.20]^m [0.30]^n$ .....Exp (i) $(r_2) 5.07 \times 10^{-5} = k [0.20]^m [0.10]^n$ .....Exp (ii) $(r_3) 1.43 \times 10^{-4} = k [0.40]^m [0.05]^n$ .....Exp (iii) From experiment (i) and (ii) $\left(\frac{r_2}{r_1}\right) = \frac{5.07 \times 10^{-5} \text{Ms}^{-1}}{5.07 \times ^{-5} \text{Ms}^{-1}} = \frac{\text{k}(0.20)^{\text{m}} (0.10)^{\text{n}}}{\text{k}(0.20)^{\text{m}} (0.30)^{\text{n}}}$ 0.10 0.30 or $3^n = 1$ 3<sup>n</sup> = 3<sup>o</sup> $\Rightarrow$ n = 0 *.*.. From experiment (i) and (iii) $=\frac{1.43\times10^{-4}\,\text{Ms}^{-1}}{5.07\times10^{-5}\,\text{Ms}^{-1}}\ =\ \frac{k(0.40)^m(0.05)^n}{k(0.20)^m(0.10)^n}$ <u>r</u>3 r1 $2.8 = (2)^{m}$ or m log2 = log 2.8 m × 0.3010 = 0.4472 $n = \frac{0.4472}{0.3010} = 1.49$

Thus, order of reaction with respect to A is 1.49 and order with respect to B is zero. So rate law is, Rate k [A]<sup>1.49</sup> [B]<sup>0</sup>

#### Q.6 Calculate the half-life of a first order reaction from their rate constants given below:

(a) 200 s<sup>-1</sup> (b) 2 min<sup>-1</sup> (c) 4 years<sup>-1</sup> CHEMICAL KINETICS

**Sol.** (a) 
$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{200} = 3.465 \times 10^{-3} \text{ s}$$

(b) 
$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{2} = 3.465 \times 10^{-1} \text{ min}$$

(c) 
$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{4} = 0.17325$$
 years

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Q.7 The half-life for radioactive decay of <sup>14</sup>C is 5730 years. An archaeological artifact containing wood has only 80% of the <sup>14</sup>C found in a living tree. Estimate the age of the sample.

$$t_{1/2} = 5730 \text{ years}$$

If  $R_0$  is the initial <sup>14</sup>C activity in a living tree = 100

Activity in the dead wood R = 80

The nuclear radioactive decay follows the first order kinetics so

$$t = \frac{2.303}{k} \log \frac{[R_0]}{[R]}$$
  

$$k = \frac{0.693}{t_{1/2}}$$
  

$$t = \frac{2.303 \times t_{1/2}}{0.693} \log \frac{100}{80} = 1845.4 \text{ years}$$

- The rate constant for a first order reaction is 60 s<sup>-1</sup>. How much time will it take to reduce the Q.8 initial concentration of the reactant to its 1/16th value?
- Sol.

$$k = \frac{2.303}{t} \log \frac{[R_0]}{[R]}$$
  

$$t = \frac{2.303}{k} \log \frac{[R_0]}{[R]}$$
  

$$[R_0] = 1, \text{ then } [R] = 1/16$$
  

$$k = \frac{2.303}{60} \log \frac{1}{1/16} = 0.0462 \text{ s}$$

During nuclear explosion, one of the products is <sup>90</sup>Sr with half-life of 28.1 years. If 1 µg of <sup>90</sup>Sr Q.9 was absorbed in the bones of a newly born baby instead of calcium, how much of it will remain after 10 years and 60 years if it is not lost metabolically?

Sol.  

$$T_{1/2} \operatorname{Sr}^{90} = 28.1 \text{ years, } k = \frac{0.693}{t_{1/2}}, k = \frac{0.693}{28.1} \text{ year}^{-1}$$
We know,  

$$k = \frac{2.303}{k} \log \frac{[R_0]}{[R]}$$
Now,  

$$t = \frac{2.303}{k} \log \frac{[R_0]}{[R]}$$
At t = 10 year 10 =  $\frac{2.303 \times 28.1}{0.693} \log \frac{[R_0]}{[R]}$ 

$$\log \frac{[R_0]}{[R]} = 0.1070$$

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$$\frac{[R_0]}{[R]} = \text{antilog} (0.1070) = 1.279$$

So,

$$[R] = \frac{1\mu g}{1.279} = 0.7818 \, \mu g$$

At t = 60 year 60 = 
$$\frac{2.303 \times 28.1}{0.693} \log \frac{[R_0]}{[R]}$$
  
 $\log \frac{[R_0]}{[R]}$  = antilog 0.9409  
= 4.374  
So,  $[R] = \frac{1\mu g}{4.374} = 0.228 \ \mu g.$ 

Q.10 For a first order reaction, show that time required for 99% completion is twice the time required for the completion of 90% of reaction.

Sol.

 $t = \frac{2.303}{k} \log \frac{[R_0]}{[R]}$ 99% completion means If  $[R_0] = 100,$ [R] = 100 - 99 = 1 $t_{99\%} = \frac{2.303}{k} \log \frac{100}{l}$  $=\frac{2.303}{k}\log 10^2 \frac{2.303}{k}$ x 2 90% completion means If  $[R_0] = 100,$ [R] = 100 - 90 = 10 $t_{90\%} = \frac{2.303}{k} \log \frac{[R_0]}{[R]}$  $=\frac{2.303}{k}\log\frac{100}{10}$  $=\frac{2.303}{k}\log 10$  $=\frac{2.303}{k}$  $\frac{t_{99\%}}{t_{90\%}} = \frac{2.303 \times 2}{k} \times \frac{k}{2.303} = 2$ *.*..  $t_{99\%} = 2 \times t_{90\%}$ or

If

#### Q.11 A first order reaction takes 40 min for 30% decomposition. Calculate $t_{1/2}$ .

Sol.

$$t_{1/2} = \frac{0.693}{k}$$
$$k = \frac{2.303}{t} \log \frac{[R_0]}{[R]}$$

30% decomposition means that

 $[R_{0}] = 100,$  [R] = 100 - 30 = 70  $k = \frac{2.303}{k} \log \frac{100}{70} = \frac{2.303}{k} \log \frac{10}{7}$   $k = \frac{2.303}{40} \times 0.1549 = 8.918 \times 10^{-3} \text{ min}^{-1}$   $t_{1/2} = \frac{0.693}{k}$ 

$$= \frac{0.693}{8.918 \times 10^{-3}} \operatorname{min}^{-1}$$
  
= 77.7 min.

Q.12 The following data were obtained during the first order thermal decomposition of SO<sub>2</sub>Cl<sub>2</sub> at constant volume:

 $\begin{array}{c|c} SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g) \\ \hline Experiment & Time/s^{-1} & TotalPressure/atm \\ \hline 1 & 0 & 0.5 \\ \hline 2 & 100 & 0.6 \\ \end{array}$ 

#### Calculate the rate of the reaction when total pressure is 0.65 atm.

**Sol.** Suppose initial pressure of  $SO_2Cl_2$  is Pi and its pressure decreases by x atm after time t then  $SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g)$ Initial pressure (at t = 0) 0.5 atm 0 0

Pressure (at time = t) 0.05 - x x x x P<sub>total</sub> at time t = 0.5 - x + x + x = 0.5 + x atm i.e., 0.6 = 0.5 - x or x = 0.6 - 0.5 = 0.1 atm Now, Pi = 0.5 atm and P(at time 100 sec) = 0.5 - x = 0.5 - 0.1 = 0.4 atm (a) Evaluation of k : 2 303 Initial pressure

$$k_{100} = \frac{2.303}{t} \log \frac{0.5}{0.4}$$
$$= \frac{2.303}{100} \log 1.25$$
$$= \frac{2.303}{100} 0.0969 = 2.23 \times 10^{-3} \text{ s}^{-1}$$

(b) Rate at  $P_{t} = 0.65$  atm

 $P_{SO_2Cl_2}$  at total pressure of 0.65 atm

 $P_{SO_2Cl_2} = 2Pi - P_t = 1 - 0.65 = 0.35 atm$ 

Rate = k 
$$P_{SO_2Cl_2}$$
 = 2.23 × 10<sup>-3</sup> × 0.35 = 7.8 × 10<sup>-4</sup> atm s<sup>-1</sup>.



## Q.13 The rate constant for the decomposition of hydrocarbons is 2.418 × 10<sup>-5</sup> s<sup>-1</sup> at 546 K. If the energy of activation is 179.9 kJ mol<sup>-1</sup>, what will be the value of pre-exponential factor?

Sol.

 $log A = logk + \frac{E_a}{2.303 \text{ RT}}$ = log 2.418 × 10<sup>-5</sup> s<sup>-1</sup> +  $\frac{179900 \text{ J mol}^{-1}}{2.303 \times 8.314 \text{ J k}^{-1} \text{ mol}^{-1} \times 546 \text{ K}}$ = - 4.6184 + 17.21 log A = - 4.6184 + 17.21 = 12.5916 Taking antilog of both sides A = antilog 12.5916 = 3.9 × 10<sup>-12</sup> s<sup>-1</sup>.

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Q.14 The decomposition of A into product has value of k as 4.5 ×10<sup>3</sup> s<sup>-1</sup> at 10°C and energy of activation 60 kJ mol<sup>-1</sup>. At what temperature would k be 1.5 ×10<sup>4</sup> s<sup>-1</sup>?

Sol. We know that, 
$$\log \frac{\kappa_2}{\kappa_1} = \frac{L_a}{2.303 \text{ R}} \left[ \frac{T_2 - T_1}{T_1 T_2} \right]$$
  
 $\log \frac{1.5 \times 10^4}{4.5 \times 10^3} = \frac{60000}{2.303 \times 8.314} \left[ \frac{T_2 - 283}{283 T_2} \right]$   
 $0.5228 = 3133.62 \left[ \frac{T_2 - 283}{283 T_2} \right]$   
or  $\frac{0.5228}{3133.62} = \frac{T_2 - 233}{283 T_2}$   
 $1.67 \times 10^{-4} \times 283 = \frac{T_2 - 283}{T_2}$   
 $0.0472 T_2 = T_2 - 283$   
 $T_2 - 0.0472 T_2 = 283$   
 $0.9528 T_2 = 283$   
Hence,  $T_2 = \frac{283}{0.9528} = 297.02 \text{ K}$ .

١.

Q.15 The time required for 10% completion of a first order reaction at 298 K is equal to that required for its 25% completion at 308. If the value of A is  $4 \times 10^{10}$ s<sup>-1</sup>, calculate k at 308 K and E<sub>a</sub>.

$$k_{298} = \frac{2.303}{k} \log \frac{[R_0]}{[R]} = \frac{2.303}{k} \log \frac{100}{90} \qquad \dots \dots \dots (i)$$
$$k_{308} = \frac{2.303}{t} \log \frac{100}{75} \qquad \dots \dots \dots \dots \dots (ii)$$

Similarly,

Sol.

Dividing equation (ii) by equation (i), we get

$$\frac{k_{308}}{k_{298}} = \frac{\frac{2.303}{t}\log\frac{100}{75}}{\frac{2.303}{t}\log\frac{100}{90}}$$

As time required for 10% completion = time required for 25% completion.

 $\frac{k_{308}}{k_{298}} = \frac{\log 100/75}{\log 100/90} = \frac{0.1249}{0.0457} = 2.733$ ÷ According to Arrhenius equation  $\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]$  $log 2.733 = \frac{E_a}{2.303 \times 8.314} \left\lceil \frac{308 - 298}{308 \times 298} \right\rceil$  $\mathsf{E}_{\mathsf{a}} = \frac{0436 \times 2.303 \times 8.314}{1.089 \times 10^{-4}}$ or  $=\frac{8.36}{1089\times10^{-4}}$ = 76658 J mol<sup>-1</sup>  $=A.e^{-E_a/RT}$ k<sub>308</sub> Now,  $\log k_{308} = \log 4 \times 10^{10} - \frac{E_a}{2.303 R} \times \frac{1}{308}$ 1 or  $= 10.602 - \frac{76658}{2.303 \times 8.314 \times 308}$ = 10.602 - 12.998 = - 2.3 % = antilog (-2.396) or k<sub>308</sub>  $= 4.02 \times 10^{-3} \text{ s}^{-1}$ 

Q.16 The rate of reaction quadruples when the temperature changes from 298 K to 313 K. Calculate the energy of activation of the reaction assuming that it does not change with temperature.

T<sub>1</sub> = 293 K ; T<sub>2</sub> = 313 K

According to Arrhenius equation

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left[ \frac{T_2 - T_1}{T_1 T_2} \right]$$
$$E_a = 2.303 R \times \left[ \frac{T_1 T_2}{T_2 - T_1} \right] \log \frac{k_2}{k_1}$$
Now, 
$$\frac{T_1 T_2}{T_2 - T_1} = \frac{293 \times 313}{313 - 293} = 4585.45 \text{ K}$$

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$$\log \frac{k_2}{k_1} = \log \frac{4}{1} = \log 4 = 0.6021$$

$$E_{a} = \frac{2.303 \times 8314 \times JK^{-1}mol^{-1} \times 293 \times 313}{313 - 293}log\frac{4}{1}$$
$$E_{a} = \frac{2.303 \times 8314 \times 293 \times 313 \times 0.6021}{20}$$
$$= 52863.33 J mol^{-1} = 52.86 kJ mol^{-1}$$

# Q.17 Express the rate of the following reactions in terms of the concentrations of reactants and products

(i) 
$$2NO_{2}(g) + F_{2}(g) \rightarrow 2NO_{2}F(g)$$

- (ii)  $5Br^{-}(aq) + BrO_{3}^{-}(aq) + 6H^{+}(aq) \rightarrow 3Br_{2}(aq) + 3H_{2}O(I)$
- **Sol.** (i) For the given reaction,

$$2NO_2(g) + F_2(g) \rightarrow 2NO_2F(g)$$

Rate of reaction = 
$$\frac{-1}{2} \frac{d[NO_2]}{dt} = -\frac{d[F_2]}{dt} = +\frac{1}{2} \frac{d[NO_2]}{dt}$$

(ii) For given reaction,

Rate of reaction = 
$$\frac{-1}{5} \frac{dBr^{-}}{dt} = -d \frac{BrO_3^{-}}{dt} = \frac{-1}{6} \frac{dH^{+}}{dt} = \frac{1}{3} \frac{dBr_2}{dt}$$

# Q.18 A first order reaction has specific rate constant 10<sup>-3</sup> sec<sup>-1</sup>. How muct time time will it take for 10 g to reduce to half of the quantity?

**Sol.** Half-life period for the first order reaction is given by the expression.

 $k = 10^{-3} \text{ sec}^{-1}$ 

 $t_{0.5} = \frac{0.693}{k}$ 

Now,

*.*..

$$t_{0,5} = \frac{0.693}{10^{-3}} = 693$$
 seconds

Q.19 60 per cent of a first order reaction was completed in 60 minutes. When was it half completed?Sol. Using first order rate constant equation.

$$k = \frac{2.303}{t} \log \frac{a}{a - x}$$
In first case:  

$$k = \frac{2.303}{60 \text{ min}} \log \frac{100}{100 - 60}$$
.....(i)  
in second case:  

$$k = \frac{2.303}{t} \log \frac{100}{100 - 50}$$
.....(ii)

Equating the two equations (i) and (ii), we get

$$\frac{2.303}{60 \text{ min}} \log \frac{100}{40} = \frac{2.303}{t} \log \frac{100}{50}$$

or 
$$t = \frac{\frac{60 \times \log 2}{\log \frac{10}{4}}}{= 45.4 \text{ min.}} = \frac{\frac{60 \times 0.3010}{1 - 0.6020} \text{ min}}{= 45.4 \text{ min.}}$$

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CHEMICAL KINETICS

## Q.20 A first orer reaction is 20% complete in 10 minutes. Calculates the time for 75% completion of the reaction.

0.000 400

**Sol.** For a first order reaction,  $k = \frac{2.303}{t} \log \frac{a}{(a-x)}$ 

Substituting the given values, we get

- Q.21 The half-life of a chemical reaction at a particular concentration is 25 minutes. When the concentration is doubled, the half-life becomes 50 minutes. Find the order of reaction.
- **Sol.** Suppose the initial concentration in the first case is a mol L<sup>-1</sup>. Then

$$[A_{0}]_{1} = a_{1}(t_{1/2})_{1} = 25 \text{ minutes}$$
and
$$[A_{0}]_{2} = 2a_{1}(t_{1/2})_{2} = 50 \text{ minutes}$$
Now,
$$\frac{(t_{1/2})_{1}}{(t_{1/2})_{2}} = \left\{ \frac{[A_{0}]_{1}}{[A_{0}]_{2}} \right\}^{n-1}$$
So,
$$\left( \frac{a_{1}}{2a_{1}} \right)^{n-1} = \left( \frac{1}{2} \right)^{n-1} \text{ or } \frac{1}{2} = \left( \frac{1}{2} \right)^{n-1}$$

$$\therefore \qquad 1 = n - 1$$

$$n = 2$$

Hence, the reaction is of second order



### EXERCISE – I UNSOLVED PROBLEMS

- **Q.1** The rate of decomposition of substance A becomes eight times when its concentration is doubled. What is the order of the reaction?
- **Q.2** The following rate data were obtained at 300 K for the reaction

2A +	$B \rightarrow$	C +	D
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Exp.No.	[A](mol/L)	[B](mol/L)	Rate of formation of D(mol/L/min)
1	0.1	0.1	6×10 <sup>-3</sup>
2	0.3	0.2	7.2×10 <sup>-2</sup>
3	0.3	0.4	2.40 × 10 <sup>-1</sup>
4	0.4	0.1	2.40×10 <sup>-2</sup>

Determine the rate law and rate constant for reaction.

- **Q.3** Define collision frequency, threshold energy and activation energy.
- **Q.4** The rate of a particular reaction triples when temperature changes from 50°C to 100°C. Calculate the activation energy of reaction.
- Q.5 What is the catalyst? How does it effects the rate of reaction?
- **Q.6** From the rate expression for the following reactions determine the order of reaction and the dimensions of the rate constants.

(i)  $3NO(g) \rightarrow N_2O(g) + NO_2(g)$ ;

(ii)  $H_2O_2(aq) + 3I^-(aq) + 2H^+(aq) \rightarrow 2H_2O(I) + I_3^-$ ;

(iii)  $CH_3CHO(g) \rightarrow CH_4(g) + CO(g)$ ;

(iv)  $C_2H_5Cl(g) \rightarrow C_2H_4(g) + HCl(g)$ ;

**Q.7** For the reaction  $2A + B \rightarrow A_{2}B$ 

the rate = k[A] [B]<sup>2</sup> with k =  $2.0 \times 10^6$  mol<sup>-2</sup> L<sup>2</sup>s<sup>-1</sup>. Calculate the initial rate of the reaction when [A] = 0.1 mol L<sup>-1</sup>, [B] = 0.2 mol L<sup>-1</sup>. Calculate the rate of reaction after [A] is reduced to 0.06 mol L<sup>-1</sup>.

**Q.8** A reaction is second order with respect to a reactant. How is the rate of reaction affected if the concentration of the reactant is

(i) doubled

(ii) reduced to half

Rate =  $k[NO]^2$ 

Rate =  $k[H_2O_2][I^-]$ 

Rate =  $k[C_2H_5CI]$ 

Rate =  $k[CH_3CHO]^{3/2}$ 

- **Q.9** Sucrose decomposes in acid solution into glucose and fructose according to the first order rate law, with  $t_{1/2} = 3.00$  hours. What fraction of sample of sucrose remains after 8 hours.
- **Q.10** Show that in case of a first order reaction, the time required for 99.9% of the reaction take place is ten times that required for half of the reaction.
- **Q.11** The half life of a reaction  $A \rightarrow B$  is 8 minutes. How long it takes [A] to reach 25% of the initial concentration?
- **Q.12** For a first order reaction, calculate the ratio between the time to complete three fourth of the reaction and the time taken to complete half of the reaction.

CHEMICAL KINETICS



0.1	A first order decomposition reaction takes 40 minutes for 30% decomposition. Calculate its tvalue
Q.2	The decomposition of phosphine, 4 $PH_{3(g)} \rightarrow P_{4(g)} + 6 H_{2(g)}$ has the rate law, rate = k [PH <sub>3</sub> ]. The rate contant is 6.0 × 10 <sup>-4</sup> s <sup>-1</sup> at 300 K and activation energy is 3.05 ×10 <sup>5</sup> J mol <sup>-1</sup> . Calculate the value of rate contant at 310 K. (Give, R = 8.314 JK <sup>-</sup> mol <sup>-</sup> )
Q.3	Define the following : (i) Elementary step in a reaction (ii) Rate of a reaction
Q.4	For a decomposition reaction the values of rate constant k at two different temperatures are given below: $k_1 = 2.15 \times 10^{-8} \text{ L mol}^{-1} \text{ s}^{-1}$ at 650 K , $k_2 = 2.39 \times 10^{-7} \text{ L mol}^{-1} \text{ s}^{-1}$ at 700 K Calculate the value of activation energy for this reaction (R = 8.314 J K <sup>-1</sup> mol <sup>-1</sup> )
Q.5	Define the following :(i) Order of a reaction (ii) Activation energy of a reaction
Q.6	A first order reaction has a rate constant of 0.0051 min <sup>-1</sup> . If we begin with 0.10 M concentration of the reactant, what concentration of the reactant will be left after 3 hours ?
Q.7	<ul> <li>(a) Explain the following terms:</li> <li>(i) Order of a reaction</li> <li>(b) The rate of a reaction increases four times when the temperature changes from 300 K to 320 K. Calculate the energy of activation of the reaction, assuming that it does not change with temperature.</li> <li>(R = 8314 JK<sup>-1</sup> mol<sup>-1</sup>)</li> </ul>
Q.8	<ul> <li>(a) Explain the following terms:</li> <li>(i) Rate of a reaction</li> <li>(ii) Activation energy of a reaction</li> <li>(b) The decomposition of phosphine, PH<sub>3</sub>, proceeds according to the following equation: 4 PH<sub>a</sub>(g) → P<sub>4</sub>(g) + 6 H<sub>2</sub>(g)</li> <li>It is found that the reaction follows the following rate equation: Rate = k [PH<sub>3</sub>].</li> <li>The half-life of PH<sub>3</sub> is 37.9 s at 120°C.</li> <li>(i) How much time is required for 3/4<sup>th</sup> of PH<sub>3</sub> to decompose?</li> <li>(ii) What fraction of the original sample of PH<sub>3</sub> remains behind after 1 minute?</li> </ul>
Q.9	Define 'activation energy' of a reaction.
Q.10	The thermal decomposition of $HCO_2H$ is a first order reaction with a rate constant of $2.4 \times 10^{-3} \text{ s}^{-1}$ at a certain temperature. Calculate how long will it take for three-fourths of initial quantity of $HCO_2H$ to decompose. (log $0.25 = -0.6021$ )
Q.11	What do you understand by the rate law and rate constant of a reaction? Identify the order of a reaction if the units of its rate constant are : (i) $L^{-1}$ mol s <sup>-1</sup> (ii) L mol <sup>-1</sup> s <sup>-1</sup>
Q.12	The rate of a reaction increases four times when the temperature changes from 300 K to 320 K. Calculate the energy of activation of the reaction, assuming that it does not change with temperature. $(R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1})$
Q.13	(a) For a reaction A + B $\rightarrow$ P, the rate law is given by, r = k[A] <sup>1/2</sup> [B] <sup>2</sup> What is the order of this reaction ? (b) A first order reaction is found to have a rate constant k = 5.5 × 1 <sup>-14</sup> s <sup>-1</sup> . Find the half life of the reaction.
Q.14	The rate of a reaction becomes four times when the temperature changes from 293 K to 313 K. Calculate the energy of activation ( $E_a$ ) of the reaction assuming that it does not change with temperature. [R = 8.314 J K <sup>-1</sup> mol <sup>-1</sup> , log 4 = 0.6021]
	Answers
Q.1 Q.4	n = 3Q.2Rate = $k[A][B]^2$ , 6 mol <sup>-2</sup> L <sup>2</sup> S <sup>-1</sup> 22.012 kJ/moleQ.7 $3.89 \times 10^{-9}$ mole litre <sup>-1</sup> s <sup>-1</sup>

- **Q.4** 22.012 kJ/mole **Q.8** (i) 4 times, (ii) 1/4 times **Q.10**  $t_{99.9\%} = 10 \times t_{50\%}$
- 0.158 M. Q.9 **Q.11** 16 min

**Q.12** 2