### CHAPTER / 04

# **Chemical Kinetics**

#### **Topics** Covered

Rate of Chemical Reaction, Order and Molecularity of a Chemical Reactions

- Types of Chemical Reactions
- Rate of a Reaction
- Rate Expressions and Rate Constant
- Factors Affecting Rate of Reactions
- Molecularity of a Reaction

Order of a Chemical Reaction

Integrated Rate Equations

- Rate Equations of First Order Reactions
- Rate Equations of Zero Order Reactions
- Fractional-Life Period

Activation Energy and Collision Theory of Chemical Reactions

- Activation Energy
- Arrhenius Equation
- Collision Theory of Unimolecular Reactions

The word kinetics is derived from the Greek word, 'kinesis' meaning 'movement'.

Chemical kinetics is the study of chemical reactions with respect to reaction rates, effect of various factors affecting the rate of reaction, rearrangement of atoms and the formation of intermediates. The factors that affect the rate of a reaction are concentration, temperature, pressure and catalyst.

## **TOPIC ~01** Rate of Chemical Reaction, Order and Molecularity of a Chemical Reactions

#### **Types of Chemical Reactions**

The chemical reactions on the basis of the speed can be classified into the following categories:

#### (i) Fast or Instantaneous Reactions

These are the reactions which are completed immediately. These reactions occur so fast that, it is practically impossible to measure the exact speed of these reactions.

e.g. NaCl 
$$(aq)$$
 + AgNO<sub>3</sub> $(aq) \longrightarrow$  AgCl $(s)$   $\downarrow$  + NaNO<sub>3</sub> $(aq)$ 

 $2\mathrm{KMnO_4} + 8\mathrm{H_2SO_4} + 10\mathrm{FeSO_4} \longrightarrow \mathrm{K_2SO_4} + 2\mathrm{MnSO_4} + 5\mathrm{Fe_2(SO_4)_3} + 8\mathrm{H_2O}$ 

#### (ii) Moderate Reactions

There are many reactions which proceed at measurable speed. The rates of these reactions can be conveniently measured.

e.g.  $C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$ Sucrose Glucose Fructose  $CH_3COOC_2H_5 + NaOH \longrightarrow CH_3COONa + C_2H_5OH$ Ethyl acetate Sodium acetate Ethyl alcohol

#### (iii) Extremely Slow Reactions

These are the reactions which take a long time to complete. These reactions proceed with very slow speed and it is not possible to measure the exact speed of these reactions.

e.g. 
$$Fe + H_2O + CO_2 \longrightarrow Fe(OH)(HCO_3)$$
  
Rust

#### **Rate of a Reaction**

The rate of a chemical reaction means the speed with which the reaction takes place. Just as the speed of a vehicle is expressed in terms of distance travelled per unit time, the speed or the rate of a chemical reaction can be defined as the change in concentration of reactants or products per unit time.

It can be expressed in terms of

- (i) the rate of decrease in concentration of any one of the reactants.
- (ii) the rate of increase in concentration of any one of the products.

For a simple hypothetical reaction,  $R \longrightarrow P$ One mole of the reactant R produces one mole of the product P. If  $[R]_1$  and  $[P]_1$  are the concentrations of reactant R and product P, respectively at time  $t_1$  and  $[R]_2$  and  $[P]_2$  are their concentrations at time  $t_2$ , then

$$\Delta t = t_2 - t_1$$
  
 $\Delta R = [R]_2 - [R]_1 \text{ or, } \Delta P = [P]_2 - [P]_1$ 

(Here, the square brackets are used to express molar concentration)

Rate of disappearance of R

$$= \frac{\text{Decrease in concentration of } R}{\text{Time taken}} = -\frac{\Delta[R]}{\Delta t} \qquad \dots (i)$$

Rate of appearance of P

$$=\frac{\text{Increase in concentration of }P}{\text{Time taken}} = +\frac{\Delta[P]}{\Delta t} \qquad \dots (\text{ii})$$

Since,  $\Delta[R]$  is a negative quantity (as concentration of reactants is decreasing), it is multiplied by -1 to make the rate of the reaction a positive quantity.

#### Units of Rate of Reaction

From the Eq. (i) and (ii), it is clear that unit of rate is concentration time<sup>-1</sup>.

If concentration is in mol  $L^{-1}$  and time is in second, then the units of rate of reaction will be mol  $L^{-1}s^{-1}$ .

However, in gaseous reactions when the concentration of gases is in terms of their partial pressure, the unit of rate of their reaction will be atm  $s^{-1}$ .

#### Average Rate of a Reaction

The average rate of reaction is the appearance of product or disappearance of reactants over a long time interval.

$$\therefore \qquad r_{\rm av} = -\frac{\Delta[R]}{\Delta t} = +\frac{\Delta[P]}{\Delta t}$$

#### Instantaneous Rate of a Reaction

Reaction rate, at a particular moment of time is called instantaneous rate of reaction.

$$\therefore \qquad r_{\text{inst}} = -\frac{d[R]}{dt} = +\frac{d[P]}{dt}$$

As  $\Delta t \rightarrow 0$ , Instantaneous rate = Average rate It is determined from the slope of the graph as given below:



Determination of instantaneous and average rate of a reaction

#### Rate Expression and Rate Constant

Rate of reaction at a given temperature may depend on concentration of reactants and products. Representation of the rate of reaction in terms of concentration of the reactants is called the **rate law**, **rate equation** or **rate expression**.

Consider a general reaction,  $aA + bB \longrightarrow cC + dD$ 

where, a, b, c and d are stoichiometric coefficient of reactants and products.

The rate law for this reaction is

Rate 
$$\propto [A]^x [B]^x$$

where, *x* and *y* are determined experimentally and may be or may not be equal to stoichiometric coefficient of the reactant. Above equation can be written as,

$$\operatorname{Rate} = \frac{-d[R]}{dt} = k[A]^{x}[B]^{2}$$

where, *k* is the proportionality constant called **rate constant**.

#### Rate Constant (Specific Reaction Rate)

The rate constant of a reaction is equal to the rate of reaction when the concentration of each of the reactants is unity. For reaction,  $aA+bB \longrightarrow$  Products,

Rate law is given by,

Rate 
$$\propto [A]^a [B]^b$$
  
Rate =  $k [A]^a [B]^b$ 

So, k = rate constant.

The general unit of rate constant is  $\text{mol}^{1-n} L^{n-1} s^{-1}$ where, *n* represents the overall sum of the powers appearing in the rate law. For a gaseous reaction, unit of rate constant is  $\text{atm}^{1-n} s^{-1}$ .

#### **Distinction between Rate of Reaction and Rate Constant**

	Rate of reaction	Rate constant
(i)	It is the change in concentration of reactant or product per unit time.	It is constant of proportionality in rate law equation.
(ii)	At any instant of time, it depends upon molar concentration and temperature of reactants at that time.	It depends upon temperature but is independent of concentration of reactant.
(iii)	Its units are always $mol L^{-1} time^{-1}$ .	Its units depends upon order of reaction.

#### Factors Affecting Rate of Reactions

Rate of a chemical reaction depends upon the experimental conditions, like concentration of one or more reactants (pressure in case of gases), temperature, catalyst and surface area of the reactants.

#### (i) Nature of the Reactants

Rates of reactions are influenced by the nature of reactants. The reactivity of a substance depends on the ease with which the specific bonds are broken or formed. The rate of reaction is fast, if it involves ionic species. On the other hand, rate of molecular reactions and oxidation-reduction reactions are quite slow.

#### (ii) Concentration of Reactants

Reactions occur with greater speed when concentration of the reactants is high.

Conversely, reaction rate decreases as the concentrations of the reactants decrease.

#### (iii) Effect of Temperature

Temperature influences the rate of reaction. Reactions occur with greater speed at higher temperature. Speed of a reaction nearly doubles on  $10^{\circ}$  C rise in temperature.

#### (iv) Presence of Catalyst

A catalyst alters the speed of reaction. It helps to attain the equilibrium quickly. It participates in the reaction without being consumed.

#### (v) Surface Area of the Reactants

Smaller the particle size, greater the surface area and faster is the reaction. So, powdered form of catalyst is better catalyst.

#### (vi) Effect of Radiation

Rate of reaction increased by the use of certain radiations. The photons of these radiations having frequencies (v) possess sufficient energies (E = hv) to break certain bonds of reactants.

#### Molecularity of a Reaction

According to the collision theory, a reaction may take place, the atoms, ions or molecules of the reactants must come close together simultaneously and collide with one another.

Therefore, the number of reacting species (atoms, ions or molecules) taking part in an elementary reaction, which must collide simultaneously in order to bring about a chemical reaction is called molecularity of a reaction.

 In case of decomposition of NH<sub>4</sub>NO<sub>2</sub> and O<sub>2</sub>F<sub>2</sub>, the molecularity is 1 and it is unimolecular reaction.

$$\begin{array}{rcl} \mathrm{NH_4NO_2} & \longrightarrow & \mathrm{N_2} + 2\mathrm{H_2O} \\ \mathrm{O_2F_2} & \longrightarrow & \mathrm{O_2} + \mathrm{F_2} \end{array}$$

• The decomposition of HI is a bimolecular reaction as, it involves collision of two molecules.

$$2 \text{HI} \longrightarrow \text{H}_2 + \text{I}_2$$

- The reaction between NO and  ${\rm O}_2$  is a trimolecular reaction as collision of three molecules result into the product.

$$2NO + O_2 \longrightarrow 2NO_2$$

- Reactions with molecularity greater than three are not found, as probability of more than three molecules colliding simultaneously and react to form product is small.
- The slowest step of a reaction is the rate determining step of a chemical reaction and decides the overall rate of reaction.

Consider the reaction,

$$2\mathrm{N}_2\mathrm{O}_5 \ \longrightarrow \ 4\mathrm{NO}_2 + \mathrm{O}_2$$

According to the rate law,

Rate of reaction =  $k [N_2O_5]$ 

So, this reaction must takes place in two steps in such a way that the slowest step should involve only one molecule of N<sub>2</sub>O<sub>5</sub>.

Step I 
$$N_2O_5 \xrightarrow{\text{Slow}} NO_2 + NO_3$$
  
Step II  $N_2O_5 + NO_3 \xrightarrow{\text{Fast}} 3NO_2 + O_2$ 

The first step, being slow, is the rate determining step. Since, the rate determining step is unimolecular, so it has order one.

#### **Order of a Chemical Reaction**

For a general reaction,  $aA + bB \longrightarrow cC + dD$ Rate =  $k [A]^x [B]^y$ 

Here, x and y calculated experimentally indicate how sensitive the rate is to the change in concentration of Aand B. Sum of these exponents, i.e. x + y gives the overall order of a reaction, whereas x and y represent the order with respect to the reactants A and B, respectively.

Hence, the sum of the powers of the concentration of the reactants in the rate law expression is called the order of that chemical reaction.

Order of a reaction can be 0, 1, 2, 3 and even a fraction. A zero order reaction means that the rate of reaction is independent of the concentration of reactants and the reaction is extremely fast.

Taking SI units of concentration mol  $L^{-1}$  and time(s) the unit of *k* for different reaction order are given below:

- For zero order (n = 0) reaction = mol L<sup>-1</sup>s<sup>-1</sup>
- For first order (n = 1) reaction  $= s^{-1}$
- For second order (n = 2) reaction = mol<sup>-1</sup>L s<sup>-1</sup>

• For *n*th order reaction,

$$k = \frac{\text{Concentration}}{\text{Time}} \times \frac{1}{(\text{Concentration})^n} = (\text{mol } L^{-1})^{1-n} s^{-1}$$

#### **Zero Order Reaction**

A zero order reaction means that the rate of reaction is independent of the concentration of reactants and the reaction is extremely fast.

$$\mathrm{H}_{2}(g) + \mathrm{Cl}_{2}(g) \xrightarrow{h\nu} 2\mathrm{HCl}(g)$$

#### **First Order Reaction**

The reactions in which only one reactant molecule undergoes chemical change, are called first order reaction.

In these reactions, concentration of only one reacting substance changes during chemical reaction.

e.g. 
$$N_2O_5 \longrightarrow N_2O_4 + \frac{1}{2}O_2$$

#### Second Order Reaction

The reactions in which rate is determined by the variation of two concentration terms or the rate of the reaction is proportional to the second power of the concentration of a single reacting substance.

e.g. 
$$A + B \longrightarrow$$
 Products  
 $2A \longrightarrow$  Products

#### Third Order Reaction

The reaction in which sum of the exponents of the concentration of the reactant species is 3, are called third order reactions.

e.g. 
$$2A + B \longrightarrow \text{Products}$$
  
 $A + 2B \longrightarrow \text{Products}$ 

#### **Fractional Order Reaction**

There are some reactions having fractional order of reaction.

e.g. 
$$CH_3CHO \longrightarrow CH_4 + CO$$
  
Here, order =  $\frac{3}{2}$ 

Comparision between molecularity and order of a reaction as follows:

Molecularity of a reaction	Order of a reaction
The number of reacting species which must collide simultaneously in order to bring about a chemical reaction is called molecularity of a reaction.	The sum of powers of the concentrations of the reactants in the rate law expression is called the order of that chemical reaction.
Molecularity is always a whole number value.	Order may have zero, whole number or fractional values.
Molecularity is a theoretical concept.	Order is determined experimentally.
Molecularity is applicable to elementary reactions only. For complex reactions, it has no meaning.	Order is applicable to elementary as well as complex reactions.
For simple reactions, molecularity can be obtained from the stoichiometry of the equations.	For simple reactions, order may or may not be equal to the number of molecules of the reactants as seen from the balanced equation.

## **PRACTICE** QUESTIONS

#### Exams', Textbook's Other Imp. Questions

#### **1 MARK** Questions

#### **Exams' Questions**

- **Q.1** The overall order of reaction which has rate expression rate =  $k A^{1/2} B^{3/2}$  is [2018] (a) 1 (b) 2 (c) 3 (d) zero
- (a) 1 (b) 2 (c) 3 (d) zero **Sol** (b) Given, rate =  $k A^{1/2} B^{3/2}$
- Thus, overall order of reaction  $=\frac{1}{2} + \frac{3}{2} = 2$

Therefore, the reaction is said to be of second order.

- Q.2 What is the unit of rate constant of the first order reaction? [2014, 2009, 2003, Textbook]
- **Sol** s<sup>-1</sup> is the unit of rate constant for first order reaction.
- Q.3 The unit of rate constant for zero order reaction is ......[2011]
- **Sol** mol  $L^{-1}s^{-1}$ .

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Q.4 Define molecularity of a reaction. [2006]
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- **Sol** Molecularity is defined as the number of reacting species in an elementary reaction undergoing simultaneous collision in order to bring about a chemical reaction.
- **Q.5** What is the unit of rate constant for the second order reaction?

[2005, 2002, 2000 Instant, 2000, Textbook]

- **Sol**  $mol^{-1}L s^{-1}$  is the unit of rate constant for second order reaction.
- **Q.6** Calculate the order of a reaction having the rate expression, rate =  $k [A]^{1/2} [B]^{1/2}$ . [2004]
- **Sol** The order of reaction is  $\frac{1}{2} + \frac{1}{2} = 1$ .
- Q.7 What is the reaction order, if the unit of rate constant is L mol<sup>-1</sup>s<sup>-1</sup>? [2004, Textbook]
- Sol It is the second order reaction.

#### Important Questions

- Q.8 The specific rate constant of a first order reaction depends upon the(a) concentration of the reactant
  - (b) concentration of the product

(c) time

(d) temperature

- **Sol** (d) The specific rate constant of a first order reaction depends upon the temperature, its value does not depend upon concentration of reactant and product and time.
- **Q.9** In which of the following cases, does the reaction go farthest to completion?
  - (a)  $k = 10^2$  (b)  $k = 10^{-2}$  (c) k = 10 (d) k = 1
- **Sol** (a) More the value of the ratio of [product]/[reactant], further the reaction will go. The reaction having  $k = 10^2$  will go farthest to

completion because the ratio [product/reactant] is maximum in option (a).

(d) 0

**Q.10** Rate expression of a chemical change is  $\frac{dx}{dt} = k[A]^{2}[B] [C]^{0}$ 

> The order of the reaction is (a) 2 (b) 3 (c) 1

- **Sol** (b) Since, here three reactant are present but the order with respect to (A) is two and order with respect to [B] [C] is one and zero respectively. Hence, overall order for this expression will be 3.
- **Q.11** The unit of the rate constant for the second order reaction is

(a) $mol^{-1} L s^{-1}$	(b) mol $L^{-1} s^{-1}$
(c) $s^{-1}$	(d) mol $L^{-1}s$

- **Sol** (a) Formula for *n*th order reaction  $(\text{mol } L^{-1})^{1-n} s^{-1}$ For second order reaction value of n = 2, hence  $(\text{mol } L^{-1})^{1-2} s^{-1}$  or  $\text{mol}^{-1} L s^{-1}$ .
- **Q.12** The reaction,  $2Na + Cl_2 \longrightarrow 2NaCl$  is found to

follow 3rd order kinetics, its molecularity is (a) 1 (b) 2

- (c) 3 (d) 4
- **Sol** (c) According to molecularity, the number of reacting species (atoms, ions, or molecules) taking part in an elementary reaction is known as molecularity.

In  $2Na + Cl_2 \longrightarrow 2NaCl$ , two molecules of Na and one molecule of  $Cl_2$  part in elementary reaction, hence its molecularity will be 3.

Q.13 The rate law for the reaction.

 $RCl + NaOH(aq) \longrightarrow ROH + NaCl is given by,$ Rate =  $k_1$  [*RCl*]. The rate of reaction will be

- (a) doubled on doubling the concentration of NaOH
- (b) halved on reducing the concentration of alkyl
- halide to one half (c) increased on decreasing the temperature of the
- reaction (d) unaffected by increasing the temperature of the
- reactionSol (b) The rate of reaction of given reaction is k, [RCl]It means rate of reaction depends upon concentration of RCl, so halved on reducing the concentration of alkyl halide rate will be one half.Also, the rate of reaction depends on temperature,

so increasing the temperature it will increased.

**Q.14** When  $AgNO_3$  solution is added to aq.NaCl, a

white precipitate is obtained. This reaction is

- (a) slow (b) with measurable speed
- (c) instantaneous (d) None of these
- **Sol** (c) When  $AgNO_3$  solution is added to aq. NaCl, a white precipitate is obtained immediately. There reaction occur so fast, so it is a instantaneous reaction. NaCl(aq) + AgNO<sub>3</sub>(aq)  $\longrightarrow$  AgCl(s)  $\downarrow$  + NaNO<sub>3</sub>(aq)
- **Q.15** Which one of the following does not influence the rate of reaction?
  - (a) Nature of reactant(b) Concentration of reactant(c) Temperature(d) Molecularity
- **Sol** (d) The rate of reaction depends on nature and concentration of reactant and temperature but molecularity does not influence it.
- **Q.16** The rate at which a substance reacts is proportional to
  - (a) equivalent weight (b) molecular weight
  - (c) number of moles (d) number of moles per litre
  - **Sol** (d) According to law of mass action, the rate at which substance reacts is proportional to its active mass (number of mole per litre).
- **Q.17** The rate law for the single step reaction,

 $2A + B \longrightarrow 2C$  is given by (a) rate = k [A] [B] (b) rate =  $k [A]^2 [B]$ (c) rate = k [A] [B] (d) rate =  $k [A]^2 [B]^0$ 

**Sol** (b) Consider the following reaction:

$$2A + B \longrightarrow 2C$$

The rate of a reaction is given as:

Rate = 
$$k[A]^2[B]$$

- **Q.18** If the rate of reaction is given by, rate =  $[A][B]^2$ , then the reaction is
  - (a) first order with respect to A
  - (b) second order with respect to B
  - (c) third order overall
  - (d) All of the above
  - **Sol** (d) Rate of reaction, rate =  $[A] [B]^2$ .

According to this expression, order of reaction with respect to [A] will be first order and with respect to [B] will be second order because it is proportional to the second power of the concentration of B. And overall reaction will be third order. (Order of reaction) n = 1 + 2 = 3 (third order).

Q.19 The rate law of the reaction,

 $2A + B \longrightarrow 2C$  is represented as,

Rate =  $k [A]^{2}[B]$ . If *A* is taken in large excess, the order of the reaction will be

(a) three (b) two (c) one (d) zero

**Sol** (c)  $2A + B \longrightarrow 2C$ 

Rate =  $k[A]^2[B]$ 

If A is taken in large excess then the rate of reaction does not depends upon concentration of [A]. It is pseudomolecular first order reaction. The rate of reaction depends only on concentration [B]. Thus, the order of the reaction is 1.

**Q.20** For the reaction,  $H_2(g) + Br_2(g) \Longrightarrow 2HBr(g)$ , the

reaction rate =  $k[H_2] [Br_2]^{1/2}$ . Which of the

following statement is correct for this reaction?

- (a) Molecularity of the reaction is 2
- (b) Molecularity of the reaction is 3/2
- (c) The unit of k is s<sup>-1</sup>
- (d) None of the above
- **Sol** (a) Statement (a) is correct as two molecules of the reactants take part in a chemical reaction.
- **Q.21** For a reaction,  $A + B \longrightarrow X + Y$ , if concentration of A is doubled without altering that of B, rate of the reaction gets doubled. If concentration of B is increased nine times without altering that of A, rate of the reaction gets tripled. Order of the reaction is

(a) 
$$1\frac{2}{3}$$
 (b)  $1\frac{1}{2}$  (c) 2 (d) 0

**Sol** (b) The rate of reaction can be written as:  $r = k [A]^{1} [B]^{\nu_{2}}$ 

Hence, order of reaction  $= 1 + \frac{1}{2} = 1\frac{1}{2}$ 

**Q.22** The decomposition of dimethyl ether leads to the formation of  $CH_4$ ,  $H_2$  and CO and the reaction rate is given by rate =  $k[CH_3OCH_3]^{3/2}$ .

The rate of reaction is followed by increase in pressure in a closed vessel, so the rate can also be expressed in terms of partial pressure of dimethyl ether, i.e. rate =  $k(p_{CH_3OCH_3})^{3/2}$ .

If the pressure is measured in bar and time in minutes, then what are the units of rate and rate constant?

**Sol** Unit of rate = bar min<sup>-1</sup>

Unit of 
$$k = \frac{\text{Rate}}{[P_{\text{CH}_3\text{OCH}_3]}^{3/2}} = \frac{\text{bar min}^{-1}}{(\text{bar})^{3/2}} = \text{bar}^{-1/2} \text{min}^{-1}$$

**Q.23** Nitric oxide reacts with hydrogen to give nitrogen and water.

$$2NO + 2H_2 \longrightarrow N_2 + 2H_2O$$

The kinetics of this reaction is predicted by the following steps:

What is the predicted rate law?

- Sol Slowest step of the reaction mechanism determines the rate of the reaction. So, the rate law is, Rate =  $k [NO]^2 [H_2]$
- **Q.24** What is the rate of disappearance of hydrogen in the reaction?

$$3H_2 + N_2 \longrightarrow 2NH_3$$

**Sol** Rate of disappearance of hydrogen =  $-\frac{1}{3} \frac{d [H_2]}{dt}$ 

#### **2 MARK** Questions

#### **Exams' Questions**

- Q.25 What is the difference between order of reaction and molecularity of reaction? Give two distinctions. [2015]
  - Or Distinguish between order and molecularity of a reaction. [Textbook]
  - Sol Distinctions between order of reaction and molecularity of reaction

Order	Molecularity
1. The sum of powers of the concentrations of the reactants in the rate law expression is called the order of that chemical reaction.	The number of reacting species which must collide simultaneously in order to bring about a chemical reaction is called molecularity of a reaction.
2. Order may have zero, whole number or fractional values.	Molecularity is always a, whole number value.

- Q.26 Name two factors which influence the rate of reaction. [2002, 2000, Textbook]
  - Sol Molar concentration of reactants and temperature are the two factors which influence the rate of reaction. (2)

#### Important Questions

**Q.27** For a reaction,  $P \longrightarrow Q$  the rate becomes eight times when concentration of P is doubled. What is the order of the reaction?

Sol Let 
$$r = k [P]^n$$
 ...(i)  
 $8 r = [2P]^n$  ...(ii)

$$8 r = [2P]^{n} \qquad \dots(11)$$
  
Dividing Eq. (i) by Eq. (i)  
$$\frac{8r}{r} = \frac{k [2P]^{n}}{k [P]^{n}}$$
  
or 
$$[2]^{3} = [2]^{n} \qquad (1)$$

Therefore, order of the reaction is 3.

**Q.28** For the reaction,  $2A + B \longrightarrow A_2B$ the rate =  $k [A] [B]^2$  with  $k = 2.0 \times 10^{-6} \text{ mol}^{-2} \text{ L}^2 \text{s}^{-1}$ .

Calculate the initial rate of reaction when  $[A] = 0.1 \text{ mol } \text{L}^{-1}$ ,  $[B] = 0.2 \text{ mol } \text{L}^{-1}$ . Also, calculate the rate of reaction after [A] is reduced to 0.06 mol  $\text{L}^{-1}$ .

Sol (i) Case I Initial rate = 
$$k [A] [B]^2$$
 (given)  
=  $(2.0 \times 10^{-6} \text{mol}^{-2} \text{ L}^2 \text{ s}^{-1})$   
 $\times (0.1 \text{ mol } \text{L}^{-1}) \times (0.2 \text{ mol } \text{L}^{-1})^2$ 

$$= 8.0 \times 10^{-9} \text{ mol } \text{L}^{-1} \text{ s}^{-1}$$
 (1/2)

(1)

(ii) **Case II** Concentration of A at a particular time =  $0.06 \text{ mol } \text{L}^{-1}$ 

Amount of A reacted =  $(0.1 - 0.06) = 0.04 \text{ mol } \text{L}^{-1}$ 

Amount of *B* reacted =  $\frac{1}{2} \times 0.04 \text{ mol } \text{L}^{-1}$ 

 $= 0.02 \text{ mol } \text{L}^{-1}$ 

Concentration of *B* at a particular time  
= (0.2 - 0.02) mol L<sup>-1</sup>= 0.18 mol L<sup>-1</sup> (1/2)  
Rate = 
$$k [A] [B]^2$$
  
= (2.0×10<sup>-6</sup>mol<sup>-2</sup>L<sup>2</sup>s<sup>-1</sup>)  
× (0.06 mol L<sup>-1</sup>)× (0.18 mol L<sup>-1</sup>)<sup>2</sup>

 $= 3.89 \times 10^{-9} \text{mol } \text{L}^{-1} \text{s}^{-1}$  (1)

#### **<u>3 MARK</u>** Questions

**Q.29** Under which condition the rate of reaction becomes equal to the specific reaction rate? Write the expressions for the rate of reaction of  $PCl_5 \longrightarrow PCl_3 + Cl_2$ . [2019] *Sol* Rate of reaction equal to the specific reaction rate (i.e. rate constant), when concentration of reactants is unity, i.e. for the reaction,

$$PCl_5 \longrightarrow PCl_3 + Cl_3$$

Rate (r) = k [concentration]<sup>1</sup>

Expression for rate of reaction of  ${\rm PCl}_5 \longrightarrow {\rm PCl}_3$  +  ${\rm Cl}_2$  is as follows :

Rate  $(r) = k [PCl_5]^1$ 

[:: The given reaction is of first order] (3)

#### Important Questions

- **Q.30** The ionisation constant of  $NH_4^+$  in water is  $5.6 \times 10^{-10}$  at 25°C. The rate constant for the
  - $\begin{array}{ll} \mbox{reaction of NH}_4^+ \mbox{ and OH}^- \mbox{ to from NH}_3 \mbox{ and H}_2 O \\ \mbox{at 25}^{\circ} C \mbox{ is } 3.4 \times 10^{-10} \mbox{ L mol}^{-1} \mbox{ sec}^{-1}. \mbox{ Calculate} \\ \mbox{the rate constant for proton transfer from water} \\ \mbox{to NH}_3. \end{tabular}$

Sol NH<sub>3</sub> + H<sub>2</sub>O → NH<sub>4</sub><sup>+</sup> + O H; 
$$K_b = 3.4 \times 10^{-10} \text{ L mol}^{-1} \text{s}^{-1}$$
  
NH<sub>4</sub><sup>+</sup> + H<sub>2</sub>O → NH<sub>4</sub>OH + H<sup>+</sup>;  $K_a = 5.6 \times 10^{-10}$   
 $K_{\text{NH}_3} (K_{\text{base}}) = \frac{K_f}{K_b}$   
 $\frac{K_w}{K_{\text{acid}}} = \frac{K_f}{K_b}$  [As,  $K_{\text{acid}} \times K_{\text{base}} = K_w$ ]  
 $\frac{10^{-14}}{5.6 \times 10^{-10}} = \frac{K_f}{3.4 \times 10^{-10}}$   
 $\therefore \qquad K_f = 6.07 \times 10^{-15} \text{ s}^{-1}$  (3)

**Q.31** The following results have been obtained during the kinetic studies of the reaction,  $2A + B \longrightarrow C + D.$ 

Exp.	$[A]$ /mol $L^{-1}$	$[B]$ mol $\mathrm{L}^{\!-\!1}$	Initial rate of formation of [D]mol L <sup>-1</sup> min <sup>-1</sup>
1.	0.1	0.1	$6.0 imes10^{-3}$
2.	0.3	0.2	$7.2  imes 10^{-2}$
3.	0.3	0.4	$2.88  imes 10^{-1}$
4.	0.4	0.1	$2.40  imes 10^{-2}$

Determine the rate law and the rate constant for the reaction.

Sol Rate law may be, expressed as,

Rate = 
$$k [A]^x [B]^y$$

$$(\text{Rate})_1 = 6.0 \times 10^{-3} = k \ (0.1)^x \ (0.1)^y \qquad \dots (i)$$

$$(\text{Rate})_2 = 7.2 \times 10^{-2} = k \ (0.3)^x \ (0.2)^y \qquad \dots (ii)$$

$$(\text{Rate})_3 = 2.88 \times 10^{-1} = k \ (0.3)^x \ (0.4)^y \qquad \dots (\text{iii})$$

$$(\text{Rate})_{4} = 2.40 \times 10^{-2} = k \ (0.4)^{x} \ (0.1)^{y} \qquad \dots \text{(iv)}$$
$$\frac{(\text{Rate})_{1}}{(\text{Rate})_{4}} = \frac{6.0 \times 10^{-3}}{2.40 \times 10^{-2}} = \frac{k \ (0.1)^{x} \ (0.1)^{y}}{k \ (0.4)^{x} \ (0.1)^{y}}$$
$$\frac{1}{4} = \frac{(0.1)^{x}}{(0.4)^{x}} = \left(\frac{1}{4}\right)^{x}$$
$$x = 1 \qquad (1/2)$$
$$\frac{(\text{Rate})_{2}}{(\text{Rate})_{3}} = \frac{7.2 \times 10^{-2}}{2.88 \times 10^{-1}} = \frac{k \ (0.3)^{x} \ (0.2)^{y}}{k \ (0.3)^{x} \ (0.4)^{y}}$$

or 
$$\frac{1}{4} = \frac{(0.2)^y}{(0.4)^y} = \left(\frac{1}{2}\right)^y$$
  
 $\therefore \qquad y = 2$  (1/2)

Now, rate law expression is given by

$$Rate = k [A] [B]^2$$
(1)

**Rate constant** (k) can be determined by placing the values of A, B and rate of formation of D. By taking the values from experiment 2.

Rate = 
$$k [A] [B]^2$$
  

$$k = \frac{\text{Rate}}{[A] [B]^2} = \frac{7.2 \times 10^{-2} \text{mol } \text{L}^{-1} \text{ min}^{-1}}{(0.3 \text{ mol } \text{L}^{-1}) (0.2 \text{ mol } \text{L}^{-1})^2}$$

$$= 6.0 \text{ mol}^{-2} \text{L}^2 \text{min}^{-1}$$
or,  $k = 6.0 \text{ mol}^{-2} \text{L}^2 \text{min}^{-1}$  (1)

#### **7 MARK** Questions

#### **Exams' Questions**

or

*:*..

- Q.32 (i) What is molecularity of a reaction? Illustrate with examples.
  - (ii) Derive the rate constant expression for the reaction  $A \longrightarrow B + C$ . [2013]
  - Sol (i) Refer to the text on page 68. (3)
    - (ii) Refer to the text on pages 67 and 68. (4)
- **Q.33** Writes notes on distinction between molecularity of reaction and order of reaction.
  - [2011, 2009, 2003, 2000, Textbook] Sol Refer to text on page 69. (7)

#### **Important Questions**

- Q.34 (i) What do you mean by the term 'chemical kinetics'? What are the different types of chemical reactions? Explain.
  - (ii) A chemical reaction, 2X → 4Y + Z in gas phase occurs in a closed vessel. The concentration of Y is found to increase by 5×10<sup>-3</sup> mol L<sup>-1</sup> in 10 s. Determine (a) rate of appearance of Y, (b) rate of disappearance of X.

(a) Rate of appearance of  

$$Y = \frac{d[Y]}{dt} = \frac{5 \times 10^{-3} \text{ mol } \text{L}^{-1}}{10 \text{ s}}$$

$$= 5 \times 10^{-4} \text{ mol } \text{L}^{-1} \text{s}^{-1}$$
(b) Rate =  $-\frac{1}{2} \frac{d[X]}{dt} = +\frac{1}{2} \frac{d[Y]}{dt}$ 

$$2 \quad dt \qquad 4 \quad dt$$
∴ Rate of disappearance of X
$$\frac{-d[X]}{dt} = \frac{2}{4} \times \frac{d[4Y]}{dt} = \frac{1}{2} \times 5 \times 10^{-4}$$

$$= 2.5 \times 10^{-4} \text{ mol } \text{L}^{-1} \text{ s}^{-1} \qquad (2)$$

- Q.35 (i) Define the term 'average rate' and 'instantaneous rate'.
  - (ii) For the following reaction,

 $2X + Y + Z \longrightarrow X_2Y + Z$ , the rate law has been determine to be =  $k [X] [Y]^2$  with  $k = 2.0 \times 10^{-6}$  mol<sup>-2</sup>L<sup>2</sup>s<sup>-1</sup>. For this reaction, find out the initial rate of reaction with

#### **TOPIC TEST 1**

**1.** The inversion of cane sugar is a ..... reaction though its molecularity is .....

[Ans. First order, two]

- ..... is always a whole number value and never a fraction or zero. [Ans. Molecularity]
- **3.** What is rate of reaction? Give its unit.
- **4.** Give the difference between fast reaction and slow reaction.
- **5.** Write the order of a reaction whose rate constant (*k*) has the same units as the rate of reaction.
- 6. The kinetics of the given reaction is  $2NO + 2H_2 \longrightarrow N_2 + 2H_2O$  is explained by the steps as follows:
  - (i)  $2NO + H_2 \longrightarrow N_2 + H_2O_2$  (Slow)
  - (ii)  $H_2O_2 + H_2 \longrightarrow 2H_2O$  (Fast) What is the predicted rate law?

~ ~

1 - 1

1 7 -1 577

LTT 0 4

Sol

(

(3)

7. NH<sub>3</sub> decomposes as follows:

$$2\mathrm{NH}_{3} \longrightarrow \mathrm{N}_{2} + 3\mathrm{H}_{2}$$
$$-\frac{d[\mathrm{NH}_{3}]}{dt} = k_{1}[\mathrm{NH}_{3}]; + \frac{d[\mathrm{N}_{2}]}{dt} = k_{2}[\mathrm{NH}_{3}]$$
and  $+ \frac{d[\mathrm{H}_{2}]}{dt} = k_{3}[\mathrm{NH}_{3}]$ 

Derive the ratio between  $k_1, k_2$  and  $k_3$ .

- **8.** For a chemical reaction, what are the factors which influence the rate of a reaction?
- 9. (i) State the 'rate law' for chemical reaction.(ii) What is meant by the order of reaction being
  - zero?(iii) How does the value of rate constant vary with reactant concentration?
- **10.** For the reaction,  $2SO_2 + O_2 \longrightarrow 2SO_3$ , the rate of reaction with respect to  $O_2$  is 0.48 Ms<sup>-1</sup>. Find the rate of reaction w.r.t.  $SO_2$  and  $SO_3$ .

## **TOPIC ~02** Integrated Rate Equations

#### Rate Equations of First Order Reactions

In this class of reactions, the rate of the reaction is proportional to the first power of the concentration of the reactant R.

For the reaction,  $R \longrightarrow P$ 

Rate = 
$$-\frac{d[R]}{dt} = k[R]$$
 or  $\frac{d[R]}{[R]} = -kdt$ 

In the beginning when  $t = 0, R = [R]_0$ ,  $[R]_0$  being the initial concentration of the reactant

or  $k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$ 

Here,  $[R]_1$  and  $[R]_2$  are concentrations of the reactants at time  $t_1$  and  $t_2$ , respectively.

$$k = \frac{2.303}{t_2 - t_1} \log \frac{[R]_1}{[R]_2} \qquad \dots (i)$$

The first order rate Eq. (i) can also be written as:

$$k = \frac{2.303}{t} \log \frac{R_0}{R}$$
 or,  $\log \frac{R_0}{R} = \frac{kt}{2.303}$ 

• If we plot a graph between  $\log [R]_0 / [R]$  vs t, we get a straight line with the slope = k/2.303 as shown in the figure (b).



e.g. Decomposition of nitrogen pentaoxide and dissociation of  $PCl_5$  are examples of 1st order reaction.

#### **Characteristic of First Order Reactions**

- (i) The unit of rate constant is  $s^{-1}$ .
- (ii) Rate constant remains unaffected by the change in concentration.
- (iii) Graph plotted between  $\log a x$  and t is found to be linear.

#### **Rate Equations of Zero Order Reactions**

It means that the rate of the reaction is proportional to zeroth power of the concentration of reactants. Consider the reaction.

$$R \longrightarrow P$$
Rate =  $-\frac{d[R]}{dt} = k[R]^0 = k \times 1$ 

$$d[R] = -kdt$$
hoth sides  $[R] = -kt + I$ 

Integrating both sides, [R] = -kt + I

where, I is constant of integration.

Initially, at t = 0, the concentration of the reactant  $R = [R]_0$ , where  $[R]_0$  being the initial concentration of the reactant.

From Eq. (i), we have

$$[R]_0 = -k \times 0 + I$$

Substituting  $I = [R]_0$  in the Eq. (i)

$$[R] = -kt + [R]_0 \qquad \dots (ii)$$

Simplifying Eq. (ii) gives,

$$k = \frac{[R]_0 - [R]}{t}$$
 ...(iii)

If we plot [R] against (t), we get a straight line with slope
 = -k and intercept equal to [R]<sub>0</sub> as shown in the figure below.



Variation in the concentration - time plot for a zero order reaction

Zero order reactions are not so common and they occur under special conditions. Some enzyme catalysed reactions and reactions which occur on metal surfaces are few examples of zero order reactions.

#### **Characteristic of Zero Order Reactions**

- (i) Unit of rate constant for zero order is mol  $L^{-1}s^{-1}$ .
- (ii) A graph of concentration of product (x) against time (t) for such reaction gives a straight line passing through the origin.

...(i)

#### **Fractional-Life Period**

It is the time required to complete a particular fraction of a reaction.

#### Half-Life Period

The time in which the concentration of a reactant is reduced to one half of its initial concentration is called the half-life of that reaction. It is represented as  $t_{1/2}$ .

(i) For a zero order reaction  $k = \frac{[R]_0 - [R]}{t}$ 

At  $t = t_{1/2}$ ,  $[R] = \frac{1}{2} [R]_0$ 

The rate constant at  $t_{1/2}$  becomes

$$k = \frac{[R]_0 - 1/2 [R]_0}{t_{1/2}}$$
$$t_{1/2} = \frac{[R]_0}{2k}$$

It is clear that  $t_{1/2}$  for a zero order reaction is directly proportional to the initial concentration of the reactants and inversely proportional to the rate constant.

(ii) For the first order reaction,

$$k = \frac{1}{t} \ln \frac{[R]_0}{[R]} \quad \text{or,} \quad k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$$
  
At  $t_{1/2}$ ,  $[R] = \frac{[R]_0}{2}$   
Therefore,  $k = \frac{2.303}{t_{1/2}} \log \frac{[R]_0}{[R]_0/2}$   
or  $k = \frac{2.303}{t_{1/2}} \log 2 = \frac{2.303}{t_{1/2}} \times 0.301$   
or  $t_{1/2} = \frac{0.693}{k}$ 

Therefore, for zero order reaction,  $t_{1/2} \propto [R]_0$ . For first order reaction,  $t_{1/2}$  is independent of  $[R]_0$ .

<b>Integrated rate</b>	laws for the	reactions of	zero and	first order
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Order	Reaction type	Differential rate law	Integrated rate law	Straight line plot	Half-life	Units of k
0	$R \longrightarrow P$	$\frac{d[R]}{dt} = -k$	$kt = [R]_0 - [R]$	[R] vs t	$\left[R\right]_{0}/2k$	$\begin{array}{c} \text{conc. time}^{-1} \text{ or} \\ \text{mol } \text{L}^{-1} \text{s}^{-1} \end{array}$
1	$R \longrightarrow P$	$\frac{d[R]}{dt} = -k[R]$	$[R] = [R]_0 e^{-kt} \text{ or} kt = \ln \{[R]_0 / [R]\}$	$\ln [R] vs t$	$\ln 2/k$	$\rm time^{-1}~\rm or~s^{-1}$

## **PRACTICE** QUESTIONS

#### Exams', Textbook's Other Imp. Questions

#### **1 MARK** Questions

#### **Exams' Questions**

Q.2 Acid hydrolysis of ethyl acetate is [2015, 10] (a) zero order (b) first order (c) second order (d) third order

**Sol** (b) Acid hydrolysis of ethyl acetate is as follows:  $CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$ 

The concentration of water is not considered in calculation as its concentration does not get altered much with time. Hence, it is first order reaction.

- **Q.3** Which of the following reaction is a zero order reaction? [2014, 2011] (a)  $2NO + O_2 \longrightarrow 2NO_2$ (b)  $H_2 + Cl_2 \longrightarrow 2HCl$ (c)  $CH_3COOC_2H_5 + H_2O \Longrightarrow CH_3COOH + C_2H_5OH$ (d)  $CH_3COOC_2H_5 + NaOH \longrightarrow CH_3COONa + C_2H_5OH$ 
  - **Sol** (b)  $H_2 + Cl_2 \longrightarrow 2HCl$  is an example of zero order reaction because the rate of the reaction is proportional to zero power of the concentration of reactants.

Q.4 What will be the amount of  $I^{128}(t_{1/2} = 25 \text{ min})$  left after 50 min? [2013, Textbook] (a) One-half (b) One-fourth (c) One-third (d) One-eight Sol (b) Half-life period is 25 min. Hence, the amount of

**Sol** (b) Half-life period is 25 min. Hence, the amount of  $I^{128}$  becomes half in  $t_{1/2}$ . After 50 min, it becomes  $\frac{1}{4}$  th.

**Q.5** In a first order reaction,  $A \longrightarrow B$ , if k is rate constant and the initial concentration of the reactant A is 0.5 M, then half-life is [2008]

(a) 
$$\frac{\log 2}{k}$$
 (b)  $\frac{\ln 2}{k}$ 

- **Sol** (b) For 1st order reaction,  $k = \frac{2.303}{t_{1/2}} \log 2$ 
  - or  $t_{1/2} = \frac{2.303 \log 2}{k} = \frac{\ln 2}{k}$  (ln 2 = 2.303 log 2)

(c)  $\frac{\log 2}{k\sqrt{0.5}}$ 

**Q.6** What is the order of the reaction given below?  $N_2O_5(g) \rightleftharpoons N_2O_4(g) + \frac{1}{2}O_2(g)$ [2007]

Sol The order of the reaction is one.

**Q.7** What is the half-life period of a reaction having rate constant  $6.93 \times 10^{-4} \text{ s}^{-1}$ ?

[2002, 2001, Textbook]

(d)  $\frac{0.693}{0.5 k}$ 

**Sol** Given that, rate constant  $(k) = 6.93 \times 10^{-4} \text{ s}^{-1}$ As the units of rate constant is  $\text{s}^{-1}$ . Thus, the reaction is first order reaction.

: 
$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{6.93 \times 10^{-4}} = \frac{0.693 \times 10^4}{6.93} = 1 \times 10^3 \,\mathrm{s}$$

#### Important Questions

Q.7 The hydrolysis of ethyl acetate in acid medium is a reaction of the [Textbook]

(a) zero order (b) first order

(c) second order (d) third order

**Sol** (b) The hydrolysis of ethyl acetate in acidic medium is a first order reaction because rate of reaction depends only upon concentration of ester.

e.g. 
$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^-} CH_3COOH + C_2H_5OH$$
  
Rate =  $k$ [Ester].

- Q.9 75% of a first order reaction was completed in 32 minutes, 50% of the reaction will be completed in
  - (a) 24 min (b) 16 min (c) 8 min (d) 22 min
- $\pmb{Sol}~(b)$  We know, the rate equation for first order reaction is

$$k = \frac{2.303}{t} \log \frac{a}{a - x} = 2.303$$
$$k = \frac{2.303}{t} \log \frac{100}{100 - 75} = \frac{2.303}{32} \log \frac{100}{25} = \frac{2.303}{32} \log 4$$
$$k = 0.0432 \text{ min}^{-1}$$

[Here, a = 100 mol / L, x = 75 mol / LAfter 32 min.,(a - x) = 25 mol / L]

For 50% reaction completion,

$$t = \frac{2.303}{k} \log \frac{a}{a - x}$$

or 
$$t = \frac{2303}{0.0432} \log \frac{100}{50} = \frac{2303}{0.0432} \times \log 2 = 16$$
 minute.

- Q.10 The isotope 19 K<sup>42</sup> has a half-life of about 12 hours. What fraction of the initial concentration of 19 K<sup>42</sup> remains after 48 hours.
  (a) 1/4
  (b) 1/8
  (c) 1/12
  (d) 1/16
  - **Sol** (d) Half-life period is 12 hours. Hence, the amount of  $_{19}K^{42}$  becomes half in  $t_{1/2}$ . After 48 h, it becomes  $\frac{1}{16}$  th.
- **Q.11**  $t_{1/2}$  for zero order reaction is

(a)  $\propto a$  (b)  $\propto a^{1/2}$  (c)  $\propto a^2$  (d)  $\propto a^3$ 

(a)  $\approx a$  (b)  $\approx a$  (c)  $\approx a$  (c)  $\approx a$ Sol (a) For zero order reaction,  $t_{1/2} \approx a$  because  $t_{1/2} = \frac{[R]_0}{2k}$ .

It is clear that,  $t_{1/2}$  for zero order reaction is directly proportional to the initial concentration of the reactants.

#### Q.12 The half-life of a radioactive element is 1580 years. How long will it take to reduce to 1/4th of its original mass ? (a) 3160 yr (b) 796 yr

- (a) 5100 yr (b) 750 y.
- (c) 1580 yr (d) 6320 yr
- **Sol** (a) Half-life period is 1580 years. Hence, it will reduce to  $\frac{1}{4}$  th of its original mass in 3160 years.
- **Q.13** If 'a' is the initial concentration of a substance which reacts according to zero order kinetic and 'k' is rate constant, the time for the reactant to go to completion is

(a) 
$$\frac{a}{k}$$
 (b)  $\frac{k}{a}$  (c)  $\frac{2}{ka}$  (d)  $\frac{2k}{a}$ 

**Sol** (a) The integrated rate law for zero order kinetics is given as:

$$[A] = [A]_0 - kt$$

[A] =concentration of substance left after time t

- $[A]_0$  = initial concentration of the substance
- k = rate constant of the reaction

It the initial concentration of the substance = aConcentration after reaction gets completed = 0

$$0 = a - kt$$

 $t = \frac{1}{k}$ 

Q.14 A zero order reaction is one

- (a) in which the difference of concentration of product and reactant is zero
- (b) in which concentration of the reactants do not change with time.
- (c) in which one of the reactants is in large excess
- (d) in which reactants do not react
- **Sol** (b) Zero order reaction is a chemical reaction, where the rate does not vary with the increase or decrease in the concentration of the reactants.

Q.15 The half-life period of a reaction is 100 minutes. In 400 min the initial concentration of 2.0g will become

(a) 0.25g (b) 0.75g (c) 0.125g (d) 0.1g

Sol (c) The half-life period of a reaction is 100 minutes. After 400 minutes, the initial concentration 2 g will become 0.125 g. Initial conc. 2 g  $\xrightarrow{100 \text{ min}}$  1 g  $\xrightarrow{100 \text{ min}}$ .

iitial conc. 2 g 
$$\xrightarrow{100 \text{ min}}$$
 1 g  $\xrightarrow{100 \text{ min}}$ .  
0.50 g  $\xrightarrow{100 \text{ min}}$  0.25 g  $\xrightarrow{100 \text{ min}}$  0.125 g

**Q.16** Half-life period of any first order reaction is

- (a) directly proportional to initial concentration of reactant
- (b) half of the rate constant
- (c) same for all reactions
- (d) independent of initial concentration of reactant

(d) For first order reaction, we know that 
$$k = \frac{2.303}{\log \frac{[A]_0}{1 + 1}}$$

or

$$t = [A]$$

$$t = \frac{2.303}{k} \log \frac{[A]_0}{[A]}$$

$$t = t_{1/2} \text{ then, } [A] = \frac{1}{2} [A]_0$$

$$t_{1/2} = \frac{2.303}{k} \log \frac{[A]_0}{\frac{1}{2} [A]_0} = \frac{2.303}{k} \log 2$$

$$t_{1/2} = \frac{0.693}{k} \qquad [\because \log 2 = 0.3010]$$

It is quite clear from the above expression that the half-life period for first order reaction does not depend upon initial concentration of the reaction.

- Q.17 The hydrolysis of ester in alkaline medium is `
  (a) biomolecular reaction (b) thermomolecular reaction
  (c) first order reaction (d) zero order reaction
  - Sol (a) Hydrolysis of ester in alkaline medium  $CH_3COOC_2H_5 + NaOH \longrightarrow CH_3COONa + C_2H_5OH$ The rate law equation is

Rate =  $k [CH_3COOC_9H_5] [NaOH]$ 

According to rate law equation, the order of this reaction will be second order and it is a bimolecular reaction. Because two molecules part in the stoichiometry of this reaction.

**Q.18** The decomposition of  $N_2O_5$  by

 $2N_2O_5 \longrightarrow 4NO_2 + O_2$  follows first order kinetics. Hence,

- (a) the reaction is biomolecular
- (b) the reaction is unimolecular
- (c)  $t_{1/2} \propto a^0$
- (d) None of the above

$$\pmb{Sol}~(c)$$
 The decomposition of  $N_2O_5$ 

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

Experimentally, it is found that rate of reaction  $\sim [N_2O_5]$ Hence, it will be first order reaction and half-life of first order reaction is directly proportional to the initial concentration of reactant.

 $t_{1/2} \propto a^0$ 

- **Q.19** Which of the following rate law applies to a second order reaction involving only one reactant?
  - (a) Rate is directly proportional to concentration.
  - (b) Rate is directly proportional to the square root of concentration
  - (c) Rate is equal to square of concentration
  - (d) Rate is proportional to the square of concentration
  - **Sol** (d) The second order reaction is one whose rate is proportional to the square of the concentration of one reactant. These generally have the form  $2A \longrightarrow$  products.
- **Q.20** In a second order reaction,  $2A \longrightarrow$  products, the concentration is halved. The half-life of the reaction is
  - (a) halved (b) doubled
  - (c) becomes four fold (d) unaltered
  - **Sol** (b) The half-life of a second order reaction depends on the initial concentration the half-life is given by,

$$t_{1/2} = \frac{1}{k[A]_0}$$

Two of the same reactant (A) combine in a single elementary step,  $2A \longrightarrow P$ , thus, if the concentration is halved, then the half-life of the reaction will be doubled.

**Q.21** For a first order reaction,  $X \longrightarrow$  products, the concentration of X changes from 0.1 M to 0.025 M in 40 min. The rate of reaction when the concentration of X is 0.01 M is (a)  $2.73 \times 10^{-5}$  M/min (b)  $3.47 \times 10^{-4}$  M/min (c)  $3.92 \times 10^{-5}$  M/s (d)  $2.82 \times 10^{-4}$  M/s

Sol (b) For 1st order reaction,

$$k = \frac{1}{t} \ln \frac{a}{a-x}$$

$$k = \frac{1}{40} \ln \frac{0.1}{0.025} \implies k = \frac{1}{40} \ln 4$$
Rate,  $r = k [X]^1 = \frac{1}{40} \ln 4 (0.01) = \frac{2 \ln 2}{40} (0.01)$ 

$$= 3.46 \times 10^{-4} \text{ M/min}$$

- Q.22 For a first order reaction, the time taken to reduce the initial concentration by a factor of 1/4 is 20 min. The time required to reduce initial concentration by a factor of 1/16 is
  (a) 20 min (b) 80 min (c) 40 min (d) 160 min
  - **Sol** (c) Time taken to reduce initial concentration by a factor of  $\frac{1}{4} = 20$  min

Time taken to reduce initial concentration by a factor of  $\frac{1}{2} = 20 \text{ min}$ 

Half-life =  $\frac{20}{2}$  = 10 min.

Time required to reduce the concentration upto 1/16 need four half-lives or 40 min.

- Q.23 Photochemical combination of hydrogen and chlorine is an example of ..... order reaction.
  - Sol Photochemical combination of hydrogen and chlorine is an example of zero order reaction.
- Q.24 The half-life time of first order reaction ...... on initial concentration. (Correct the sentence)
  - Sol The half-life time of first order reaction is independent on initial concentration.

#### **2 MARK** Questions

#### **Exams' Questions**

Q.25 C-11 is a radioisotope of carbon. Its half-life is 20 min. What fraction of the initial number of C-11 atoms in a sample will have decayed away after 80 min? [2015]

Sol Number of half lives 
$$=\frac{80\min}{20\min} = 4$$
  
Fraction of the substance left  $=\frac{1}{2^n} = \frac{1}{2^4} = \frac{1}{16} = 0.625$   
Decayed fraction  $= 1 - 0.625 = 0.375$  (2)

- Q.26 What is zero order reaction? Give one example. [2010, 2001, Textbook]
- Sol A reaction is said to be of zero order if its rate is independent of concentration of reactants for e.g. decomposition of N<sub>2</sub>O on hot platinum surface. (1)

$$N_2 O \longrightarrow N_2 + \frac{1}{2} O_2$$
 (1)

- Q.27 For a first order reaction, it takes 16 min to complete 50% reaction. How much time does it take to complete 75% reaction? [2006]
  - **Sol** Given that,  $t_{1/2} = 16 \min$

:. Rate constant, 
$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{16 \text{ min}}$$
 (1/2)

For first order reaction,  $t = \frac{2.303}{k} \log \frac{a}{a-x}$ 

For 25% reaction, 
$$a = 100$$
,  $(a - x) = 100 - 75 = 25$  (1/2)  
2.303  $\log 100 - 2.303 \times 16 \min \log 4$ 

- Q.28 The rate constant of a first order reaction is  $k = 7.39 \times 10^{-5}$  s<sup>-1</sup>. Find the half-life of the [2002, Textbook] reaction.
  - Sol From the relation, Half-life,  $t_{1/2} = \frac{0.693}{k} = \frac{0.693}{7.39 \times 10^{-5} \text{ s}^{-1}} = 156.3 \text{ min}^{-1}$
- Q.29 Calculate the rate constant of a reaction (first order) which is 90% complete in 10 min. [20

Sol From the first order equation,  
Rate constant, 
$$k = \frac{2.303}{t} \log \frac{a}{(a-x)}$$
  
As  $a = 100$  then  $(a - x) = 100 - 90 = 10$   
Then,  $k = \frac{2.303}{10 \text{ min}} \log \frac{100}{10} = \frac{2.303}{10} \log 10$   
 $= 0.2303 \text{ min}^{-1} = 13.818 \text{ s}^{-1}$  (2)

#### Important Questions

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

**Sol** 
$$a = 100, a - x = 100 - 30 = 70, t = 40 \min$$

For 1st order reaction,  

$$k = \frac{2.303}{t} \log \frac{a}{(a-x)} = \frac{2.303}{40 \min} \log \frac{100}{70} = \frac{2.303}{40} \log \frac{10}{7}$$

$$= \frac{2.303}{40} \log 1.428 = \frac{2.303}{40} \times 0.1548$$

$$k = 8.91 \times 10^{-3} \min^{-1} \qquad (1)$$
Also,  $t_{1/2} = \frac{0.693}{k} = \frac{0.693}{8.91 \times 10^{-3} \min^{-1}} = 77.78 \min$ 

$$t_{1/2} = 77.78 \min \qquad (1)$$

#### **3 MARK** Questions

#### **Exams'** Questions

- Q.31 The half-life of a radioactive element is 69.3 days. Find out the time taken for a given sample of the element to be reduced to 1/10<sup>th</sup> of its initial activity. [2016]
- **Sol** Given, Half-life period;  $t_{1/2} = 69.3$  days (1) All radioactive disintegration reactions are first order reactions.
  - : Disintegration constant,

$$\lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{69.3} = 0.01 \text{ days}^{-1}$$
(1)

Time, 
$$t = \frac{2.303}{\lambda} \log \frac{N_0}{N}, N_0 = 100$$
  
 $N = 100 - \frac{1}{10} \text{ of } N_0 = 100 - \frac{1}{10} \times 100 = 90$   
 $t = \frac{2.303}{0.01} \log \frac{100}{90} \Rightarrow t = 10.5 \text{ days}$  (1)

- Q.32 In a first order reaction, the reactant concentration decreases from 0.8 M to 0.4 M in 15 min. What is the time taken for the concentration to change from 0.1 M to 0.025 M? [2017]
  - **Sol** Let, a = 0.8 M, a x = 0.4 M, t = 15 min.

For first order reaction,

k

$$=\frac{2.303}{t}\log\frac{a}{a-x}=\frac{2.303}{15}\log\frac{0.8}{0.4}=0.462\,\mathrm{min}^{-1}$$

 $\therefore$  Time taken for 0.1 M to 0.025 M can be calculated as:

$$t = \frac{2.303}{k} \log \frac{a}{a-x} = \frac{2.303}{0.0462} \log \frac{0.1}{0.025} = 30 \text{ min}$$
(3)

#### Important Questions

**Q.33** The decomposition of  $N_2O_5$  according to the equation,  $2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$ 

is a first order reaction. After 30 minutes from the start of the decomposition in a closed vessel, the total pressure developed is found to be 284.5 mm of Hg and on complete decomposition, the total pressure is 584.5 mm of Hg. Calculate the rate constant of the reactions. [Textbook]

**Sol** Suppose, initial pressure of  $N_2O_5$  is P mm

Decrease in pressure of  $N_2O_5$  after time t = p mm

	$2N_2O_5(g$	$g \longrightarrow 4NO_2$	(g) +	$O_2(g)$
Initial pressure	P	0	0	P
Pressure after 30 min.	P- $2p$	4p	р	P + 3p
Final pressure	0	4p	p	5p
Total pressure	=4p + p	=5 <i>p</i>		
Final pressure	=584.5 n	nm		
:. ·	5p = 584.5	$5 \text{ mm} \Rightarrow p = 1$	16.9	9 mm

Pressure after 30 min is 284.5 mm

:.  $p + 3p = 284.5 \Rightarrow p = 55.8 \text{ mm}$ Using rate equation for first order

$$k = \frac{2.303}{t} \log \frac{P}{P - p}$$
  

$$\therefore \qquad k = \frac{2.303}{30 \times 60 \sec} \log \frac{116.9}{61.1} = 3.70 \times 10^{-4} \sec^{-1}$$
(3)

**Q.34** Sucrose decomposes in acid solution into glucose and fructose according to the first order rate law with  $t_{1/2} = 3.00$  hr. What fraction of sample of sucrose remains after 8 hr?

Sol For first order reactions,

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{(3.0 \text{ hr})} \text{ or } t = \frac{2.303}{k} \log \frac{[R]_0}{[R]}$$
(1)

or 
$$\log \frac{[R]_0}{[R]} = \frac{k \times t}{2.303}$$
,  $\log \frac{[A]_0}{[A]} = \frac{0.693}{3 \text{ hr}} \times \frac{8 \text{ hr}}{2.303} = 0.8024$   
 $\frac{[A]_0}{[A]} = \text{antilog } 0.8024 = 6.345$   
 $[A]_0 = 1 \text{ M}, \ [A] = \frac{[A]_0}{6.345} = \frac{1 \text{ M}}{6.345} = 0.1576 \text{ M}$ 

After 8 hr, sucrose left = 0.1576 M

#### **7 MARK** Questions

#### **Exams' Questions**

- **Q.35** (i) Derive an expression for the rate constant of a first order reaction. How does the rate constant relate to the half-life period?
  - (ii) Prove that for the first order reaction, the time required for 99% completion of the reaction is twice the time required to complete 90% of the reactions. [2012 Instant, 2018]
  - Sol (i) Refer to the text on pages 75 and 76. (4) (ii) Case I If a = 100, (a - x) = (100 - 99) = 1For 99% completion of the reaction,

$$t_{99\%} = \frac{2.303}{k} \log \frac{100}{1} = \frac{2.303}{k} \log 10^2 = \frac{2.303 \times 2}{k}$$
$$t_{99\%} = \frac{4.606}{k} \qquad \dots (i) \ (1\%)$$

*Case* II If a = 100, (a - x) = (100 - 90) = 10

For 90% completion of the reaction

$$t_{90\%} = \frac{2.303}{k} \log \frac{100}{10} = \frac{2.303}{k} \log 10 = \frac{2.303}{k} \dots$$
(ii)

On dividing Eq. (i) by Eq. (ii), we get

$$\frac{t_{99\%}}{t_{90\%}} = \frac{4.606}{k} \times \frac{k}{2.303} = 2$$

It means that time required for 99% completion of the reaction is twice the time required to complete 90% of the reaction. (1<sup>1</sup>/<sub>2</sub>)

- Q.36 Derive an expression for rate constant of first order reaction. Define half-life period? A first order reaction takes 69.3 min for 50% completion. How much time will be needed for 80% completion? [2018, 2005, 2002, Textbook]
  - Sol Derivation of expression for rate constant of first order reaction and half-life period. Refer to the text on pages 75 and 76. (4)

As we know that, for first order,

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{69.3 \text{ min}} = 0.01 \text{ min}^{-1}$$
(1)

Suppose that t be the time taken for 80% completion.

$$t = \frac{2.303}{k} \log \frac{100}{100 - 80} = \frac{2.303}{10^{-2} \text{min}^{-1}} \log 5$$
 (1)

$$= 230.3 \times 0.6989 = 160.97 \,\mathrm{min} \tag{1}$$

#### Important Questions

**Q.37** During nuclear explosion one of the products is <sup>90</sup>Sr with half-life of 28.1 yr. If 1 µg of <sup>90</sup>Sr was absorbed in the bones of a newly born baby instead of calcium, how much of it will remain after 10 yr and 60 yr if it is not lost metabolically?

**Sol** 
$$t_{1/2} = 28.1 \text{ yr}, \ k = \frac{0.693}{t_{1/2}} = \frac{0.693}{28.1} \text{ yr}^{-1}$$
 (1)

For first order reaction, 2.303

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

**Case I** 
$$a = 1 \mu g$$
;  $t = 10$  yr;  $k = \frac{0.693}{28.1}$  yr<sup>-1</sup>  
 $10$  yrs  $= \frac{2.303}{0.693} \times 28.1 \log \frac{a}{(a-x)}$  (1)  
 $\log \frac{a}{(a-x)} = \frac{10 \text{ yr} \times 0.693}{28.1} = 0.107$ 

$$\log \frac{1}{(a-x)} = \frac{1}{2.303 \times 28.1} =$$

**TOPIC TEST 2** 

1. The order of hydrolysis of sucrose

$$\begin{array}{ccc} C_{12}H_{22}O_{11}(g) + H_2O(l) \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6 \text{ is} \\ (a) \ zero & (b) \ 1 \\ (c) \ 2 & (d) \ 3 & [Ans. (b)] \end{array}$$

- **2.** For a first order reaction, the rate constant  $1.15 \times 10^{-3} s^{-1}$ . The time of completion of 50% reaction is
  - (a) 10 min
     (b) 7 min

     (c) 4 min
     (d) 8 min
     [Ans. (a)]
- **3.** For a first order reaction, the half-life period is equal to ......  $[Ans. \frac{0.693}{K}]$
- **4.** Define half-life period.
- 5. What is the order of radioactive decay?
- **6.** The rate constant for a reaction of zero order in X is 0.0060 mol L<sup>-1</sup> s<sup>-1</sup>. How long will it take for the initial concentration of X to fall from 0.10 M to 0.075 M?

$$\frac{a}{(a-x)} = \text{antilog } (0.107) = 1.279$$
 (1)

$$(a - x) = \frac{a}{1.279} = \frac{(1\mu g)}{1.279} = 0.7819 \,\mu g$$

Amount left after 10 yr = 
$$0.7819 \mu g$$
 (1)

**Case II** 
$$a = 1 \mu g$$
,  $t = 60 \text{ yr}$ ;  $k = \frac{0.693}{28.1} \text{ yr}^{-1}$   
 $60 \text{ yrs} = \frac{2.303}{0.693/28.1} \times \log \frac{a}{(a-x)}$  (1)

$$\log \frac{a}{(a-x)} = \frac{(60) \times 0.693 / 28.1}{2.303} = 0.642$$

$$\frac{a}{(a-x)} = \text{antilog } 0.642 = 4.385$$
 (1)

$$(a - x) = \frac{a}{4.385} = \frac{(1\mu g)}{4.385} = 0.2280 \,\mu g \tag{1}$$

Amount left after 60 yr =  $0.2280 \,\mu g$ 

(

- **7.** A first order reaction is found to have a rate constant,  $k = 5.5 \times 10^{-14} \text{ s}^{-1}$ . Calculate the half-life of the reaction.
- **8.** A first order reaction has a rate constant  $1.15 \times 10^{-3}$ s<sup>-1</sup>. How long will 5 g of this reactant take to reduce to 3 g?
- 9. (i) A reactant has half-life of 20 min.
  - (a) Determine the rate constant for the first order reaction.
  - (b) What fraction of the reactants will left after an hour of reaction has occurred?
  - (ii) A first order decomposition reaction takes 45min for 30% decomposition then find out its  $t_{\rm 1/2}$  value.
  - **10.** The half-life period of a first order reaction is 60 min. Calculate the time required for the completion of 99% of the reaction.

## **TOPIC ~03** Activation Energy and Collision Theory of Chemical Reactions

#### **Activation Energy**

Most of the chemical reactions are accelerated by increase in temperature. The concept of activation energy is important to understand why a mixture of oxygen and hydrogen remains unreacted at room temperature but undergoes a vigorous change if an electric spark is passed through it.

$$2H_2 + O_2 \xrightarrow{\text{Electric}} 2H_2O$$

The molecules undergoing a chemical reaction must possess a minimum amount of energy, so that the collisions between themselves result in a reaction. This minimum amount of energy is called **threshold** energy  $(E_{\rm th})$ .

The reaction can take place only when reactants have energy more than or equal the thershold energy.

Thus, the excess energy supplied to the reactant molecules to attain threshold energy for undergoing chemical reaction is called activation energy.

Thus, activation energy  $(E_a)$  = Threshold energy  $(E_{th})$ - Average energy possessed by reactant molecules  $(E_r)$ .

Some energy is released when the activated complex (intermediate) decomposes to form products. Therefore, the final enthalpy of the reaction depends upon the nature of reactants and products.



In the above graph,  $E_a$  = energy of activation of reactants  $E_p$  = energy of activation of products. When  $E_p > E_a$ , the reaction is **exothermic** and when  $E_p < E_a$ , the reaction is **endothermic**. To convert reactants into products they have to cross an energy barrier (also called potential barrier) and achieve the threshold energy as shown in the figure, which has been obtained by plotting potential energy *versus* reaction coordinate.

#### **Determination of Activation Energy**

Activation energy can be calculated through Arrhenius equation. In Arrhenius equation,  $k = Ae^{-E_a/RT}$ , the factor  $e^{-E_a/RT}$  represents the fraction of molecules that have kinetic energy more than the activation energy  $(E_a)$ .

It is clear from Arrhenius equation that increasing the temperature or decreasing the activation energy will result in an increase in the rate of the reaction and an exponential increase in the rate constant.

Taking natural logarithm on both sides, the Arrhenius equation becomes,  $\ln k = -\frac{E_a}{RT} + \ln A$ 

The plot of  $\ln k$  versus 1/T gives a straight line.

Slope of this plot gives the value of  $-\frac{E_a}{R}$  and the intercept gives the value of  $\ln A$ .



 $E_a$  and A can also be determined from the rate constants

it two different temperatures.  

$$\ln k = -\frac{E_a}{RT} + \ln A \text{ or } \log k = -\frac{E_a}{2.303 RT} + \log A$$

Let  $k_1$  and  $k_2$  be the rate constants at temperatures  $T_1$  and  $T_2$ . Then,

$$\log k_{1} = -\frac{E_{a}}{2.303 RT_{1}} + \log A \qquad \dots (i)$$

$$\log k_2 = -\frac{E_a}{2.303 RT_2} + \log A$$
 ...(ii)

A = constant for the given reactions. Subtracting Eq. (i) from Eq. (ii), we have

$$\log k_2 - \log k_1 = \frac{E_a}{2.303 RT_1} - \frac{E_a}{2.303 RT_2}$$
$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]$$
$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left[ \frac{T_2 - T_1}{T_1 T_2} \right]$$

#### **Arrhenius Equation**

Most of the chemical reactions are accelerated by increase in temperature.

It has been found that for a chemical reaction with rise in temperature by 10°C, the rate constant is nearly doubled. The exact dependence of rate of reaction can be determined by Arrhenius equation.

#### Collision Theory of Unimolecular Reactions

It is based on kinetic theory of gases. According to this theory, the reactant molecules are assumed to be hard spheres and reaction is postulated to occur when molecules collide with each other.

The number of collisions per second per unit volume of the reaction mixture is called **collision frequency** (Z).  $E_a$  is another factor which affects the rate of chemical reactions. For a bimolecular reaction,

 $\begin{array}{ccc} A+B & \longrightarrow & {\rm Products} \\ {\rm Rate \ of \ reaction \ can \ be \ expressed \ as:} \\ {\rm Rate \ } = Z_{AB} e^{-E_a/RT} \end{array}$ 

where,  $Z_{AB}$  is the collision frequency of the reactants A and B and  $e^{-E_{a'}RT}$  is the fraction of molecules with energies equal to or greater than  $E_{a}$ .

When Arrhenius equation,  $k = Ae^{-\vec{E}_a/RT}$  is compared with the above equation, (A) can be related to the collision frequency (Z). Not all the collisions result into product. Collisions in which molecules have sufficient kinetic energy (which is also called **threshold energy**) and proper orientation result into breaking of bond between the reacting species and formation of new bonds to form products. These collisions are referred to as the **effective collisions**.

### Threshold energy = activation energy + energy possessed by reacting species

Collisions of the reactant molecules with proper orientation result into bond formation. Collisions with improper orientation make the molecules bounce back with no product formation.

#### Limitations of Collision Theory

This theory explains the results of a number of reactions, but it does not give satisfactory results in some cases as it considers atoms/molecules to be hard spheres and ignores their structural aspect.

## **PRACTICE** QUESTIONS

#### Exams', Textbook's Other Imp. Questions

#### **1 MARK** Questions

#### **Exams' Question**

#### Sol faster.

#### Important Questions

- **Q.2** A large increase in the rate of reaction for a small rise in temperature is due to
  - (a) increase in number of collision
  - (b) increase in the number of activated molecules
  - (c) lowering of activation energy
  - (d) shortening of the mean free path  $% \left( {{{\mathbf{x}}_{i}}} \right)$
- **Sol** (b) Increasing the temperature increases reaction rates because of more is the number of effective collisions, more will be rate of reaction.

The increase in temperature results in increase in kinetic energy of molecule.

Q.3 The rate constant k'<sub>a</sub> of one reaction is found to be double that of the rate constant k''<sub>a</sub> of another reaction. Then the relation between the corresponding activation energies of the two reactions E'<sub>a</sub> and E''<sub>a</sub> can be represented as,
(a) E<sub>a</sub>'> E''<sub>a</sub>
(b) E<sub>a</sub>'< E''<sub>a</sub>
(c) E<sub>a</sub>' = E''<sub>a</sub>
(d) E<sub>a</sub>' = 4E''<sub>a</sub>

 $=2k_{2}$ 

(c) 
$$E_{a'} = E_{a'}^{"}$$
  
Sol (b)  $k_{a'}^{'} / k_{a'}^{"} = \frac{2}{1}$  or  $k_{a}^{'}$ 

i.e., 
$$k_{a}^{'} > k_{2}$$
  
Using Arrhenius equation,  
 $k = Ae^{-E_{a}/RT}$ 

therefore, if k is high,  $E_a$  is low. Hence,  $E'_a < E''_a$ 

**Q.4** Rate of reaction can be expressed by Arrhenius equation as  $k = Ae^{-E_a/RT}$ . In this equation,  $E_a$  represents

- (a) the energy below which colliding molecules will not react
- (b) the energy above which all the colliding molecules will react
- (c) the fraction of molecules with energy greater than the activation energy of the reaction
- (d) the total energy of the reacting molecules at the temperature  $\left(T\right)$
- **Q.5** The rate constant  $k_1$  and  $k_2$  for two different reactions are  $10^{16}e^{-2000/T}$  and  $10^{15}e^{-1000/T}$  respectively. The temperature at which  $k_1$  is equal to  $k_2$  is
  - (a) 1000 K (b) 2000 K (c)  $\frac{1000}{2.303}$  K (d)  $\frac{2000}{2.303}$  K

**Sol** (c) Given, 
$$k_1 = 10^{16} e^{-2000/T}$$
,  $k_2 = 10^{15} e^{-1000/T}$ 

As, 
$$k_1 = k_2$$
 then,  $10^{16} e^{-2000/T} = 10^{15} e^{-1000/T}$ 

or,  $10 e^{-2000/T} = e^{-1000/T}$ 

Taking log on both side, we get

$$\ln 10 - \frac{2000}{T} = -\frac{1000}{T}$$
  
or 
$$2.303 - \frac{2000}{T} = -\frac{1000}{T}$$
  
or 
$$\frac{1000}{T} = 2.303 \text{ or } T = \frac{1000}{2.303} \text{ K}$$

- **Q.6** For an endothermic reaction where,  $\Delta H$  represent the enthalpy of the reaction in k J/mol, the minimum value for energy of activation will be (a) less than  $\Delta H$  (b) zero (c) equal to  $\Delta H$  (d) more than  $\Delta H$
- Sol (d) In endothermic reactions, energy of reactants is less than that of the products. Potential energy diagram for endothermic reaction is

where,  $\boldsymbol{E}_a$  = activation energy of forward reaction

 $E'_a$  = activation energy of backward reaction  $\Delta H$  = enthalpy of the reaction

the reaction 
$$E_{a} = E_{a}^{'} + \Delta H$$

Thus,  $E_a > \Delta H$ 

- **Q.7** The reaction having activation energy equal to ..... is impossible.
- *Sol* The reaction having activation energy equal to zero is impossible.
- **Q.8** Minimum amount of energy that must be required for the collision between reactant molecules in a reaction is known as .........
- Sol threshold energy.

- **Q.9** The number of collisions per second per unit volume of the reaction mixture is called ........
- Sol collision frequency
- **Q.10** How is energy of activation related to rate constant of a reaction?
- **Sol** Rate constant is related to activation energy by Arrhenius equation,  $k = A e^{-E_a/RT}$ .
- **Q.11** The activation energy of a reaction is zero. Will the rate constant of a reaction depend upon temperature? Give suitable reason.
- **Sol** No, the activation energy of a reaction is never zero. When,  $E_a = 0$ , then  $k = Ae^{-E_a/RT} = A$

#### **2 MARK** Questions

#### **Exams' Questions**

Q.12 Define activation energy. What is<br/>Arrhenius equation?[2008]SolThe energy required to form the intermediate,<br/>called activated complex is known as activation<br/>energy  $(E_a)$ .(1)The temperature dependence of rate of chemical

reaction is expressed by Arrhenius equation,  $k = Ae^{-E_a/RT}$  (1)

- Q.13 On the basis of activation energy, how can you explain slow and fast reaction? [2003]
  - Sol A fast reaction has low activation energy, where a large number of reactant molecules will be able to form activated complex and formation of products take place. A reaction with high activation energy is slow reaction. (2)

#### Important Questions

e.g.

- **Q.14** What is the role of activated complex in a chemical reaction?
  - **Sol** When the reactant molecules absorb energy, their bonds are loosened and there is formation of new loose bonds between them. This intermediate thus, formed is known as activated complex or transition state complex, which is highly unstable and immediately dissociates into products and some energy is released during this dissociation.

- **Q.15** What will be the effect of temperature on rate constant?
- **Sol** The rate constant for a reaction is nearly doubled with 10°C rise in temperature. The reason is that the number of effective collisions becomes almost double. The exact dependence of the rate of reaction can be given by Arrhenius equation;  $k = Ae^{-E_a/RT}$ , where, A is called frequency factor and  $E_a$  is the activation energy of the reaction. (2)

#### **3 MARK** Questions

#### **Exams' Questions**

- **Q.16** The rate constants of a reaction at 500 K and 700K are  $0.025 \text{ sec}^{-1}$  and  $0.075 \text{ sec}^{-1}$  respectively. Calculate the energy of activation of the reaction.  $(R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1} \text{ and } \log 3 = 0.477)$  [2019]
  - **Sol** Given,  $T_1 = 500$  K,  $T_2 = 700$  K

Rate constant  $(k_1) = 0.025 \text{ sec}^{-1}$ 

Rate constant  $(k_2) = 0.075 \text{ sec}^{-1}$  $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$ 

n = 0.5145 mor

From Arrhenius equation,  

$$k_0 \quad E \quad \begin{bmatrix} T_0 - T_1 \end{bmatrix}$$

$$:: \log \frac{R_2}{k_1} = \frac{E_a}{2.303R} \left[ \frac{I_2 - I_1}{T_1 \cdot T_2} \right]$$
or
$$E_a = \frac{2.303 \times R \times T_1 \times T_2 \times \log 3}{T_2 - T_1} \left[ :: \log \frac{k_2}{k_1} = \log \frac{0.075}{0.025} = \log 3 \right]$$

$$E_a = \frac{2.303 \times 8.314 \times 500 \times 700 \times 0.477}{700 - 500}$$

$$E_a = 15986.43 \text{ J mol}^{-1} = 15.99 \text{ kJ mol}^{-1}$$
(3)

#### **7 MARK** Questions

#### **Exams' Questions**

- Q.17 Write a note on 'activation energy'. [2012, 03, 01]Sol Refer to the text on pages 82. (7)
- **Q.18** First order reaction,  $A \rightarrow B$  requires activation energy of 70 kJ mol<sup>-1</sup>. When a 20% solution of Awas kept at 25°C for 20 min. 25% decomposition took place. What will be percentage decomposition in the same time in a 30% solution maintained at 40°C? Assume that activation energy remains constant in this range of temperature.
  - Sol We know that the fraction of reactants reacted in a first order reaction is independent of initial concentration. So, we need not worry about the terms 20% solution and 30% solution.

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

Given, t = 20 min., a = 100, (a - x) = 100 - 25 = 75 $\therefore \qquad k = \frac{2.303}{20} \log \frac{100}{75} = 1.44 \times 10^{-2} \text{ min}^{-1}$ 

Let,  $k_2$  be the rate constant of this reaction at 40°C. According to Arrhenius equation,

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]$$
$$\log k_2 = \frac{70 \times 10^3 \text{ J mol}^{-1}}{2.303 \times 8.314 \text{ JK}^{-1} \text{ mol}^{-1}} \left[ \frac{1}{298\text{K}} - \frac{1}{313 \text{ K}} \right]$$
$$k_2 = 5.56 \times 10^{-2} \text{ min}^{-1}$$

Now, again using first order reaction

 $\log \frac{a}{a-x} = \frac{k}{2.303}, t = \frac{5.56 \times 10^{-2} \text{ min}^{-1}}{2.303} \times 20 \text{ min.} = 0.33$ 

: Percentage of A remaining = 33%

Percentage of A reacted = 100 - 33 = 67%

- Q.19 (i) Derive rate equation for first order reaction.
  - (ii) What is Arrhenius equation?
  - (iii) For a hypothetical reaction, the mean potential energies of reactants and products are 40 and 25 kcal per mol respectively. Calculate the activation energies of the forward and the reverse reactions if the threshold energy is 65 kcal. Also calculate the heat of the reaction. [2011 Instant]
    Sol (i) Refer to the text on page 75 (2)

л	(1)	merer	to the	UCAU	011	page 15.	(4)	'
	(ii)	Refer	to the	text	on	page 83.	(2)	)

 (ii) Refer to the text of page 05.
 (iii) Given that Mean potential energies of reactants = 40 kcal/mol.

Mean potential energies of products = 25 kcal/mol.

From the equation,

Threshold energy = Activation energy + energy possessed by reacting species

65 =Activation energy + 40

Activation energy of reactants = 25 kcal/mol (1)

Similarly, activation energy of products

$$= 40 \text{ kcal/mol}$$
(1)

Heat of reaction = Energy of product

Energy of reactant

=25-40=-15 kcal/mol (1)

Thus, (-) sign shows that reaction is exothermic.

**Q.20** Write note on:

	(i)	Activation energy	(ii) Arrhenius equation	ı
	(iii)	Half-life period	[2007,	, 2003]
Sol	(i)	Refer to the text on	pages 82.	(3)
	(ii)	Refer to the text on	page 83.	(2)

(iii) Refer to the text on pages 76. (2)

#### **TOPIC TEST 3**

- **3.** What is the value of slope in the plot of log k versus  $\frac{1}{T}$  (for Arrhenius equation)?
- 4. Define activation energy.
- 5. What are effective collision?
- **6.** What is the change in the activation energy if temperature is raised by 10°C?

- The rate of the most of the reactions becomes double when their temperature is raised from 298K to 308K. Calculate their activation energy.
- **8.** (i) Write Arrhenius equation.
  - (ii) Define collision frequency.
  - (iii) What is the limitation of collision theory?
- **9.** All effective collisions do not result in a chemical change. Explain with the help of an example.
- 10. The rate constant of a reaction is  $1.50 \times 10^7 \text{ s}^{-1}$  at 50°C and  $4.5 \times 10^7 \text{ s}^{-1}$  at 100°C. Evaluate the Arrhenius parameters A and  $E_a$ .

# | Chapter Test |

#### **1 MARK** Questions

- **1** In a first order reaction, reactant concentration '*C*' varies with time 't' as
  - (a) C decreases with 1/t
  - (b)  $\log C$  decreases with 1/t
  - (c)  $\frac{1}{C}$  increases linearly with t
  - (d)  $\log C$  decreases linearly with t
- 2 Which of the following statement(s) is/are true? (a) For zero order reaction,  $t_{1/2} \propto [R]_0$ 
  - (b) For first order reaction,  $t_{1/2}$  is independent of  $[R]_0$
  - (c) Both (a) and (b) (d) None of the above
- 3 Select the incorrect statement.
  - (a) Larger the value of  $E_a$ , smaller the value of rate constant (k)
  - (b) Larger the value of  $E_a$ , greater is the effect on the value of *k* for a given temperature change
  - (c) At lower temperature, increase in temperature causes more change in the value of *k* than at higher temperature (d) k is affected by change in concentration

[Ans. 1.(d), 2.(c), 3.(d)]

- **4** The order of a reaction whose rate law is rate  $k[A]^{3/2}[B]^{1/2}$  is ...... [Ans. 2]
- **5** Give an example of pseudo first order reaction.
- 6 Compute the half-life of a first order reaction whose  $\left[ \text{Hint: } E_{1/2} = \frac{0.693}{k} \right]$ rate constant is  $5 \,\mathrm{s}^{-1}$ . [Ans. 0.13865]
- 7 Given an example of zero order reaction. [Textbook]

#### **2 MARK** Questions

8 The activation energy of a reaction is 94.14 kJ mol<sup>-1</sup> and the value of rate constant at 298 K is  $18 \times 10^{-5}$  s<sup>-1</sup>. Calculate the frequency factor or pre-exponential factor, A. [Hint: Use Arrhenius equation]

[Ans. 11.754]

- 9 For which type of reactions, order and molecularity have the same value. Give an example.
- 10 Find the molecularity of the reaction,

 $\operatorname{Cl} \longrightarrow \frac{1}{2} \operatorname{Cl}_2(g)$ . Give the potential energy diagram to explain activation energy.

11 For a reaction,  $P \longrightarrow Q$ , the rate becomes 27 times when concentration of P is tripled. What is the order of the reaction?

12 If the rate constants of a reaction are  $1 \times 10^3 \, \text{s}^{-1}$  and  $2 \times 10^3 \text{ s}^{-1}$  at 27°C and 37°C, respectively. Calculate the activation energy  $(E_a)$  of the reaction.

 $[Ans. 53.6 \text{ kJ mol}^{-1}]$ 

13 State the role of activated complex in a reaction and state its relation with activation energy.

#### **3 MARK** Questions

- 14 Discuss various factors influencing the rate of reaction.
- **15** Thermal decomposition of a compound is of first order. If 50% of a sample of the compound is decomposed in 120 minutes how long would it take for 90% of the compound to decompose? [Textbook]

**Hint:** Use formula 
$$t = \frac{2.303}{k} \log \frac{a}{a-x}$$

[Ans. 400 minutes]

- **16** Define the following terms: (i) Order of reaction (ii) Threshold energy (iii) Collision frequency
- **17** The rate constant for a first order reaction is  $60 \text{ s}^{-1}$ . How much time will it take to reduce the concentration of the reactant of 1/10th of its initial value? **Hint:** Use formula  $t = \frac{2.303}{b} \log \frac{a}{a-x}$

and the cost formula 
$$t = k$$
 is a  $k$ 

[Ans. 0.03845]

#### 7 MARK Questions

- 18 Explain the terms
  - molecularity and order of a reaction. Give one example from each of first and second order reactions. A 0.1 M HCN solution



contained 0.2 moles of KCN per litre of the solution. What was the hydronoum ion concentration of the solution. ( $K_a$  for HCN  $= 7.2 \times 10^{-10})$  [Ans.  $3.6 \times 10^{-10}$  mol/L] [Textbook]

- **19** Answer the following questions on the basis of the given curve for a first order reaction.  $R \longrightarrow P$ 
  - Concentratior (i) Find the relation between slope of this line and rate constant.
  - (ii) If the slope is  $2 \times 10^{-4} \text{s}^{-1}$ , then calculate the rate constant.

 $\bigcirc$ 

Time (t)