

## CHEMICAL KINETICS

### 4.1 Rate of a Chemical Reaction :

#### Q. Define rate of reaction ?

**Solution :** The rate of a reaction can be defined as the change in concentration of a reactant or product in unit time. To be more specific, it can be expressed in terms of : (i) the rate of decrease in concentration of any one of the reactants, or (ii) the rate of increase in concentration of any one of the products.

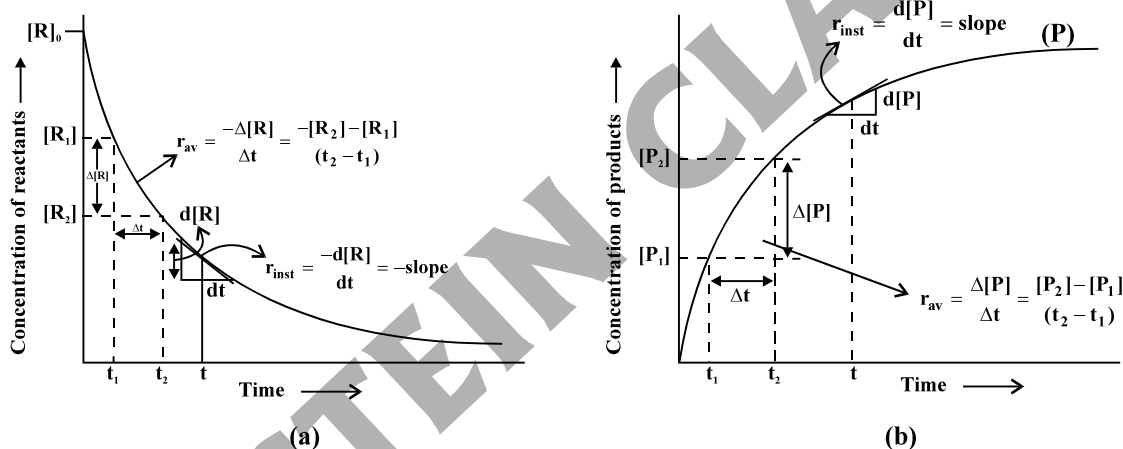
#### Q. Express the average rate of reaction for the following reaction : $R \rightarrow P$ .

**Solution :** Rate of disappearance of R =  $\frac{\text{Decrease in concentration of R}}{\text{Time taken}} = -\frac{\Delta[R]}{dt}$ .

Rate of formation of P =  $\frac{\text{Increase in concentration of P}}{\text{Time taken}} = \frac{\Delta[P]}{dt}$ . Average rate of reaction depends upon the change in concentration of reactants or products and the time taken for that change to occur.

#### Q. Show graphically instantaneous and average rate of a reaction for reactant and product $R \rightarrow P$ .

**Solution :**



**Q. From the concentration of  $C_4H_9Cl$  (butyl chloride) at different times given below, calculate the average rate of reaction :  $C_4H_9Cl + H_2O \rightarrow C_4H_9OH + HCl$  during different intervals of time.**

|                                |       |        |        |        |        |        |        |        |       |
|--------------------------------|-------|--------|--------|--------|--------|--------|--------|--------|-------|
| t/s                            | 0     | 50     | 100    | 150    | 200    | 300    | 400    | 700    | 800   |
| $[C_4H_9Cl]/\text{mol L}^{-1}$ | 0.100 | 0.0905 | 0.0820 | 0.0741 | 0.0671 | 0.0549 | 0.0439 | 0.0210 | 0.017 |

[NCERT Solved Example 4.1]

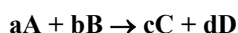
**Solution :** 1.90, 1.70, 1.58, 1.40, 1.22, 1.10, 1.04, 0.4

#### Q. Define instantaneous rate.

**Solution :** The rate of a particular moment of time we determine the instantaneous rate. It is obtained when we consider the average rate at the smallest time interval say  $dt$  (i.e., when  $\Delta t$  approaches zero). Hence, mathematically for an infinitesimally small  $dt$  instantaneous rate is given by for reaction  $R \rightarrow P$ .

$$\text{As } \Delta t \rightarrow 0 \text{ or } r_{\text{inst}} = \frac{-d[R]}{dt} = \frac{d[P]}{dt}.$$

**Q. For the following reaction at any instant find the relation between rate of reaction between reactants and products.**



**Solution :** At any instant rate of reaction of reactants or products are same.

For the reaction  $aA + bB \rightarrow cC + dD$

$$\text{Instantaneous rate} = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt}$$

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

–ve sign. indicates decrease of conc. of reactants with time t.

$$\text{Rate of disappearance of A} = -\frac{d[A]}{dt}; \text{Rate of disappearance of B} = -\frac{d[B]}{dt}$$

$$\text{Rate of formation of C} = \frac{d[C]}{dt}; \text{Rate of formation of D} = \frac{d[D]}{dt}$$

Rate of reaction and rate of formation or rate of disappearance expression can be same if stoichiometric coefficient is one.

**Q. Write the relation between average rate of reaction for reactants and products for following reaction :** (a)  $2\text{HI}(\text{g}) \rightarrow \text{H}_2(\text{g}) + \text{I}_2(\text{g})$  (b)  $5 \text{Br}^-(\text{aq}) + \text{BrO}_3^-(\text{aq}) + 6\text{H}^+(\text{aq}) \rightarrow 3 \text{Br}_2(\text{aq}) + 3\text{H}_2\text{O}(\text{l})$ .

**Solution :** (a)  $2\text{HI}(\text{g}) \rightarrow \text{H}_2(\text{g}) + \text{I}_2(\text{g})$

$$\text{Average rate of reaction} = -\frac{1}{2} \frac{\Delta[\text{HI}]}{\Delta t} = \frac{\Delta[\text{H}_2]}{\Delta t} = \frac{\Delta[\text{I}_2]}{\Delta t}$$

(b)  $5 \text{Br}^-(\text{aq}) + \text{BrO}_3^-(\text{aq}) + 6\text{H}^+(\text{aq}) \rightarrow 3 \text{Br}_2(\text{aq}) + 3\text{H}_2\text{O}(\text{l})$

$$\text{Average rate of reaction} = -\frac{1}{5} \frac{\Delta[\text{Br}^-]}{\Delta t} = \frac{\Delta[\text{BrO}_3^-]}{\Delta t} = \frac{1}{6} \frac{\Delta[\text{H}^+]}{\Delta t} = \frac{1}{3} \frac{\Delta[\text{Br}_2]}{\Delta t} = \frac{1}{3} \frac{\Delta[\text{H}_2\text{O}]}{\Delta t}$$

**Q. What are the different factors on which rate of reaction depends ?**

**Solution :** Rate of a chemical reaction is influenced by (a) Nature of reactants (b) Temperature (c) Catalyst (d) Surface area of reactants (e) Change in concentration of reactants or product and the time taken for change to occur.

**Q. What are the units of rate of reaction ?**

**Solution :** (i) If concentration is in  $\text{mol L}^{-1}$  and time is in seconds then the units will be  $\text{mol L}^{-1}\text{s}^{-1}$  (ii) However, in gaseous reactions, when the concentration of gases is expressed in terms of their partial pressures, then the units of the rate equation will be  $\text{atm s}^{-1}$ .

**Q. The decomposition of  $\text{N}_2\text{O}_5$  in  $\text{CCl}_4$  at 318K has been studied by monitoring the concentration of  $\text{N}_2\text{O}_5$  in the solution. Initially the concentration of  $\text{N}_2\text{O}_5$  is  $2.33 \text{ mol L}^{-1}$  and after 184 minutes, it is reduced to  $2.08 \text{ mol L}^{-1}$ . The reaction takes place according to the equation :**



**Calculate the average rate of this reaction in terms of hours, minutes and seconds. What is the rate of production of  $\text{NO}_2$  during this period ? [NCERT Solved Example 4.2].**

**Solution :** (i)  $4.07 \times 10^{-2} \text{ mol L}^{-1}/\text{h}$  (ii)  $6.79 \times 10^{-4} \text{ mol L}^{-1}/\text{min}$  (iii)  $1.13 \times 10^{-5} \text{ mol L}^{-1}\text{s}^{-1}$  (iv)  $2.72 \times 10^{-3} \text{ mol L}^{-1}\text{min}^{-1}$ .

**Q. For the reaction  $\text{R} \rightarrow \text{P}$ , the concentration of a reactant changes from  $0.03 \text{ M}$  to  $0.02 \text{ M}$  in 25 minutes. Calculate the average rate of reaction using units of time both in minutes and seconds.**

**Solution :**  $6.66 \times 10^{-6} \text{ mol litre}^{-1} \text{ second}^{-1}$

**Q. In a reaction,  $2\text{A} \rightarrow \text{Products}$ , the concentration of A decreases from  $0.5 \text{ mol L}^{-1}$  to  $0.4 \text{ mol L}^{-1}$  in 10 minutes. Calculate the rate during this interval.**

**Solution :**  $5 \times 10^{-3} \text{ mole minutes}^{-1}$

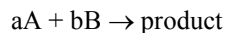
#### 4.2 Factors Influencing Rate of a Reaction :

**Q. Define rate law or rate equation or rate expression.**

**Solution :** The representation of rate of reaction in terms of concentration of the reactants is known as rate law. It is also called as rate equation or rate expression.

Rate law is the expression in which reaction rate is given in terms of molar concentration of reactants with each term raised to some power, which may or may not be same as the stoichiometric coefficient of the reacting species in a balanced chemical equation.

For a reaction :



rate =  $k[A]^m[B]^n$  ..... [A], [B] are the molar concentrations or active masses.

$k$  = rate constant or specific rate constant or velocity constant

Order of reaction w.r.t. A =  $m$ ; order of reaction w.r.t. B =  $n$

Overall order of reaction =  $m + n$ .

**Q. Define order of a chemical reaction.**

**Solution :** The order of the reaction is defined as the sum of the powers of the concentration of the reactants in the rate law expression of the reaction. It is an experimental property derived from the experimental rate law. It will change with conditions. It may be an integer, fractional or even zero. A zero order of reaction means that the rate of reaction is independent of the concentration of reactants.

**Q. Calculate the overall order of a reaction which has the rate expression (a) Rate =  $k[A]^{1/2}[B]^{3/2}$  (b) Rate =  $k[A]^{3/2}[B]^{-1}$ . [NCERT Solved Example 4.3]**

**Solution :** (a) second order (b) half order.

**Q. What are the elementary and complex reaction ?**

**Solution :** The reactions taking place in one step are called **elementary reactions**. When a sequence of elementary reactions (called mechanism) gives us the products, the reactions are called **complex reactions**.

**Q. Derive the units of rates of rate constant.**

**Solution :** For a general reaction  $aA + bB \rightarrow cC + dD$

Rate =  $k[A]^x[B]^y$ , where  $x + y = n =$  order of the reaction

$$k = \frac{\text{Rate}}{[A]^x[B]^y}$$

$$= \frac{\text{concentration}}{\text{time}} \frac{1}{(\text{concentration})^n}$$

$$k = \frac{1}{\text{time}} \times \frac{1}{[\text{Conc.}]^{n-1}}$$

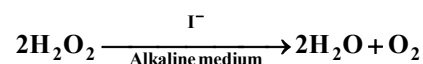
**Q. Identify the reaction order from each of the following rate constants. (i)  $k = 2.3 \times 10^{-5} \text{ L mol}^{-1} \text{ s}^{-1}$  (ii)  $k = 3 \times 10^{-4} \text{ s}^{-1}$ . [NCERT Solved Example 4.4]**

**Solution :** (i) second order reaction (ii) first order reaction

**Q. Define molecularity of a reaction with examples.**

**Solution :** 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 whereas for complex reaction it has no significance. For e.g., (i) in decomposition of ammonium nitrite. It is a unimolecular reaction  $\text{NH}_4\text{NO}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O}$  (ii) Bimolecular reactions involve simultaneous collision between two species, for example, dissociation of hydrogen iodide  $2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$  (iii) Trimolecular or termolecular reactions involve simultaneous collision between three reacting species, for example,  $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$ . The probability that more than three molecules can collide and react simultaneously is very small. Hence, the molecularity greater than three is not observed.

**Q. Which step controls the rate of a complex reaction in the following reaction mechanism. Also write the rate law expression.**



(i)  $\text{H}_2\text{O}_2 + \text{I}^- \rightarrow \text{H}_2\text{O} + \text{IO}^-$  [slow step]

(ii)  $\text{H}_2\text{O}_2 + \text{IO}^- \rightarrow \text{H}_2\text{O} + \text{I}^- + \text{O}_2$  [fast step]

$$\text{Solution : Rate} = \frac{-d[\text{H}_2\text{O}_2]}{dt} = k[\text{H}_2\text{O}_2][\text{I}^-]$$

The overall rate of the reaction is controlled by the slowest step in a reaction called the rate determining step.

**Q. Write the difference between order and molecularity of a reaction.**

**Solution :**

| <b>Molecularity</b>  | <b>Order</b>  |
|--|---|
| 1. In elementary reactions, it is the total number of atoms or molecules taking part in the balanced equation, whereas for the complex reactions it has no significance. | 1. The order of the reaction is defined as the sum of the powers of the concentration terms represented in the rate expression of the reaction. |
| 2. It is the theoretical concept based on the number of molecules of an elementary equation  | 2. It is an experimental property derived from the experimental rate law.   |
| 3. It will not change with the change in conditions i.e. temperature, pressure etc.  | 3. It will change with conditions.  |
| 4. It is always an integer i.e. never be zero  | 4. It may be an integer, fractional or even zero.   |

For elementary reactions the order and molecularity may be same or different. For Pseudo molecular reaction – order and molecularity are different

units of rate : mol, L<sup>-1</sup> time<sup>-1</sup>

**Q. For a reaction, A + B → Product, the rate law is given by, r = k[A]<sup>1/2</sup>[B]<sup>2</sup>. What is the order of the reaction ?**

**Solution :** 2.5

**Q. The conversion of the molecules X and Y follows second order kinetics. If the concentration X is increased to three times, how will it affect the rate of formation of Y ?**

**Solution :** increase 9 times

#### 4.3 Integral Rate Equations :

**Q. Derive the integrated rate equation for zero order chemical reaction ?**

**Solution :** Zero order reaction means that the rate of the reaction is proportional to zero power of the concentration of reactants. Consider the reaction



$$\text{at } t = 0 \quad \text{A}_0 \quad 0$$

$$\text{at time } t \quad \text{A}_0 - x \quad x$$

Let A<sub>0</sub> = initial concentration of reactant.

A<sub>0</sub> - x = remaining concentration of reactant at time 't'

x = concentration of reactant decomposed at time 't'.

Rate law expression for zero order reaction is r = k[A]<sup>0</sup>

$$\frac{-d[\text{A}]}{dt} = k$$

$$d[\text{A}] = -kdt$$

$$\text{integrating both sides } [\text{A}] = -kt + I \quad \dots(i)$$

where I is the constant of integration.

At t = 0, the concentration of the reactant is [A<sub>0</sub>]

Substituting in Eq. (i) [A<sub>0</sub>] = -k × 0 + I

$$[\text{A}_0] = I$$

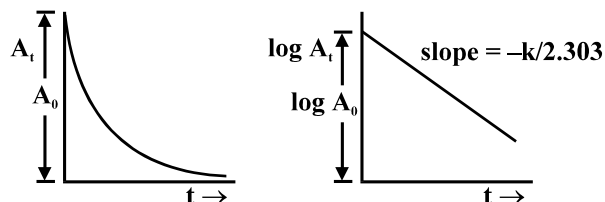


First order rate equation (ii) can also be written in the form of as follows :

$$k = \frac{2.303}{t} \log \frac{A_0}{(A_0 - x)}$$

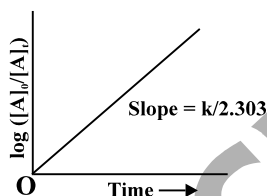
**Q. Draw the log[A] vs. time graph for first order reaction. Also draw the graph of A<sub>t</sub>(concentration) vs. time for first order reaction.**

**Solution :**



**Q. Plot a graph for first order reaction  $\log [A]_0/[A]_t$  vs. time.**

**Solution :**

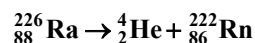


**Q. Give the examples of first order reaction.**

**Solution :** (i) Hydrogenation of ethene is an example of first order reaction,  $C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$

Rate =  $k [C_2H_4]$

(ii) All natural and artificial radioactive decay of unstable nuclei take place by first order kinetics.



Rate =  $k[\text{Ra}]$

**Q. The initial concentration of  $N_2O_5$  in the following first order reaction**

$N_2O_5(g) \rightarrow 2NO_2(g) + 1/2O_2(g)$  was  $1.24 \times 10^{-2} \text{ mol L}^{-1}$  at 318 K. The concentration of  $N_2O_5$  after 60 minutes was  $0.20 \times 10^{-2} \text{ mol L}^{-1}$ . Calculate the rate constant of the reaction at 318 K.

[NCERT Solved Example 4.5]

**Solution :**  $k = 0.0304 \text{ min}^{-1}$

**Q. Consider first order gas phase reaction  $A(g) \rightarrow B(g) + C(g)$ . Let  $p_i$  is the initial pressure of A and  $p_t$  is the total pressure at time t. Derive the integrated rate equation for such reaction.**

**Solution :**  $A(g) \rightarrow B(g) + C(g)$

Total pressure  $p_t = p_A + p_B + p_C$  (pressure units)

$p_A$ ,  $p_B$  and  $p_C$  are the partial pressures of A, B and C, respectively. If x atm be the decrease in pressure of A at time t and one mole each of B and C is being formed, the increase in pressure of B and C will also be x atm each.

|           |                 |   |       |   |       |
|-----------|-----------------|---|-------|---|-------|
|           | A(g)            | → | B(g)  | + | C(g)  |
| At t = 0  | $p_i$ atm       |   | 0 atm |   | 0 atm |
| At time t | $(p_i - x)$ atm |   | x atm |   | x atm |

where,  $p_i$  is the initial pressure at time  $t = 0$ .

$$p_t = (p_i - x) + x + x = p_i + x$$

$$x = (p_t - p_i)$$

$$\begin{aligned} \text{where, } p_A &= p_i - x = p_i - (p_t - p_i) \\ &= 2p_i - p_t \end{aligned}$$

$$k = \left( \frac{2.303}{t} \right) \left( \log \frac{p_i}{p_A} \right) = \frac{2.303}{t} \log \frac{p_i}{(2p_i - p_t)}$$

**Q. The following data were obtained during the first order thermal decomposition of  $N_2O_5(g)$  at constant volume :  $2N_2O_5(g) \rightarrow 2N_2O_4(g) + O_2(g)$**

| S.No. | Time/s | Total Pressure/(atm) |
|-------|--------|----------------------|
| 1.    | 0      | 0.5                  |
| 2.    | 100    | 0.512                |

**Calculate the rate constant.**

**Solution :**  $4.98 \times 10^{-4} s^{-1}$

**Q. Define Half-Life of a reaction.**

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

**Q. Derive the Half-Life of zero order reaction.**

**Solution :** For a zero order reaction, rate constant is given as follows :

$$k = \frac{[A]_0 - [A]_t}{t}$$

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

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

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

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

**Q. Derive the Half-Life expression for first order reaction.**

**Solution :** For first order reaction :  $k = \frac{2.303}{t} \log \frac{[A]_0}{[A]_t}$

$$\text{at } t_{1/2} [A]_t = [A]_0 - [A]_0/2$$

$$[A]_t = [A]_0/2$$

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

$$\text{or } t_{1/2} = \frac{2.303}{k} \log 2$$

$$t_{1/2} = \frac{2.303}{k} \times 0.301$$

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

It can be seen that for a first order reaction, half-life period is constant i.e., it is independent of initial concentration of the reacting species.

**Q.** A first order reaction is found to have a rate constant,  $k = 5.5 \times 10^{-14} \text{s}^{-1}$ . Find the half-life of the reaction. [NCERT Solved Example 4.7]

**Solution :**  $1.26 \times 10^{14} \text{s}$

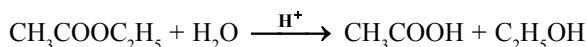
**Q.** Show that in a first order reaction, time required for completion of 99.9% is 10 times of half-life ( $t_{1/2}$ ) of the reaction.

**Solution :** 10

#### 4.4 Pseudo First Order Reaction :

**Q.** What are the pseudo first order reaction ? Give example.

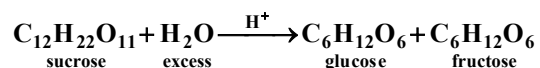
**Solution :** The order of a reaction is some times alter by conditions. For e.g., in ester hydrolysis concentration of water does not get alter much during the course of reaction. Thus it behaves as a first order reaction. Such reaction is called pseudo first order reaction.



Rate =  $k' [\text{CH}_3\text{COOC}_2\text{H}_5] [\text{H}_2\text{O}]$  the term  $[\text{H}_2\text{O}]$  can be taken as constant. The equation, thus, becomes

Rate =  $k [\text{CH}_3\text{COOC}_2\text{H}_5]$  where  $k = k' [\text{H}_2\text{O}]$

Inversion of cane sugar is another pseudo first order reaction.



Rate =  $k [\text{C}_{12}\text{H}_{22}\text{O}_{11}]$

**Q.** Hydrolysis of methyl acetate in aqueous solution has been studied by titrating the liberated acetic acid against sodium hydroxide. The concentration of the ester at different times is given below :

|                       |        |        |        |        |
|-----------------------|--------|--------|--------|--------|
| t/min                 | 0      | 30     | 60     | 90     |
| C/mol L <sup>-1</sup> | 0.8500 | 0.8004 | 0.7538 | 0.7096 |

Show that it follows a pseudo first order reaction, as the concentration of water remains nearly constant (55 mol L<sup>-1</sup>), during the course of the reaction. What is the value of  $k'$  in this equation ?

Rate =  $k' [\text{CH}_3\text{COOCH}_3][\text{H}_2\text{O}]$

**Solution :**  $K' = 3.64 \times 10^{-5} \text{ mol}^{-1} \text{ L min}^{-1}$

**Q.** A first order reaction has a rate constant  $1.15 \times 10^{-3} \text{s}^{-1}$ . How long will 5 g of this reactant take to reduce to 3 g ?

**Solution :** 443.8 s

**Q.** Time required to decompose  $\text{SO}_2\text{Cl}_2$  to half of its initial amount is 60 minutes. If the decomposition is a first order reaction, calculate the rate constant of the reaction.

**Solution :**  $1.925 \times 10^{-4} \text{s}^{-1}$

#### 4.5 Temperature Dependence of the Rate of a Reaction :

**Q.** What is the effect of rise in temperature on chemical reaction ? Also give the Arrhenius relation for rate constant.

**Solution :** The rate of chemical reaction generally increases on increasing in temperature. It has been found that for a chemical reaction with rise in temperature by 10, the rate constant is nearly doubled.

$$\text{Temperature coefficient} = \frac{\text{Rate constant (T+10)}^{\circ}\text{C}}{\text{rate constant at T}^{\circ}\text{C}}$$

Variation of rate constant  $k$  with temperature  $T(\text{K})$  is given by Arrhenius equation.

$$k = Ae^{-E_a/RT}; \ln k = \ln A - \frac{E_a}{RT}; \log k = \log A - \frac{E_a}{2.303RT}$$

Where  $A$  is called the frequency factor or the pre-exponential factor. Collectively  $A$  and  $E_a$  are called the Arrhenius parameters of the reaction,  $E_a$  is called activation energy.

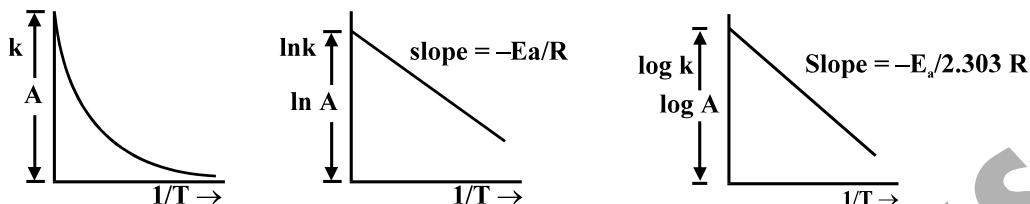


when  $T \rightarrow \infty$ , then  $k = A$

when temperature is change from  $T_1$  K to  $T_2$  K having the same activation energy and Arrhenius constant

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

Graph on Arrhenius equation are as follows :

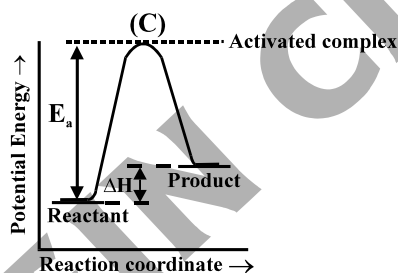


**Q. Define temperature coefficient.**

**Solution :** Temperature coefficient of a reaction is defined as the ratio of rate constant at two temperatures differing by 10 K (generally 25° and 35°C). Observed value usually lies between 2 and 3 for most of the reactions.

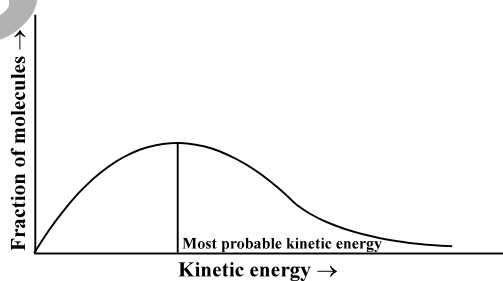
**Q. Define activation energy ? Plot the potential energy vs. reaction coordinate diagram.**

**Solution :** Activation energy : The energy required to form this intermediate, called activated complex (C), is known as activation energy ( $E_a$ ).



**Q. Explain the distribution of kinetic energy by plotting fraction of molecules ( $N_E/N_T$ ) with a kinetic energy Vs. kinetic energy graph given by Boltzmann and Maxwell.**

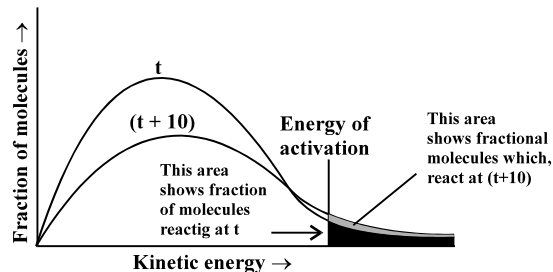
**Solution :**



According to them, the distribution of kinetic energy may be described by plotting the fraction of molecules ( $N_E/N_T$ ) with a given kinetic energy (E) vs kinetic energy. Here,  $N_E$  is the number of molecules with energy E and  $N_T$  is total number of molecules.

**Q. What is the effect of temperature change on the Maxwell graph showing the distribution of kinetic energy ?**

**Solution :**



Increasing the temperature of the substance increase the fraction of molecules, which collide with energies greater than  $E_a$ . It is clear from the diagram that in the curve at  $(t + 10)$ , the area showing the fraction of molecules having energy equal to or greater than activation energy gets doubled leading to doubling the rate of a reaction.

In the Arrhenius equation, the factor  $e^{-E_a/RT}$  corresponds to the fraction of molecules that have kinetic energy greater than  $E_a$ .

**Q. The rate constant of a reaction at 500K and 700K are  $0.02s^{-1}$  and  $0.07s^{-1}$  respectively. Calculate the values of  $E_a$  and A. [NCERT Solved Example 4.10]**

**Solution :** 18230.8 J, 1.61

**Q. The first order rate constant for the decomposition of ethyl iodide by the reaction**



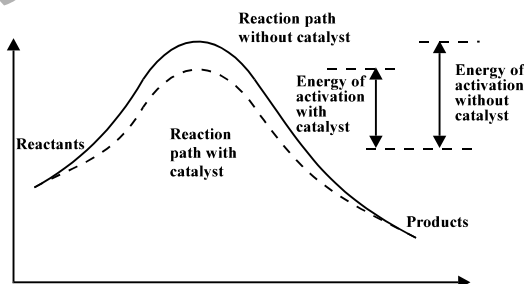
**at 600 K is  $1.60 \times 10^{-5} s^{-1}$ . Its energy of activation is 209 kJ/mol. Calculate the rate constant of the reaction at 700K. [NCERT Solved Example 4.11]**

**Solution :**  $6.36 \times 10^{-3} s^{-1}$

**Q. What is the effect of adding the catalyst on the spontaneous reaction ?**

**Solution :** A catalyst is a substance which alters the rate of a reaction without itself undergoing any permanent chemical change.

The action of the catalyst can be explained by intermediate complex theory. According to this theory, a catalyst participates in a chemical reaction by forming temporary bonds with the reactants resulting in an intermediate complex. This has a transitory existence and decomposes to yield products and the catalyst.



It is believed that the catalyst provides an alternate pathway or reaction mechanism by reducing the activation energy between reactants and products and hence lowering the potential energy barrier.

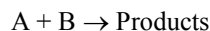
It is clear from Arrhenius equation that lower the value of activation energy faster will be the rate of a reaction.

A catalyst does not alter Gibbs energy,  $\Delta G$  of a reaction. It catalyses the spontaneous reactions but does not catalyse non-spontaneous reactions. It is also found that acatalyst does not change the equilibrium constant of a reaction rather, it helps in attaining the equilibrium faster, that is, it catalyses the forward as well as the backward reactions to the same extent so that the equilibrium state remains same.

#### 4.6 Collision Theory of Chemical Reactions :

**Q. Explain the collision theory of chemical reaction.**

**Solution :** 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 known as collision frequency ( $Z$ ). Another factor which affects the rate of chemical reactions is activation energy (as we have already studied). For a bimolecular elementary reaction



rate of reaction can be expressed as

$$\text{Rate} = Z_{AB} e^{-E_a/RT}$$

where  $Z_{AB}$  represents the collision frequency of reactants, A and B and  $e^{-E_a/RT}$  represents the fraction of molecules with energies equal to or greater than  $E_a$ . Comparing with Arrhenius equation, we can say that  $A$  is related to collision frequency.

The value of rate constant fairly accurately for the reactions that involve atomic species or simple molecules but for complex molecules significant deviations are observed. The reason could be that all collisions do not lead to the formation of products. The collision in which molecules collide with sufficient kinetic energy (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.

To account for effective collisions, another factor  $P$ , called the probability or steric factor is introduced. It takes into account the fact that in a collision, molecules must be properly oriented i.e.,

$$\text{Rate} = PZ_{AB} e^{-E_a/RT}$$

Thus, in collision theory activation energy and proper orientation of the molecules together determine the criteria for an effective collision and hence the rate of a chemical reaction.

Collision theory also has certain drawbacks as it considers atoms/molecules to be hard spheres and ignores their structural aspect.

**Q. What will be the effect of temperature on rate constant ?**

**Q. The rate of the chemical reaction doubles for an increase of 10K in absolute temperature from 298K. Calculate  $E_a$ .**

**Q. The activation energy for the reaction  $2\text{HI}(\text{g}) \rightarrow \text{H}_2 + \text{I}_2(\text{g})$  is  $209.5 \text{ kJ mol}^{-1}$  at 581 K. Calculate the fraction of molecules of reactants having energy equal to or greater than activation energy ?**

## NCERT EXERCISE

4.1 From the rate expression for the following reactions, determine their order of reaction and the dimensions of the rate constant.

- (i)  $3\text{NO}(\text{g}) \rightarrow \text{N}_2\text{O}(\text{g})$  ; Rate =  $k[\text{NO}]^2$   
 (ii)  $\text{H}_2\text{O}_2(\text{aq}) + 3\text{I}^-(\text{aq}) + 2\text{H}^+ \rightarrow 2\text{H}_2\text{O}(\text{l}) + \text{I}_3^-$  ; Rate =  $k[\text{H}_2\text{O}_2][\text{I}^-]$   
 (iii)  $\text{CH}_3\text{CHO}(\text{g}) \rightarrow \text{CH}_4(\text{g}) + \text{CO}(\text{g})$  ; Rate =  $k[\text{CH}_3\text{CHO}]^{3/2}$   
 (iv)  $\text{C}_2\text{H}_5\text{Cl}(\text{g}) \rightarrow \text{C}_2\text{H}_4(\text{g}) + \text{HCl}(\text{g})$  ; Rate =  $k[\text{C}_2\text{H}_5\text{Cl}]$

4.2 For the reaction :  $2\text{A} + \text{B} \rightarrow \text{A}_2\text{B}$ , the rate =  $k[\text{A}][\text{B}]^2$  with  $k = 2.0 \times 10^{-6} \text{ mol}^{-2} \text{ L}^2 \text{ s}^{-1}$ . Calculate the initial rate of the reaction when  $[\text{A}] = 0.1 \text{ mol L}^{-1}$  and  $[\text{B}] = 0.2 \text{ mol L}^{-1}$ . Calculate the rate of reaction after  $[\text{A}]$  is reduced to  $0.06 \text{ mol L}^{-1}$ .

4.3 The decomposition of  $\text{NH}_3$  on platinum surface is zero order reaction. What are the rates of production of  $\text{N}_2$  and  $\text{H}_2$  if  $k = 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$  ?

4.4 The decomposition of dimethyl ether leads to the formation of  $\text{CH}_4$ ,  $\text{H}_2$  and  $\text{CO}$  and the reaction rate is given by, Rate =  $k[\text{CH}_3\text{OCH}_3]^{3/2}$ . The rate of reaction is followed by increase in pressure in a closed vessel, so the rate can also be expressed in terms of the partial pressure of dimethyl ether, i.e.

Rate =  $k(\text{p}_{\text{CH}_3\text{OCH}_3})^{3/2}$ . If the pressure is measured in bar and time in minutes, then what are the units of rate and rate constant ?

4.5 Mention the factors that affect the rate of a chemical reaction.

4.6 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 ?

4.7 What is the effect of temperature on the rate constant of a reaction ? How can this temperature effect on the rate constant be represented quantitatively ?

4.8 In a pseudo first order hydrolysis of an ester in water, the following result were obtained :

|                             |      |      |      |       |
|-----------------------------|------|------|------|-------|
| t/s                         | 0    | 30   | 60   | 90    |
| [Ester] mol L <sup>-1</sup> | 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.

4.9 A reaction is first order in A and second order in B.

- (i) Write the differential rate equation.  
 (ii) How is the rate affected on increasing the concentration of B three times ?  
 (iii) How is the rate affected when concentrations of both A and B are doubled ?

4.10 In a reaction between A and B, the initial rate of reaction ( $r_0$ ) was measured for different initial concentrations of A and B as given below :

|                                      |                       |                       |                       |
|--------------------------------------|-----------------------|-----------------------|-----------------------|
| A/mol L <sup>-1</sup>                | 0.20                  | 0.20                  | 0.40                  |
| B/mol L <sup>-1</sup>                | 0.30                  | 0.10                  | 0.05                  |
| $r_0/\text{mol L}^{-1}\text{s}^{-1}$ | $5.07 \times 10^{-5}$ | $5.07 \times 10^{-5}$ | $7.16 \times 10^{-5}$ |

What is the order of reaction with respect to A and B ?

4.11 The following result have been obtained during the kinetic studies of the reaction :  $2\text{A} + \text{B} \rightarrow \text{C} + \text{D}$

| Experiment | [A]/mol L <sup>-1</sup> | [B]/mol L <sup>-1</sup> | Initial rate of formation of D/mol L <sup>-1</sup> min <sup>-1</sup> |
|------------|-------------------------|-------------------------|--|
| I          | 0.1                     | 0.1                     | $6.0 \times 10^{-3}$   |
| II         | 0.3                     | 0.2                     | $7.2 \times 10^{-2}$   |
| III        | 0.3                     | 0.4                     | $2.88 \times 10^{-1}$  |
| IV         | 0.4                     | 0.1                     | $2.40 \times 10^{-2}$  |

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

- 4.12 The reaction between A and B is first order with respect to A and zero order with respect to B. Fill in the blanks in the following table :

| Experiment | [A]/mol L <sup>-1</sup> | [B]/mol L <sup>-1</sup> | Initial rate/mol L <sup>-1</sup> min <sup>-1</sup> |
|------------|-------------------------|-------------------------|--|
| I          | 0.1                     | 0.1                     | $2.0 \times 10^{-2}$                               |
| II         | —                       | 0.2                     | $4.0 \times 10^{-2}$                               |
| III        | 0.4                     | 0.4                     | —  |
| IV         | —                       | 0.2                     | $2.0 \times 10^{-2}$                               |

- 4.13 Calculate the half-life of a first order reaction from their rate constants given below :

(i)  $200 \text{ s}^{-1}$                       (ii)  $2 \text{ min}^{-1}$                       (iii)  $4 \text{ years}^{-1}$

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

- 4.15 The experimental data for the decomposition of N<sub>2</sub>O<sub>5</sub>, [2N<sub>2</sub>O<sub>5</sub> → 4NO<sub>2</sub> + O<sub>2</sub>] in gas phase at 318 K are given below :

| t/s  | 0    | 400  | 800  | 1200 | 1600 | 2000 | 2400 | 2800 | 3200 |
|--|------|------|------|------|------|------|------|------|------|
| $10^2 \times [\text{N}_2\text{O}_5]/\text{mol L}^{-1}$ | 1.63 | 1.36 | 1.14 | 0.93 | 0.78 | 0.64 | 0.53 | 0.43 | 0.35 |

- (i) What is the rate law ?  
 (ii) Calculate the rate constant.  
 (iii) Calculate the half-life period from k.
- 4.16 The rate constant for a first order reaction is  $60 \text{ s}^{-1}$ . How much time will it take to reduce the initial concentration of the reactant to its  $1/16^{\text{th}}$  value ?
- 4.17 During nuclear explosion, one of the products is <sup>90</sup>Sr with half-life of 28.1 years. If  $1 \mu\text{g}$  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 years and 60 years if it is not lost metabolically.
- 4.18 For a first order reaction, show that time required for 99% completion is twice the time required for the completion of 90% of reaction.
- 4.19 A first order reaction takes 40 min for 30% decomposition. Calculate  $t_{1/2}$ .
- 4.20 For the decomposition of azoisopropane to hexane and nitrogen at 543 K, the following data are obtained :

| t (sec) | P(mm of Hg) |
|---------|-------------|
| 0       | 35.0        |
| 360     | 54.0        |
| 720     | 63.0        |

Calculate the rate constant.

- 4.21 The following data were obtained during the first order thermal decomposition of SO<sub>2</sub>Cl<sub>2</sub> at a constant volume.



| Experiment | Time/s <sup>-1</sup> | Total pressure/atm |
|------------|----------------------|--------------------|
| 1          | 0                    | 0.5                |
| 2          | 100                  | 0.6                |

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

- 4.22 The rate constant for the decomposition of N<sub>2</sub>O<sub>5</sub> at various temperatures is given below :

| T/ <sup>o</sup> C             | 0      | 20   | 40   | 60  | 80   |
|-------------------------------|--------|------|------|-----|------|
| $10^5 \times k/\text{s}^{-1}$ | 0.0787 | 1.70 | 25.7 | 178 | 2140 |

- 4.23 The rate constant for the decomposition of hydrocarbons is  $2.418 \times 10^{-5} \text{ s}^{-1}$  at 546 K. If the energy of activation is 179.9 kJ/mol, what will be the value of pre-exponential factor ?

- 4.24 Consider a certain reaction  $A \rightarrow \text{Product}$  with  $k = 2.0 \times 10^{-2} \text{ s}^{-1}$ . Calculate the concentration of A remaining after 100 s if the initial concentration of A is  $1.0 \text{ mol L}^{-1}$ .
- 4.25 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 the sample of sucrose remains after 8 hours ?
- 4.26 The decomposition of hydrocarbon follows the equation  $k = (4.5 \times 10^{11} \text{ s}^{-1}) e^{-28000 \text{ K}/T}$ . Calculate  $E_a$ .
- 4.27 The rate constant for the first order decomposition of  $\text{H}_2\text{O}_2$  is given by the following equation :  

$$\log k = 14.34 - 1.25 \times 10^4 \text{ K}/T$$
 Calculate  $E_a$  for this reaction and at what temperature will its half-period be 256 minutes ?
- 4.28 The decomposition of A into product has value of k as  $4.5 \times 10^3 \text{ s}^{-1}$  at  $10^\circ\text{C}$  and energy of activation  $60 \text{ kJ mol}^{-1}$ . At what temperature would k be  $1.5 \times 10^4 \text{ s}^{-1}$  ?
- 4.29 The time required for 10% completion of a first order reaction at 298K is equal to that required for its 25% completion at 308K. If the value of A is  $4 \times 10^{10} \text{ s}^{-1}$ . Calculate k at 318K and  $E_a$ .
- 4.30 The rate of a reaction quadruples when the temperature changes from 293 K to 313 K. Calculate the energy of activation of the reaction, assuming that it does not change with temperature.

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## ANSWERS

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- 4.1 (i)  $\text{L mol}^{-1} \text{ s}^{-1}$  (ii) Same as in (i) (iii)  $\text{L}^{1/2} \text{ mol}^{-1/2} \text{ s}^{-1}$  (iv)  $\text{s}^{-1}$
- 4.2  $3.89 \times 10^{-9} \text{ mol L}^{-1} \text{ s}^{-1}$
- 4.3  $2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$ ,  $7.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$
- 4.4  $\text{bar minutes}^{-1}$ ,  $\text{bar}^{-1/2} \text{ minutes}^{-1}$
- 4.6 (i) rate becomes 4 times (ii) rate becomes one-fourth
- 4.8 (i)  $4.67 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$  (ii)  $1.98 \times 10^{-2} \text{ s}^{-1}$
- 4.9 (i)  $\frac{dx}{dt} = k[A][B]^2$  (ii) rate increases 9 times (iii) rate increases 8 times
- 4.10  $A = 0.5$ ,  $B = 0$
- 4.11  $\text{Rate} = k[A][B]^2$ ,  $k = 6.0 \text{ mol}^{-2} \text{ L}^2 \text{ min}^{-1}$
- 4.12  $[A] = 0.2 \text{ mol L}^{-1}$ ,  $\text{Rate} = 0.08 \text{ mol L}^{-1} \text{ min}^{-1}$ ,  $[A] = 0.1 \text{ mol L}^{-1}$
- 4.13 (i)  $3.47 \times 10^{-3}$  seconds (ii) 0.35 minutes (iii) 0.173 years
- 4.14 1845 years
- 4.15 (i)  $\text{Rate} = k[\text{N}_2\text{O}_5]$  (ii)  $4.82 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$  (iii) 1438 s
- 4.16  $4.62 \times 10^{-2} \text{ s}$
- 4.17 0.7842  $\mu\text{g}$  and 0.227  $\mu\text{g}$
- 4.18 2
- 4.19 77.7 min.
- 4.20  $2.20 \times 10^{-3} \text{ s}^{-1}$
- 4.21  $7.8 \times 10^{-4} \text{ atm s}^{-1}$
- 4.23  $3.912 \times 10^{12} \text{ s}^{-1}$
- 4.24  $0.1354 \text{ mol L}^{-1}$
- 4.25 0.158
- 4.26 0.135 M
- 4.27 239.33 kJ/mol,  $T = 669 \text{ K}$
- 4.28  $24^\circ\text{C}$
- 4.29  $E_a = 479.77 \text{ kJ mol}^{-1}$ ,  $k = 5.70 \times 10^{-70} \text{ s}^{-1}$
- 4.30  $52.862 \text{ kJ mol}^{-1}$

## ADDITIONAL QUESTIONS AND PROBLEMS

- Q. The specific rate constant for a particular reaction is  $2.34 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$  at 370 K and  $7.50 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1}$  at 400 K. Calculate the activation energy for the reaction. [ $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$ ].
- Q. What will be the initial rate of reaction if its rate constant is  $10^{-3} \text{ s}^{-1}$  and the concentration of the reactant is  $0.2 \text{ mol L}^{-1}$ ? What fraction of the reactant will be converted into the products in 200 seconds?
- Q. What is meant by inversion of sugar?
- Q. State the role of activated complex in a reaction and state its relation with activation energy.
- Q. What is the temperature coefficient of the reaction?
- Q. The reaction  $\text{SO}_2\text{Cl}_2 \rightarrow \text{SO}_2 + \text{Cl}_2$  is a first order reaction with half-life  $3.15 \times 10^4 \text{ s}$  at  $320^\circ\text{C}$ . What percentage of  $\text{SO}_2\text{Cl}_2$  would be decomposed on heating at  $320^\circ\text{C}$  for 90 minutes?
- A. 11.2%
- Q. For the reaction at 500 K,  $\text{NO}_2(\text{g}) + \text{CO}(\text{g}) \rightarrow \text{CO}_2(\text{g}) + \text{NO}(\text{g})$  the proposed mechanism is as follows  
Find the rate law expression
- (i)  $\text{NO}_2 + \text{NO}_2 \rightarrow \text{NO} + \text{NO}_3$  (slow)                      (ii)  $\text{NO}_3 + \text{CO} \rightarrow \text{CO}_2 + \text{NO}_2$  (fast)
- A.  $\frac{dx}{dt} = k[\text{NO}_2]^2$
- Q. What will be the initial rate of reaction if its rate constant is  $10^{-3} \text{ s}^{-1}$  and the concentration of the reactant is  $0.2 \text{ mol L}^{-1}$ ? What fraction of the reactant will be converted into the products in 200 seconds?
- A. 18%
- Q. A first order reaction is 20% complete in 20 minutes. Calculate the time it will take the reaction to complete 80%.
- A. 144.2 min.
- Q. For the decomposition of  $\text{N}_2\text{O}_5$  at 298 K, the rate law is  $\frac{d[\text{N}_2\text{O}_5]}{dt} = k[\text{N}_2\text{O}_5]$ . Starting with 2.5 moles of  $\text{N}_2\text{O}_5(\text{g})$  in a five litre container, how many moles per litre of  $\text{N}_2\text{O}_5$  would remain after 75 seconds if rate constant for the reaction is  $16.8 \times 10^{-3} \text{ s}^{-1}$ ?
- A.  $0.1418 \text{ mol L}^{-1}$
- Q. The rate constant for the first order decomposition of  $\text{N}_2\text{O}_5$  at  $45^\circ\text{C}$  is  $3.00 \times 10^{-2} \text{ min}^{-1}$ . If the initial concentration of  $\text{N}_2\text{O}_5$  is  $2.00 \times 10^{-3} \text{ mol L}^{-1}$ , how long will it take for the concentration to drop to  $5.00 \times 10^{-4} \text{ mol L}^{-1}$ ?
- A. 46.2 min.
- Q. Consider the following data for the reaction  $\text{A} + \text{B} \rightarrow \text{Products}$ .
- | Run | Initial conc. [A] | Initial conc. [B] | Initial Rate [ $\text{mol L}^{-1} \text{ s}^{-1}$ ] |
|-----|-------------------|-------------------|---|
| 1.  | 0.10 M            | 1.00 M            | $2.1 \times 10^{-3}$                                |
| 2.  | 0.20 M            | 1.00 M            | $8.4 \times 10^{-3}$                                |
| 3.  | 0.20 M            | 2.00 M            | $8.4 \times 10^{-3}$                                |
- Determine the order of the reaction with respect to 'A' and with respect to 'B' and the overall order of the reaction.
- A. 2
- Q. Distinguish between rate of reaction and rate constant.
- Q. What is the effect of catalyst on activation energy and why?
- Q. Why do reaction rate depend upon temperature?
- A. Rate of reaction depends upon number of molecules possessing a minimum energy which undergo effective collisions. The energy of molecules depends upon temperature because kinetic energy is directly proportional to temperature, therefore, rate of reaction depends upon temperature.