The order of a reaction is sometimes altered by conditions. There are many reactions which obey first order rate law although they are higher order reactions. Consider the hydrolysis of ethyl acetate which is a chemical reaction between ethyl acetate and water. In reality, it is a second order reaction and concentration of both ethyl acetate and water affect the rate of the reaction. But water is taken in large excess for hydrolysis, therefore, concentration of water is not altered much during the reaction. Thus, the rate of reaction is affected by concentration of ethyl acetate only. For example, during the hydrolysis of 0.01 mol of ethyl acetate with 10 mol of water, amounts of the reactants and products at the beginning (t = 0) and completion (t) of the reaction are given as under.

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$$

	$CH_3COOC_2H_5$	H_2O	CH_3COOH	C_2H_5OH
$t = 0$	0.01 mol	10 mol	0 mol	0 mol
t	0 mol	9.99 mol	0.01 mol	0.01 mol

The concentration of water does not get altered much during the course of the reaction. So, the reaction behaves as first order reaction. Such reactions are called **pseudo first order reactions**.

Inversion of cane sugar is another pseudo first order reaction.

$$\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$\text{Rate} = k\ [C_{12}H_{22}O_{11}]$$

Intext Questions

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

4.6 Time required to decompose SO_2Cl_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.

4.4 Temperature Dependence of the Rate of a Reaction

Most of the chemical reactions are accelerated by increase in temperature. For example, in decomposition of N_2O_5, the time taken for half of the original amount of material to decompose is 12 min at 50°C, 5 h at 25°C and 10 days at 0°C. You also know that in a mixture of potassium permanganate ($KMnO_4$) and oxalic acid ($H_2C_2O_4$), potassium permanganate gets decolourised faster at a higher temperature than that at a lower temperature.

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

The temperature dependence of the rate of a chemical reaction can be accurately explained by **Arrhenius equation** (4.18). It was first proposed by Dutch chemist, J.H. van't Hoff but Swedish chemist, Arrhenius provided its physical justification and interpretation.

$$k = A\ e^{-Ea\ /RT} \qquad (4.18)$$

where *A* is the Arrhenius factor or the **frequency factor**. It is also called pre-exponential factor. It is a constant specific to a particular reaction. *R* is gas constant and E_a is activation energy measured in joules/mole (J mol $^{-1}$).

It can be understood clearly using the following simple reaction

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

According to Arrhenius, this reaction can take place only when a molecule of hydrogen and a molecule of iodine collide to form an unstable intermediate (Fig. 4.6). It exists for a very short time and then breaks up to form two molecules of hydrogen iodide.

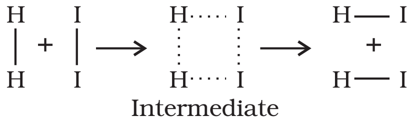

Fig. 4.6: *Formation of HI through the intermediate*

The energy required to form this intermediate, called **activated complex** (C), is known as **activation energy (E_a)**. Fig. 4.7 is obtained by plotting potential energy vs reaction coordinate. Reaction coordinate represents the profile of energy change when reactants change into products.

Some energy is released when the complex decomposes to form products. So, the final enthalpy of the reaction depends upon the nature of reactants and products.

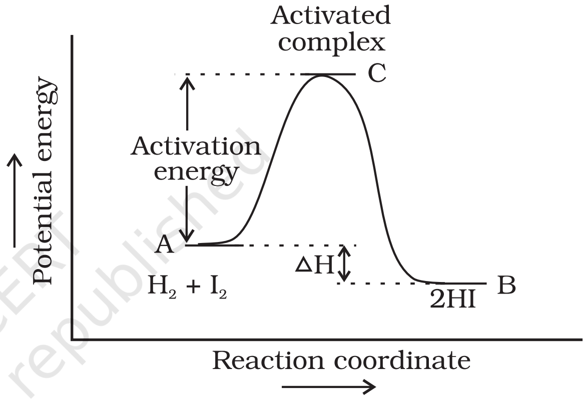

Fig. 4.7: *Diagram showing plot of potential energy vs reaction coordinate*

All the molecules in the reacting species do not have the same kinetic energy. Since it is difficult to predict the behaviour of any one molecule with precision, Ludwig Boltzmann and James Clark Maxwell used statistics to predict the behaviour of large number of molecules. 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 (Fig. 4.8). Here, N_E is the number of molecules with energy *E* and N_T is total number of molecules.

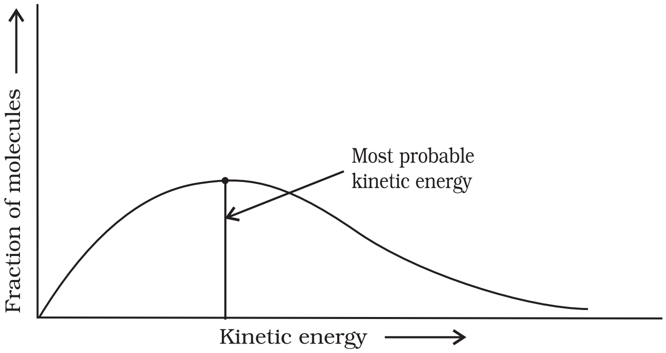

Fig. 4.8: *Distribution curve showing energies among gaseous molecules*

The peak of the curve corresponds to the **most probable kinetic energy**, i.e., kinetic energy of maximum fraction of molecules. There are decreasing number of molecules with energies higher or lower than this value. When the

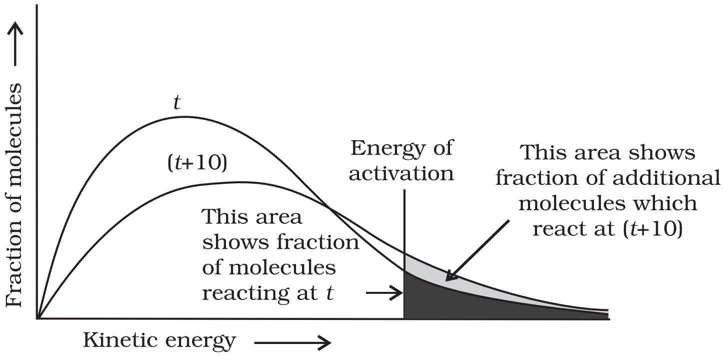

Fig. 4.9: *Distribution curve showing temperature dependence of rate of a reaction*

temperature is raised, the maximum of the curve moves to the higher energy value (Fig. 4.9) and the curve broadens out, i.e., spreads to the right such that there is a greater proportion of molecules with much higher energies. The area under the curve must be constant since total probability must be one at all times. We can mark the position of E_a on Maxwell Boltzmann distribution curve (Fig. 4.9).

Increasing the temperature of the substance increases 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 (4.18) the factor $e^{-E_a/RT}$ corresponds to the fraction of molecules that have kinetic energy greater than E_a. Taking natural logarithm of both sides of equation (4.18)

$$\ln k = -\frac{E_a}{RT} + \ln A \tag{4.19}$$

The plot of ln k vs 1/T gives a straight line according to the equation (4.19) as shown in Fig. 4.10.

Thus, it has been found from Arrhenius equation (4.18) 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.

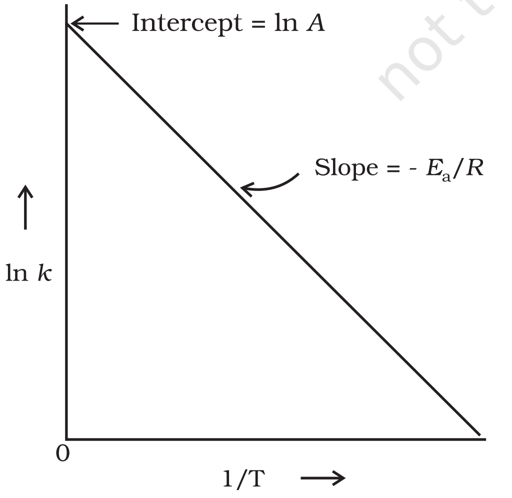

Fig. 4.10: *A plot between ln k and 1/T*

In Fig. 4.10, slope = $-\frac{E_a}{R}$ and intercept = ln A. So we can calculate E_a and A using these values.

At temperature T_1, equation (4.19) is

$$\ln k_1 = -\frac{E_a}{RT_1} + \ln A \tag{4.20}$$

At temperature T_2, equation (4.19) is

$$\ln k_2 = -\frac{E_a}{RT_2} + \ln A \tag{4.21}$$

(since A is constant for a given reaction)

k_1 and k_2 are the values of rate constants at temperatures T_1 and T_2 respectively.

Subtracting equation (4.20) from (4.21), we obtain

$$\ln k_2 - \ln k_1 = \frac{E_a}{RT_1} - \frac{E_a}{RT_2}$$

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \qquad (4.22)$$

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

Example 4.9 The rate constants of a reaction at 500K and 700K are 0.02s^{-1} and 0.07s^{-1} respectively. Calculate the values of E_a and A.

Solution

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

$$\log \frac{0.07}{0.02} = \left(\frac{E_a}{2.303 \times 8.314 \, \text{JK}^{-1}\text{mol}^{-1}}\right)\left[\frac{700-500}{700 \times 500}\right]$$

$$0.544 = E_a \times 5.714 \times 10^{-4}/19.15$$

$$E_a = 0.544 \times 19.15/5.714 \times 10^{-4} = 18230.8 \text{ J}$$

Since $k = Ae^{-Ea/RT}$

$$0.02 = Ae^{-18230.8/8.314 \times 500}$$

$$A = 0.02/0.012 = 1.61$$

Example 4.10 The first order rate constant for the decomposition of ethyl iodide by the reaction

$$C_2H_5I(g) \rightarrow C_2H_4\ (g) + HI(g)$$

at 600K is 1.60 × 10^{-5} s^{-1}. Its energy of activation is 209 kJ/mol. Calculate the rate constant of the reaction at 700K.

Solution We know that

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