

LECTURE 10

NCERT

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 ($\text{H}_2\text{C}_2\text{O}_4$), potassium permanganate gets decolourised faster at a higher temperature than that at a lower temperature.

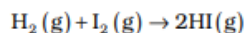
It has been found that **for a chemical reaction with rise in temperature by 10° , the rate constant is nearly doubled.**

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.

$$k = A e^{-E_a/RT} \quad (4.18)$$

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



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.

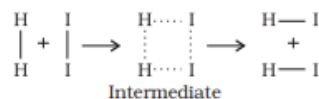


Fig. 4.6: Formation of HI through the intermediate

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.

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.

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

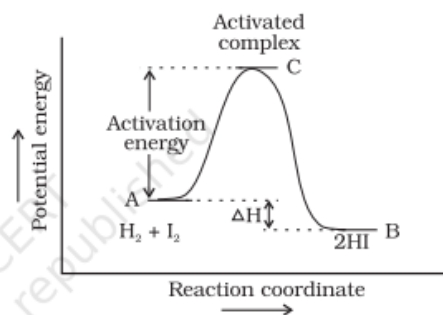


Fig. 4.7: Diagram showing plot of potential energy vs reaction coordinate

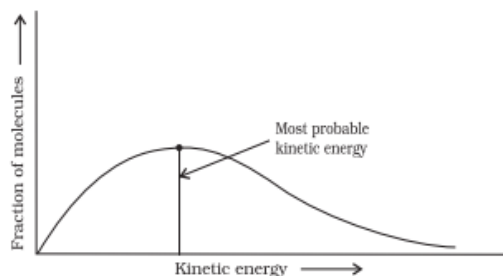


Fig. 4.8: Distribution curve showing energies among gaseous molecules