Paper : Physical Chemistry
Topic : Chemical Kinetics

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Effect of Temperature on Reaction Rates :-

The temperature has a significant effect on the rate of a reaction. It has been observed experimentally that an increase of temperature increases the rate of reaction and hence the rate constant. As a rule, an increase of temp. by $10°C$ doubles the reaction rate. The ratio of rate constants of a reaction at two different temperatures differing by $10°C$ is known as the _temperature coefficient_ of the reaction. The temps. usually selected for this purpose are $25°C$ and $35°C$. i.e.

$$\text{Temperature Coefficient} = \frac{k_{35}}{k_{25}} = 2 \text{ to } 3$$

The value of the temperature coefficient for most of the reactions is close to 2 and in some cases it approaches even 3.

For example :

(i) Temperature coefficient for the decomposition of HBr in aqueous solution is 1.9.

(ii) Temperature coefficient for

$$CH_3I + C_2H_5ONa \longrightarrow CH_3OC_2H_5 + NaI$$

is 2.9.

(iii) For the reaction $NO + \frac{1}{2} O_2 \longrightarrow NO_2$, the rate of reaction is slightly decreased as the temperature is increased and so this reaction has fractional temperature coefficient.

Arrhenius Equation :–

In 1884, van't Hoff predicted that the value of equilibrium constant varies with temp. and that a plot of log k versus 1/T must be linear with negative slope for most of the reactions. Arrhenius, in 1889, extended his idea and proposed a mathematical relation between rate constant and absolute temperature of a reaction which is known as Arrhenius Equation. It is based on the following assumptions :

(a) All the molecules present in the system can not take part in the chemical reaction.

(b) It is only a certain number of molecules which react to yield products. Such molecules are called active molecules.

(c) Those molecules who do not take part in chemical reaction are called passive molecules.

(d) An equilibrium must exist between active and passive molecules.

$$\text{Passive Molecules} \rightleftharpoons \text{Active Molecules}$$

(e) When temperature is raised, the equilibrium between active and passive molecules shifts towards the right. This increases the number of active molecules which may take part in chemical reaction and thus increases the reaction rate. It means passive molecules may become active by absorbing heat energy.

The Arrhenius equation is given by as

$$k = A \cdot e^{-Ea/RT} \qquad —①$$

where k is rate constant, T is the absolute temperature, R is the gas constant, Ea is the energy of activation for the reaction, and A is an experimentally determined quantity called the pre-exponential factor. The pre-exponential factor has the same unit as that of rate constant k. The unit of k for a first order reaction is s^{-1}, which is also the unit of frequency. Hence, A is also called the frequency factor. In the above equation, Ea and A are the Arrhenius parameters.

Calculation of Ea using Arrhenius Equation :
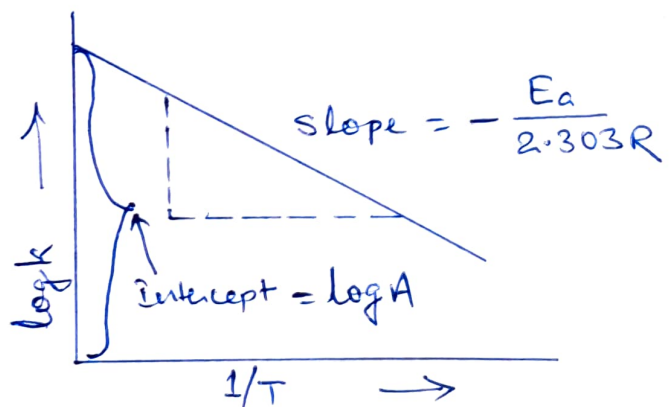
The Arrhenius equation

$$k = A \cdot e^{-Ea/RT}$$

Taking log we get-

$$\ln k = \ln A - \frac{Ea}{RT} \qquad —②$$

or, $$\log k = -\frac{Ea}{2.303 RT} + \log A \qquad —③$$

Comparing this equation with that of a straight line, $y = mx + c$, a plot of $\log k$ versus $1/T$ should be a straight-line with a slope $-Ea/2.303R$ and intercept $\log A$.

Thus, by measuring the slope of the line, we can calculate the value of Ea. And from the intercept, we can calculate the value of A.

Calculation of Ea from the values of k at two Temperatures :-

The logarithamic form of Arrhenius equation is

$$\ln k = -\frac{Ea}{RT} + \ln A$$

The rate constant, k, is measured at two different temperatures. If k_1 is the specific rate constant at temperature T_1 and k_2 at another temperature T_2 then from the above equation we have

$$\ln k_1 = -\frac{Ea}{RT_1} + \ln A \quad \text{and}$$

$$\ln k_2 = -\frac{Ea}{RT_2} + \ln A$$

On substraction, we get-

$$\ln k_2 - \ln k_1 = \left(-\frac{Ea}{RT_2}\right) - \left(-\frac{Ea}{RT_1}\right)$$

or, $$\frac{\ln k_2}{\ln k_1} = \frac{Ea}{RT_1} - \frac{Ea}{RT_2}$$

or, $$\ln\left(\frac{k_2}{k_1}\right) = \frac{Ea}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

or, $$\ln\frac{k_2}{k_1} = \frac{Ea}{R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

or, $$\log\frac{k_2}{k_1} = \frac{Ea}{2.303R}\left(\frac{T_2 - T_1}{T_1 \cdot T_2}\right)$$

This is the Integrated Arrhenius Equation. Thus, knowing the rate constants at two different temperatures, the energy of activation Ea can readily be determined.

Further, when Ea and specific rate constant at one temperature are known, then specific rate constant at any other temperature can be evaluated.

Energy of Activation, Ea :—

Appearance of Ea factor in the Arrhenius equation leads to the fact that before the reaction occurs, reactant molecules must be activated, i.e. they possess energy in excess of a certain amount. These activated molecules will then collide and lead to the reaction to yield products. Collisions between molecules which are not activated, will be of nouse and no reaction will take place. The minimum energy which the molecules must have in order to react before the reaction takes place is known as the Activation Energy.

It follows from the concept of activation that reactants are not directly converted into products. The molecules first acquire energy to form an activated complex and then this activated complex decomposes into products.

Reactants $\rightleftharpoons$ Activated Complex $\longrightarrow$ Products
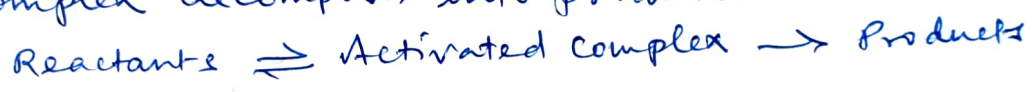
In other words, there exists an energy barrier between the reactants and products. If the reactant molecules can cross the energy barrier, they will be converted into products. This can be shown in the figure given below :
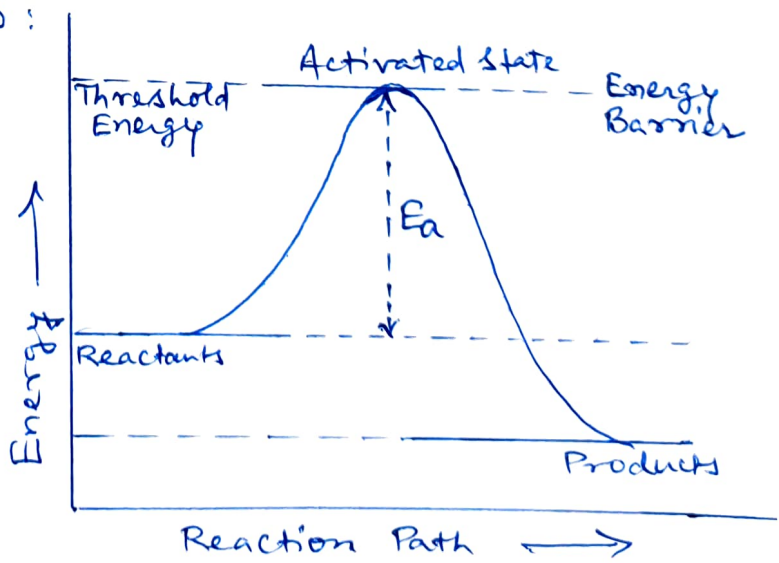
It is evident from the figure that there is a certain minimum energy (threshold energy) which the colliding molecules must acquire before they are capable of reacting. Most of the molecules,

however, have much less kinetic energy than the threshold energy. This excess energy that the reactant molecules must acquire in order to react to yield products is known as activation energy, E_a.

i.e. E_a = Threshold Energy – Energy actually possessed by reactant molecules

Thus, there is an energy barrier placed between reactants and products. This barrier has to be crossed before reactants yielding products. Only those molecules which collide with a kinetic energy greater than E_a are able to get over the barrier and react. The molecules colliding with kinetic energies less than E_a fail to surmount the barrier. The collisions between them are unproductive and the molecules simply bounce off one another.

Therefore, the energy of activation, E_a, is defined as the minimum amount of extra energy required by reactant molecules to get converted into product-molecules.

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Recommended Books :—

1. Principles of Physical Chemistry
   By Puri, Sharma and Pathania

2. A Textbook of Physical Chemistry
   By K. K. Sharma and L. K. Sharma

3. Essentials of Physical Chemistry
   By Bahl, Bahl and Tuli.