Effect of Temperature on Reaction Rates

It has been found that an increase in temperature generally increases the rate of a reaction. In majority of cases it has been seen that the rate of a reaction increases by a factor of 2 or 3 for every 10^0C rise in temperature. This is empirically given by the relation

$$\frac{k_{t+10}}{k_t} \approx 2 \text{ or } 3$$

However, more correct dependence of k on temperature is given by Arrhenius equation

$$\frac{d\ln k}{dt} = \frac{E_a}{RT^2} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (65)$$

Where E_a is called the ***activation energy*** of the reaction and is characteristic of the reaction. It is the threshold energy that the reactant molecules must have in order to react. Integration of Eq.(65) yields

$$\ln k = -E_a/RT + I \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (66)$$

$$\log k = -\ E_a/2.303RT + I' \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (67)$$

$$\mathbf{k = Ae^{-Ea/RT}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (68)$$

where I is the integration constant. The factor A is called the pre-exponential factor or the frequency factor. Equation (67) suggests that a plot of logk versus 1/T should be a straight line for many reactions as shown in Fig .9

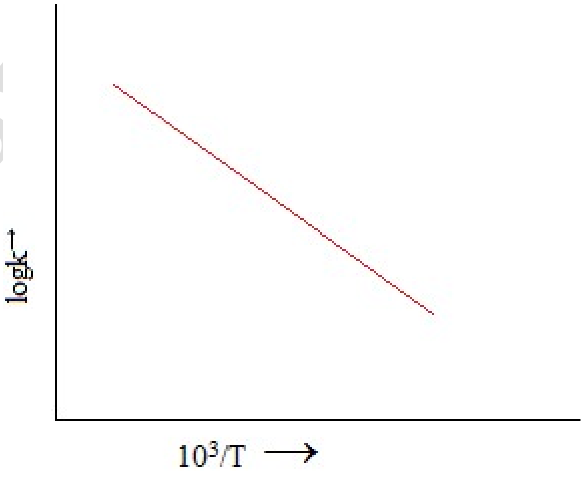


Figure 9: Plot of logk versus 1/T

The slope of the plot is equal to $-E_a/2.303R$ and the intercept equal to I'. From the slope of this plot the activation energy can be evaluated. However, if we integrate eq.(65) between the limits $k=k_1$ at $T=T_1$ and $k=k_2$ at $T=T_2$, then

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

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

$$= \frac{E_a}{R}\left[\frac{T_2-T_1}{T_1 T_2}\right]$$

or

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2-T_1}{T_1 T_2}\right] \quad \ldots\ldots\ldots\ldots\ldots (69)$$

From this equation it is evident that the activation energy, E_a, can be obtained from the value of the rate constant at two different temperatures.

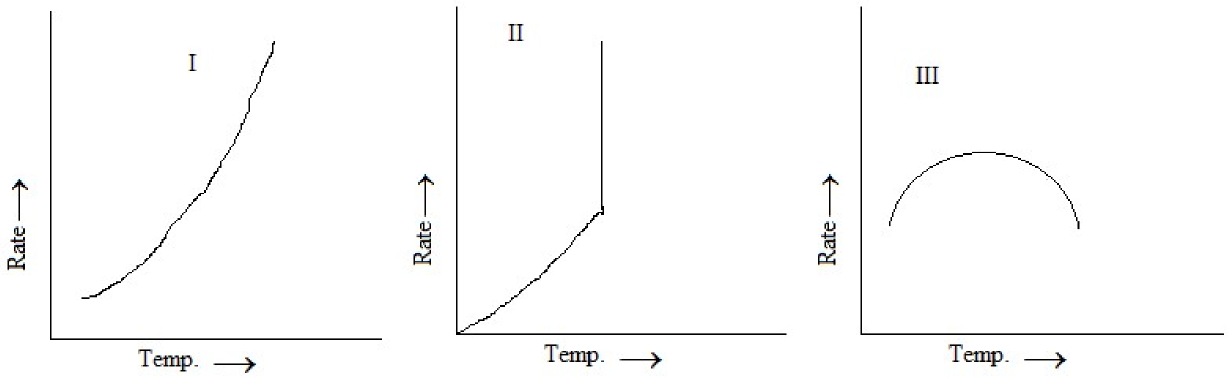


Figure 10: Various types of curves showing variation of rate with temperature

Arrhenius equation shows that the rate of a reaction increases exponentially with rise in temperature (fig.10). Curve of type I is generally obtained for most of the reaction. For explosive reaction, curve of type II is obtained whereas curve III is obtained for enzyme catalysed reactions.

The energy of Activation:

In Arrhenius equation appearance of E_a suggests that molecule must acquire a certain amount of energy before they could undergo chemical reactions. This means that before the chemical reaction to occur the molecules must be activated, i.e., they must be raised to a higher energy state. ***The minimum energy which the reacting molecules must possess before the reaction to occur is known as the energy of activation.*** According to the concept of activation, the transformation of the reactions into the products does not take place directly. The reacting molecules, however, must acquire sufficient energy to cross an activation energy barrier. This idea may be made clear with the help of a schematic diagram as shown in the **fig. 11** for the reaction A→B.

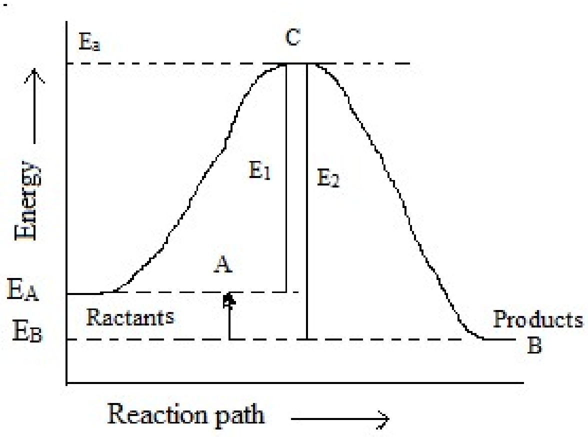


Figure 11: Energy of activation

Let E_A represent the average energy of the reactants and E_B those of the products. Even if E_A is greater than E_B, the reactants A will not be directly converted into the products B. The reacting molecules must first attain the minimum energy E_a, for the reaction to occur. Molecules at C having energy E_a, are said to be in an activated state. The excess energy (E_a- E_A), which the reactant molecules must absorb in order to become activated and react, is the energy of activation E_1 for the forward direction, i.e, A→C

Energy of activation= Energy of the activated state- Energy of the reactants

$$E_1 = E_a - E_A$$

When the activated complex decomposes into the products, energy (E_2) is given out. This can be taken as the energy of activation of the process B→C, i.e.,

$$E_2 = E_a - E_B$$

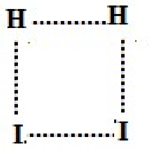
Thus, the difference ΔE, between E_A and E_B is given as, $\Delta E = E_1 - E_2 = (E_a - E_A) - (E_a - E_B) = E_B - E_A$

ΔE is simply the difference in energy between the products and reactant and is known as the enthalpy of the reaction at constant volume. This means that when the activated complex decomposes into the products, it gives out an energy E_2 which is equal to the energy absorbed by the reactant molecules from A to C plus the enthalpy of the reaction. If $E_2 > E_1$, the reaction is evidently exothermic, whereas if $E_2 < E_1$,the reaction is endothermic.

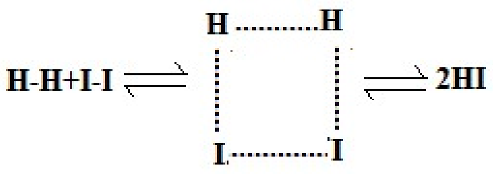
Application of the idea of activation of energy to the reaction:

$$\text{H-H} + \text{I-I} \rightleftharpoons 2\text{HI}$$

When two molecules (H_2 and I_2) are far apart and the total energy of the system is equal to the potential energy of H_2 and I_2, this part of the reaction is represented by the horizontal portion of the curve in fig. 11.As the molecule approach each other, H-H and I-I bonds being to stretch and HI bond being to form. The energy starts increasing and is represented by the rising portion of the curve .HI bond formation increases and that of H-H and I-I bonds breakage increases, a point is reached when the energy is maximum (point C). At this point the activated complex of the type shown below is formed:



The point C in the curve is called the transition state. A slight distortion of the bond in the form of compression of HI bond and stretching of H-H and I-I bonds results in the activated complex to pass through the transition state yielding the products as follows:



❖ Collision Theory of Reaction Rates

The collision theory attempts to account for the observed kinetics of reactions in terms of kinetic molecular theory. This theory has been found to be satisfactory for gaseous reactions and postulates that the reacting molecules must collide. If collision is the only requirement for a reaction to occur then the rate of the reaction should be proportional to the number of collisions between the reacting molecules. In order to explain this discrepancy, it is assumed that molecules are activated and only those molecules processing energy equal to or greater than the activation energy are able to form the products. Furthermore, in many cases it is assumed that molecules must be properly oriented so that rearrangements of atoms can occur with minimum expenditure of energy and time.

Thus, in collision theory the essential requirements for reactions to occur are :

i) **Collision between the reactant molecules.**

ii) Activated of molecules and

iii)Proper orientation of the reacting molecules at the time of collision.

For a biomolecular gaseous reaction

$$A+A \xrightarrow{k} \text{Product(s)}$$

The rate of the reaction is given by

$$-\frac{d[A]}{dt} = k[A]^2$$

If the concentration of A is 1 mol dm^{-3}, we get

$$-\frac{d[A]}{dt} = k \qquad \text{.............................. (70)}$$

According to the collision theory the rate of the reaction is given by

$$-\frac{d[A]}{dt} = k = Z_{11}q \qquad \text{....................(71)}$$

Where Z_{11} is the number of collision between the reacting molecules per second per dm^3 and q is the fraction of the total number of molecules which are activated. The values of Z_{11} and q can be calculated from the kinetic theory of gases. Z_{11} is given by

$$Z_{11} = \frac{1}{2}\sqrt{2}\ \pi\sigma^2(n')^2C_{av} \qquad \text{.....................(72)}$$

$$q = \frac{n^*}{n'}e^{-E_a/RT} \qquad \text{.............................. (73)}$$

Where σ is the collision diameter and C_{av} the average velocity of the molecules in dm per second, n^* the number of molecules per dm having energy equal to or more than the activation energy E_a and n' is the total number of molecules per dm^3. Substituting the value of C_{av} in eq (72)

, we get

$$Z_{11} = \frac{1}{2}\sqrt{2}\ \pi\sigma^2(n')^2\sqrt{\frac{8RT}{\pi M}} \qquad \text{........................(74)}$$

$$=2\sigma^2(n')^2\sqrt{\frac{\pi RT}{M}}$$

……………………………….(75)

The number of collisions per second between two unlike molcules1 and 2 is given by

$$Z_{12}=n'_1 n'_2\left(\frac{\sigma_1+\sigma_2}{2}\right)^2\sqrt{\frac{8\pi kT}{\mu}}$$

…………..(76)

Where $n'_1$and n'_2 are the number of molecules per dm^3 of reactants 1and 2 , $\sigma_1$and σ_2 are the collision diameters of the molecules 1 and 2 and μ is the reduced mass given by

$$\frac{1}{\mu}=\frac{1}{m_1}+\frac{1}{m_2}$$

Hence the expression for the rate of a reaction involving identical molecules is given by

$$\text{Rate}=qZ_{11}=2\sigma^2(n')^2\sqrt{\frac{\pi RT}{M}}\,e^{-E_a/RT}$$

…………………. (77)

And for different reactant molecules

$$\text{Rate}=qZ_{12}=n'_1 n'_2\left(\frac{\sigma_1+\sigma_2}{2}\right)^2\sqrt{\frac{8\pi kT}{\mu}}\,e^{-E_a/RT}$$

……………………….. (78)

Comparison of Eq.(77) and (68) shows that the pre-exponential factor A in the Arrhenius equation is equal to Z_{11}.

The results predicted by Eq.(77) and (78) can be compared with the experimental values of the rate constants.

Discrepancy between experimental and calculated value of k –introduction of steric factor:

Take the example of dissociation of a mole of HI per dm^3 at 556K. The value of activation energy for the reaction has been found to be 185.0 kJ, the collision diameter for HI is $3.5\text{X}10^{-9}$ dm, the molar mass is $1.28\ \text{X}10^{-1}$kg mol^{-1} and the number of molecules per dm^3 is $6.023\text{X}10^{23}$. Substituting these values in eq. (75), we obtain

$$Z_{11}=2\sigma^2(n')^2\sqrt{\frac{\pi RT}{M}}$$

$$=2x(3.5x10^{-9}dm)^2(6.023x10^{23}dm^{-3}\left(\frac{3.14x8.314x10^2kg\ dm^2s^{-2}K^{-1}mol^{-1}x556K}{1.28x10^{-1}kgmol^{-1}}\right)^{1/2}$$

$=2.99X10^{34}s^{-1}dm^{-3}$

The number of colliding molecules per second per dm^3 is twice the value of Z_{11}, i.e $5.98x10^{34}$.

The fraction of total number of molecules, q, is given by

$q=e^{-Ea/RT}$

$=exp[-(185x10^3)/(8.314x556)]=5.2x10^{-18}$

Hence $k=qZ_{11}=5.98x10^{34}x5.2x10^{-18}=3.12x10^{17}$ molecules/dm^3/sec

If this value is divided by Avogadro constant, we get the rate constant in units of $mol^{-1}dm^3s^{-1}$.

Therefore, $k=5.2x10^{-7}\ mol^{-1}dm^3s^{-1}$

The experimental value of k has been found to be $3.5\ x10^{-7}\ mol^{-1}dm^3s^{-1}$.

The agreement between these values is quite satisfactory indicating the validity of the theory. However, the agreement between the calculated and the observed values has been found to hold only for simple biomolecular gaseous reactions and in solutions where the reacting molecules are simple. For reaction involving complex molecules, the experimental rates are quite different from the calculated values. In order to account for the observed discrepancy it is further postulated that the molecules must be properly oriented at the time of the collision and an additional term is introduced in expression for the rate of the reaction i.e.,

$k=PZ_{11}e^{-Ea/RT}$ ……………………… (79)

where P is referred to as ***the probability*** or ***steric factor*** and is related to the geometry of the molecule. It is a measure of the deviation from the calculated value. It can have values ranging from unity to about 10^{-9} for slow reactions.