Chemical Kinetics (Note -2)

The Arrhenius Equation:

The Arrhenius equation is an expression that provides a relationship between the rate constant (of a chemical reaction), the absolute temperature, and the A factor (also known as the pre-exponential factor). The expression of the Arrhenius equation is:

$$k = Ae^{-E_a/RT}$$

Arrhenius Equation

Where,

- k denotes the rate constant of the reaction
- A denotes the pre-exponential factor which, in terms of the collision theory, is the frequency of correctly oriented collisions between the reacting species
- e is the base of the natural logarithm (Euler's number)
- E_a denotes the activation energy of the chemical reaction (in terms of energy per mole)
- R denotes the universal gas constant
- T denotes the absolute temperature associated with the reaction (in Kelvin)

If the activation energy is expressed in terms of energy per reactant molecule, the universal gas constant must be replaced with the Boltzmann constant (k_B) in the Arrhenius equation.

Arrhenius Plot

When logarithms are taken on both sides of the equation, the Arrhenius equation can be written as follows:

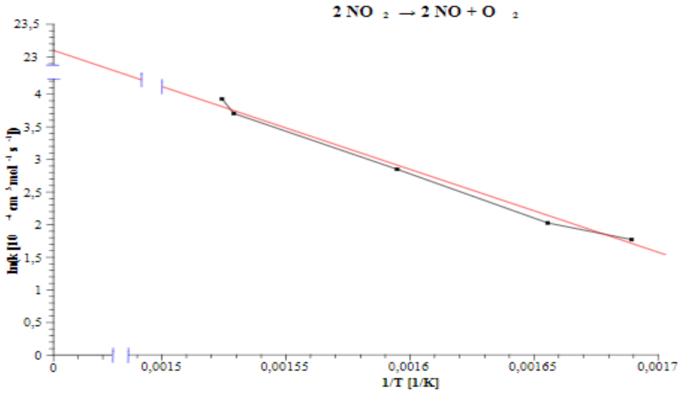
$$\ln k = \ln(Ae^{-Ea/RT})$$

Solving the equation further:

$$\ln k = \ln(A) + \ln(e^{-Ea/RT})$$

$$\ln k = \ln(A) + (-E_a/RT) = \ln(A) - (E_a/R)(1/T)$$

Since ln(A) is a constant, the equation corresponds to that of a straight line ($y = mx + c$) whose slope (m) is $-E_a/R$. When the logarithm of the rate constant (ln K) is plotted on the Y-axis and the inverse of the absolute temperature (1/T) is plotted on the X-axis, the resulting graph is called an Arrhenius plot.



Arrhenius Plot

The Arrhenius plot for the decomposition of nitrogen dioxide is illustrated above.

Arrhenius Equation for a reaction taking place at two different temperatues

Considering a chemical reaction at two different temperatures T_1 and T_2, whose corresponding rate constants are k_1 and k_2 respectively, the logarithmic form of the Arrhenius equation is:

$\ln k_1 = \ln(A) – E_a/RT_1$

$\ln k_2 = \ln(A) – E_a/RT_2$

Subtracting eqn (2) from eqn (1)

$$\ln(k_1) - \ln(k_2) = {E_a}/{RT_2} - {E_a}/{RT_1}$$

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

Arrhenius Equation and the Pre-Exponential Factor (A)

The symbol ‘A’ in the Arrhenius equation denotes the pre-exponential factor or the frequency factor. This factor deals with the collisions between molecules and can be thought of as the frequency of correctly oriented collisions between molecules that have sufficient energy to spark a chemical reaction.

The pre-exponential factor is often represented by the following equation:

$A = \rho Z$

Where Z is the frequency factor (frequency of collisions) and ρ is the steric factor (deals with orientation of molecules).

The value of A must be determined experimentally since it assumes different values for different reactions. It is also dependent on the temperature at which the reaction is taking place. The units of A are dependent on the order of the reaction. For example, the value of 'A' for a second-order rate constant is expressed in $L.mol^{-1}.s^{-1}$ (or $M^{-1}s^{-1}$, since $M = mol.L^{-1}$) and that of a first-order rate constant is expressed in s^{-1}.

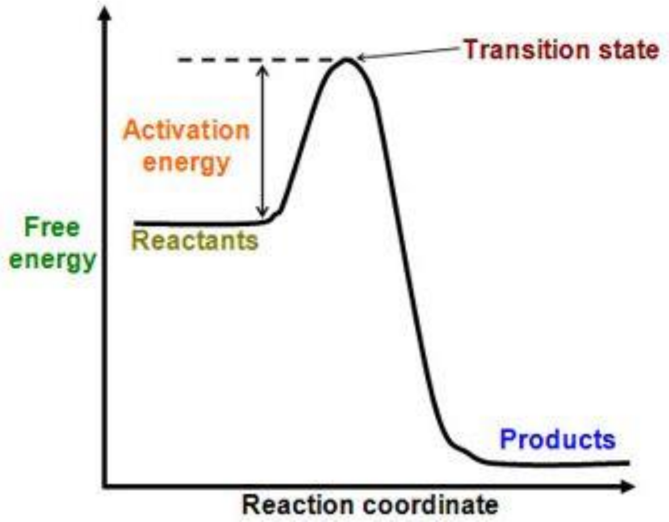
Collision Theory:

According to this theory, for chemical reaction to occur, there must be collisions between the reactant molecules. However all the collisions between molecules are not effective. Only those collisions in which the colliding molecules are associated with a certain minimum energy called the threshold energy result in chemical reaction.

A certain minimum energy which the colliding molecules must acquire to undergo a chemical reaction is called Threshold Energy. However most of the molecules have much lesser Kinetic energy than the threshold energy. The excess energy that the reactant molecules having energy less than the threshold energy must acquire in order to react to yield products is known as activation energy.

Thus,

Activation Energy=Threshold Energy – Energy actually possessed by molecules



From the Kinetic theory of gases, the number of bimolecular collisions per second per cm^3 among molecules of one species is given by $Z = 2n^2d^2(\frac{8\pi KT}{\mu})^{1/2}$

For a reaction n involving two different gases A and B, the rate of bimolecular collisions between unlike molecules per second unit voliume is given by $Z_{AB} = n_A n_B (d_{av})^2 (\frac{8\pi KT}{\mu})^{1/2}$ n_A and n_B are the numbers of A and B molecules, respectively and d_{av} is the average collision diameter defined as ${(d_A+d_B)}/{2}$ and μ is the reduced mass defined as $\mu = \frac{M_A M_B}{(M_A+M_B)}$. In terms of molar masses M_A and M_B

$$Z_{AB} = n_A n_B (d_{av})^2 \left[\frac{(M_A + M_B)8\pi rT}{M_A M_B}\right]^{1/2}$$

Activated Complex Theory (ACT) of Bimolecular Reactions:

According to Activated Complex Theory (ACT) or Transition State Theory (TST), the bimolecular reaction between two molecules A_2 and B_2 progresses through the formation of the so-called activated complex which then decomposes to yield the product AB, as illustrated below

$$A_2 + B_2 \rightleftharpoons (A_2B_2)^{\neq} \rightarrow 2AB$$

or,

$$\begin{array}{ccccc} A-A & & A\ldots.A & & A \quad\; A \\ + & \rightleftharpoons & \vdots \quad\; \vdots & \rightarrow & | \; + \; | \\ B-B & & B\ldots.B & & B \quad\; B \end{array}$$

(1)The activated complex is regarded as a separate entity and ut is always equilibrium with the reactant molecules.

$$A + B \leftrightarrows X$$
$$c_A \quad c_B \quad c^{\neq}$$

The equilibrium constant $k^{\neq} = \frac{c^{\neq}}{c_A c_B}$

$$c^{\neq} = k^{\neq} c_A c_B$$

(2)The activation energy (E) of the reaction is the additional energy which the reactant molecules acquire to form the activated complex (X)

(3) The activated complex must have one of uts vibrational degrees of freedom which would be quite unstable. The frequency of such vibration will be low and the average energy will be of the order of kT. If v be the frequency of this vibration

$$hv = kT$$

$$v = \frac{kT}{h}$$

This frequency would give the rate at which complex would break up into products

$$rate = vc^{\neq}$$

$$rate = vk^{\neq}c_A c_B$$

If k_1 is the rate constant of the reaction

$$rate = k_1 c_A c_B$$

Comparing the above two equations

$$k_1 = vk^{\neq} = \frac{kT}{h}k^{\neq}$$

$k^{\neq}$ can be expressed in terms of thermodynamic quantities

$$RTlnk^{\neq} = \Delta G^{\neq}$$

$$k^{\neq} = e^{-\Delta G^{\neq}/RT} = e^{-(\Delta H^{\neq} - T\Delta S^{\neq})/RT}$$

$$= e^{\Delta S^{\neq}/R}\ e^{-\Delta H^{\neq}/RT}$$

$$k_1 = \frac{kT}{h}k^{\neq} = \frac{kT}{h}e^{\Delta S^{\neq}/R}\ e^{-\Delta H^{\neq}/RT}$$