

## ST. LAWRENCE HIGH SCHOOL A JESUIT CHRISTIAN MINORITY INSTITUTION STUDY MATERIAL FOR CHEMISTRY (CLASS-12) <u>TOPIC-</u> CHEMICAL KINETICS <u>PREPARED BY</u>: MR. ARNAB PAUL CHOWDHURY SET NUMBER-03 DATE: 06.07.2020



**Chemical kinetics**, also known as **reaction kinetics**, is the branch of physical chemistry that is concerned with understanding the rates of chemical reactions. It is to be contrasted with thermodynamics, which deals with the direction in which a process occurs but in itself tells nothing about its rate. Chemical kinetics includes investigations of how experimental conditions influence the speed of a chemical reaction and yield information about the reaction's mechanism and <u>transition states</u>, as well as the construction of mathematical models that also can describe the characteristics of a chemical reaction.

## Chemical Reactions on the Basis of Rate of Reaction:

- 1. **Fast/instantaneous reactions** Chemical reaction which completes in less than Ips (10<sup>-12</sup> s) time, is known as fast reaction. It IS practically impossible to measure the speed of such reactions, e.g., ionic reactions. Organic substitution reactions.
- 2. <u>Slow reactions</u> Chemical reactions which completes in a long time from some minutes to some years are called slow reactions. e.g., rusting of iron. Transformation of diamond etc.
- 3. <u>Moderately</u> slow reactions Chemical reactions which are intermediate between slow and fast reactions are called moderately slow reactions.



Chemical Kinetics also called reaction kinetics deals with the study of rates of chemical reactions. Some of the factors affecting the rate of reaction are:

### 1) Nature of reactants



#### What is the Rate Law?

The rate law (also known as the rate equation) for a chemical reaction is an expression that provides a relationship between the rate of the reaction and the concentrations of the reactants participating in it.

#### Rate of Reaction

Rate of a chemical reaction IS the change in the concentration of any one of the reactants or products per unit time. It is expressed in mol  $L^{-1} s^{-1}$  or  $Ms^{-1}$  or atm time<sup>-1</sup> units.

#### **Rate of reaction**

= (decrease/increase in the concentration of reactant/product/time taken)

This rate of reaction is known as average rate of reaction  $(r_{av}).(r_{av} \text{ can be calculated by dividing the concentration difference by the time interval}). For a chemical reaction,$ 

For a chemical reaction,
$aA + bB \longrightarrow cC + dD$
Average rate of reaction $(r_{av}) = -\frac{1}{a} \frac{\Delta[A]}{\Delta t} = -\frac{1}{b} \frac{\Delta[B]}{\Delta t}$
$= \frac{1}{c} \frac{\Delta[C]}{\Delta t} = \frac{1}{d} \frac{\Delta[D]}{\Delta t}$
Rate of disappearance of $A = -\frac{\Delta[A]}{\Delta t}$
Rate of disappearance of $B = -\frac{\Delta[B]}{\Delta t}$
Rate of appearance of $C = \frac{\Delta[C]}{\Delta t}$
Rate of appearance of $D = \frac{\Delta[D]}{\Delta t}$

#### Instantaneous Rate of Reaction

Rate of a chemical reaction at a particular moment of time, is known as the instantaneous rate of reaction.

For reaction,

For reaction, 
$$R \longrightarrow P$$
  
 $r_{ins} = -\frac{\Delta[R]}{\Delta t} \text{ or } \frac{\Delta[P]}{\Delta t} \text{ as } \Delta \rightarrow d$   
 $\Rightarrow r_{inst} = -\frac{d[R]}{dt} = \frac{d[P]}{dt}$ 

Methods for measuring reaction rate (i) pH measurement, (ii) change in optical activity, (iii) change in pressure, (iv) change in conductance.

Slowest step of a reaction was called rate determining step by Van't Hoff.

#### **Expression**

For a reaction given by:

#### $aA + bB \rightarrow cC + dD$

Where a, b, c, and d are the stoichiometric coefficients of the reactants or products, the rate equation for the reaction is given by:

#### Rate $\propto$ [A]<sup>x</sup>[B]<sup>y</sup> $\Rightarrow$ Rate = k[A]<sup>x</sup>[B]<sup>y</sup>

Where,

- [A] & [B] denote the concentrations of the reactants A and B.
- x & y denote the partial reaction orders for reactants A & B (which may or may not be equal to their stoichiometric coefficients a & b).
- The proportionality constant 'k' is the rate constant of the reaction.

It is important to note that the expression of the rate law for a specific reaction can only be determined experimentally. The rate law expression cannot be obtained from the balanced chemical equation (since the partial orders of the reactants are not necessarily equal to the stoichiometric coefficients).

#### **Reaction Orders**

#### Order of Reaction



The sum of the partial orders of the reactants in the rate law expression gives the overall <u>order</u> of the reaction.

If Rate =  $k[A]^{x}[B]^{y}$ ; overall order of the reaction (n) = x+y

The order of a reaction provides insight into the change in the rate of the reaction that can be expected by increasing the concentration of the reactants. For example:

- If the reaction is a zero-order reaction, doubling the reactant concentration will have no effect on the reaction rate.
- If the reaction is of the first order, doubling the reactant concentration will double the reaction rate
- In second-order reactions, doubling the concentration of the reactants will quadruple the overall reaction rate.
- For third-order reactions, the overall rate increases by eight times when the reactant concentration is doubled.
- Elementary Reaction:
- It is the reaction which completes in a single step.
- A reaction may involve more than one elementary reactions or steps also.
- Overall rate of reaction depends on the slowest elementary step and thus it is known as rate determining step.

#### **Molecularity of Reaction:**

- Number of molecules taking part in an elementary step is known as its molecularity.
- Order of an elementary reaction is always equal to its molecularity.
- Elementary reactions with molecularity greater than three are not known because collisions in which more than three particles come together simultaneously are rare.

**Rate Constants** 

Chemical Reaction	Molecularity
$PCI_5 \rightarrow PCI_3 + CI_2$	Unimolecular
$2HI \rightarrow H_2 + I_2$	Bimolecular
$2SO_2 + O_2 \rightarrow 2SO_3$	Trimolecular
$NO + O_3 \rightarrow NO_2 + O_2$	Bimolecular
$2CO + O_2 \rightarrow 2CO_2$	Trimolecular

Rearranging the rate equation, the value of the rate constant 'k' is given by:

 $k = Rate/[A]^{x}[B]^{y}$ 

Therefore, the units of k (assuming that concentration is represented in mol.L<sup>-1</sup> or M and time is represented in seconds) can be calculated via the following equation.  $k = (M.s^{-1})*(M^{-n}) = M^{(1-n)}.s^{-1}$ 

The units of the rate constants for zero, first, second, and n<sup>th</sup>-order reactions are tabulated below.

Reaction Order	Units of Rate Constant
0	M.s <sup>-1</sup> (or) mol.L <sup>-1</sup> .s <sup>-1</sup>
1	S <sup>-1</sup>
2	M <sup>-1</sup> .s <sup>-1</sup> (or) L.mol <sup>-1</sup> .s <sup>-1</sup>
n	M <sup>1-n</sup> .s <sup>-1</sup> (or) L <sup>(-1+n)</sup> .mol <sup>(1-n)</sup> .s <sup>-1</sup>

### **Differential Rate Equations**

Differential rate laws are used to express the rate of a reaction in terms of the changes in reactant concentrations (d[R]) over a small interval of time (dt). Therefore, the differential form of the rate expression provided in the previous subsection is given by:

 $-d[R]/dt = k[A]^{x}[B]^{y}$ 

Differential rate equations can be used to calculate the instantaneous rate of a reaction, which is the reaction rate under a very small time interval. It can be noted that the ordinary rate law is a differential rate equation since it offers insight into the instantaneous rate of the reaction.

### **Integrated Rate Equations**

Integrated rate equations express the concentration of the reactants in a chemical reaction as a function of time. Therefore, such rate equations can be employed to check how long it would take for a given percentage of the reactants to be consumed in a chemical reaction. It is important to note that reactions of different orders have different integrated rate equations.

#### **Characteristics of rate constant**

- 1. Greater the value of rate constant, faster is the reaction.
- 2. Each reaction has a particular value of rate constant at a particular temperature.
- 3. The value of rate constant for the same reaction changes with temperature.
- 4. The value of rate constant for a reaction does't depend upon the concentration of the reactants.



## **Integrated Rate Equation for Zero-Order Reactions**

The integrated rate equation for a <u>zero-order reaction</u> is given by:

 $kt = [R_0] - [R]$  (or)  $k = ([R_0] - [R])/t$ 

#### Where,

- [R<sub>0</sub>] is the initial concentration of the reactant (when t = 0)
- [R] is the concentration of the reactant at time 't'
- k is the rate constant

### Integrated Rate Equation for First-Order Reactions

The integrated rate law for first-order reactions is:

 $kt = 2.303log([R_0]/[R]) (or) k = (2.303/t)log([R_0]/[R])$ 

#### **Integrated Rate Equation for Second-Order Reactions**

For second-order reactions, the integrated rate equation is:

 $kt = (1/[R]) - (1/[R_0])$ 

## **Solved Examples on the Rate Law**

#### Example 1

For the reaction given by  $2NO + O_2 \rightarrow 2NO_2$ , The rate equation is: Rate =  $k[NO]^2[O_2]$ 

Find the overall order of the reaction and the units of the rate constant.

**Ans.** The overall order of the reaction = sum of exponents of reactants in the rate equation = 2+1 = 3

The reaction is a third-order reaction. Units of rate constant for 'n<sup>th</sup>' order reaction = M<sup>(1-n)</sup>.s<sup>-1</sup>

Therefore, units of rate constant for the third-order reaction =  $M^{(1-3)}$ .s<sup>-1</sup> =  $M^{-2}$ .s<sup>-1</sup> = L<sup>2</sup>.mol<sup>-2</sup>.s<sup>-1</sup>

#### Example 2

For the first-order reaction given by  $2N_2O_5 \rightarrow 4NO_2 + O_2$  the initial concentration of  $N_2O_5$  was 0.1M (at a constant temperature of 300K). After 10 minutes, the concentration of  $N_2O_5$  was found to be 0.01M. Find the rate constant of this reaction (at 300K).

Ans. From the integral rate equation of first-order reactions:

 $k = (2.303/t)\log([R_0]/[R])$ Given, t = 10 mins = 600 s Initial concentration, [R\_0] = 0.1M Final concentration, [R] = 0.01M Therefore, rate constant, k = (2.303/600s)log(0.1M/0.01M) = 0.0038 s<sup>-1</sup> The rate constant of this equation is 0.0038 s<sup>-1</sup> To learn more about the rate law and other important concepts such as the <u>half life of a</u> <u>chemical reaction</u>, register with BYJU'S and download the mobile application on your smartphone.

### Differential and Integrated Rate Laws:

Zero Order Reactions:



<u>For Reaction:</u>  $A \rightarrow$  Product

 $[\mathsf{A}]_0\text{-}[\mathsf{A}]_{\mathsf{t}} = k_0 t$ 

Where,

 $[A]_{0} =$  Initial concentration of A

 $[A]_t$  = Concentration of A at time t.

 $k_0$  = Rate constant for zero order reaction.

## Half Life:

 $t_{1/2} = [A]_0/2k$ 

Unit of rate constant = mol dm<sup>-3</sup>s<sup>-1</sup>

## Examples:

- Enzyme catalyzed reactions are zero order with respect to substrate concentration.
- Decomposition of gases on the surface of metallic catalysts like decomposition of HI on gold surface.

First Order Reactions:



## $A \rightarrow Product$ $(\Delta [A] /A) = -k_1 \Delta t$

#### or $k_1=(2.303/t)\log([A]_0/[A]_t)$

### Half Life:

 $t_{1/2} = 0.693/k_1$ 

Half life is independent of the initial concentration of the reactant for a first order reaction. Units of  $k_1 = s^{-1}$ 

## Examples:

 $N_{2}O_{5} \rightarrow 2NO_{2} + 1/2O_{2}$   $Br_{2} \rightarrow 2Br$   $2HNO_{3} \rightarrow 2NO + H_{2}O$   $H_{2}O_{2} \rightarrow H_{2}O + 1/2O_{2}$ 

#### Pseudo First Order Reactions:

These are the reactions in which more than one species is involved in the rate determining step but still the order of reaction is one.

Examples:

- Acid hydrolysis of ester: CH<sub>3</sub>COOEt + H<sub>3</sub>O<sup>+</sup> →CH<sub>3</sub>COOH + EtOH
- Inversion of cane sugar:

• Decomposition of benzenediazonium halides  $C_6H_5N=NCI+H_2O \rightarrow C_6H_5OH+N_2+HCI$ 

## Half – Life of a nth Order Reaction:

 $kt_{1/2} = (2^{n-1}-1)/(n-1)[A_0]^{n-1}$ 

Where, n = order of reaction  $\neq 1$ 

Methods to Determine Order of Reaction



(ii) Initial rate method In this method, the order of a reaction is determined by varying the concentration of one of the

reactants while others are kept constant.

(iii) Integrated rate law method In this method out different integrated rate equation which gives the most constant value for the rate constant corresponds to a specific order of reaction.

(iv) Half-life period ( $t_{1/2}$ ) method In general half-life period ( $t_{1/2}$ ) of a reaction of nth order is related to initial concentration of the reactant as



This method is employed only when the rate law involved only one concentration term.

(v) Ostwald's isolation method This method is employed in determining the order of complicated reactions by isolating one

of the reactants so far as its influence on the reaction rate is concerned.

#### **Temperature DCOEFFICIENT of Reaction RATE**

The temperature coefficient of a chemical reaction is defined as the ratio of the specific reaction rates of a reaction at two temperature differing by 10°C.

 $\mu$  = Temperature coefficient=  $k_{(r+10)}/k_t$ 

Let temperature coefficient of a reaction be '  $\mu$  ' when temperature is raised from T<sub>1</sub>to T<sub>2</sub>; then the ratio of rate constants or rate may be calculated as

$$\frac{k_{T2}}{k_{T1}} = \mu^{\frac{T_2 - T_1}{10}} = \mu^{\frac{\Delta T}{10}}$$
$$log \frac{k_{T2}}{k_{T1}} = \mu^{\frac{T_2 - T_1}{10}} = \Delta T log\mu$$
$$\frac{k_{T2}}{k_{T1}} = antilog[\frac{\Delta T}{10}] log\mu$$

Its value lies generally between 2 and 3.

#### Parallel Reactions:

The reactions in which a substance reacts or decomposes in more than one way are called parallel or side reactions.



If we assume that both of them are first order, we get.

$$-\frac{d[A]}{dt} = (k_1 + k_2)[A] = k_{av}[A]$$

 $k_1$  = fractional yield of  $B \times k_{av}$ 

 $k_2$  = fractional yield of C ×  $k_{av}$ 

If  $k_1 > k_2$  then

 $A \rightarrow B$  main and

 $A \rightarrow C$  is side reaction

Let after a definite interval x mol/litre of B and y mol/litre of C are formed.

$$\frac{x}{y} = \frac{k_1}{k_2}$$
  
i.e  
$$\frac{\underline{d[B]}}{\underline{dt}}$$
$$\frac{\underline{d[C]}}{\underline{dt}} = \frac{k_1}{k_2}$$

This means that irrespective of how much time is elapsed, the ratio of concentration of B to that of C from the start (assuming no B and C in the beginning ) is a constant equal to  $k_1/k_2$ .



### Sequential Reactions:

This reaction is defined as that reaction which proceeds from reactants to final products through one or more intermediate stages. The overall reaction is a result of several successive or consecutive steps.

 $A \rightarrow B \rightarrow C \text{ and so on}$  $A \stackrel{k_1}{\rightarrow} B \stackrel{K_2}{\rightarrow} C$ 

$$-\frac{d[A]}{dt} = k_1[A] \dots (i)$$

$$\frac{d[B]}{dt} = k_1[A] - K_2[B] \dots (ii)$$

$$\frac{d[C]}{dt} = k_2[B] \dots (iii)$$
Integrating equation (i), we get
$$[A] - [A]_o e^{-k_1 t}$$

$$[\mathbf{B}] = \frac{k_1[\mathbf{A}]_0}{k_2 - k_1} \left[ \mathbf{e}^{-\mathbf{k}_1 t} - \mathbf{e}^{-\mathbf{k}_2 t} \right]$$

$$[\mathbf{C}] = \frac{[\mathbf{A}]_0}{k_2 - k_1} \left[ k_2 \left( 1 - \mathbf{e}^{-\mathbf{k}_1 t} \right) - k_1 \left( 1 - \mathbf{e}^{-\mathbf{k}_2 t} \right) \right]$$

$$\mathbf{t}_{\max} = \frac{1}{k_1 - k_2} \ln \frac{k_1}{k_2}$$

$$\mathbf{B}_{\max} = [\mathbf{A}]_o \left[ \frac{k_2}{k_1} \right]^{k_2 k_1 - k_2}$$

## What is 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 preexponential factor; can be visualised as the frequency of correctly oriented collisions between reactant particles). It provides insight into the dependence of <u>reaction rates</u> on the absolute temperature. The expression of the Arrhenius equation is:

$$k = A e^{-E_a/RT}$$

Arrhenius Equation

Where,

• k denotes the rate constant of the reaction

- A denotes the pre-exponential factor which, in terms of the <u>collision theory</u>, is the frequency of correctly oriented collisions between the reacting species
- e is the base of the natural logarithm (Euler's number)
- E<sub>a</sub> 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. The Arrhenius equation was put forward by the Swedish chemist Svante Arrhenius in the year 1889.

## **Graphical Representation of the Arrhenius Equation**

For the decomposition reaction undergone by nitrogen dioxide (given by  $2NO_2 \rightarrow 2NO + O_2$ ), a graph plotted with the rate constant (k) on the Y-axis and the absolute temperature (T) on the X-axis is provided below. Note that the rate of the reaction increases as the temperature increases.



Arrhenius Equation Graph

## **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.

## **Does the Arrhenius Equation Account for Catalysts?**

The function of a catalyst is to lower the <u>activation energy</u> required by a reaction. Therefore, the lowered activation energy (accounted for by the catalyst) can be substituted into the Arrhenius equation in order to obtain the rate constant for the catalyzed reaction.

The exponential part of the Arrhenius equation ( $-E_a/RT$ ) accounts for an exponential increase in the value of the rate constant for any decrease in the activation energy. Since the rate of a chemical reaction is directly proportional to the rate constant of that reaction, the decrease in activation energy results in an exponential increase in the reaction rate.

It is important to note that the rates of uncatalyzed reactions are more severely affected by temperature than the rates of catalyzed reactions. This is because the activation energy is in the numerator of the exponential term  $-E_a/RT$  and the absolute temperature is in the denominator. Since the activation energy of the catalyzed reaction is relatively low, the effect of temperature on the rate constant is more visible in the corresponding uncatalyzed reaction.

## 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** = ρΖ

Where Z is the frequency factor (frequency of collisions) and  $\rho$  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 <u>order of the reaction</u>. For example, the value of 'A' for a second-order rate constant is expressed in L.mol<sup>-1</sup>.s<sup>-1</sup> (or M<sup>-1</sup>s<sup>-1</sup>, since M = mol.L<sup>-1</sup>) and that of a first-order rate constant is expressed in s<sup>-1</sup>.

## **Eliminating the A Factor from the Arrhenius Equation**

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:

 $\ln k_1 = \ln(A) - E_a/RT_1$ 

 $\ln k_2 = \ln(A) - E_a/RT_2$ 

The second equation can be rearranged to get the value of ln(A):

 $\ln (A) = \ln(k_2) + E_a/RT_2$ 

Substituting the value of ln(A) in the equation for  $ln(k_1)$ , the following equations can be obtained:

 $ln(k_1) = ln(k_2) + E_a/RT_2 - E_a/RT_1$ 

Shifting  $ln(k_2)$  to the LHS, the value of  $ln(k_1) - ln(k_2)$  becomes:

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

The LHS of the equation is of the form ln(x) - ln(y), which can be simplified to ln(x/y). Also, the term 'E<sub>a</sub>/R' is a common factor to both the terms in the RHS. Therefore, the entire equation can be simplified as follows: ln(k1k2)=-EaR(1T1-1T2)

## **Solved Exercises**

#### Example 1

The activation energy of a chemical reaction is 100 kJ/mol and its A factor is 10 M<sup>-1</sup>s<sup>-1</sup>. Find the rate constant of this equation at a temperature of 300 K.

Given,

E<sub>a</sub> = 100 kJ.mol<sup>-1</sup> = 100000 J.mol<sup>-1</sup>

 $A = 10 M^{-1}s^{-1}$ , ln(A) = 2.3 (approx.)

T = 300 K

**Ans.** The value of the rate constant can be obtained from the logarithmic form of the Arrhenius equation,

 $\ln k = \ln(A) - (E_a/RT)$ 

 $\ln k = 2.3 - (100000 \text{ J.mol}^{-1})/(8.314 \text{ J.mol}^{-1}.\text{K}^{-1})*(300\text{K})$ 

ln k = 2.3 – 40.1

ln k = -37.8

 $k = 3.8341^*10^{-17} \text{ M}^{-1}\text{s}^{-1}$  (from the units of the A factor, it can be understood that the reaction is a <u>second-order reaction</u>, for which the unit of k is M<sup>-1</sup>s<sup>-1</sup>)

Therefore, the value of the rate constant for the reaction at a temperature of 300K is approximately  $3.8341*10^{-17} \text{ M}^{-1}\text{s}^{-1}$ .

#### Example 2

At a temperature of 600 K, the rate constant of a chemical reaction is 2.75\*10<sup>-8</sup> M<sup>-1</sup>s<sup>-1</sup>. When the temperature is increased to 800K, the rate constant for the same reaction is 1.95\*10<sup>-7</sup>M<sup>-1</sup>s<sup>-1</sup>. What is the activation energy of this reaction?

Given,

T<sub>1</sub> = 600K

k<sub>1</sub> = 2.75\*10<sup>-8</sup> M<sup>-1</sup>s<sup>-1</sup>.

T<sub>2</sub> = 800K

 $K_2 = 1.95 * 10^{-7} M^{-1} s^{-1}$ 

**Ans.** When the A factor is eliminated from the Arrhenius equation, the following equation is obtained:

 $\ln(k_1/k_2) = (-E_a/R)(1/T_1 - 1/T_2)$ 

Substituting the given values in the equation, the value of E<sub>a</sub> can be determined:

 $\ln(2.75*10^{-8}/1.95*10^{-7}) = (-E_a/8.314 \text{ J}.\text{K}^{-1}.\text{mol}^{-1})*(0.00041\text{K}^{-1})$ 

 $\ln(0.141) = (E_a)^*(-0.0000493) J^{-1}.mol$ 

E<sub>a</sub> = (-1.958)/(-0.0000493)J.mol<sup>-1</sup> = 39716 J.mol<sup>-1</sup>

The activation energy of the reaction is approximately 39716 J.mol<sup>-1</sup>.

### **Effect of Temperature:**

Temperature is one of the parameters that can affect the rate of a chemical reaction considerably. We have often seen milk boiling on a gas stove. The rate at which a specific quantity of milk boils depends on the flame of the stove. If the flame height is maximum, the milk boils in less time and if the flame height is minimum, the milk takes more time to boil. Here the flame height resembles temperature.



If the temperature is high, the milk attains its boiling point in less time and if the temperature is low, the milk takes more time to attain its <u>boiling point</u>. The boiling of milk is not the only reaction that gets affected by temperature. Most of the chemical reactions show a change in their reaction rate with the varying in temperature.

It has been observed that the rate constant for a chemical reaction gets doubled for every 10°C rise in temperature. Until 1889, there was no fixed way to physically measure the temperature dependence of the rate of a chemical reaction. In 1889, Svante Arrhenius extended the work of J.H van't Hoff and proposed an equation that related temperature and the rate constant for a reaction quantitatively. The proposed equation was named as Arrhenius Equation.

## Activated complex (or transition state)

Activated complex is the highest energy unstable intermediate between the reactants and products and gets decomposed immediately (having very short life), to give the products. In this state, bonds of reactant are not completely broken while the bonds of products are not completely formed.



**Threshold energy (E<sub>T</sub>)** The minimum amount of energy which the reactant must possess in order to convert into products is known as threshold energy.

Activation energy ( $E_a$ ) The additional amount of energy, required by the reactant so that their energy becomes equal to the threshold value is known as activation energy.

$$\Rightarrow E_a = E_T - E_R$$

Lower the activation energy, faster is the reaction.

Different reactions have different rates because their activation energies are different.

Larger the value of Eo, smaller the value of rate constant and greater is the effect of a given temperature rise on K

Important points about Arrhenius equation

(i) If  $\mathfrak{R}_2$  and  $\mathfrak{R}_1$  are rate constant at temperature  $T_2$  and  $T_1$ ; then

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

ii) Fraction of molecules with energy equal to or greater than the activation energy is called Boltzmann factor and is given by

$$x = \frac{n}{N} = e^{-E_a/RT}$$
$$\log x = \frac{-E_a}{2.303 RT}$$

(iii) E<sub>a</sub> is constant for a particular reaction.

(iv)  $E_a$  does't depend on temperature, volume, pressure, etc., but gets affected by catalyst. In the Arrhenius equation, when  $T \rightarrow \infty$  then  $\Re = Ae^\circ = A$  when  $E_a = 0, k = A$  and the rate of reaction becomes independent temperature.

Role of Catalyst in a Chemical Reaction

A catalyst is a chemical substance which alters the rate of a reaction WIthout itself undergoing any permanent chemical change.

In the chemical reactions, catalyst provides an alternate pathway or reaction mechanism by reducing the activation energy between reactants and products and hence. lowering the potential energy barrier as shown.



In the presence of catalyst, activation energy decreases and hence.

$$\frac{k_P}{k_a} = e^{(E_a - E_P)RT} = e^{\Delta E/RT}$$

Where, P denotes presence of catalyst and a denotes absence of catalyst.

## **Theory of Reaction Rates**

## **Collision Theory**

According to this theory, the reactant molecules are assumed to be hard spheres and the reaction is postulated to occur, when molecules collide with each other.

The number of collisions between the reacting molecules taking place per second per unit volume is known as collision frequency  $(Z_{AB})$ .

But only those collisions in which the colliding species are associated with certain minimum amount of energy and collide in proper orientation result in the product formation, such collisions are called **fruitful collisions or effective collision**.

Here, rate = -(dv/dt) = collision frequency x fraction of effective collision

#### $= Z_{AB} \times f = Z_{AB} \times e^{-E_a/RT}$

where,  $Z_{AB}$  represents the collision frequency of reactants, A and B e<sup>-E</sup>a<sup>/RT</sup> represents the fraction of molecules with energies equal to or greater than Ea.

So, to account for effective collisions, another factor, P called the probability or steric factor is introduced.

## So, rate = PZ<sub>AB</sub>e<sup>-E</sup>a<sup>/RT</sup> The Activated Complex Theory or Transition State Theory

 $\mathsf{Reactants} \Leftrightarrow \mathsf{Activated} \ \mathsf{complex} \rightarrow \mathsf{Products}$ 

This theory is based on the fact that bond cleavage and bond formation, involved in a chemical reaction, must occur simultaneously. Hence, the reactants are not converted directly into the products. There is an energy barrier or activated complex [intermediate product with partially formed bond] between the reactants and products. The reactants must cross this energy barrier before converting into products. The height of the barrier determines the threshold energy.

## **Photochemical Reactions**

Chemical reactions that occur on exposure to visible radiation are called photochemical reactions.

- 1. The rate of a photochemical reactions is affected by the the intensity of light.
- 2. Temperature has little effect on photochemical reactions.

Quantum yield or quantum efficiency of a photochemical reaction,

 $\phi$  = (number of reactant molecules reacting in a given time / number of photons (quanta) of light absorbed ill the same time)

# CHEMISTRY REVISION NOTES CHAPTER CHEMICAL KINETICS

- **Chemical kinetics:** It is the branch of chemistry that deals with the study of reaction rates and their mechanisms.
- Rate of reaction: It is the change in concentration of reactant (or product) in unit time.
- The unit of rate of reaction is mol L-1s-1.
- $A + B \rightarrow C + D$

Rate of disappearance of  $A = \frac{-d[A]}{dt}$ where d[A] is small change in conc. of 'A' and dt is small interval of time Rate of disappearance of  $B = \frac{-d[B]}{dt}$ Where d[B] is small change in conc. of 'B' and dt is small interval of time +d[C]

Rate of appearance of  $C = \frac{+d[C]}{dt}$ 

Where d[C] is small change in conc. of 'C' and dt is small interval of time +d[D]

Rate of appearance of  $D = \frac{+d[D]}{dt}$ Where d[D] is small change in conc. of 'D' and dt is small interval of time Rate

- Rate law or rate equation: It is the expression which relates the rate of reaction with concentration of the reactants. The constant of proportionality 'k' is known as rate constant.
- Average rate: It is the rate of reaction measured over a long time interval.
- Average rate  $= \frac{\Delta x}{\Delta t}$

where is  $\Delta x$  change in concentration and  $\Delta t$  is large interval of time.

• Instantaneous rate: It is the rate of reaction when the average rate is taken over a dx

particular moment of time. Instantaneous rate  $= \overline{dt}$ . where dx is small change in conc. and dt is the smallest interval of time.

It is the expression which relates the rate of reaction with concentration of the reactants.

- **Rate constant:** When the concentration of reactants is unity, then the rate of reaction is known as rate constant. It is also called specific reaction rate. The constant of proportionality 'k' is known as rate constant.
- **Molecularity of a reaction:** The total number of atoms, ions or molecules of the reactants involved in the reaction is termed as its molecularity. It is always in whole number and is never more than three. It cannot be zero.

• Order of a reaction: The sum of the exponents (power) of the concentration of reactants in the rate law is termed as order of the reaction. It can be in fraction. It can be zero also.

If rate law expression for a reaction is Rate = k [A]x [B]y Then its order of reaction = x + y

- Order cannot be determined with a given balanced chemical equation. It can be experimentally determined.
- Integrated rate law for zero order reaction:  $\mathsf{R} \rightarrow \mathsf{P}$

$$\frac{dx}{dt} = k[R]^0$$
$$k = \frac{[R_0] - [R]}{t}$$

If we plot a graph between concentration of R vs time t, the graph is a straight line with slope equal to -k and intercept is equal to [Ro].

- Half- life of a reaction: The time taken for a reaction, when half of the starting material has reacted is called half- life of a reaction.
- For zero order reaction, the half-life time is  $t_{1/2} =$

$$_{1/2} = \frac{[R_0]}{2k}$$

- For first order reaction, the half-life time is  $t_{1/2} = \frac{0.693}{k}$ , where 'k' is rate constant. It is independent of initial concentration for first order reaction.
- Rate law for first order reaction:  $R \rightarrow P$

$$k = \frac{2.303}{t} \log \frac{[R_0]}{[R]}$$

where 'k' is rate constant or specific reaction rate, [Ro] is initial molar conc., [R] is final molar conc. after time 't'.

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

where 'a' is initial conc. reacted in time 't' final conc., after time 't' is (a - x).

- If we plot a graph between ln[R] with time, we get a straight line whose slope = k and intercept ln[Ro].
- To calculate rate constant for first order gas phase reaction of the type

$$A(g) \rightarrow B(g) + C(g)$$

$$k = \frac{2.303}{t} \log \frac{p_1}{(2p_i - p_t)}$$

 $t = t^{-105} (2p_i - p_t)$ Where pi is initial pressure of A, pt is total pressure of gaseous mixture containing A , B, C

 $p_{t} = p_{A} + p_{B} + p_{C}$ 

• **Pseudo first order reaction:** The reaction which is bimolecular but order is one is called pseudo first order reaction. This happens when one of the reactants is in large excess.Example – Acidic hydrolysis of ester (ethyl acetate).

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

- Activation energy (Ea): It is extra energy which must be possessed by reactant molecules so that collision between reactant molecules is effective and leads to the formation of product molecules.
- Arrhenius equation of reaction rate: It gives the relation between rate of reaction and temperature.

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

$$\ln k = \ln A - E_a/RT$$
  

$$\log k = \log A - \frac{E_a}{E_a}$$

 $g \kappa = \log A - \frac{1}{2.303RT}$ 

where k = rate constant, A = frequency factor, Ea = energy of activation R = gas constant, T = temperature in Kelvin,

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

• Probability factor or Steric factor

## $Rate = PZ_{AB}.e^{\frac{-E_a}{RT}}$

Where ZAB represents the collision frequency of reactants, A and B,  $e^{\frac{-E_{a}}{RT}}$  represents the fraction of molecules with energies equal to or greater than Ea and P is called the probability or steric factor.

- Mechanism of reaction: It is the sequence of elementary processes leading to the overall stoichiometry of a chemical reaction.
- Activated complex: It is an unstable intermediate formed between reacting molecules. Since, it is highly unstable and it readily changes into product.
- Rate determining step: It is the slowest step in the reaction mechanism.
- The number of collisions per second per unit volume of the reaction mixture is known as collision frequency (Z).

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